DEVELOPMENT OF S-TRIAZINE BASED HYPERBRANCHED AROMATIC POLYAMINES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
Doctor of Philosophy

By

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Dedicated to my

parents

ABSTRACT

BACKGROUND

Non-linear highly branched polymers such as dendritic polymers have attracted considerable attention of almost all classes of scientists and technologists. This is because of their improved physical and chemical properties, generated from their unique architectural features. These dendritic polymers not only possess large number of surface functionality but they also exhibit unique rheological properties like low melt and solution viscosities because of globular and non-entangled structures. The dendritic polymers include both dendrimers and hyperbranched polymers. Dendrimers are monodisperse and perfectly regular-branched structures, whereas hyperbranched polymers are polydisperse, less regular and have more defective branched structures. However, the synthesis of dendrimers needs more stringent reaction conditions and time consuming laborious processes. Hence their large-scale production is very difficult. On the other hand, the synthesis of hyperbranched polymers is much easier, involves only single step and no need of any purification, and thus can be produced in large scale without any great difficulty. Thus the research on hyperbranched polymers has gained much attention to the scientists for their different value-added applications. Hyperbranched polymers are generally synthesized from AB_X ($X \geq 2$) type monomers but the availability of this type of monomers is limited. For the synthesis of these monomers, very tedious and cumbersome organic synthetic routes are also required, most of the cases. To overcome these problems, recently a simple and a useful $A_2 + B_3$ approach has been utilized for synthesis of such hyperbranched polymers. However, this approach also has its own merits and demerits like other approaches. Here the polymerization process is very easy and simple, offers higher yield and almost tailored structure. But the gelation is very common problem in this approach and leads to gel type products. If this could be avoided then it is a very successful approach.

The polymers with heterocyclic moiety show important physical, chemical and thermal properties. A few number of published reports described the synthesis and the

properties of heterocyclic linear polymers with s-triazine moiety. In these approaches the solubility and the processability of heterocyclic polymers have been improved, as well as thermal stability is also maintained. This includes polyesters, polyamides, polyimides, polyazomethines, polyureas, polycyanurates, polyamines, polyethers, etc. Thus, the development of such hyperbranched polymers with s-triazine unit is expected to exhibit very interesting and unusual properties of the polymers.

Again, the unique architecture of hyperbranched macromolecules makes them interesting candidate as a blend component/polymeric additive for commercial linear polymers along with many other applications. Since these additives are organic and *macromolecular in nature, so they eliminate all the common problems such as leaching,* migration, volatilization, etc. which are observed in the case of conventional small molecular additives. Further, because of large number of active functionality on the surface of the dendritic polymers, the effectiveness will be much more. Thus hyperbranched polymers will be expected to act as a high performance additives to different linear base polymers. Further, design of hyperbranched polymers with s-triazine unit in the backbone, may offer high thermostability and flame retardancy. Many hyperbranched polymers viz. polyphenylene, polyesters, poly(ether amide), polyamides, poly(amide ester), etc. are utilized as blend components to improve many desirable levels of properties for different well-known linear polymers.

OBJECTIVES OF THE PRESENT INVESTIGATION

The main objectives of the present investigations are as follows.

(a) To synthesize the hyperbranched aromatic polyamines by a simple and an economically favorable technique using cyanuric chloride as one of the monomers.

(b) To characterize the synthesized polyamines by different spectroscopic and analytical techniques.

(c) To study the physical, thermal and optical properties of the above polyamines by different techniques.

(d) To utilize a hyperbranched polyamine as multipurpose polymeric additive for commercial linear polymers.

(e) To use a hyperbranched polyamine as a crosslinker for thermosetting resins.

(g) To utilize the hyperbranched polyamines as matrices for nanoparticles synthesis.

THE THESIS

Chapter One deals with the general introduction of hyperbranched polymers with special emphasis on hyperbranched polyamines. It is a brief review on hyperbranched polymers, which describes the importance, history, general techniques, characterization, properties and applications of such polymers. This chapter also describes the scope and objectives along with the plan and methodology of the present investigation.

Work on **Chapter Two** includes the synthesis and characterizations of the hyperbranched polyamines. Six hyperbranched polyamines have been synthesized by one pot nucleophilic displacement polymerization technique via $A_2 + B_3$ approach using commercially available relatively low cost monomers such as aromatic diamines (as A_2 monomer) and cyanuric chloride (as B_3 monomer). The hyperbranched polyamines are designated as HPs, HPm, HPo, HPa, HPb and HPd for the diamines; 4,4′-diaminodiphenylsulfone, 4,4′-diaminodiphenylmethane, 4,4′-oxydianiline, 4,4′-(1,4-phenylenediisopropylidene) bisaniline, 4,4′-(1,3-phenylenediisopropylidene) bisaniline and 4,4′-(4,4′-isopropylidenediphenyl-1,1′-diyldioxy) dianiline respectively for this study. End capping reactions were performed with benzoyl chloride, 4-hydroxybezaldehyde and methyl red for HPs and HPo hyperbranched polyamines respectively. The synthesized polymers have been successfully characterized by UV-visible, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques and elemental analysis data. The values of degree of branching (DB) of the hyperbranched polyamines were calculated from ^{1}H-NMR spectroscopy and indicate that the polymers are more like hyperbranched rather than linear or dendrimer.

Chapter Three involves the description of physical, thermal and fluorescence properties of the synthesized hyperbranched aromatic polyamines. From this study, it has been shown that the hyperbranched polyamines containing s-triazine ring exhibit good thermostability under the nitrogen atmosphere, self-extinguishing characteristics and good solubility in highly polar solvents. The fluorescence study shows that the polymers exhibit emission in the blue to yellow region from 350 to 650 nm with maxima at about 455 nm and the emission influenced by concentration of polymer solution, pH of the medium, nature of end capping, and the presence of metal ion.

Chapter Four reports the studies on hyperbranched polyamine as multipurpose macromolecular additives for commercial linear polymers like low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC). The compounding of polymers was carried out in a Brabender plasticorder at dose level of 1 phr, 5 phr and 7.5 phr of hyperbranched polyamine (HPs) separately for both the cases. This hyperbranched polyamine has good compatibility with PVC and LDPE though the degree of compatibility with PVC is higher than LDPE. It improved the processability, physical and mechanical properties for both the linear polymers. However, the improvement is significant in case of PVC. The retention properties after heat aging as well as after leaching in different chemical media of the linear polymers also proved the good capability of hyperbranched polyamine. This prevents degradation, leaching and migration of hyperbranched polyamine compared to the conventional antidegradant, IPPD. Also this chapter describes hyperbranched polyamines as polymeric flame retardant additives for the above commercial linear polymers up to dose level of 7.5 phr. The flame retardancey was measured by limiting oxygen index (LOI) test. The results show that the polyamines (HPs, HPa) improve the flame retardancy of the linear polymers. The synergist effect was also observed in polyamine (HPa) with widely used commercial flame retardant additive, triphenylphosphine oxide for both the linear polymers.

Chapter Five describes the studies on synthesis of metal nanoparticles such as silver and copper using hyperbranched polyamine (HPd and HPb) as matrices. It has been shown that metal nanoparticles are highly stable. and well dispersed in these matrices. The synthesized nanoparticles were characterized by using different spectroscopic and analytical techniques such as FT-IR, UV-visible, X-ray diffraction, SEM, TEM, etc. The antimicrobial activities of the nanoparticles were tested against the particular microbes at different concentrations of active agent by using the diffusion disc technique. The result shows that the antimicrobial activity increases with the increase of concentration of the active agent.

Chapter Six involves the use of a hyperbranched polyamine (HPb) as a crosslinker for thermosetting resins such as vegetable oil based poly(ester amide) and commercially available bisphenol A based epoxy resins. The studies show that the hyperbranched polyamine not only enhances the rate of crosslinking reaction but it also improves many desirable performance characteristics especially the thermostability, flame retardancy, hardness, impact strength, chemical resistance, etc. of the cured resins.

Chapter Seven, the last chapter of thesis includes the concluding remarks, highlights of the findings and future scope of the present investigation. The highlights of the present investigation are as follows.

i) Triazine based six hyperbranched polyamines have been synthesized from commercially available relatively low cost monomers by an $A_2 + B_3$ approach.
ii) The synthesized polyamines were characterized successfully by the conventional analytical and spectroscopic techniques.
iii) The physical, thermal and fluorescence properties of these hyperbranched polyamines were studied in details.
iv) The synthesized polyamines were used as multipurpose polymeric additives for commercially available linear polymers such as plasticized PVC and LDPE, for the first time.
v) The flame retardancy of the hyperbranched polyamines was measured by limiting oxygen index (LOI) test and found to be self extinguishing in nature.
vi) The hyperbranched polyamines act effectively as polymeric flame retardants for linear plasticized PVC and LDPE even at low dose level. They also exhibit synergistic effect with commercial flame retardant additive, triphenylphosphine oxide.
vii) The hyperbranched polyamine act as an effective crosslinking agent for vegetable oil based poly(ester amide) resin as well as for a commercially available epoxy resin.
viii) Metal nanoparticles such as silver and copper have been synthesized within hyperbranched polyamine matrices and the biological activity of such nanoparticles has been studied.

DECLARATION

I do hereby declare that the thesis entitled *"Development of s-Triazine Based Hyperbranched Aromatic Polyamines"*, submitted to the Department of Chemical Sciences, Tezpur University, is a record of original research work carried out by me. All sources of assistance have been assigned due acknowledgment. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or Institute for any other degree, diploma or award.

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All helps received by him from various sources have been duly acknowledged.

No part of this thesis has been reproduced elsewhere for award of any other degree.

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The committee recommends for the award of the degree of Doctor of Philosophy.

Principal Supervisor	External Examiner
Date:	Date:

PREFACE

Dendritic polymers are one important class of advanced frontier macromolecules in polymer science and technology. They include both dendrimers and hyperbranched polymers. These macromolecules are novel and versatile because of their unique architectural features of highly branched non-entangled structures with large numbers of active surface functionalities. Because of their unique structural features, they possess a large variety of unusual properties like low viscosity, high solubility, high reactivity, interior cavity, etc. These unique characteristics render them in a wide range of valuable applications including medicinal to polymeric additives. Although hyperbranched polymers are less symmetric and possess large number of defects unlike the more perfect dendrimer, they are also having almost equal potential in many applications.

The main objective of the present thesis is to develop hyperbranched aromatic polyamines with s-triazine moiety for multipurpose uses. In the present study, attempt has been made to synthesize, characterize and to evaluate properties of six hyperbranched aromatic polyamines. The physical, thermal and fluorescence properties of these polyamines are investigated. The low viscosity, high solubility, intense fluorescence and good thermostability with self-extinguishing behavior are the main characteristics of these polyamines. Thus these hyperbranched polyamines are tried to utilize as multipurpose polymeric additives for commercially linear polymers. They are also utilized as potential agents for thermosetting resins and as matrices for preparation of fine, well dispersed and stable metal nanoparticles.

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LIST OF SYMBOLS AND ABBREVIATIONS

AB$_X$	general formula of monomer with A and B as two different functionalities and x is number of functionality
b.p.	boiling point
c.c.	cubic centimeter
cm	centimeter(s)
CMC	critical micelle concentration
CYC	cyanuric chloride
DB	degree of branching
deg. C/ ^{O}C	degree centigrade
dL	decilitre(s)
DMAc	*N,N′*-dimethyl acetamide
DMF	*N,N′*-dimethyl formamide
DMSO	*N,N′*-dimethyl sulfoxide
DOP	dioctyl phthalate
DTA	differential thermal analysis
DSC	differential scanning calorimetry
EL	electroluminescence
eV	electron volt
FT-IR	Fourier transform infrared
g	gram(s)
GPC	gel permeation chromatography
h	hour(s)
HBP	hyperbranched polymer
HDPE	high density polyethylene
IGA	isogravimetric analysis
IPPD	N-Isopropyl N′-phenyl *p*-phenyl diamine
K	Kelvin
kHz	kilo-hertz

kN	kilo-newton
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
LOI	limiting oxygen index
m	meter(s)
min	minute(s)
mL	mili liter(s)
mm	mili meter(s)
mmol	mili mole
mol	mole
m.p.	melting point
M_n	number average molecular weight
M_w	weight average molecular weight
N	Newton
NMR	nuclear magnetic resonance
nm	nano meter(s)
NMP	*N*-methylpyrrolidone
Nu	Nucleophile
phr	part per hundred of base polymer
ppm	parts per million
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
rpm	rotation per minute
s	second(s)
SEM	scanning electron microscope
T_d	decomposition temperature
TEM	transmission electron microscopy
Temp	temperature
T_g	glass transition temperature
TG	thermogravimetry
TGA	thermogravimetric analysis
THF	tetrahydrofuran

TMS	tetramethyl silane
TPO	triphenylphosphine oxide
UTM	universal testing machine
UV	ultraviolet
v	volume
w	weight
XRD	X-ray diffraction
%	percentage
η_{inh}	inherent viscosity
λ_{max}	wavelength maximum
θ	scattering angle

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ACKNOWLEDGMENT

It is my greatest pleasure to express my gratitude to all of them, who have directly or indirectly influenced and encouraged over the course of my studies and my life in general.

First of all, I would like to express sincere gratitude and humble respect to my Ph.D. supervisor Dr. Niranjan Karak for his supports, advices and wonderful companion throughout my Ph.D. work. It would have been impossible to complete this thesis without his assistance in each and every step and continuous encouragement. He not only shared the joy of success but frustrations of failure as well throughout the course of research work. It was a wonderful experience for me to learn the chemistry from an excellent teacher like him. Besides chemistry; his suggestions, corrections and advices made the things much easier to me.

It is my honor to acknowledge the present and former Head of the Department Prof. N. S. Islam and Prof. T. K. Maji for administrative supports to me during my stay and valuable advices throughout my Ph.D. work at Tezpur University.

I would also like to express my sincere gratitude and humble respect to Prof. S. K. Dolui, Dean of Science and Technology, for his valuable suggestions and help during my research work.

I would also like to thank the members of my doctoral committee for their timely help and advices. I express my thanks and sincere gratitude to all the Faculty members of Department of Chemical Sciences for their valuable suggestions and advices. My special thanks go to Mr. B. Gohain for his unforgettable help.

I would like to express my sincere thanks to Mr. D. Bharali, Mr. P. S. Baruah, Mr. B. Saikia, Mr. Satyajit Das, Mr. H. Gogoi, Mr. B. G. Chetry and Hirnyada.

I am delighted to say thanks to my two seniors Dr. Jyotishmoy Borah and Dr. Nandini Dutta who have taught me for the first time how to perform a reaction in laboratory. They even suggested me how to start writing a thesis.

I will never forget the contributions of my laboratory colleagues Suvangshu, Harekrishna, Uday, Nitul, Goutam. In every step, from lab work to thesis writing, they extended their helping hands. I am really fortunate to have lab mates like them.

Besides my lab mates, I would like to thank Binod, Lakhya, Jatin for their technical and moral support. They even read every single line of my thesis and tried to correct it. I am really fortunate to have friends like them.

I am grateful to Mr. Upamanyu Das, Mr. Sudhir Roy, Mr. Kulakamal Senapati and Dr. Abu Pharad Hussain for their kind help during my research work.

I would like to extent my heartiest thanks to my friends and well wishers, Dr. A. Patra, Miss Sumana, Dr. Tapasi Kataki, Dr. Surashree Sarma, , Dr. Ilias Ali, Dr. Rashmi R. Devi, Dr. Raju Ojah, Dr. Palash M Saikia, Poritosh Da, Pankaj Da, Rabiulda, Diganta, Ajanta Ba, Muhsina, Anamika, Nirmala, Parasha, Pubali, Bulumoni, Mridula, Suresh, Gunin, Isha, Surajit, Sivaprasad, Subrata, and others who directly or indirectly help to prepare my Ph.D. thesis.

I am also thankful to IIT Guwahati, RSIC Shillong, IISc Bangalore and other institutions for their helps in analyzing and testing works.

My special thanks go to CSIR, New Delhi for financial support to me as SRF.

I am grateful to Mrs. Susmita Karak for her encouragement and co-operation.

My words fail to express my gratitude and sincere regard to my parents, dadu-dida and my terrific grandmother for their great encourage and endless love that will always be in my heart. I would like to acknowledge my brother, sisters and brother-in-law for their well wishes and encouragement in my life. The little nephews Rima, Ria, Babai, tatai being a bundle of joy whose presence only are enough for me to keep my spirit up.

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CHAPTER ONE

General Introduction

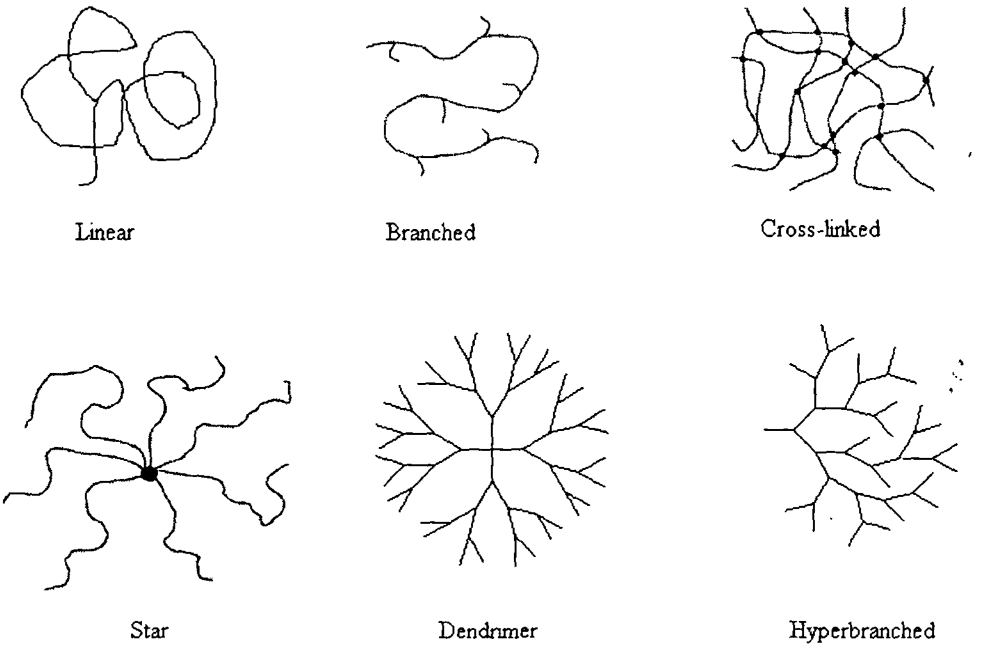
1.1. Introduction

A strong demand on high quality polymeric products inclines the polymer scientists to produce their materials with novel and innovative ideas. The creation of even a little branching in a linear polymer has already been proved to be a useful effort to modify the properties and processing characteristics of that polymer. Hence the design of a new polymer with unique architectural feature such as symmetric three-dimensional highly branched structure leads to some unusual and useful properties.

Over the last two decades, a class of such polymeric materials known as dendritic polymer has fascinated to many synthetic polymer chemists. These highly branched macromolecules resemble tree like in growth, structure and appearance. As the fourth major class of polymer architecture, after the traditional types, which include linear, cross-linked and branched structures, dendritic polymers consist of mainly two sub classes: dendrimer/dendron and hyperbranched polymer, which exhibit three-dimensional (3D) globular and spherical like structural architectures.

The term 'dendrimer' is a Greek word, 'dendrons' meaning tree like and 'meros' meaning units or parts [1]. Dendrimers are also called arborols [2] or cauliflower [3], or substrate polymer [4] or cascade molecule [5]. These are unique well controlled size and symmetric structure with ideally branching units and hence the resulting structure is monodisperse with no structural defects [6-21]. The preparation requires multistep reactions, tedious isolation and purification in each step for their perfect growth. On the other hand, hyperbranched polymers are closely related to highly branched macromolecules with significantly less regular branched structures that contain certain numbers of structural defects. However, they have almost equal potential for many applications as they have almost similar properties like dendrimers. Further, even in a natural symmetric branched architecture like a tree or a full forest there are certain defects and these irregularities generate versatility in such creations.

The most important advantage of these hyperbranched polymers over more structurally regular dendrimers is their simple preparation by single step or one pot processes of AB_X ($X \geq 2$) [21-22], $A_2 + B_3$ [23] and $A_2 + BB'_2$ [24], etc. types of monomers. This allows their large scale production, which makes less expensive and hence likely to have great potential for commercialization. The schematic two-dimensional representations of linear, low branched, crosslinked, star and highly branched dendrimers and hyperbranched polymers are shown in Figure 1.1.



Linear

Branched

Cross-linked

Star

Dendrimer

Hyperbranched

Figure 1.1. Schematic representation of linear, branched, cross-linked, star, dendrimer and hyperbranched polymer

1.2. Background

Before 1940, branched molecular structures had been considered to be responsible for the insoluble and intractable materials formed during polymerization [25]. The history of highly branched macromolecules can be dated to the middle of the 20th century, when P.J. Flory stated an unconventional scheme for polymer synthesis in

1952 [26]. This was theoretical concept of the synthesis of condensation polymers from multifunctional monomers (AB_X, $X \geq 2$) without gelation.

The practical synthesis of highly branched polymers was first reported by Vogtle and co-workers [3] in 1978, which involved the use of an aliphatic amine of AB_2 monomer to form a 'cascade' polymer. Even though, it can not be considered as a true dendritic polymer. Tomalia *et al.* [8] and Newkome *et al.* [2] simultaneously presented their first real dendrimers in 1985. After that a multitude of dendrimers such as poly(amido amine) [27], polyamides [28], polyethers [29], polyesters [30], etc. were synthesized. Highly branched polymer was first reported by Kricheldorf *et al.* [31] in 1982, even though the term 'hyperbranched' was first coined by Kim and Webster [32] in 1988. Ever since then, a wide variety of hyperbranched polymers have been reported in literature [33-46]. Due to their unique physical and chemical properties, and potential applications in various fields from drug-delivery to coating systems, interest in hyperbranched polymers is growing rapidly, as confirmed by increasing number of publications in each year (Figure1.2).

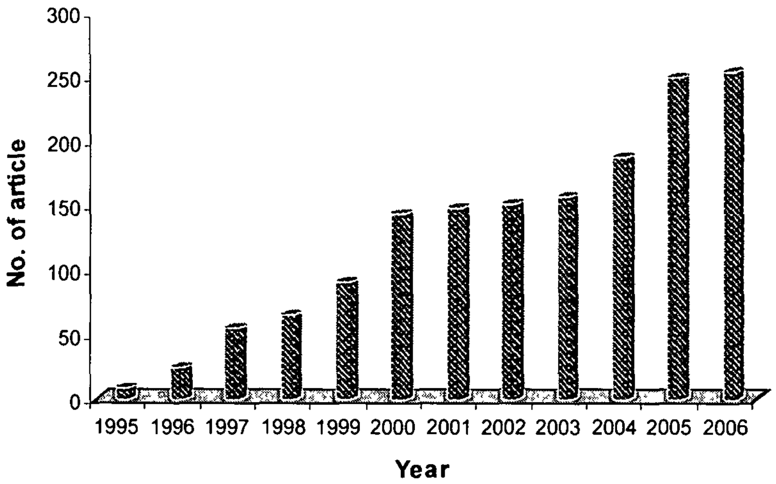


Figure 1.2. Scientific publication as a function of publication year searched by scopus (Elsevier) with hyperbranched polymer as a topic

1.3. Synthesis of hyperbranched polymers

Synthesis of hyperbranched polymer is much simpler compared to dendrimers as the former does not require protection and deprotection or multistep procedure like latter. Although there is a possibility of forming some defects in the structure by single step approach but it is more interesting because of it's less laborious and time consuming process.

1.3.1. Monomers

A variety of AB_X ($X \geq 2$ like AB_2, AB_4, AB_6 and AB_8), A_2 and B_3 monomers are used to synthesize different types of hyperbranched polymers. The structures of such monomers are shown in Table 1.1.

1.3.2. General techniques

The synthesis of hyperbranched polymer can be rationalized into two main categories. The first category contains techniques of the single monomer methodology (SSM), whereas the second one is double monomer methodology (DMM).

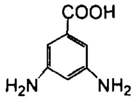
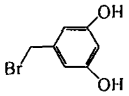
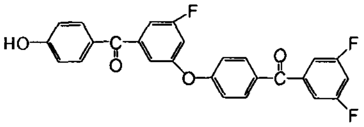
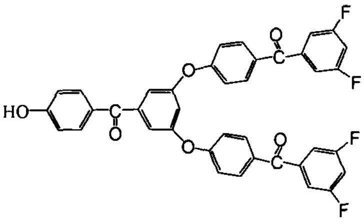
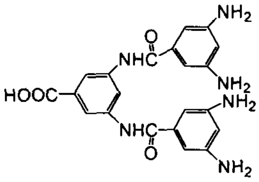
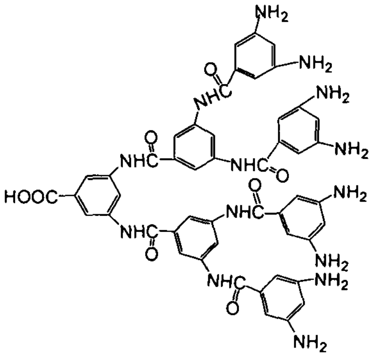
1.3.2.1. Single monomer methodology (SSM)

The SMM involves the polymerization of AB_X or a latent AB_X monomer. According to the reaction mechanism, the SMM category could be divided into four specific subcategories, viz. (i) polycondensation of AB_X monomers, (ii) self condensing vinyl polymerization (SCVP), (iii) self condensing ring opening polymerization (SCROP) and (iv) proton transfer polymerization.

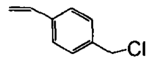
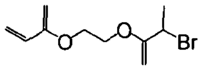
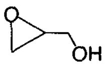
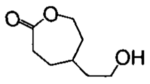
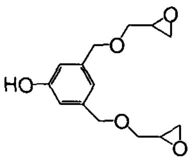
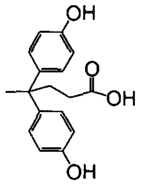
Polycondensation of AB_X monomers

In this polymerization process AB_2 type monomers are often used as starting materials because of relatively easier preparation compared to other similar monomers like AB_4, AB_6 and AB_8. As discussed by Flory [26], statistically it is impossible to have gelation caused by infinite network formation in the self-polymerization of AB_X type monomers. However, gelation may occur experimentally when undesired side reactions are involved in the polymerization process. These side reactions may also make the products insoluble in organic solvents. Gel formation can also be observed when intermolecular interactions like hydrogen bonding, and propagating molecules are strong enough to form three-dimensional networks. Dilution of the monomers in solution polymerization might be affected to avoid gelation caused by intermolecular

Table 1.1. AB_2, AB_3, AB_4, AB_8, etc. type monomers used for synthesis of hyperbranched polymers

Type	Monomer	Polymerization process	Polymer	Reference
AB_2		Self condensation	Aromatic polyamide	61
		”	Aliphatic aromatic polyether	40
AB_3		”	Poly(ether ketone)	50
AB_4		”	Poly(ether ketone)	50
		”	Polyamide	61
AB_8		”	Polyamide	61

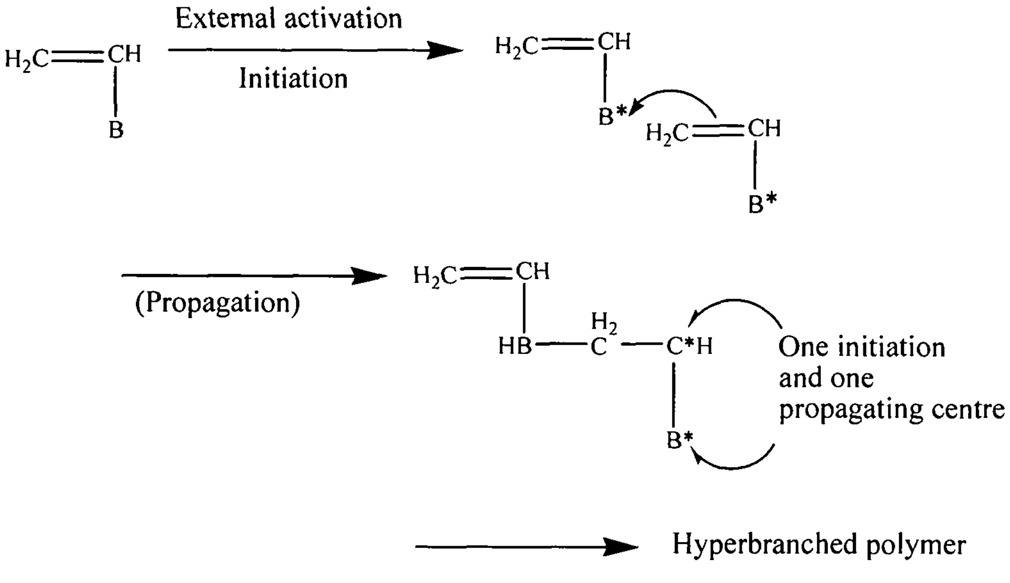
Continued

Type	Monomer	Polymerization process	Polymer	Reference
AB*		SCVP	Polystyrene	83
		"	Polyacrylate	71
Latent AB_x		SCROP	Polyglycerol	75
		"	Polyester	41
AB_2		PTP	Polyether	79
		"	Polyester	80

interactions. On the other hand, side reactions in early stage of the polymerization inhibit the formation of polymers with high molecular weight, especially when the 'A' functional group in the AB_X molecule is consumed by side reaction such as ring formation to form cyclic oligomers [37,47-49]. However, the step growth polycondensation route has been utilized extensively in the synthesis of a diverse range of hyperbranched polymers including hyperbranched polyphenylenes [21, 32-34], polyethers [40,50-52], polyesters [39,53-56], polyamides [57-61], polycarbonates [62], polyamine [63], etc.

Self condensing vinyl polymerization (SCVP)

Monomers (AB*) containing one vinyl group and one initiating moiety gives hyperbranched polymers through self condensing vinyl polymerization (SCVP), which was invented by Frechet and co-workers in 1995 [43]. In this reaction, the B group of original AB monomer is activated to generate the initiating B* site. The activated species could be a radical, cation or even a carbonium ion. B* initiates the propagation of the vinyl group A in the monomer to form a dimer with a vinyl group, a growth site and an initiating site. The dimer can function as an AB_2 monomer and undergoes further polymerization to yield the hyperbranched polymer (Scheme 1.1). On the other hand, SCVP has some disadvantages like side reaction may lead to gelation, the molecular weight distribution usually very broad and low degree of branching. In this process living/controlled polymerization systems are also included in order to avoid cross linking and gelation caused by chain transfer or dimerization reaction [64-66]. Hyperbranched polystyrene [43], polymethacrylate and polyacrylate [67-72], etc. are a few examples of synthesized hyperbranched polymers by this approach.



Scheme 1.1. Synthesis of hyperbranched polymer by SCVP approach

Self condensing ring opening polymerization (SCROP)

The third category of SMM is self condensing ring-opening polymerization of latent AB_X type monomers. This was also termed as "multibranching ring opening polymerization" by Suzuki in 1992 [73]. The monomer itself does not contain any branching point and branching points are generated through propagation reaction. Therefore, the monomer can be recognized as latent AB_X monomer. Branching units are generated during the ring opening reaction, while the starting AB monomers do not contain branching points. The polymerization is initiated by the addition of proper initiators to generate active sites, which may allow to control over the molecular weight and its distribution of the resulting polymers. Hyperbranched polyamines [73,74], polyethers [44,75-77], and polyesters [41,78], etc. have been prepared by this approach.

Proton transfer polymerization (PTP)

The last category of single monomer methodology is proton transfer polymerization. Hyperbranched polymers with epoxy or hydroxyl end groups [79-81] and hyperbranched polysiloxanes [82], etc. have been prepared by this approach.

1.3.2.2. Double monomer methodology (DMM)

The other main category is double monomer methodology (DMM) in which direct polymerization of two types of monomers or monomer pairs generates hyperbranched polymers. DMM can be divided into two main subclasses based on the selected monomer pairs and reaction pathways. The classical one is the polymerization of A_2 and B_3 monomers, which is generally called as "A_2+B_3" approach. Second one is couple monomer methodology (CMM), where the specific monomer pairs generate *in-situ* AB_X intermediate due to the non-equal reactivity of different functional groups.

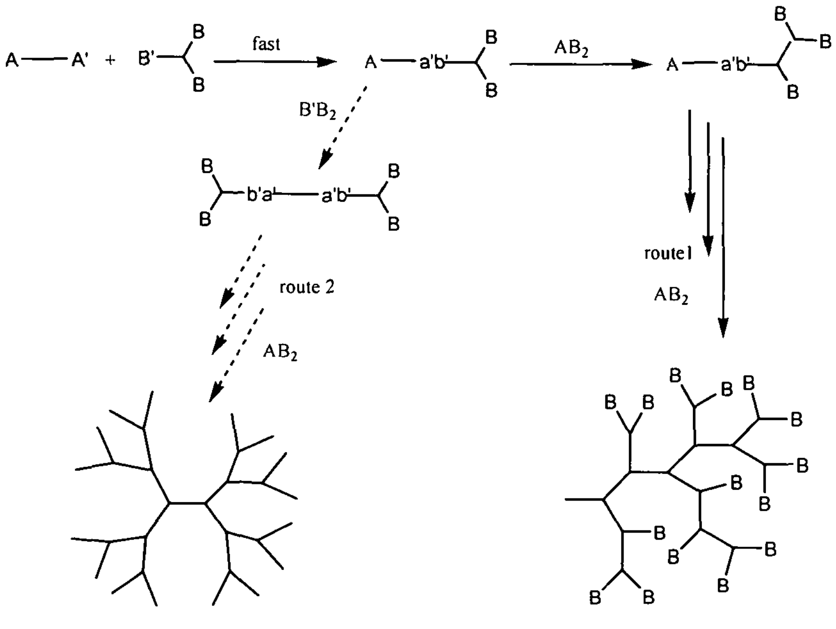
Couple monomer methodology (CMM)

Choice of suitable monomer pair is the most important step for the molecular design of a hyperbranched polymer using CMM. The basic principle of CMM is shown in Scheme 1.2. In monomer AA′, if reactivity of A is identical to A′ and B is equal to B′, then CMM is same as "A_2+B_3" approach. It is anticipated that the chance of cross-linking will be minimized if an asymmetric monomer AA′ or BB'_2 is used. If A′ is of higher reactivity than A, CMM presents as "AA′+B_3", whereas if B′ is more active than

B, then CMM presents as "A_2+$B'B_2$" polymerization systems. Using this approach Gao *et al.* reported a large number of hyperbranched polymers [84-87].

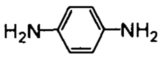
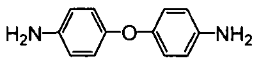
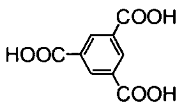
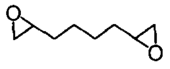
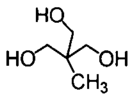
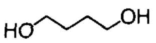
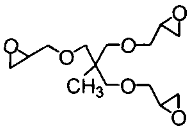
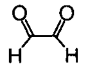
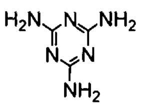
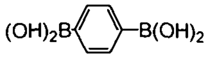
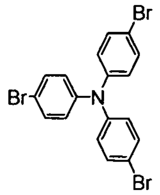
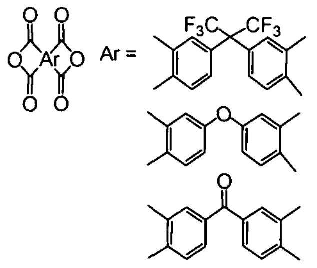
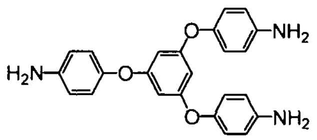
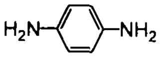
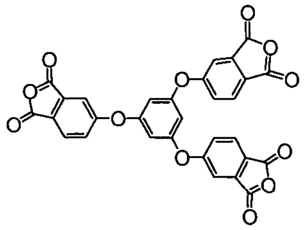
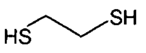
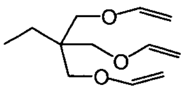
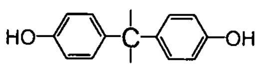
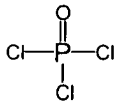
A_2+B_3 approach

As a consequence of the infrequent commercial availability of AB_X type monomers, studies have begun to focus towards the polycondensation of A_2 and B_3 monomers. The first successful example of hyperbranched polymer via the "A_2+B_3" approach was reported by Kakimoto [45], although the method had been explored to prepare cross-linked polymeric materials more than a century before [88]. The synthesis involved the reaction of diamine (A_2) and trimesic acid (B_3) to obtain hyperbranched polyamide. It is well known that direct polycondensation of A_2 and B_3 monomers generally results gelation [89-93]. Thus the crucial points of this approach are to avoid gelation and to obtain soluble three-dimensional macromolecules. In Table 1.2 lists the A_2 and B_3 type monomers reported in recent years. There have been some notable examples in literature. Polyamides [45], polycarbonates [94], polyureas [95], polyethers [96], etc. are obtained by this approach.



Scheme 1.2. Basic principle of "AA'+$B'B_2$" approach

Table 1.2. The structures of A_2 and B_3 type monomers used in $A_2 + B_3$ approach

A_2	B_3	Reference
 		49
		46
		97
		98,99
		100
		101
		102
		103
		104

1.4. Modification of hyperbranched polymers

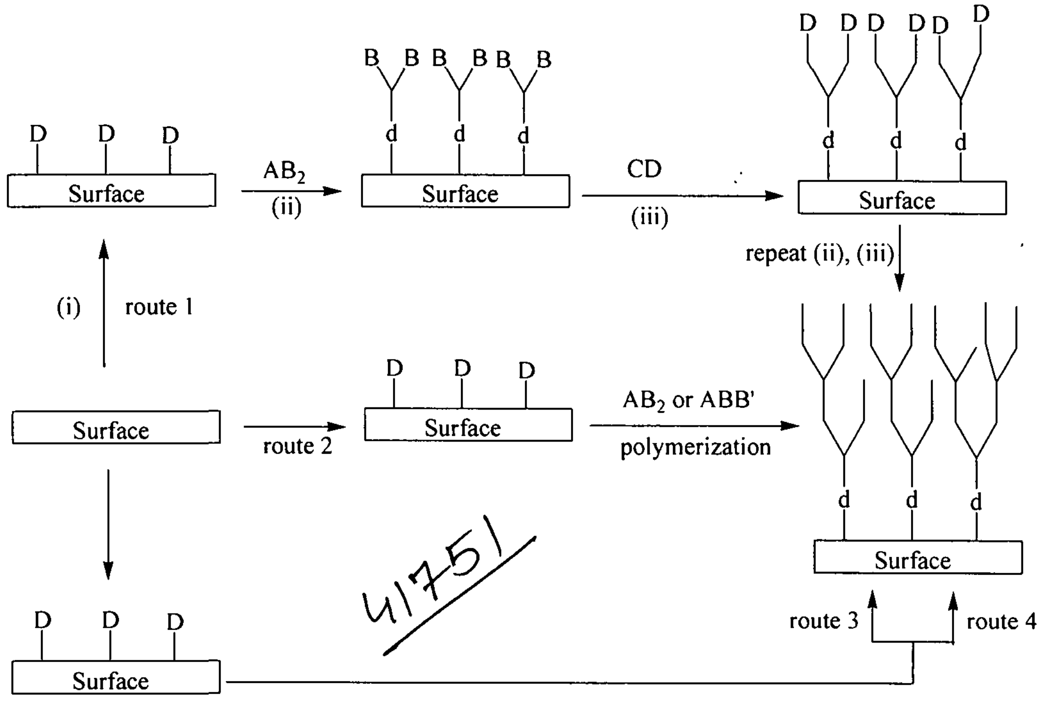
The properties of hyperbranched polymers are often affected by the nature of the backbone and the chain end functional groups, degree of branching, chain length between branching points, and the molecular weight and its distribution. Hyperbranched polymers are often modified to tailor their properties for uses in some specialized purposes. Based on the highly branched architecture and the large number of terminal functional groups of hyperbranched polymers, six modifications are generally adopted. These are (i) end-capping with short chains or special moiety containing organic molecules, (ii) terminal grafting via living polymerization, (iii) growing hyperbranched polymers on the surface or grafting from/onto the surface, (iv) hypergrafting to obtain hyperbranched polymers with a linear macromolecular core, (v) blending and (vi) crosslinking.

The large number of functional end groups attached to the linear and terminal units of hyperbranched polymers can be conventionally end-capped with organic molecules. In the end capping process three major purposes are emphasized: (a) to exclude the influence of some functional groups on the measurement of molecular weight, (b) to investigate the effect of terminal groups on the properties of hyperbranched polymers and (c) to fabricate novel functional polymeric materials. Many experiments demonstrated that the nature of the terminal functional groups strongly influenced T_g, solubility and even T_d of the hyperbranched polymers [105]. Kim *et al.* [22] investigated the influence of end groups on the T_g of hyperbranched polyphenylene. T_g can be varied over a wide range from 96 ^{O}C to 223 ^{O}C by the proper modification of hyperbranched polymers without any change in the backbone. Similarly, the fluoro-terminated hyperbranched poly(ether ketone)s [50] made from AB_2, AB_3, AB_4 monomers differ in DB (0.49, 0.39, 0.71 respectively), but have the same T_g (162 ^{O}C). It seems that several factors such as rigidity, polarity, length and steric hindrance of the terminal functional groups can influence T_g of the resulting polymers. The thermal and mechanical characteristics of hyperbranched polymers can be conventionally manipulated via the end capping method on the basis of relationship between terminal group and property [106]. It is found that solubility of the hyperbranched polymers is dependent on both the nature of the terminal functional groups and its branched structure. The polymer with polar end groups is soluble in polar solvents and the non-polar terminated polymer is soluble in apolar solvents. For examples, fluoro-terminated hyperbranched polymers [50] is sparingly soluble in DMF and totally insoluble in DMSO and aqueous solutions, while the phenolic terminated polymer is soluble in DMF, DMSO, and in aqueous KOH solutions.

Terminal grafting can also be called "grafting form" [106]. Grafting polymers from macromolecular initiators prepared by modification of the functional groups of hyperbranched polymers affords core-shell multi-arm star polymers or hyperstars [107-114]. Three polymerization methods such as, anionic, cationic and living/controlled radical polymerizations have been adopted to fabricate the hyperstars in such cases. Some properties such as polarity, solubility, flexibility of the hyperbranched scaffolds, can be conventionally tailored through thermal grafting modification. Most of the hyperbranched cores used for the above are polyols.

The method to modify the specific surface or interface with hyperbranched polymers or to graft hyperbranched polymers onto the surface is denoted as "surface growing" [106]. The grafted hyperbranched polymers are typically anchored to a surface by one end of the polymer chain, such that the polymer can extend away from the surface [115]. Surface growing is an efficient strategy to fabricate inorganic/organic-hyperbranched polymer hybrid materials to improve the properties of surface objects. Four routes have been developed in these modifications and functionalizations as shown in Scheme 1.3. Route I can be called as "graft on graft" approach. The reaction procedure is similar to the step-by-step synthesis methodology like dendrimers. Functional groups (D) are firstly introduced onto the surface, followed by reaction of AB_2 monomers with D groups and then reaction with CD monomers. Repeated reaction between AB_2 and CD grows hyperbranched polymers with numerous functional groups onto the surface. Route II is "grafting from" technique of surface initiating polymerization in which the initiating functional groups are incorporated onto the surface and then, initiate the polymerization of AB_2 or latent AB_2 (ABB′) monomers. In route III, "grafting to" approach is used, where prepared hyperbranched polymers are covalently linked to a prepared surface. And route IV, which is called as "surface adsorption", where hyperbranched polymers are directly assembled or absorbed onto the surface. A series of solid matrixes such as gold (Au), silica (SiO_2), silicon wafer (Si), aluminaium (Al), porous alumina (Al_2O_3), C_{60}, carbon black, polyethylene (PE), polypropylene (PP), and chitosan powder (CP), have been adopted as a supporting substrates for functionalized hyperbranched polymers [116-127].

Hypergrafting represents the grafting of hyperbranched macromolecules to a multifunctional polymeric core and the resulting hybrid material is called "hypergrafted polymer" [106]. If the core used is a linear polymer, a new sort comb-like polymer cylinder is formed. Frechet *et al.* [128] prepared hypergrafted polystyrene (PS) and its copolymers that resulted to PS cylinders. Although the literature published on hypergrafted polymers is limited, this new class of polymers is likely to receive more attention and be widely explored.



Scheme 1.3. Growth of hyperbranched polymer on a surface

Due to the low melt viscosity, hyperbranched polymers offer application as melt modifiers or blend components. The modification of hyperbranched polymers by bleding have been adopted for different purposes. Kim *et al.* (21) blended hyperbranched polyphenylene with polystyrene. The resulting blends exhibited improved thermal stability and a reduced melt viscosity at high temperature and high share rates. Blends of hyperbranched polyesters [129] with different linear polymers such as polyesters [129, 130], polyamides [129], polycarbonate [129], poly(vinyl chloride) and poly(vinyl acetate) [131] have been studied with regard to compatibility and change in mechanical properties. Khadir *et al.* [132-133] prepared an absorbescent polystyrene and blended it with linear polystyrene and poly(methyl methacrylate). The properties of these blends were changed with arm length of the absorbent polymers. PP and HDPE were widely used as dye carriers by blending with hyperbranched polymers [134-135]. In tubular film blowing process of LLDPE, hyperbranched polyester successfully acted as a process aid [136]. Further, hyperbranched polymers have been used as compatilizers [137], dispersers [138], etc.

Again, a large number of reactive groups are predominantly at the surface of the structure, upon reaction, in combination with the dense structure, make the hyperbranched polymers more readily accessible for reaction. Thus, they are particularly applicable to almost any crosslinking reaction. Characteristics feature of all hyperbranched polyesters, polyethers, polyamines are their very low viscosities, which are quite advantageous with respect to epoxy processing. Applications of hyperbranched polymer in epoxy resin have extensively been studied [139-143]. Also hyperbranched polymer was used as high performance thermoset for bismalimide [144-145] and vinylester-urethane hybride resin [146-147] and other thermoset systems.

1.5. Characterization

Characterization of hyperbranched polymer cannot be easily carried out because of its highly branched structure with large number of functional end groups. Also possibility of structural defects of the polymer is causing complexity and broad variety in its final structures. However, hyperbranched polymers are being characterized by the conventional techniques for determination of different physical properties like solubility, viscosity, specific gravity, etc. The chemical structures are characterized by FT-IR, NMR, UV-visible spectroscopies, etc. and molecular weight is determined by size exclusion chromatography (GPC analysis) and mass spectrometry. The chemical compositions can be known from mass spectrometry and elemental analysis. Some special elements like sulfur and halogens are determined by the heteroatom analyzer using the standard Schoniger oxygen combustion method. Crystallinity and morphology of some special liquid crystalline hyperbranched polymers are characterized by X-ray diffractometer, polarized optical microscopy, scanning electron microscopy, etc. The thermal behavior of such polymers can be predicted by TGA, DTA and DSC studies. The optical and electrochemical properties are determined by fluorescence spectrophotometer, cyclic voltammeter (CV), etc.

1.5.1. Structural elucidation

In order to elucidate the exact structure of highly branched macromolecules the determination of 'degree of branching' and 'nature and number of end groups' are paramount along with conventional characterization.

Generally hyperbranched polymers are characterized by the conventional spectroscopic techniques to investigate the chemical structure. UV-visible spectroscopy is largely used to determine the functional groups present in the structures of the dendritic polymers like linear polymers. It is not only used to determine the presence of chromophoric groups or conjugation in the hyperbranched structures but also largely used to characterize the photophysical properties of the photoactive hyperbranched polymers. Fluorescence spectrophotometer is also a very useful tool for the latter case.

FT-IR technique is largely used [148] to determine the functional groups like ether, carboxyl group, ester group, amine group, hydroxyl group, unsaturation, aromatic ring, etc. present in the structure of the hyperbranched polymers. IR spectroscopy is also utilized for the determination of structural defect in some hyperbranched polymers. Also, this technique is used to monitor the progress of *in-situ* polymerization [85].

NMR can also play an important role to understand the actual structures of hyperbranched polymers. In general, ^{1}H-NMR indicates the presence of different types of chemically equivalent protons [148,149] present in the structures. ^{13}C-NMR technique is utilized [148,149,150] to find out the presence of chemically different carbon atoms of aromatic, aliphatic, unsaturated, saturated hydrocarbons, ester, ether or carboxyl group, etc. This spectroscopic technique is also used for determination of degree of branching (DB) of hyperbranched polymers as discussed in the next page.

Elemental analysis such as CHN analyzer, hetroatomanalyzer, etc. are used to determine the percentage of elements present in the structure, However, in elemental analysis of hyperbranched polymers, a slight variation is generally observed from the theoretical values based on ideal dendritic structure without any defect [63,96].

X-ray and polarizing light microscopes support to study the arrangement of molecules into liquid crystalline hyperbranched polymers. As the crystallinity of material is due to the regular packing of atom or molecules in three dimensions [151], the arrangement of molecules in hyperbranched polymers is generally not in regular fashion and hence the hyperbranched polymers are amorphous in nature, so these techniques are generally not necessary to be used.

The thermal characterizations of hyperbranched polymers are carried out by TGA, DSC and IGA techniques. By TGA and IGA techniques along with the thermostability of the polymers in different environment, the pattern of degradation, kinetics of degradation, char residue, etc. are also determined [152, 153]. Whereas DSC technique is most widely used to get the information [152, 153] about the phase change, different chemical changes like degradation, cross-linking, etc. Kinetic of cross-linking reactions can also be studied using DSC technique.

Fluorescence technique plays an important role in studies of various interactions such as hydrogen bonding and hydrophobic association of photoactive hyperbranched polymers. Some basic problems including molecular configuration, aggregation, micelle formation, phase transition, and interfacial and surface properties in solutions of such hyperbranched polymers can also be studied by this technique [154].

The molecular weight and its distribution of polymers are determined by GPC technique. In this technique macromolecules are separated according to their size in organic solvents [153]. The GPC has been used for the calculation of radius of gyration, hydrodynamic radii, polymer average molecular weight and its distribution along with Low Angle Laser Light Scattering (LALLS) and intrinsic viscosity measurement. However, it has some drawbacks, as here only approximate molecular weights of the hyperbranched polymers have been determined by comparing with polystyrene standard but the relationship between hydrodynamic volume and molecular weight is not the same for all the polymers. So to get the exact average molecular weight and its distribution mass spectrometry has been used. In this case the mass measured is more accurate because it does not compare the polymer being measured to anything.

Degree of branching

As mentioned that dendrimers are well defined fully branched polymers and hence the resulting structure is monodisperse with no structural defects. However, single step polymerization of hyperbranched polymers resulted less regular branched structures that contain certain numbers of structural defects. As a result the hyperbranched polymers have three different types of repeating units (Figure 1.3) namely dendritic unit (D) with no unreacted group, terminal units (T) with two unreacted groups and linear units (L) with one unreacted group. Thus without knowing the "degree of branching" (DB), it is very difficult to determine the actual structure of hyperbranched polymer. In 1991, Frechet described the degree of branching as a factor to explain the structure of hyperbranched polymer [39] by the following equation.

$$DB = \frac{D + T}{D+T+L}$$

where D, T and L represent the number of dendritic, terminal and linear units respectively. DB can be used as an indicator in order to compare the structure of hyperbranched polymers with the corresponding dendrimer. The degree of branching of a perfect dendrimer is equal to 1, while a linear polymer is 0. However, most of the hyperbranched polymers reported in literature have actually DBs close to 0.5. Frey has reported a modified definition of DB that is based on growth direction of hyperbranched polymers [155] by the given equation.

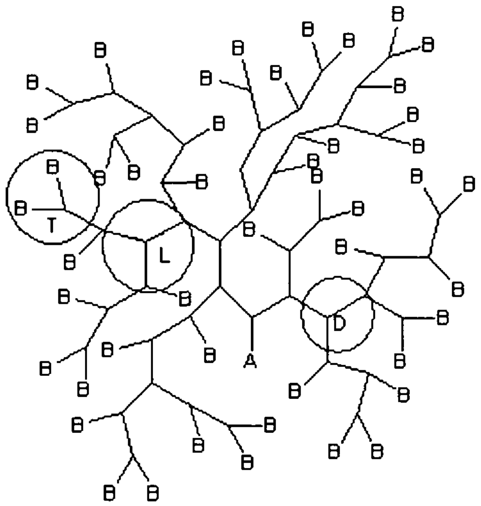


Figure 1.3. Schematic representation of a hyperbranched polymer with dendritic (D), linear (L) and terminal (T) units.

$$DB = \frac{2D}{2D+L} = \frac{D + T - N}{D + T + L - N}$$

where N is the number of molecules and D, T and L are same as earlier [39].

NMR spectroscopy is a powerful tool to determine the DB of hyperbranched polymers. In addition to ^{1}H-NMR spectroscopy, ^{13}C-NMR, ^{15}N-NMR, ^{19}F-NMR and ^{29}Si-NMR spectroscopies have also been used to determine the DB for various hyperbranched polymers [156-157]. When the polymer is composed of degradable linkages such as esters or carbonates, the DB can be calculated by the quantitative analysis for the products after degradation [62,157]. The chain ends are chemically modified and the hyperbranched skeleton is fully degraded by hydrolysis. The degradation products are identified using capillary chromatography.

It is vital importance to understand how the degree of branching affects the properties of hyperbranched polymers. The higher degree of branching, the polymer is more dendritic in nature and also exhibits the higher solubility and low viscosity.

1.6. Properties

One reason for the emerging interest in hyperbranched polymers is their unusual properties compared to the conventional linear analogs with regard to their wide range of applications. Although structure-property relationship is very useful in this regard, but still there is lack of proper investigation for this novel class of materials. This is mainly because of complexity that arises due to defects in the structure of the hyperbranched polymers. However, numbers of studies that explore the physical, rheological, thermal and mechanical properties of hyperbranched polymers are increasing steadily and also these studies are gaining considerable attention in recent days. On the other hand, because of their unique structural characteristics, new properties are resulted that creates new awareness for their different applications.

1.6.1. Physical properties

The physical properties of hyperbranched polymers are of key importance with respect to their implementation in various applications. The unique architectural molecules, which composed of successive branching units, offer some interesting properties of these polymers.

One of the most interesting properties of hyperbranched polymer is their lower solution and melt viscosity compared to their linear analogs of equivalent mass [159]. The low viscosity implies that hyperbranched polymers are not entangled due to their more compact globular like structure especially at high molecular weight [160]. The general relationship between intrinsic viscosity and molecular weight is shown in Figure 1.4. From the plot, it is clearly observed that both dendrimers and hyperbranched polymers exhibit a skewed Gaussian distribution relationship. This relationship can be related to branched structure of these macromolecules and hence do not obey the Mark-Houwink-Sakurda equation ($[\eta] = KM_w^{\alpha}$). It is well known that for linear polymers, the molecular weight (M_w) increases with the increase in intrinsic viscosity (η). Molecular weight of the dendritic polymers generally increases cubically, whereas their mass increases exponentially during the generation growth [161], thus the relationship is observed as shown in the Figure 1.4. For hyperbranched polymers, the slope is smaller than that of linear polymers although the intrinsic viscosities do not increase with increase in molecular weight. This may be due to their non-entangled and globular structures. Generally α value lies between 0.5 to 1.0 for randomly coiled linear polymers, and less than 0.5 for dendritic polymers, which suggests that they exhibit a globular shape in solution. Furthermore, the melt viscosity for linear polymers increases linearly up to a critical molar mass, where the viscosity drastically increases. This phenomenon is a consequence of the entanglement of polymer chains and is not observed for dendrimers or hyperbranched polymers. In addition for the hyperbranched polymers, higher the degree of branching lower will be the viscosity.

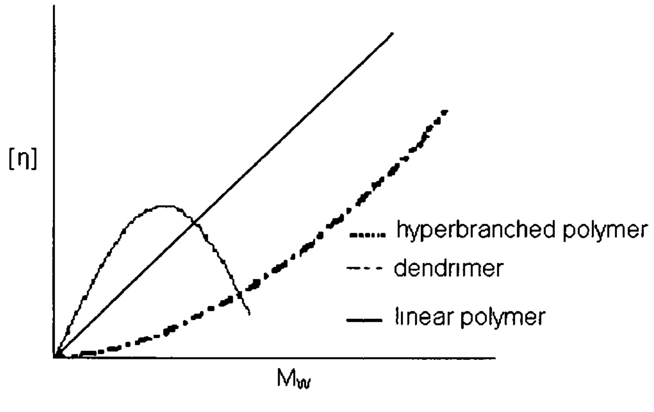


Figure 1.4. Schematic plots for the relationship between M_W and $[\eta]$

Another most important property of hyperbranched polymers that was reported to differ from those of linear analogs, was the high solubility induced by highly branched structure. This high solubility of hyperbranched polymers is mainly due to the presence of large number of surface functionality, globular shape and non-entangled structure. Also highly polar end groups such as hydroxyl, amine, carboxylates, etc. may make the polymers even water soluble. It has been reported that hyperbranched rigid aromatic polyamides are soluble in highly polar organic solvents even if the linear are insoluble in most of the common organic solvents at room temperature [28,162]. Magnusson *et al.* [163] studied the effect of solubility on DB, the higher degree of branching indicates the higher solubility of the hyperbranched polymer. The uncontrolled structures of hyperbranched polymers show no crystalline packing and definite cavities in the structures, which allow easy penetration of a solvent.

The density is a function of the molecular structure of the individual molecule and the way they packed. The hydrocarbon with no heavy atom and amorphous nature generally make the polymers with low density [164].

1.6.2. Mechanical and rheological properties

To utilize new material in any application, the evaluation of mechanical and rheological properties is very much essential. The materials must possess suitable mechanical properties and processing characteristics in order to find an appropriate use. In general the rheological property of hyperbranched polymer shows Newtonian behavior in the molten state, indicating a lack of entanglements for these polymers. The non-entangled state imposes rather poor mechanical properties and brittle polymer. The large amount of branching also makes most of these polymers amorphous in nature. However, when HBPs are used as toughening agents in resins, then enhanced flexibilities and dramatically increased toughness without affecting other properties, such as hardness and modulus have been observed [165]. The thermo-mechanical properties of the resin depend on the shell chemistry of hyperbranched polymers. Therefore, different mechanical properties have to be expected when HBPs with different chemistry are used. Moreover, a fully crosslinked HBP with large number of functionality can achieve a high crosslinking density and thus a high stiffness can be obtained. The melt behavior has been shown to be greatly affected by the structure of the end-groups where an increasing in the polarity of the end groups can raise the viscosity in several orders. It has also been found that hyperbranched polymers with different DBs differ in their rheological behavior [166]. Hyperbranched aliphatic polyethers with low DBs were found to be semicrystalline, while with high DBs were amorphous in nature and had a low melt viscosity [163].

1.6.3. Chemical properties

The hyperbranched polymers exhibit more versatile chemical properties compared to their linear analogs [167]. The spherical shape, low viscosity and high solubility, the presence of large number of functional groups at the periphery, make the hyperbranched polymers readily accessible to other substances. As a result of which they exhibit enhanced compatibility with other linear polymers and hence the mechanical properties such as initial modulus, tensile strength and compressive modulus of the linear polymers reflect the compact highly branched structure of these macromolecular architectures [160]. Also these highly branched macromolecules have a large number of functional groups and an interior that provide space as well as a microenvironment suitable for host guest chemistry [168-169] and metal nanoparticle synthesis [170-173]. Dendritic micelles are generally unimolecular and do not suffer from even the low CMC that the linear polymer based micelles do [174].

1.6.4. Thermal properties

The thermal properties of the polymers are highly important for their end application, as these properties are highly sensitive to change in temperature. The thermal stability of hyperbranched polymers is related to different factors such as chemical structure, composition, linkages, molecular weight, intra/inter molecular forces, etc. As all these factors are almost similar both for hyperbranched polymer and their linear analogs, so there is as such no difference in their thermal properties. Glass transition temperature (T_g) is one of the most important properties that has been reported for most of the hyperbranched polymers. It is demonstrated that the glass transition temperature is a function of structure, the number and nature of end groups, crosslinking, branching points, etc. For HBPs the glass transition temperature is lowered by the increasing number of end-groups, while it increased by the increase of number of branch points and the polarity of end groups. The glass transition was found to be greatly affected by the nature of the end groups and the internal monomer units [175-176]. For example, aliphatic polyester has a much lower T_g than an aromatic one

[177]. Kim and Webster [21] suggested that the glass trangition temperature of HBPs is influenced by the translational motion of molecule rather than the segmental motion. The study also showed that the properties of HBPs mostly depend on the chain length between the branching points rather than the molecular weight.

1.6.5. Electrical and optical properties

For fabrication of high performance electroluminescent (EL) devices, development of new materials with high performance and excellent properties in efficiency, stability and processability is of vital importance. Fully conjugated polymers are usually insoluble and infusible and not processable once formed, thus their application is greatly limited [178]. By introducing the flexible non-conjugated spacers into the backbone, the conjugated length of the conjugated polymers can be effectively tailored and the processability of aromatic conjugated polymers can be achieved [179], but it increased the band gap and generates a blue shifted emission spectrum. Recently, electroactive and light-emitting hyperbranched polymers are interesting for developing efficient electroluminicient devices for displays and other photonic devices, due to their synthetic simplicity, good solubility, and high fluorescence quantum yields [180-181]. Since highly branched and globular features can reduce or even eliminate strong intermolecular interaction and aggregation and hence improved solubility. The light emitting diodes made of three-dimentional polymers causes the materials to form good quality of amorphous films and to improve thermal stability and emission efficiency [182].

1.6.6. Flame retardant property

As most of the polymer are organic in nature with often high hydrogen to carbon ratio so they are combustible. Therefore considerable attention has been paid in controlling the inherent flammability of common polymer. The type of flame retardant and the quantity needed to meet the specific objective depend on the characteristics of the polymer. However, the addition of large quantity of a flame retardant may adversely influence the other properties of the base polymers and also may create processing problem. It has been found that linear polymer with halogen/nitrogen/sulfur/metal/phosphorus, etc. as special elements shows very good flame retardant characteristic [183]. As hyperbranched polymers have good compatibilizing capability with other linear polymers, so it is expected that hyperbranched polymers with similar special elements or linkages with high carbon to hydrogen ratio may also exhibit excellent flame retardant behavior. Again, due to lower viscosity of hyperbranched polymers compared to their linear analogs, they may also help in processing of the base polymer.

1.7. Present status of hyperbranched polymers

It is already discussed that the tedious and complex multistep synthesis of dendrimers results in expensive products with limited use for large scale industrial applications. For many applications, where exact structural perfection is not required, hyperbranched polymers can be the best alternatives. Unlike dendrimers, hyperbranched polymers with comparable properties can be easily synthesized by one-pot polymerization technique and hence they represent economically promising materials for large scale production. Few companies have already been produced commercially available hyperbranched polymers in large scale (Table 1.3).

1.8. Applications

The novel physical and chemical properties such as globular and branched structures, lack of interchain entanglement, amorphous morphology, high solubility in common organic solvents, etc. of hyperbranched macromolecules render them as ideal candidates for uses in wide range of applications. As hyperbranched polymers exhibit low melt and solution viscosities and good solubility [184-185], so they are useful as resins and coating materials. It has been used as binder for various coatings such as powder coatings [186], high solid coatings [187], and flame-retardant coatings [188], etc. The most widely studied commercially available HBPs in the field of coating are Boltron^{TM} (hyperbranched aliphatic polyesters) [186,189] and Hybrane^{TM} [hyperbranched poly(ester amide)s] [167]. For the purpose of UV-curing, the HBPs are generally end capped with methacrylate or acrylate groups [187,188,189]. Resin based HBPs are lower viscosities and higher curing rates than those of linear unsaturated polymers. The lack of mechanical strength for thermoplastic hyperbranched polymers make them more suitable as additives. Based on their unique properties, hyperbranched polymers can be applied as tougheners for thermosets [190-192], crosslinkers, adhesive

Table 1.3. Some commercial hyperbranched polymers and their manufacturers with potential applications

Commercial name	Polymer type	Manufacturer company/ country	Application field
Hybrane^{TM} i) Hybrane^{TM}-H1200 ii) Hybrane^{TM}-H1500 iii) Hybrane PS2550	Poly(ester amide)	DSM Fine chemicals / Netherlands	Extractive distillation and solvent extraction Blend component
Boltron^{TM} - Hx i) Boltron^{TM}-H20 ii) Boltron^{TM}-H30	Aliphatic polyester	Perstorp Ltd/ Sweden	Extractive distillation and solvent extraction Process aid
Polyimine®	Poly(ethylene imine)	BASF AG/ Germany	Liquid printing ink
Polyglycerol®	Aliphatic polyether	Hyperpolymers GmbH/ Germany	Biomedical

agents [143,193,194], compatilizers [195], process aids, etc. [196] and blend components [136,142,197,198]. The effects of hyperbranched polymers on the curing behavior of tetrafunctional epoxy resin were investigated [143] and these materials were widely used as high performance composite matrices in aerospace/aircraft industries.

Because of good solubility and excellent processability aromatic conjugate hyperbranched polymers are widely studied as device application [199-201]. The hyperbranched macromolecular structure favors exciton confinement and decreases intrachain and interchain exciton annihilation, thereby improving EL efficiency [202]. It has been reported that coumarines (2H-1-benzopyran-2-ones) containing HBPs are widely used as laser dyes and light emitters because of their good photostability and high quantum yield of photoluminescence [203]. Compared with their linear analogs, the light harvesting hyperbranched polythiophene have a much broader distribution of conjugation lengths, which makes them potentially better light absorbing materials for efficient photovoltaic as well as light emitting devices [204]. In addition to p-π and π-π conjugation systems described above, a new structural class of σ-π conjugated hyperbranched poly(2,5-silylthiophenes) has been reported [205].

Compounds possessing donor and acceptor chromophores may exhibit non-linear optical (NLO) properties. A hyperbranched polymer with 4-(2-cyano-2-methoxy-carbonylvinyl) aniline may be used as a second order NLO chromophore [206]. Hyperbranched poly(triphenyl amine) [207] is used as a conducting polymer.

Hyperbranched polyamine [63] showed magnetic properties similar or superior to that of its linear analog along with better proceesability because of its higher solubility compared to latter.

A solid polymeric electrolyte should meet the requirements of amorphous nature, high solvating power for appropriate ions, good ion transport and electrochemical solubility. It is well known that oligo(ethylene glycol) segments satisfy the last three requirements, and hyperbranched polymers are usually amorphous. Thus, hyperbranched macromolecules possessing ethylene glycol (EG) chains have been used as novel polymeric electrolytes or ion-conducting elastomers. Hawker and coworkers [208] first prepared hyperbranched poly(ether ester)s using EG segments with good yield and high molecular weight. The influences of terminal groups, the length of the EG unit, the composites of the linear polymeric electrolytes blended and the addition of filler on properties of the hyperbranched polymeric electrolytes have profound effets on their ultimate applications [208-212]. Composite polymer electrolytes based on PEO, HBP, $BaTiO_3$, and $LiN(CF_3SO_2)$ salt were fabricated, and used as the electrolyte for all solid state lithium polymer batteries [212].

Because of the three-dimentional character of hyperbranched macromolecules, some guest molecules can be encapsulated into their interior cavities. Therefore, hyperbranched polymers and their derivatives can be used as nanomaterials for host-guest encapsulation and the fabrication of organic-inorganic hybrids, and even directly used as nanoreactors for some chemical reactions [106]. The hyperbranched polyglycerols (PGs) with a hydrophilic core and a hydrophobic shell were used as amphiphilic materials [213]. Water soluble dyes such as Congo red, bromophenol blue and rose Bengal can be encapsulated irreversibly into these amphiphilic core-shell nanocapsules via phase transfer from the water phase to the organic phase. Comparison of these results with those obtained from the linear analogs suggests that the hyperbranched topology plays a crucial role in the supramolecular encapsulation [214].

Furthermore, $PdCl_2$ or $Pd(OAc)_2$ were successfully encapsulated into nanocapsules based on hyperbranched PG [215]. Hyperbranched polymers can also be utilized in nanoimprint lithography [216].

Because of low cost and well-defined structure with multifunctional terminal groups and narrow polydispersity of hyperbranched aromatic polyamides are used as biomaterials for protein immobilization [217]. It was observed that a hyperbranched poly(amino ester) with terminal amino groups is minimally toxic and shows relatively high trransfection efficiency for DNA [218]. Pyrene-labeled hyperbranched poly(sulfone amine) with hydrophobic shell and hydrophilic core can be used as a micelle [219]. Both thermotropic liquid crystalline hyperbranched polyesters [220] or polyethers [51] and lyotropic liquid crystalline hyperbranched polyamides [61] have been used as supramolecular materials.

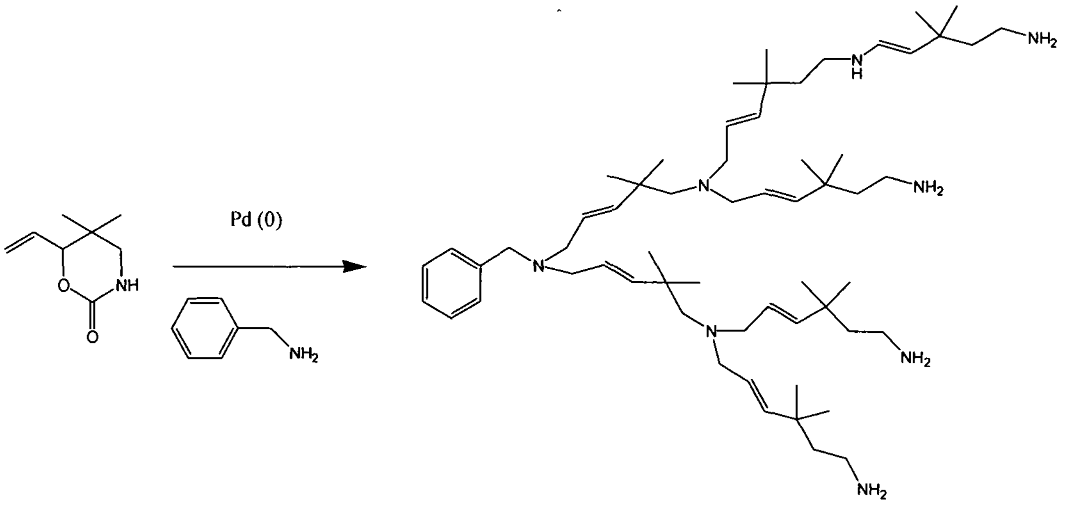
During the last decade, a number of research groups started focusing on hyperbranched polymer membranes [221]. Among the studies, the uses of hyperbranched polymers as high-performance gas separation membranes are particularly promising [222,223]. In general, polyamide membranes are of considerable interest in gas separation applications due to their high gas selectivity, low crosslinking density and excellent mechanical and thermal stability. The organic-inorganic hybrid membranes based on phosphoric acid and hyperbranched aliphatic polyesters were used as electrolytes for polymer electrolyte membrane fuel cells [224].

Liquid-liquid extraction is a separation process, which is a competition with distillation. A number of reports have been published, which were discussing the separation of components by means of hyperbranched polymers as extractant [221]. Hyperbranched polymers show high selectivity, remarkable loading capacities, no vapor pressure, completely low melt and solution viscosities, non-toxic, as well as remarkable thermal and chemical stabilities as extractant.

1.9. A short review on hyperbranched polyamine

Poly(propylene imine) (PPI) is a novel kind of dendrimer. It is widely used in drug and gene delivery, macromolecular building block, nanotechnology and supramolecular science [225] because of its unique chemical and physical properties. Its analog hyperbranched poly(ethylene imine) (HPEI) can be prepared by ring opening polymerization of ethylene imine, has been developed commercially (under the Dow trade name of Montrek) [226]. A number of studies using HPEI as a PPI alternative in many fields as mentioned above have been published [225]. However, up to now a little work has been performed on preparing actual hyperbranched polyamines, which are discussed below.

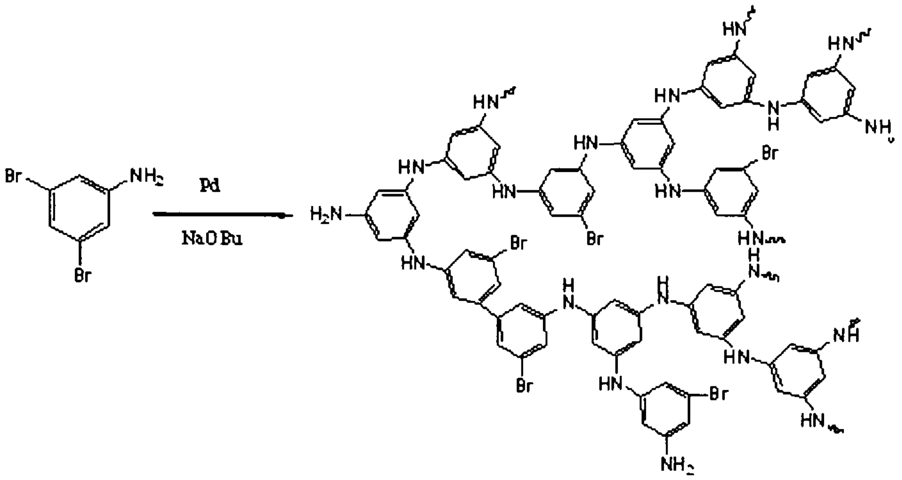
In 1992 Suzuki *et al.* [73] first reported hyperbranched polyamine by using self condensing ring opening polymerization. The polymerization of 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one cyclic monomer [73] was initiated by the addition of benzylamine and proceeded at room temperature with evaluation of CO_2 (Scheme 1.4).



Scheme 1.4. Synthesis of hyperbranched polyamine by SCROP

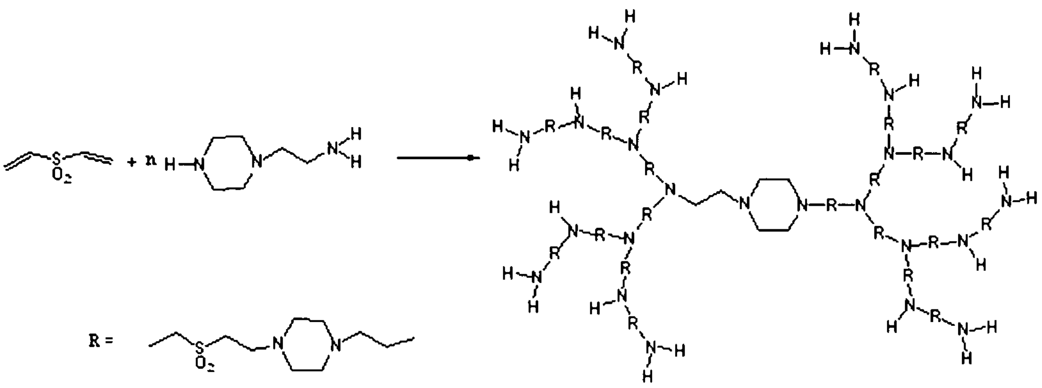
It was reported that π-allyl palladium complex was the key intermediate for this polymerization. As a consequence of poor solubility of these polyamines in organic solvents, the resultant hyperbranched polyamines were treated with n-butyl isocyanate (n-BuNCO) to end cap all 1^O and 2^O -amines present in the structure for their different analyses. The hyperbranched polyamines found to have DB of 0.61 as determined from ^{1}H-NMR spectra and molecular weights 2700-3000 g/mol as determined by GPC. In 1998, the same researchers had also published another excellent report on ring opening polymerization using 5-methyleneperhydro-1,3-oxazin-2-one as the monomer [74]. The resulting polymer was insoluble in MeOH, $CHCl_3$, DMF and H_2O but soluble in MeOH / $CHCl_3$ (3/1 v/v) mixture and in aqueous solution of HCl.

In 1998 Mayer *et al.* synthesized hyperbranched polyamine via one-step polycondensation of AB_x type monomer [63]. The step growth polycondensation route has been utilized extensively in the synthesis of a diverse range of hyperbranched systems to tailor different functionalities. The polymerization of 3,5-dibromoaniline as the AB_2 type monomer proceeded in the presence of a Pd-catalyst, a ligand and a base. 2,2'-Bis(diphenyl phosphino)-1,1'-binapthyl (BINAP) was an effective ligand for the formation of diphenylamine backbone (Scheme 1.5). The resulting hyperbranched polymer was soluble in organic solvents and the weight average molecular weight was found to be 7000 g/mol as measured by GPC. This polyamine showed magnetic properties similar or superior to that of its linear analogs.



Scheme 1.5. Synthesis of hyperbranched polyamine by AB_x type monomer

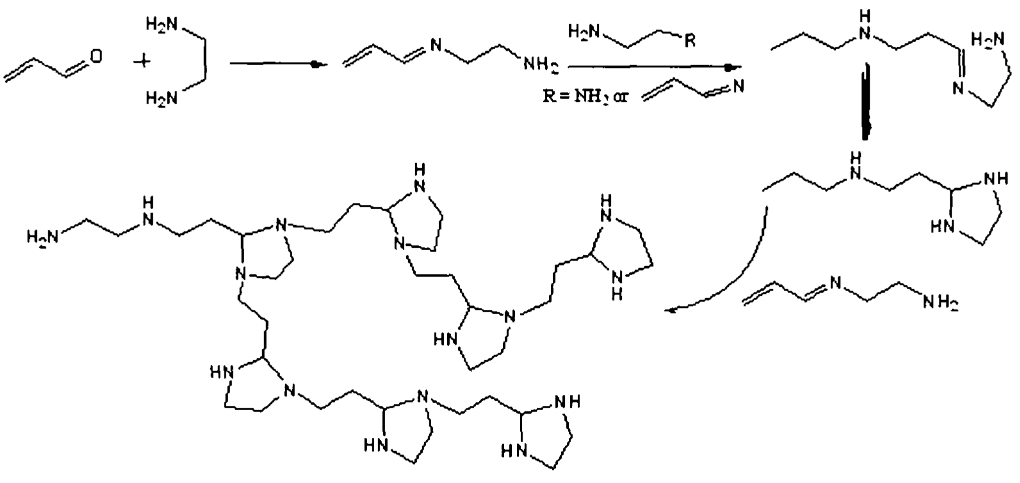
In 2000 Yan and Gao [84] reported the use of A_2 and BB'_2 monomer for design of a hyperbranched poly(sulfone amine) using DMM approach. In BB'_2 monomer, both B and B′ groups are different from each other. The difference in reactivity may be attributed to the distinction in chemical environment. Through this approach hyperbranched poly(sulphone amine)s was successfully synthesized from 1-(2-aminoethyl) piperazine (BB'_2) and divinyl sulphone (A_2) without any catalyst (Scheme 1.6) [84]. Polymerization was carried out in DMF under mild temperature (20-60) ^{0}C, when the feed ratio was 1:1, no gelation was observed for a total monomer concentration bellow 7.0 mol/L. The authors also reported a few hyperbranched poly(sulphone amine)s by using this approach [106].



Scheme 1.6. Synthesis of hyperbranched poly(sulfone amine) by A_2 + BB'_2 approach

The degree of branching, thermal behavior and mechanical properties of the polymers could be controlled by the feed ratio of the monomers. "A_2+B_2+BB'_2" approach, the A_2 and BB'_2 monomers are the same as those of A_2+BB'_2 approach [84], and B_2 is the molecule with two secondary amino groups for hyperbranched polyamines. Recently, Yan and Gao have described the synthesis of hyperbranched polyamine by using this approach [42]. During the polymerization process, the rapid reaction between A and B groups results the formation of an AB'_2 type intermediate. The linear units formed from the reaction of A and B_2 also are embedded AB'_2 species, which indicated that the segment between two branching points and the number of linear units can be adjusted by the feed ratio of B_2 to BB'_2.

More recently Liu *et al.* [227] synthesized hyperbranched polyamines containing imidazolidine rings in a step-growth manner based on the reaction of acrolein with ethylene diamine (Scheme 1.7). Sodium borohydride has been used to reduce the imidazolidine group and open the ring to give a stable hyperbranched polyamine. The resulting hyperbranched polyamines found to have DB of 0.55-0.70 as determined from ^{1}H-NMR spectra and molecular weights (M_w) range ca. 1400-1700 g/mol as determined by GPC.



Scheme 1.7. Synthesis of hyperbranched polyamine by step growth polymerization

1.10. Limitation of earlier works on hyperbranched polyamines

From the main features of the foregoing discussion, the following limitations of earlier works have been found on hyperbranched polyamines.

(i) The monomers used for synthesis of hyperbranched polyamines are mostly uncommon and difficult to purify. Also most of the synthetic methods are critical.

(ii) Even though it is established that the monomers required for $A_2 + B_3$ approach can be easily obtained commercially but no one has tried for this approach using the common monomer for polyamines.

(iii) Cyanuric chloride, despite of being an easily available commercial chemical with s-triazine unit possesses three different reactivities of chlorine atoms and therefore controlling of reactions are very easy, but utilization of this chemical directly to synthesize hyperbranched polyamine is not found.

(iv) Even though a few hyperbranched polyamines have been reported, but polymer with s-triazine in main chain is not found. Also the hyperbranched polymers with thermostable s-triazine unit are expected to exhibit high thermostability, flame retardancy, optical properties, etc.

(v) The highly branched aromatic polyamines with large number of $-NH_2$ end groups are not studied at all to establish their important properties like antioxidant, flame retardant, process aid, crosslinker, etc.

(vi) The hyperbranched aromatic polyamines containing primary, secondary and tertiary nitrogens in their structures may be very useful as matrix for the preparation of metal nanoparticles, but this aspect has not been looked upon.

So, it appears that there is a lack of systematic and comprehensive study on development of hyperbranched polyamines with s-triazine ring in the main chain using cyanuric chloride as one of the monomers.

1.11. Scope and objectives of the present investigation

Thus there is a scope to synthesize hyperbranched polyamines using cyanuric chloride, as it has many advantages. Due to the presence of rigid triazine moiety, which makes the polyamines thermally stable, and also the presence of special elements such as nitrogen or halogen in polymer backbone may result excellent flame retardant characteristic. Again, it has been already pointed out that the hyperbranched polyamine may exhibit many interesting properties for their different end applications. Therefore, the following questions may arise in the mind on development of hyperbranched polyamines with s-triazine ring.

1. Whether hyperbranched polyamines with s-triazine ring in the main chain can be synthesized by a simple method?
2. Whether cyanuric chloride could be used directly as one of the monomers in above synthetic method?
3. Whether such hyperbranched polymers will exhibit different physical and chemical properties like low viscosity, high solubility, flame retardancy, optical behavior, etc.?
4. Whether the hyperbranched polyamines could be used as matrices for preparation of metal nanoparticles, as crosslinkers for different resins, multipurpose polymeric additives for commercial linear polymers, etc.?

Under this background, the main objectives of the present investigations, therefore, are as follows.

(a) To synthesize the hyperbranched aromatic polyamines by a simple and an economically favorable technique using cyanuric chloride as one of the monomers.

(b) To characterize the synthesized polyamines by different spectroscopic and analytical techniques.

(c) To study the physical and thermal properties of the above polyamines by different techniques.

(d) To utilize a hyperbranched polyamine as multipurpose polymeric additive for commercial linear polymers.

(e) To use a hyperbranched polyamine as a crosslinker for thermosetting resins.

(g) To utilize the hyperbranched polyamines as matrices for nanoparticles synthesis.

(h) To investigate the optical property of hyperbranched polyamines.

1.11. Plan of work

To fulfill the above objectives for the present investigation, the following plans of work have been adopted.

(i) A state of art literature survey will be conducted in the area of hyperbranched polyamine.

(ii) Different aromatic diamines as A_2 monomer and cyanuric chloride as B_3 monomer will be utilized for synthesis of hyperbranched polyamines by employing a simple method.

(iii) The characterization of the synthesized polyamines will be performed by the conventional techniques such as elemental analysis, FT-IR, UV, NMR spectroscopy, XRD, etc.

(iv) Studies on the physical, thermal and optical properties of the hyperbranched polyamines will be performed by the measurement of different properties such as solubility, viscosity, thermal stability and fluorescence respectively.

(v) Studies on antioxidant, processability, mechanical and thermal properties of the linear base polymers with a hyperbranched polyamine will be carried out. The polymers will be compounded by mechanical mixing in a Brabender plasticorder under the required processing conditions.

(vi) The flame retardant behavior of the hyperbranched polyamines and their use as polymeric flame retardant additives in commercial linear polymers will be investigated.

(vii) Studies on crosslinking efficiency of a hyperbranched polyamine for a vegetable oil based poly(ester amide) resin as well as a commercially available epoxy resin.

(viii) Synthesis of biological active nanoparticles in the hyperbranched polyamine matrices and study of their biological activity.

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CHAPTER TWO

Synthesis and Characterization of Hyperbranched Polyamines

2.1. Introduction

Linear aromatic polyamides, polyimides and polyamines are known as important high performance polymers because of their excellent thermal, mechanical and chemical properties [1]. However, most of the above polymers are practically insoluble in common organic solvents at ambient temperature because of their rigid structures. The incorporation of branched structure in such polymers makes them easily processable for their unique properties [1].

The first synthesis of highly branched system was experimentally reported by Vogtle and co-workers [2] in 1978. However, the syntheses of hyperbranched polymers have lately attracted considerable attention after Kim and Webster synthesized the homopolymers of AB_x type monomers to form hyperbranched polyphenylenes [3, 4] by the single step process. Since then, a wide variety of hyperbranched polymers have been reported in the literature [5, 6] not only by step growth polymerization but also by chain growth polymerization. Most of the hyperbranched polymers have been synthesized by using AB_2 type monomers as starting materials. The monomers like AB_3 [7-10], AB_4 [11, 12], and very few AB_6 [12] and AB_8 [13] are also reported in literature. However, the infrequent commercial availability of such monomers, studies have been started to focus the use of A_2 and B_3 monomers in the polycondensation reactions.

Like any other approach, $A_2 + B_3$ approach also has its own merits and demerits. Here the polymerization process is very easy and simple, which offers high yield and often-tailored structure [14-25]. But experience reveals that the gelation is a very common problem in such kind of approach and leads to useless products.

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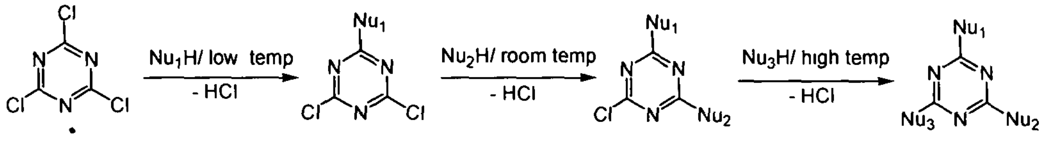
*Parts of this work have been published in J Appl Polym Sci, **2007**, 106, 95-102.*

The ideal conditions for gelation in this case as described by Flory [26] are based on the following assumptions. These are (i) *equal reactivity of 'A' or 'B' group at every moment of this reaction, (ii) no intermolecular cyclization, and (iii) the reaction is being restricted between an 'A' and a 'B' groups.* If these could be avoided then gelation will not occur. Also the success of this approach is dependent upon many factors including the ratio of functionalities, solvent and reagent purity and time as well as temperature of the reaction.

The polymers with heterocyclic moiety show important physical, chemical and thermal properties. As an approach to improve the solubility and the processabality of heterocyclic polymers, while maintaining the thermal stability, a good number of published reports described the synthesis and the properties of heterocyclic polymers with s-triazine moiety [27-33]. On the other hand, although a large variety of hyperbranched polymers have been reported in literature using difunctional (A_2) and trifunctional (B_3) monomers, but only a very few scattered reports [34, 35] were found on synthesis of s-triazine based hyperbranched polymers. The literature reports that triazine is a valuable heterocyclic thermostable moiety. They have found widespread applications in the pharmaceutical, textile, plastic and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, explosives and surface active agents [36]. The most important reagent for obtaining these compounds is cyanuric chloride because of the selective reactivity of three chlorine atoms towards different nucleophiles. This results an opportunity to perform the reaction in three different steps in the same compound without any protection or deprotections, which is very much useful for synthesis of such hyperbranched polymers [36, 37].

Hence, cyanuric chloride can be used as an active trifunctional (B_3) monomer with triazine moiety for the synthesis of hyperbranched polymers. It has also been observed that in the case of aromatic nucleophilic substitution reaction of cyanuric chloride ($C_3N_3Cl_3$) the chemoselectivity can be controlled with respect to temperature and the nature of nucleophiles [$(Nu)_x$, x = 1, 2 and 3] and thus it may produce branched macromolecules (Scheme 2.1) by a single step process. It is also important to stress that cyanuric chloride is commercially available and a very inexpensive reagent, which makes its applications even more attractive.

However, the direct use of this compound to synthesize hyperbranched polyamine is not found in literature. The advantages of using cyanuric chloride in synthesis of hyperbranched polymer are not only their thermal stability but it may also lead to flame retardancy as well as impart high electron affinity for the electronic materials [38].



Scheme 2.1. Chemoselective reactivity of cyanuric chloride

Thus the synthesis and characterization of a few hyperbranched aromatic polyamines obtained from cyanuric chloride and aromatic diamines are reported in this chapter.

2.2. Experimental

2.2.1. Materials

4,4′-Diaminodiphenylsulfone (Figure 2.1) was obtained from Merck, Germany. The compound has melting point (m.p.) 174 -177 ^{0}C, purity ≥97% and molecular weight (M_w) 248.31 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as a thermostable aromatic diamine (A_2 monomer).

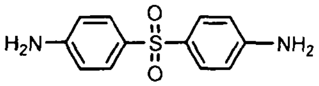


Figure 2.1. Structure of 4,4′-diaminodiphenylsulfone

4,4′-Diaminodiphenylmethane (Figure 2.2) was purchased from Merck, Germany. The compound has melting point (m.p.) 87-90 ^{0}C, purity ≥97% and molecular weight (M_w) 198 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as a simple aromatic diamine (A_2 monomer).

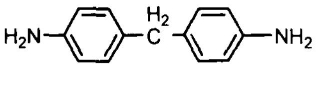


Figure 2.2. Structure of 4,4′-diaminodiphenylmethane

4,4′-Oxydianiline (Figure 2.3) was obtained from Aldrich Chemie, Germany. The compound has melting point (m.p.) 190 ^{O}C, purity ≥97% and molecular weight (M_w) 200.24 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as a flexible aromatic diamine (A_2 monomer).

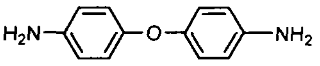


Figure 2.3. Structure of 4,4′-oxydianiline

4,4′-(1,4-Phenylenediisopropylidene) bisaniline (Figure 2.4) was obtained from Aldrich Chemie, Germany. The compound has melting point (m.p.) 163 -166 ^{O}C, purity ≥99% and molecular weight (M_w) 344.5 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as a thermostable aromatic diamine (A_2 monomer).

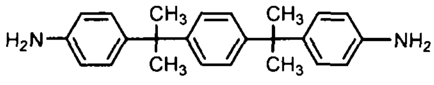


Figure 2.4. Structure of 4,4′-(1,4-phenylenediisopropylidene) bisaniline

4,4′-(1,3-Phenylenediisopropylidene) bisaniline (Figure 2.5) was purchased from Aldrich Chemie, Germany. The compound has melting point (m.p.) 110 -114 ^{O}C, purity ≥98% and molecular weight (M_w) 344.5 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as an A_2 monomer.

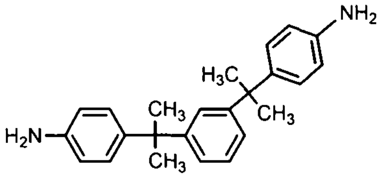


Figure 2.5. Structure of 4,4′-(1,3-phenylenediisopropylidene) bisaniline

4,4′-(4,4′-Isopropylidenediphenyl-1,1′-diyldioxy) dianiline (Figure 2.6) was obtained from Aldrich Chemie, Germany. The compound has melting point (m.p.) 127-130 ^{O}C, purity ≥98% and molecular weight (M_w) 410.52 g/mol. It was recrystallized from aqueous ethanol before used. Here it is used as a flexible aromatic diamine (A_2 monomer).

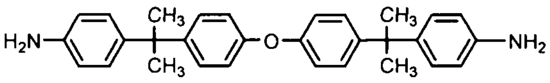


Figure 2.6. Structure of 4,4′-(4,4′-isopropylidenediphenyl-1,1′-diyldioxy) dianiline

Cyanuric chloride (Figure 2.7) was purchased from Aldrich Chemie, Germany. It has melting point (m.p.) 144-147 ^{0}C, purity ≥99% and molecular weight (M_w) 184.41 g/mol. It was recrystallized from bezene before used.

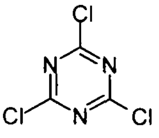


Figure 2.7. Structure of cyanuric chloride

Cyanuric chloride is an important member of triazine family. Due to its chemoselactive nature, here it is used as a B_3 monomer.

N-Ethyldiisopropylamine (Figure 2.8) was obtained from Merck, Germany. The compound has purity ≥98% and molecular weight (M_w) 410.52 g/mol. It was used as received. It is strong base and used as HCl scavenger.

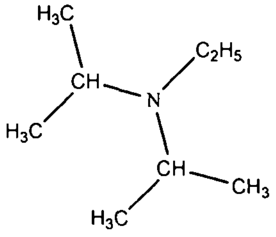


Figure 2.8. Structure of N-ethyldiisopropylamine

Methyl red ($C_{15}H_{15}N_3O_2$) was purchased from Merck, India. Its molecular weight (M_w) is 269.31 g/mol and purity is 98% and it was used as received. Actually it is used as an indicator (pH=4.4-6.2) but here it was used to end capped amino groups.

Thionyl chloride ($SOCl_2$) was obtained from LOBA Chemie, India. Its molecular weight (M_w) is 118.97 g/mol, and purity is $\geq$99%. This compound is generally used for transforming acid to acid chloride. It was used as received.

Benzoyl chloride (C_6H_5COCl) was obtained from Loba Chemie, India. Its molecular weight (M_w) is 140.57 g/mol, and purity is $\geq$99% and it was used as received. Here it was used to end capped amino groups.

4-Hydroxybenzaldehyde (p-OH-C_6H_4CHO) was obtained from Merck, Germany with melting point 114-117 ^{O}C. Its molecular weight (M_w) is 122.12 g/mol, and purity is $\geq$98.0%. It was used as received to end capped amino groups.

Calcium oxide (CaO) was obtained from SD fine Chem, Mumbai. Its molecular weight (M_w) is 56.08 g/mol and purity is 95% after ignition. The loss on ignition is 10% and impurities present are generally chloride (0.1%), sulfate (0.5%), iron (0.1%) and lead (0.02%). It was used as received to dry water of the solvents.

Molecular sieve 4AX1.5 mm has been purchased from Merck, India. Its equilibrium capacity for water at 30 ^{O}C, 75% relative air humidity is $\geq$20% and bulk density is 650-700 g/L. It was used as received to trap moisture in solvents.

N,N′-dimethylacetamide (DMAc) was purchased from SD fine Chem, India. Its purity is 99.5% with 0.1% water and 0.12% free acid as impurities. The density is 0.938-0.942 g/mL at 25 ^{O}C and boiling point (b.p.) is 165-167 ^{O}C. This was purified by the following procedure. About 500 mL of DMAc was taken in a round bottom flask and 20 g of powder calcium oxide was added into it. The solution was kept for overnight. Then it was filtered and distilled under reduced pressure. This distillate obtained was kept in an amber bottle with 4A type molecular sieves. DMAC was used as solvent.

Acetone (CH_3COCH_3) was obtained from SRL, India. It has purity $\geq$ 99.8% with water $\leq$ 0.2% and boiling point (b.p.) 64-65 ^{O}C. It was used as common solvents, as received.

Methanol (CH_3OH) was obtained from Merck, India. It has purity $\geq$ 99% with water $\leq$ 0.2% and boiling point (b.p.) 56-57 ^{O}C. It was used as solvents, as received.

2.2.2. Synthesis of hyperbranched polyamine

The hyperbranched polyamines have been synthesized by the following procedure. An appropriate amount (0.0129 mol) of aromatic diamine (A_2) was dissolved in dry freshly purified DMAc (10% (w/v)). This was taken in a 250 mL three-neck dry round bottom flask fitted with a pressure equalizing funnel, a condenser along with a drying tube and a N_2 gas inlet. When the chemicals were dissolved completely, 0.0086 mol of cyanuric chloride (B_3) solution in dry DMAc at a level of 10% concentration (w/v) and 0.0086 mol of diisopropylethylamine (DIPEA) were added dropwise for about 1 h at 0-5 ^{O}C with constant stirring. After the completion of addition, the reaction mixture was stirred for another 1 h under the same conditions, followed by raise of temperature to 40-45 ^{O}C. At this temperature, again 0.0086 mol of DIPEA was added in the reaction mixture and stirring was continued for another 2 h. Then the temperature was again raised to 85-90 ^{O}C and further 0.0086 mol of DIPEA was added. The reaction was continued for another 5-7 h under the same condition. The details of concentration of the reactants and time and yield of reaction are shown in Table 2.1. It was then cooled and poured slowly with constant stirring in 1 L of ice-cold water. The precipitate formed was collected by filtration and washed several times at first with water followed by methanol and acetone to remove the unreacted reagents. The product was dried under vacuum at temperature 45-50 ^{O}C for three days to obtain dry powder of the polymer. The hyperbranched polyamines were obtained by using A_2 diamine like 4,4′-diaminodiphenylsulfone, 4,4′-diaminodiphenylmethane, 4,4′-oxydianiline, 4,4′-(1,4-phenylenediisopropylidene) bisaniline, 4,4′-(1,3-phenylenediiso propylidene) bisaniline and 4,4′-(4,4′-isopropylidenediphenyl-1,1′-diyldioxy) dianiline are designated as HPs, HPm, HPo, HPa, HPb and HPd respectively.

2.2.3. End capping of synthesized polyamines

Preparation of end capped hyperbranched polyamine (E1, E2) with benzoyl chloride and 4-hydroxy benzaldehyde respectively

These end capping reactions of polyamine (HPs) were carried out by the following procedure. As above (section 2.2.2.), synthesis of hyperbranched polyamine (HPs was prepared first and then after a given time an excess amount (0.0035 mol, as10% solution in DMAc) of benzoyl chloride (for E1) and 4-hydroxybenzaldehyde (for E2) was added separately. An amount of 0.45 g of diisopropylethylamine (DIPEA) was added dropwise with constant stirring for E1. After the completion of addition the reaction mixture was stirred for another 1 h under the same conditions, cooled to room temperature and then poured into ice cold water for work up the product as described in section 2.2.2.

Preparation of end capped hyperbranched polyamine (E3) with methyl red

The end capping of hyperbranched polyamine (HPo) was performed by the following two step process. At first, 1.8 g (6.7 mmol) of methyl red and 5 mL of thionyl chloride were refluxed together for 6h. Then the excess thionyl chloride was removed under vacuum and the deep brown solid powder of chloride derivative of methyl red was obtained.

In the next step, 1.0 g methyl red chloride in 10 mL DMAc and 0.45 g of DIPEA were added dropwise in 1.0 g of hyperbranched polyamine (HPo) in DMAc solution with constant stirring. The mixture was stirred for 3h at 80 ^{O}C, cooled to room temperature and then poured into ice cold water. The precipitate was filtered, washed with methanol and dried under vacuum at 45 ^{O}C for 3 days.

Table 2.1. Amount of monomers, solvent and reaction time for synthesis and yield of hyperbranched polyamines

Polymer	Monomers (g)		DIPEA (g)	DMAc (mL)	Time (h)	Yield (%)
	Diamine (A_2)	CYC (B_3)				
HPs	3.72	1.84	3.88	55	11	82
HPm	2.97	1.84	3.88	48	10	90
HPo	3.00	1.84	3.88	48	9	81
HPa	5.16	1.84	3.88	70	10	80
HPb	5.16	1.84	3.88	70	10	78
HPd	6.16	1.84	3.88	80	11	75

2.2.4. Characterization techniques and instrumentation

2.2.4.1. Spectroscopic techniques

IR spectra of the hyperbranched polyamines were recorded in a FT-IR spectrometer (Impact-410, Nicolet, USA) using KBr pellet. ^{1}H-NMR and ^{13}C-NMR spectra of the polyamines were recorded in a 400 MHz NMR spectrometer (Varian, USA) using d_6-DMSO as the solvent and TMS as an internal standard. The UV-visible spectra of the polyamines were recorded in an UV spectrophotometer (Hitachi U-2001, Japan) using 0.001% solution in dry DMAc.

2.2.4.2. Analytical techniques

Elemental analyses of hyperbranched polyamines were carried out in CHN analyzer (Perkin Elmer, Model no. 2400, series II). The chlorine and sulfur contents of the polymers were determined by the standard Schoniger oxygen combustion method by a heteroatom analyzer (S.C. Deys' & Co., Kolkata).

The chlorine content of hyperbranched polyamines was determined by the Schoniger combustion method as follows. 50 mL of aqueous sodium hydroxide solution was taken in Schoniger combustion flask. 0.06-0.07 g of a polymer was weighed exactly in a small rectangular Whatmann-41 ash less filter paper. The sample with the filter paper was folded carefully and placed in the combustion flask with the help of platinum wire. The combustion chamber was flashed with sufficient amount of oxygen to burn the polymer sample completely. Then the sample was burned with the help of a filament in the chamber. After completion of the burning process, the generated gases were absorbed completely by proper shaking of the flask by the sodium hydroxide solution. Then 2 mL of phenolphthalein solution was added into the chamber. Again, 0.1N nitric acid was added drop wise to neutralize the solution in the flask. After complete neutralization 10 mL of 0.1M silver nitrate solutions was added into it. The flask was shaken vigorously and 2 mL of 40% ammonium ferric sulfate solution was added at last. Finally, the reaction mixture was titrated against the standard 0.1M ammonium thiocyanate solution. The amount of chlorine (N) in percentage is calculated by using the following equation:

$$N = (C_1V_1 - C_2V_2) X 0.0035/m X100$$

where C_1 and V_1 are the concentration and volume of $AgNO_3$ solution, C_2 and V_2 are the concentration and volume of ammonium thiocyanate solution and 'm' is the amount of polymer used in gram.

The sulfur content of hyperbranched polyamine was also determined by the Schoniger combustion method as described below.

0.0673 g of polymer was weighted exactly in a small rectangular Whatmann-41 ash less filter paper. After completion of the burning process by the same way as described above, the generated gases were absorbed completely by proper shaking of

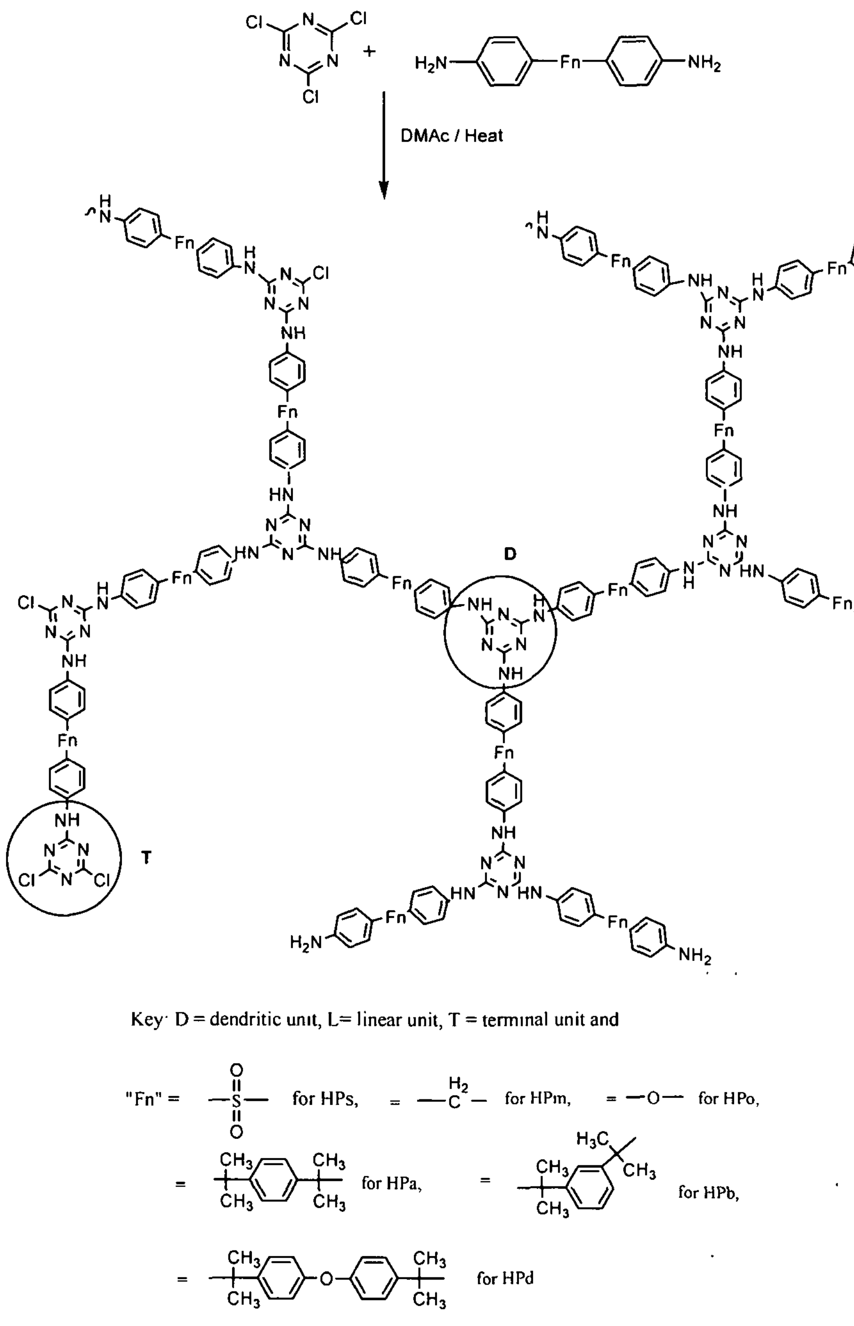
50 mL of 6% hydrogen peroxide solution in the flask. Then 2 drops of methyl red indicator were added and the solution was neutralized by adding 0.02 N sodium hydroxide solution drop wise until a yellow color was obtained. 300 mL of distilled water was introduced into the solution and the mixture was shaken for a minute. It was then transferred to a 500 mL beaker and boiled on a hot plate until the volume of solution was reduced to 50 mL. 3 mL of 0.3 N hydrochloric acid and 3 mL of 10% barium chloride solution were added consecutively with continuous stirring. Finally the beaker was covered with a watch glass and permitted to stand undisturbed for 2 h. The precipitate formed was transferred into a weighed Gooch crucible and washed several times with 25 mL of dilute hydrochloric acid solution. Then it was dried in an oven at 110 ^{O}C until a constant weight was obtained. The amount of sulfur is calculated by using the following equation.

$$\% S = (\text{Weight of } BaSO_4 \times 0.1374 \times 100) / (\text{Weight of sample})$$

2.3. Results and discussion

2.3.1. Synthesis of polymers

The s-triazine based hyperbranched polyamines were synthesized by using an A_2+B_3 approach from the corresponding aromatic diamine (A_2) and cyanuric chloride (B_3) by nucleophilic displacement polymerization reaction as shown in Scheme 2.2. The product without gel formation in an A_2+B_3 approach can only be obtained under highly restricted conditions [17, 22]. The first chlorine atom in CYC has the highest reactivity followed by the second one and the third has the lowest reactivity due to the passivation effect of amine substituents as mentioned earlier (Scheme 2.1). This was reported by the previous workers in nucleophilic substitution of chlorine atoms in 2,4,6-trichloro-s-triazine by different amine compounds [36, 37]. The substitution reaction of CYC and aromatic amine is, therefore, highly selective with respect to temperature. The first chlorine atom has been substituted at 0-5 ^{O}C, second at 40-45 ^{O}C and third at 85-90 ^{O}C by amine substituents in the polymerization reaction. This stage wise condensation reaction avoids the gel formation in the synthesized hyperbranched polymers, as no gel product was observed under the used reaction conditions of this polymerization process, as confirmed by solubility test. It has also been observed that if the temperature of the reaction was higher than the used temperature at any stage, a large amount of fume was generated and the reaction happens to be uncontrolled. Even a two-stage or a single-stage reaction resulted a gel product. The high temperature single stage reaction with simultaneous addition and high concentration of the reactants often afforded a gel, which indicates that the polymerization is uncontrollable. This is due to high rate of reaction between chlorine atoms of triazine unit and amine functional groups of aromatic diamine. The use of high reaction concentration (20%)



Key D = dendritic unit, L= linear unit, T = terminal unit and

Scheme 2.2. Synthesis of hyperbranched polyamines leads to gel formation and low yield. The use of other mol ratio (1:1) of the reactants resulted low yield and viscosity. Even in solvents like THF, DMF and DMSO the yield and viscosity of the Ps polymer were not so good. Thus the success of this approach is dependent on judicious choice of the following factors: concentration and ratio of the reactants, solvent used, purity of the reactants, reaction time and temperature, etc. The reaction was succeeded by using 3:2 mol ratio of A_2 and B_3 monomers and slow addition of a very dilute solution (<10% w/v). The reaction was further facilitated by using diisopropyl ethylamine, an active base to scavange the HCl gas, which was generated during the substitution reaction.

2.3.2. Characterization

The λ_{max} values of the HPs, HPm, HPo, HPa, HPb and HPd polymers, in DMAc solution were observed at 315 nm, 282 nm, 290 nm, 277 nm, 273 nm and 278 nm respectively (Figure 2.9), which indicate the presence of aromatic moiety with conjugation and characteristic π-π^* electronic transition in the aromatic 1,3,5-triazine moieties [39]. The higher λ_{max} values of HPs and HPo are due to the presence of higher conjugation in both the cases than the other polyamines. As the sulfonyl group and ether linkage are in conjugation with the aromatic rings in polyamines HPs and HPo respectively, so they have extended conjugation.

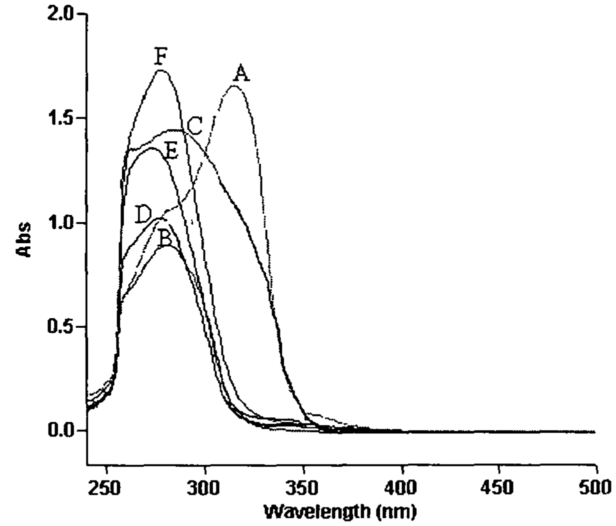


Figure 2.9. UV-visible spectra of hyperbranched polyamines (A = HPs, B = HPm, C = HPo, D = HPa, E= HPb and F= HPd)

The FT-IR spectra of the polymers indicate the presence of aromatic amine linkage, N—H (primary or secondary) at 3350-3445 cm^{-1}. The nature of the peak is mainly due to associated N—H bond as this is a weak but sharp peak [40]. The representative two spectra are shown in Figure 2.10. The N-H bending vibrations for primary and secondary aromatic amine linkages for all the polymers are found separately at 1572-1621 cm^{-1} and 1476-1511 cm^{-1} respectively. The marginal shift of these absorption values may be due to the presence of H-bonding [40]. The presence of the above peaks in the polymers confirmed occurrence of nucleophilic displacement polymerization reaction with formation of secondary amine bond. The C=N bond of the triazine moiety appears at 1416-1439 cm^{-1} in the IR spectra for all the polymers. The

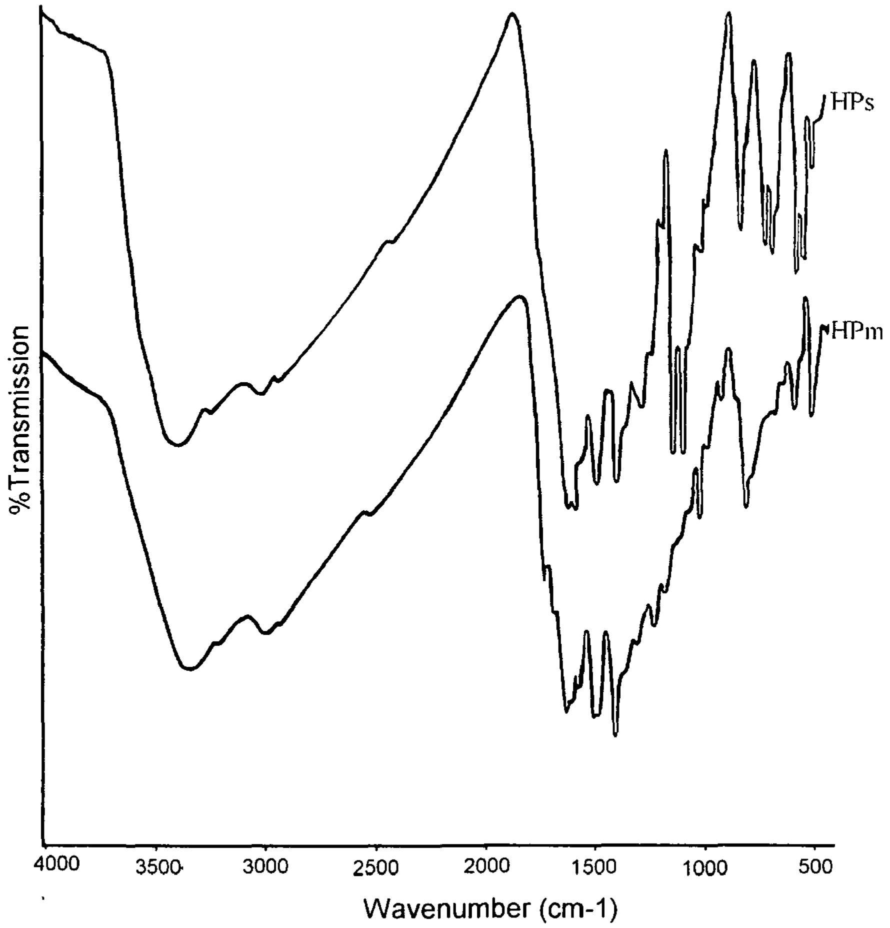


Figure 2.10. FT-IR spectra of hyperbranched polyamines

aromatic C-Cl bond was observed at 1014-1050 cm^{-1} for all cases, which indicates the displacement reaction was not completed. This was confirmed by quantitative estimation of chlorine by Schoniger oxygen combustion method (Table 2). Strong absorption bands at 1140 cm^{-1} and 1355 cm^{-1} were observed for polyamine containing sulfonyl group (HPs). The aromatic ether linkage of polymer HPo was also observed at 1235 cm^{-1}. The absorption band at 1645-1660 cm^{-1} was observed in E1 an E3 end capped polymers due to amide carbonyl group. A weak absorption band at 1556 cm^{-1} was also observed for N=N linkages in E3 end capped polymer.

The structures of the polymers were further supported by NMR studies. The ^{1}H-NMR spectra of the polymers indicate the presence of important peaks for the different types of protons [39]. Three different peaks appear for the secondary N-H protons of the polymers, which confirmed the presence of three different units viz. dendritic, linear and terminal. The peaks at δ= 10.86 ppm, δ= 9.93-9.89 ppm and δ= 9.87–9.62 ppm are due to N-H protons attached with the terminal triazine unit (triazine with two unsubstituted chlorine atoms), with the linear unit (triazine with one unsubstituted chlorine atom) and with the dendritic unit (triazine with no chlorine atom) respectively for HPs hyperbranched polyamine (Figure 2.11). Whereas the peaks at δ= 11.17 ppm, δ= 9.12 ppm and δ= 9.09 ppm for HPm (Figure 2.12), peaks at δ= 10.66 ppm, δ= 9.20 ppm and δ= 9.08 ppm for HPo (Figure 2.13), peaks at δ= 10.68 ppm, δ= 9.05 ppm and δ= 8.93 ppm for HPa (Figure 2.14), peaks at δ= 10.81 ppm, δ= 9.12 ppm and δ= 8.86 ppm for HPb (Figure 2.15) and the peaks at δ= 10.77 ppm, δ= 9.1 ppm and δ= 8.95 ppm for HPd (Figure 2.16) are due to the protons of N-H, which are attached with the terminal triazine unit, linear unit and dendritic unit respectively for each polyamine. The peaks for NH_2 protons appear at the range of δ= 3.72 to 3.03 ppm for all the polymers. The aliphatic CH_2 protons of HPm appear at δ= 3.85-3.75 ppm, whereas the aliphatic methyl protons of HPa, HPb and HPd appear at δ= 1.58-1.49 ppm. The protons for the aromatic moieties appear at δ= 5.98- 8.15 ppm for all the polymers as multiplate may be due to the presence of different types of chemical environment as a large number of conformations are possible for all polymers.

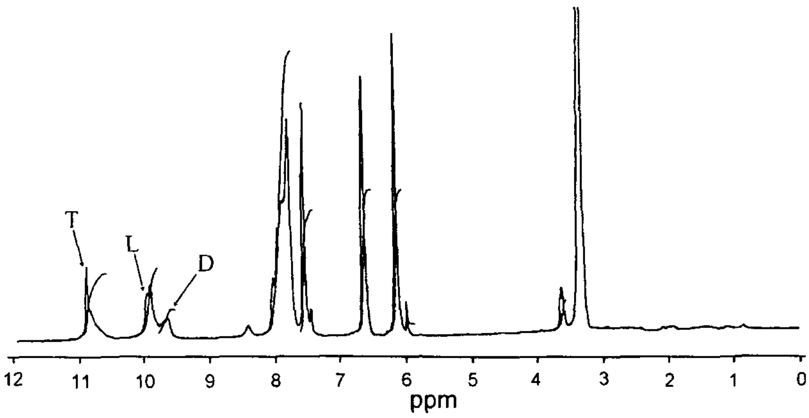


Figure 2.11. ^{1}H-NMR spectrum of hyperbranched polyamine, HPs

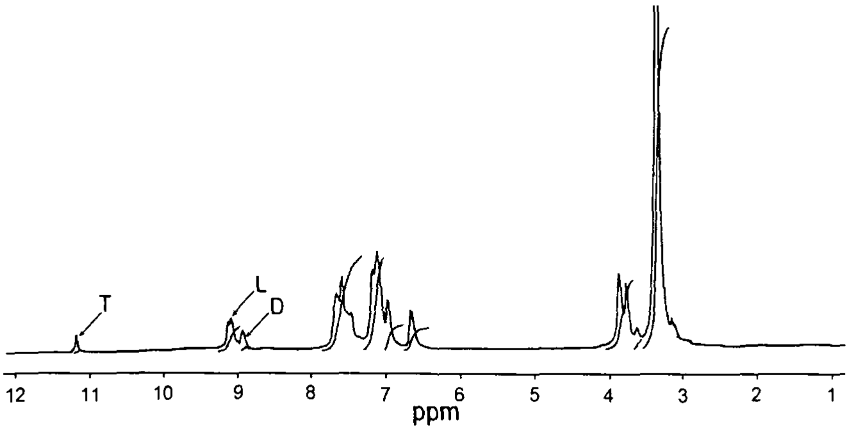


Figure 2.12. ^{1}H-NMR spectrum of hyperbranched polyamine, HPm

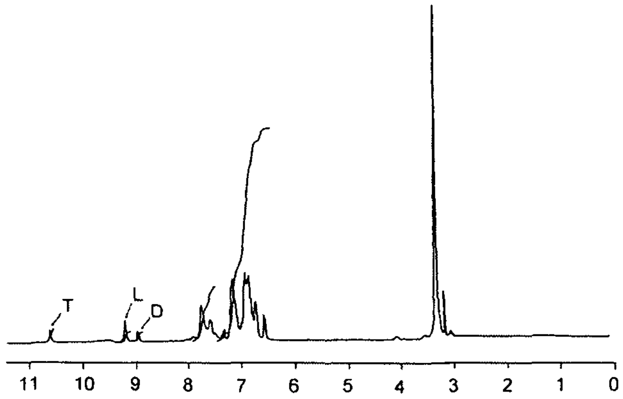


Figure 2.13. ^{1}H-NMR spectrum of hyperbranched polyamine, HPo

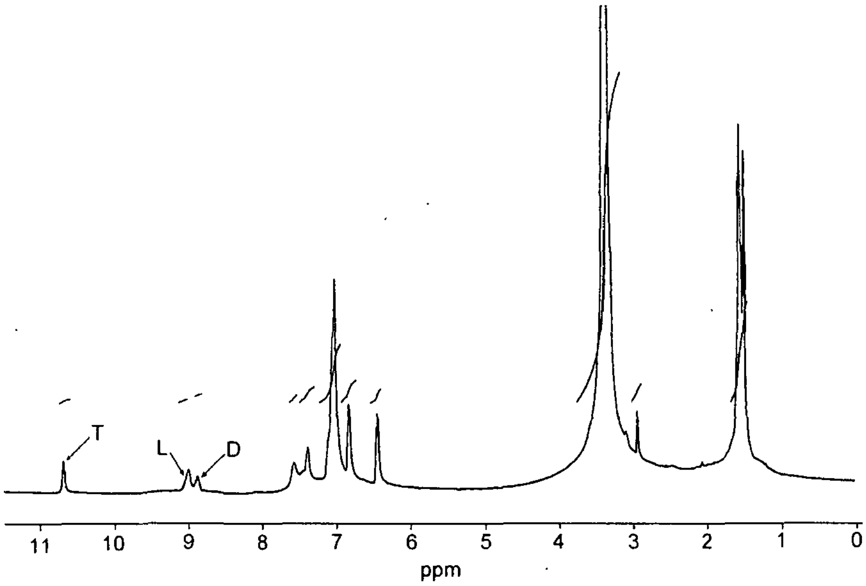


Figure 2.14. ^{1}H-NMR spectrum of hyperbranched polyamine, HPa

The ^{13}C-NMR spectra further support the structures of the polymers as shown in the Scheme 2.2 [40]. The peaks at δ= 163.9- 164.37 ppm are due to the carbon atoms present in the dendritic triazine units for the all polyamines. The peaks at δ= 153.42 ppm, δ= 126.27-129.18 ppm, δ= 113.11 ppm and δ= 120.23-121.06 ppm are due to the carbons attached with secondary N-H groups, ortho, meta and directly attached with sulfonyl groups respectively for the HPs polymer (Figure 2.17).

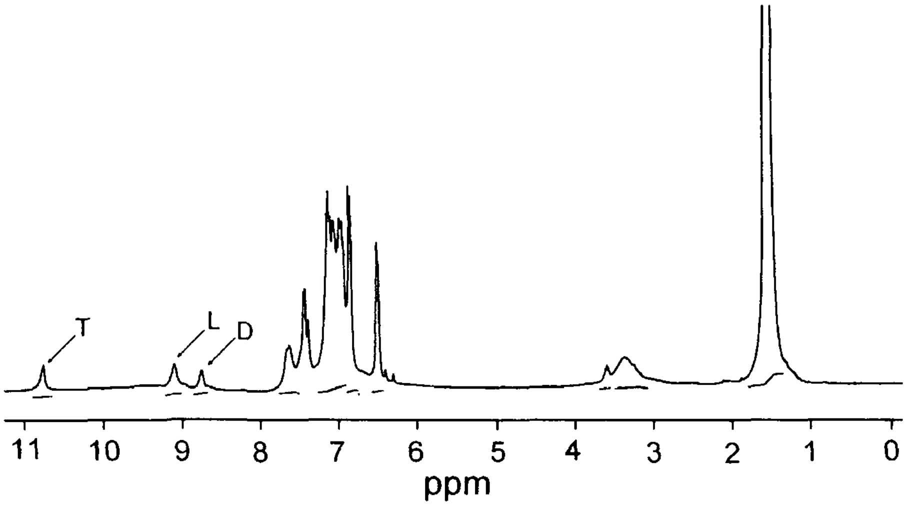


Figure 2.15. ^{1}H-NMR spectrum of hyperbranched polyamine, HPb

Whereas in HPm polymer (Figure 2.18) the peaks at δ= 135.27-137.78 ppm, δ= 119.38-121.51 ppm, δ= 128.29-129.19 ppm and δ= 115.90 ppm in ^{13}C-NMR spectra may be due to the carbons attached with secondary N-H groups, ortho, meta and directly attached with methylene groups of aromatic moiety respectively and the peak for the CH$_2$ carbon appears at δ= 53.57 ppm.

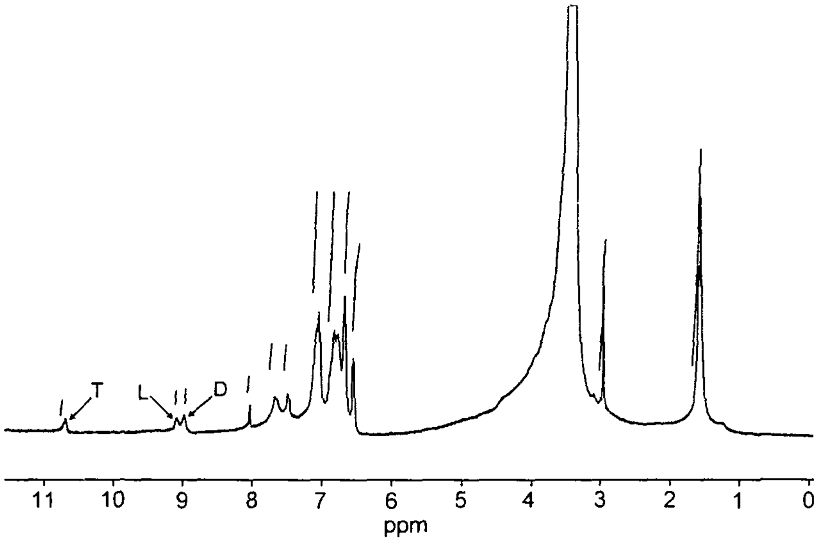


Figure 2.16. ^{1}H-NMR spectrum of hyperbranched polyamine, HPd

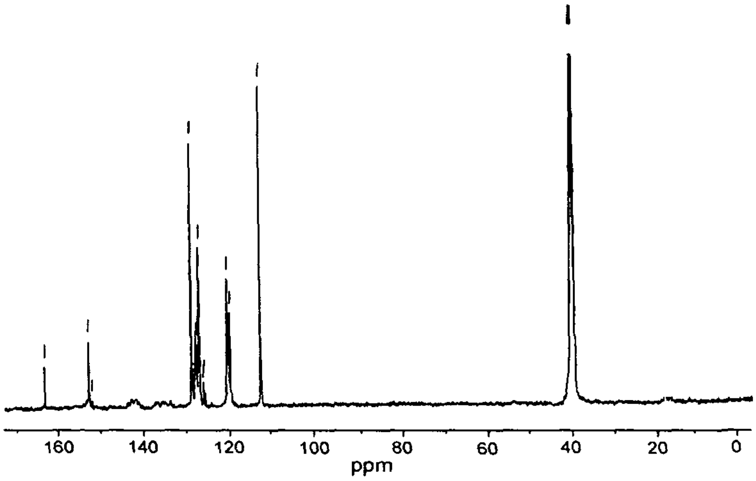


Figure 2.17. ^{13}C-NMR spectrum of hyperbranched polyamine, HPs

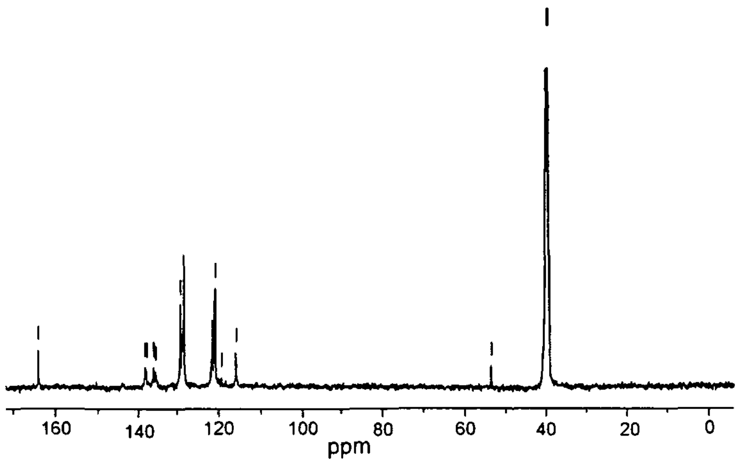


Figure 2.18. ^{13}C-NMR spectrum of hyperbranched polyamine, HPm

The ^{13}C-NMR spectrum (Figure 2.19) of HPo polymer indicates the presence of peaks at δ= 169.57 ppm, δ=163.98 ppm, δ= 152.44-143.88 ppm, δ= 135.37-131.37 ppm and peaks at δ= 123.73-114.89 ppm are due to unsubstitute chlorine atom in triazine ring, the carbon atoms present in the dendritic triazine units [41], the carbons directly attached with oxy groups, the carbon atoms directly attached with –NH groups and the carbon atoms present at ortho and meta to oxy group of amine moieties respectively [39].

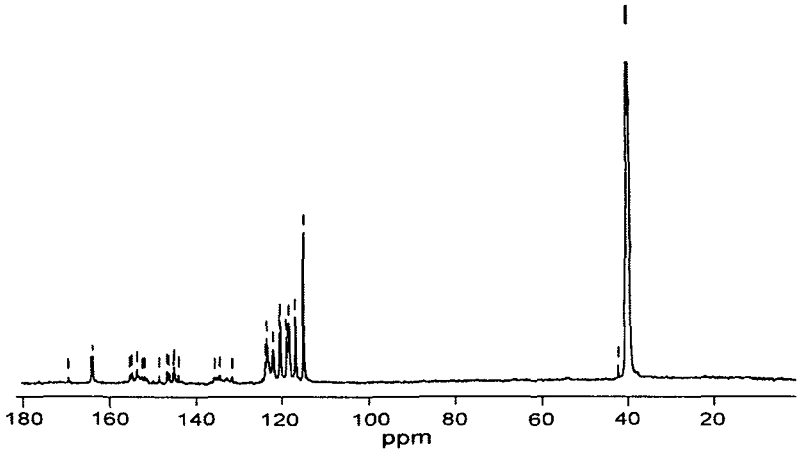


Figure 2.19. ^{13}C-NMR spectrum of hyperbranched polyamine, HPo

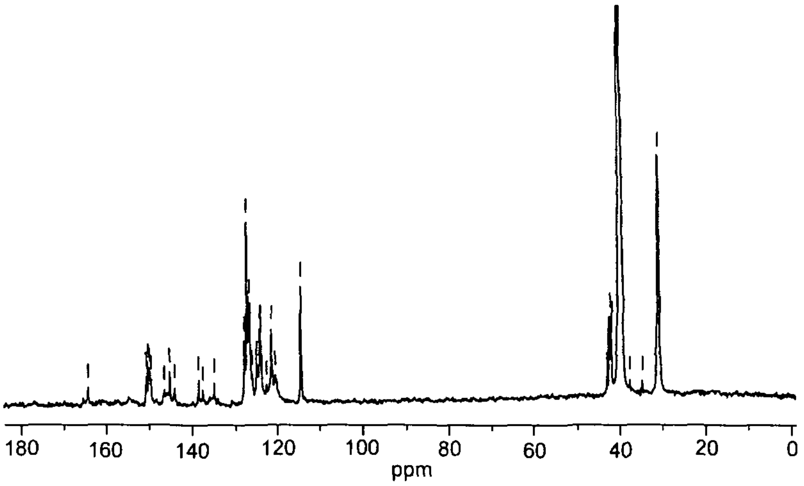


Figure 2.20. ^{13}C-NMR spectrum of hyperbranched polyamine, HPa

For HPa polyamine (Figure 2.20) the peaks at δ= 150.44-134.27 ppm may be due to the carbons attached with secondary >N-H groups and directly attached with isopropyl groups. Whereas the peaks at δ= 127.27-114.89 ppm may be due to the carbon atoms at *ortho* and *meta* to isopropyl groups of the polymer. The peaks for the carbon atoms of isopropylediene moiety appears at δ= 42.70-30.45 ppm.

All the important peaks such as carbon atoms present in the dendritic triazine units at δ= 164.31 ppm, carbons attached with secondary >N-H groups at δ= 150.44-134.27 ppm, carbon atoms at *ortho* and *meta* to isopropyl groups at δ= 127.22-121.67 ppm and carbon atoms of isopropylediene moiety at δ= 42.07-30.12 ppm are observed in the spectrum of HPb polyamine (Figure 2.21).

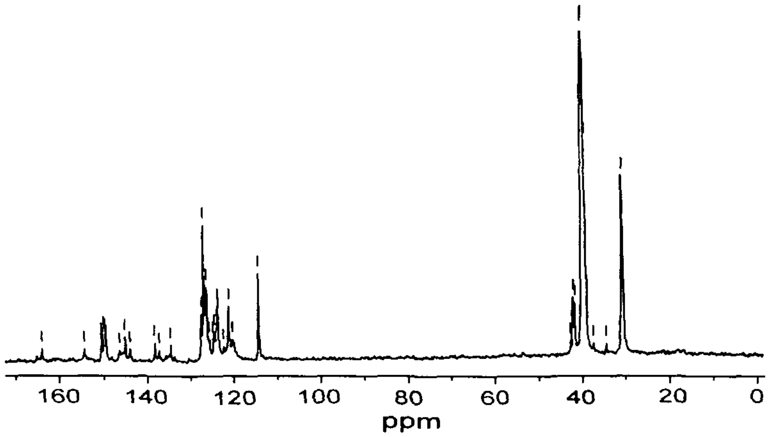


Figure 2.21. ^{13}C-NMR spectrum of hyperbranched polyamine, HPb

The ^{13}C-NMR spectrum of HPd polyamine (Figure 2.22) indicates the presence of peaks at δ= 164.21-163.98 ppm is due to the carbon atoms present in the dendritic triazine units, peaks at δ= 154.44-145.27 ppm is due to the carbons attached with secondary >N-H groups, directly attached with oxy and isopropyl groups, peaks at δ= 135.37-114.69 ppm is due to the carbon atoms at *ortho* and *meta* to oxy and isopropyl groups) and peaks at δ= 41.60-34.45 ppm appear for the carbon atoms of isopropylediene moiety.

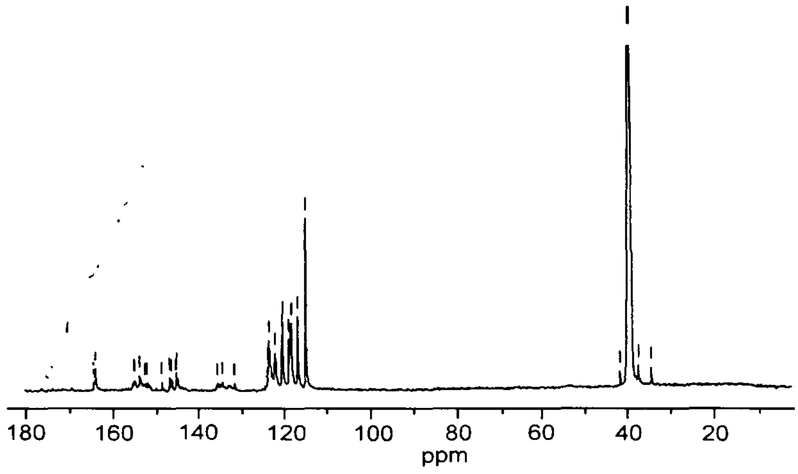


Figure 2.22. ^{13}C-NMR spectrum of hyperbranched polyamine, HPd

The elemental analysis data of the polymers (Table 2.2) also support the structures of the polymers as shown in the Scheme 2.2. The variation of the elemental analysis values from the ideal structure of dendrimer (calculated) is quite obvious as the hyperbranched structure has large structural defects and is complex in nature. Thus it is very difficult to assign the exact structure of the hyperbranched polymers.

Degree of Branching

The structural perfection of the hyperbranched polymers is usually characterized by the determination of their degree of branching (DB) of the polymer. This is determined here by [42] formulae of Frechet *et al.* as

$$DB=(D+T)/(D+T+L)..........(I)$$

where D, T, and L refer to the number of dendritic, terminal and linear units respectively in the structure of the polymer. Experimentally, DB is generally determined from NMR spectroscopy by comparing the integration of the peaks for the respective units in the hyperbranched polymer. The structure of hyperbranched polymer is indeed a block construction of above three units. In this work, the dendritic, terminal and linear units are distinguished by considering how many functional groups in the B_3 monomer (CYC) are consumed, similar to the case for hyperbranched polymers from AB_2 monomers. The dendritic, linear and terminal units have zero, one and two unreacted B functional groups (chlorine atoms) respectively. It is found that the secondary N-H linkages derived from the central aromatic (triazine) ring of the B_3 monomers are sensitive to the number of B functional groups, which are capable to assign the above three units with the help of ^{1}H-NMR measurement (Figure 2.11.-2.16). The relative amounts of the aforementioned units are calculated by the respective integration of the ^{1}H-NMR peaks. The peaks for the different units are assigned as discussed in the characterization section. The values of DB for all the

Table 2.2. Elemental analysis of hyperbranched polyamines

Polymer	Method	% of element				
		C	H	N	Cl[b]	S[b]
HPs	Calculated[a]	56.32	3.35	18.77	-	10.73
	Found	54.86	2.98	19.17	4.05	8.00
HPm	Calculated[a]	72.52	4.80	22.56	-	-
	Found	69.26	4.20	21.87	3.50	-
HPo	Calculated[a]	67.20	4.00	22.40	-	-
	Found	65.12	3.91	21.36	2.5	-
HPa	Calculated[a]	78.18	6.59	14.21	-	-
	Found	75.24	6.58	14.32	3.16	-
HPb	Calculated[a]	78.18	6.59	14.21	-	-
	Found	76.02	6.37	13.68	3.0	-
HPd	Calculated[a]	75.65	5.21	12.17	-	-
	Found	73.92	5.15	11.86	2.1	-

[a] *Calculated on basis of ideal dendritic structure with no chlorine atom*

[b] *Estimated by Schoniger combustion technique*

polymers are calculated from the integration of ^{1}H-NMR peaks and are given in Table 2.3. The results confirmed that all the polymers having near ideal hyperbranched structures (DB = 0.5) rather than linear (DB = 0) or dendrimer (DB = 1).

Table 2.3. Degree of branching (DB) of hyperbranched polyamines

Polyamine	HPs	HPm	HPo	HPa	HPb	HPd
DB	0.56	0.60	0.55	0.68	0.52	0.58

The other characteristic features of the synthesized hyperbranched polymers are discussed in details in the next chapter.

2.4. Conclusions

From this study, it has been found that the hyperbranched polyamines can be synthesized by an one-pot nucleophilic displacement polymerization technique via A_2 + B_3 approach using relatively low cost monomers. The synthesized polymers have been successfully characterized by UV-visible, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic studies and elemental analysis data. As the hyperbranched polyamines have structural defect, so it is very difficult to draw the exact structure. The values of degree of branching of these polyamines indicate that the structures of the polymers are more like hyperbranched rather than linear or dendrimer.

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CHAPTER THREE

Physical, Thermal and Fluorescence Properties of Hyperbranched Polyamines

3.1. Introduction

After more than 15 years of intensive research, the synthesis of hyperbranched polymer is certainly no longer new. The progress has been made in all directions, are covering synthesis, characterization, theory, modeling, and also potential applications [1-4]. But still it can not be called as matured or established because this research area is much active and still strongly expanding. Further, a full profile of different properties of hyperbranched polymers is still not studied comprehensively [5], except some physical properties like solution viscosity, solubility, etc. It is mainly due to defective highly branched complex structure of these polymers. Thus the interest to evaluate different properties of hyperbranched polymers is gaining tremendous potential among the scientists. The significant feature of dendritic polymers that has sparked significant interest is the belief that they could adopt a globular shape and having a large number of functionality with no entanglement, which will be reflected in their different properties.

The most interesting and widely studied properties of hyperbranched polymers over their linear analogs are higher solubility, lower solution or melt viscosity [6,7] and higher surface reactivity [8]. These improved properties are mainly due to branched and globular architecture [9,10] with large number of surface groups.

Another important characteristic property of hyperbranched polymers is their amorphous nature even though the linear analogs may be crystalline, which also influences the density of hyperbranched polymers [11]. However, liquid crystalline hyperbranched polymers have also been reported in literature, where the polymers possess highly rigid moiety and low molecular weight [12-15].

Parts of this work have been published in J Appl Polym Sci, 2007, 106, 95-102.

Again, the chemical reactivity of hyperbranched polymers towards different chemicals is high. Globular shape, large number of surface functionality, low viscosity and high solubility make the hyperbranched polymers easily accessible to other chemicals [16,17]. Thus hyperbranched polymers are much more reactive by multiple interactions with other substrates. These properties are especially helpful in curing of different thermosetting polymer systems [18].

Thermal properties of hyperbranched polymers are also extremely important for their ultimate applications. These properties especially the thermal stability is highly sensitive to change in temperature. It is indicated that T_g represents a crucial parameter for the determination of processing and servicing characteristics of materials. Generally, thermal properties of hyperbranched polymers are affected by the branched structure, bond strength, intra/intermolecular interactions, crystallinity, imperfection in structure, number of end groups, molecular weight, etc. [4]. The influence of the terminal groups of hyperbranched polymers on the thermal properties was studied in details by Hawker and Chu [19]. Further, design of hyperbranched polymers with s-triazine unit in the backbone, may offer high thermostability and flame retardancy [20,21].

Fluorescence of organic materials has been applied in many areas especially in chemical and biological sciences [22,23]. It can be observed from many organic materials, which have rigid frameworks and not many loosely coupled substituents through which vibronic energy can flow out i.e. materials with aromatic moieties, heterocyclic moieties, etc. with conjugate structures may exhibit fluorescence. Further conjugate structures with electron deficient unit such as nitrogen containing heterocyclic moiety are very interesting for this study [24,25]. The design of a polymer with heterocyclic moiety like s-triazine unit in the structure has profound effects on the physico-chemical and thermal properties as well as on its processability [26,27]. The incorporation of rigid electron deficient triazine unit in the hyperbranched polymeric structure is largely due to the ease of chemo- and thermo-selective substitution of the chlorine atoms with different nucleophiles to generate a variety of structures. Further recently, fluorescent and electroactive hyperbranched polymers with electron deficient unit are of great interest because of their highly branched globular structures which reduce the intramolecular and intermolecular aggregation behavior [28]. There are a large number of reports in the literature on the study of fluorescence property of hyperbranched polymers with different structures [29-33].

To predict any property of a polymer with known structure, the structure-property relationship is very important. However, such relationship is very difficult to establish in case of hyperbranched polymers because of their complex defective structures. So in this investigation an attempt has been made to establish a structure-property relationship on fluorescence property for hyperbranched polyamine with different structural moieties.

The influence of end groups on the properties of a linear polymer, at a sufficiently high molecular weight, is negligible. However, regardless of synthetic procedure used to obtain the hyperbranched polymers, the resulting macromolecules have a large number of end groups. The end groups have been demonstrated to be easily accessible for chemical modifications, and the nature of the end groups has been found to determine the physical properties of the hyperbranched polymers to a great extent. Therefore, the modification of the functional groups of hyperbranched polymers is of great interest for optimizing the material properties [34-36].

In this chapter, therefore, the physical, thermal and fluorescence properties of the synthesized hyperbranched polyamines are discussed.

3.2. Experimental

3.2.1. Materials

Cobalt (II) chloride hexahydrate ($CoCl_2 . 6H_2O$) was obtained from Merck, India. Its molecular weight (M_w) is 237.93 g/mol and minimum assay is 98%. The impurities present generally are sulfate (0.01%), lead (0.002%), iron (0.02%) and nickel (0.2%). It was used as received.

Cupric acetate monohydrate [$(CH_3COO)_2Cu . H_2O)$] was obtained from SD fine Chem, India. Its molecular weight (M_w) is 199.65 g/mol and minimum assay is 98%. The impurities present generally are chloride (0.005%), sulfate (0.03%) and iron (0.02%). It was used as received.

Lead (II) acetate trihydrate [$CH_3COO)_2Pb . 3H_2O$] was obtained from BDH, India. Its molecular weight (M_w) is 379.33 g/mol and minimum assay is 99%. The impurities present generally are chloride (0.005%), copper (0.002%) and iron (0.002%). It was used as received.

Nickel chloride hexahydrate ($NiCl_2 . 6H_2O$) was obtained from Ranbaxy Fine Chem. Ltd., India. Its molecular weight (M_w) is 237.71 g/mol and minimum assay is 97%. The impurities present generally are sulfate (0.05%), cobalt (0.02%) and iron (0.02%). It was used as received.

N,N'-dimethyl sulphoxide (DMSO) was purchased from Merck, India. Its purity is $\geq$99% with $\leq$0.2% water as impurity. The density is 1.09-1.10 g/mL at 25 ^{O}C and boiling point (b.p.) is 189 ^{O}C. This was purified by the following procedure. About 500 mL of DMSO was taken in a round bottom flask and 20 g of anhydrous calcium sulfate was added into it. The solution was kept for overnight. Then it was filtered and distilled under reduced pressure. This distillate obtained was kept in an amber bottle with 4A type molecular sieves.

Hydrochloric acid was obtained from Merck, India and was used as received. It has formula weight (F_w) 36.46 g/mol, purity $\geq$ 35% and the impurities present generally are sulfate (0.0005%), sulfite (0.001%), free chlorine (0.0001%) and heavy metals as lead (0.0005%), Iron (0.0002%) and arsenic (0.0001%).

Sodium hydroxide (NaOH) was obtained from Merck, India and was used as received. It has molecular weight (M_w) 40.0 g/mol and purity > 97%. It was used as received.

Anhydrous calcium sulfate ($CaSO_4$) was obtained from Qualigens, India. Its molecular weight (M_w) is 136.14 g/mol and minimum assay is 98%. It was used as received.

The hyperbranched polyamines (HPs, HPm, HPo, HPa, HPb and HPd) were obtained by using the same methods as described in experimental section of chapter two, section 2.2.2. and were used for determination of different properties. The end capped polymers (E1, E2 and E3) were also obtained by using the same methods as described in experimental section of chapter two, section 2.2.3. and were used for determination of the fluorescence property.

3.2.2. Instruments and methods

Viscosity of the polymer solutions (0·5% g/dL in DMAc) was measured by an Ubbelohde suspended level viscometer at (27±0·1) ^{O}C. The solubility of the polymers was observed in different solvents after three days at room temperature using 0·01 g of sample in 1·0 mL solvent. X-ray diffraction studies were made on the powder samples at room temperature (ca. 27 ^{O}C) on a Rigaku X-ray diffractometer (Miniflex, UK). The scanning rate used was 5.0 ^{O}min^{-1} over the range of 2θ = 10-90 ^{O} for the above study. The density of the polymers was determined by pycnometer in dry hexane at room temperature (ca. 27 ^{O}C) by the conventional liquid displacement method.

Thermogravimetric (TG) analysis and DSC measurement were carried out in Shimadzu TG 50 and DSC 60 DSC thermal analyzer respectively using the nitrogen flow rate of 30 mL/min at the heat rate of 10 ^{O}C/min.

The fluorescence spectra of the compounds were recorded in Perkin Elmer (LS55) spectrophotometer in DMSO solution.

The flame retardancy test of the polymers was carried out by measurement of limiting oxygen index (LOI) value by a flammability tester (S.C. Dey Co., Kolkata) by using modified version of the standard ASTM D 2863-77 by following formula.

$$\mathrm{LOI} = \{[O_2]/([N_2] + [O_2])\}X100$$

where $[N_2]$ = volume of nitrogen and $[O_2]$ = volume of oxygen in the oxygen-nitrogen gas mixture. The procedure is briefly described as follows.

The dry grounded powder sample was taken in a glass cup of diameter 1.0 cm and height of 1.01 cm attached with a glass rod of 80 cm, which was clamped by the sample holder. A mixture of nitrogen and oxygen gas was flown through the column in such a controlled rate that the total amount of gas mixture was 300 mL at each moment of the test. The amount of oxygen was initially low and it was increased after each trial for the same samples until it reached to the required amount. A pilot flame of (2.0±0.1) cm length was used to ignite the top of the specimen by touching it for 2 s and then it was removed. The burning of the samples was noted at the minimum concentration of oxygen in the nitrogen-oxygen gas mixture, which supports flame of the specimen for at least 30 s after removal of the pilot flame. The LOI values obtained by this technique are the average of at least three tests for each sample.

3.3. Results and discussion

3.3.1. Physical properties

The most important and significant result obtained for the hyperbranched polyamines is the solubility (Table 3.1). The hyperbranched polyamines are soluble only in highly polar solvents such as DMAc, DMF, DMSO, NMP, etc. but insoluble in most of the other solvents like hydrocarbon solvents, water, chlorinated common organic solvents, etc. This may be due to the presence of polar –NH- groups, rigid triazine units and aromatic moieties in the structures. However, this solubility behavior is superior compared to the similar type of aromatic linear polyamines [37], which may be due to the presence of large numbers of polar surface groups, non-entangled structure and globular shape of hyperbranched polymer. This high solubility not only supported the formation of hyperbranched structure but also confirmed that the polymers are not crosslinked gel products.

The inherent viscosity (η_{inh}) values of hyperbranched polyamines are mentioned in Table 3.2. The low viscosity values of all the hyperbranched polyamines are mainly due to globular and compact non-entangled structure, which makes them less viscous.

The moderate density value for all the polymers may be due to the presence of rigid aromatic triazine moiety, polar and hydrogen bonding interactions, which increases the compactness of the polymers (Table 3.2). The highest density of HPs than other polyamines is mainly due to the presence of sulfonyl group in the polymer backbone. But due to less symmetric structure of hyperbranched polymers because of structural defects, the density is not too high.

Table 3.1. Solubility behavior of the hyperbranched polyamines

Polymer	[c]Solubility							
	DMAc	DMF	DMSO	NMP	THF	Acetone	Toluene	Water
HPs	+	+	+	+	-	-	-	-
HPm	+	+	+	+	-	-	-	-
HPo	+	+	+	+	-	-	-	-
HPa	+	+	+	+	±	-	-	-
HPb	+	+	+	+	+	±	-	-
HPd	+	+	+	+	±	-	-	-

[c] key : + = soluble , - = insoluble.

The X-ray diffraction patterns (Figure 3.1) of hyperbranched polyamines donot show any sharp peak in the intensity vs. scaterring angle (2θ) curve, which indicate the polymers are amorphous in nature and hence compactness of the polymers is not so high. Since all the hyperbranched polyamines have almost similar structure so they exhibited same physical state, i.e. amorphous character.

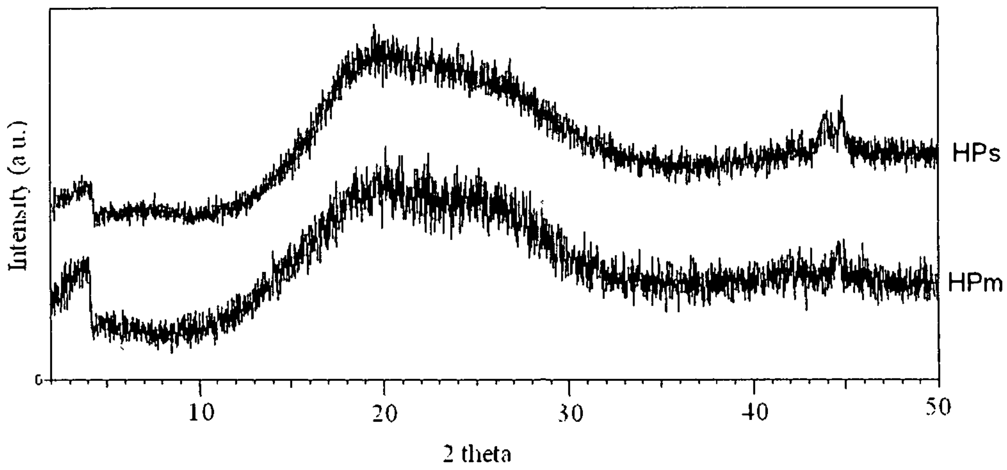

Figure 3.1. XRD deffractograms of the hyperbranched polyamines, HPs and HPm

Table 3.2. Physical properties of hyperbranched polyamines

Polymer	Color	Density (g/mL)	Viscosity [η_{inh} (gdL^{-1})]
HPs	Brown	1.29	0.23
HPm	Light brown	1.24	0.42
HPo	Light brown	1.18	0.15
HPa	Light brown	1.22	0.14
HPb	Light brown	1.18	0.14
HPd	Light brown	1.20	0.13

3.3.2. Thermal and flame retardant characteristics

The thermogravimatric analysis of hyperbranched polyamines (Figure 3.2) showed the high initial degradation temperature (about 255-305 ^{O}C) for all the cases. This high thermostability of these polyamines may be due to the presence of thermostable triazine and phenyl moiety in the structures. However, maximum stability was observed in case of HPs, where the polyamine was thermally stable up to 305 ^{O}C. The high stability of this polyamine is mainly due to the presence of sulfonyl group (O=S=O) in the polymer backbone in addition to the above thermostable moieties. The weight losses at initial decomposition temperature and 50% decomposition temperature as well as the char residue at 800 ^{0}C for the polyamines are summarized in Table 3.3. From this table, it has been seen that the char residue at 800 ^{0}C is about 46-52%, which indicated their overall high thermostability and flame retardancy characteristic. This is mainly due to the undegradable triazine and aromatic moieties. The high thermostability of polymers with triazine moiety is also reported by other researchers [37-39].

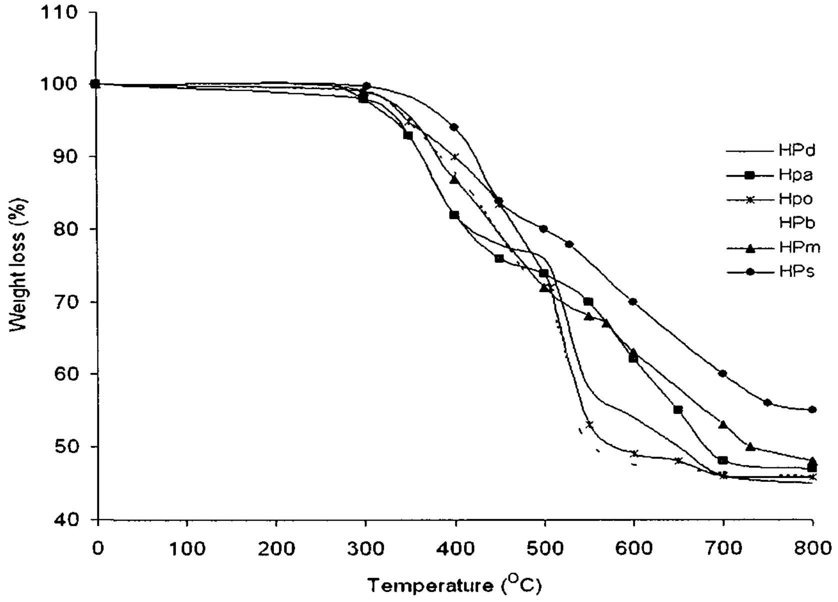

Figure 3.2. TG thermograms of hyperbranched polyamines

The self-extinguishing behavior of the polymers is also supported by high LOI value, which varies from 32-42. It has already been reported [20,21] that triazine based polymers have very good flame retardant behavior for their excellent charring effect. This is mainly due to the presence of tertiary nitrogen in their ring structures. However, the flame retardency test indicated that the HPm has lower and HPs has higher LOI value than the other polyamines (Table 3.3). This may be due to the presence of thermolabile -CH_2- moiety, which may form flammable CH_4, CH_3-CH_3, etc. molecules for HPm polymer. Whereas HPs does not possess such flammable moiety but it has non-flammable sulfur as the special element. However, the presence of methylene moiety in Pm polymer chain makes it relatively flexible than HPs, as obtained by measurement of T_g (glass transition temperature) from DSC studies (Table 3.3). In DSC studies no melting or crystallization peak was observed for all the polymers, which indicates that these hyperbranched polymers are amorphous in nature. This is further supported by the XRD study. The study indicates that the polymers have T_g within 230-243 ^{O}C, which supports the rigidity of the structure.

Table 3.3. Thermal characteristics and LOI values of the hyperbranched polyamines

Polymer	$^aT_5$ (°C)	$^bT_{50}$ (°C)	$^cCR_{800}$ (%)	^bT_g	LOI
HPs	305	-	55	240	42
HPm	255	720	48	230	32
HPo	300	695	45	238	36
HPa	298	575	46	243	38
HPb	290	555	44	236	37
HPd	260	650	45	240	35

$^aT_5$ (Temperature for 5% weight loss), $^bT_{50}$ (^{O}C) (Temperature for 50% weight loss), $^cCR_{800}$ (Char residue at 800 ^{O}C) obtained from TG curve at a heating rate 10 ^{O}C/min under the nitrogen atmosphere.

3.3.3. Fluorescence properties

Among the different classes of hyperbranched polymers, aromatic hyperbranched polyamines with s-triazine moiety have some added advantages. These include high thermostability, flame retardancy, high surface reactivity or ease of surface modification, good electronic property, good solubility, etc. Moreover, these aromatic hyperbranched polyamines are containing all three different types of nitrogen linkages viz. primary at terminal, secondary in main chain and tertiary in triazine unit. This s-triazine has also two important properties that incline to use this in this study. These are: (i) its ionization potential value is 11.67 eV, i.e. it is more electron deficient than pyridine (9.73 eV), pyridazine (10.61 eV), pyrimidine (10.41 eV) and pyrazine (10.2 eV) and (ii) unlike benzene ring, connecting three aromatic ring at 2, 4 and 6 positions of 1,3,5-triazine will not create the steric interactions of the ortho hydrogens [40]. As the terminal amino groups of the hyperbranched polyamine can easily react with a variety of other functionalities such as acid, acid chloride, anhydride, aldehyde, etc. [36, 41-43], so a number of reports have been published on the end group modification of different hyperbranched polymers to achieve many useful properties such as enhance solubility, thermostability, amphiphilic characteristics, conductivity, optical properties, etc. [30, 44-46]. Further recently, fluorescent and electroactive hyperbranched polymers with electron deficient unit are of great interest for their highly branched globular structures [47]. Thus hyperbranched aromatic polyamines with s-triazine units may be used as fluorescent materials for different applications especially in chemical and biological sciences [22-23].

The fluorescence emissions of hyperbranched polymers (0.1 g/L in DMSO) were shown in Figure 3.3. All these samples were excited within 285-290 nm wavelength of light and exhibit emission in the blue to yellow region from 350 to 650 nm with maxima at about 430-455 nm except polyamine, HPa. This may be due to the presence of aromatic moieties with s-triazine unit and large number of free amine groups in the structure of the polymers. The HPa exhibited the emission at the region 325-600 nm with maxima at about 370 nm. This may be due to the presence of electronically isolated three aromatic rings with *para* connectivity in between the two s-triazine rings. From these results, it has also been observed that HPs has the highest intensity compared to other polymers due to presence of fluorophore, O=S=O with conjugation in aromatic rings. High degree of branching makes the hyperbranched polymers more three-dimentional to avoid excimer/ aggregate formation.

Further, end capping with organic molecules or complexation with metal ions influence the fluorescence intensity of hyperbranched polymer by changing the quenching effects of the intra- or inter-molecular interactions of the different functional groups. For example, fluorescent chemosensors for selective detection of transition metal ions especially Cu^{2+} ion are rather rare [48,49], although it is a very important metal in human body and plays an important role in various physiological processes. Similarly the change of pH or concentration also affects the fluorescence intensity of the hyperbranched polymers [29-31,33]. So the effect of concentration (5-0.1 g/L in DMSO) of the polymer, pH of the medium (3.1-11.6), and metal ions has also investigated on the fluorescence characteristics of sulfone containing hyperbranched polyamine (HPs), as it shows the best result among the studied polymers. The hyperbranched polyamine (HPs) has also been end capped with benzoyl chloride and 4-

hydroxybenzaldehyde to study the influence of end groups. Further the dye molecule also enhances the conjugation and hence increases intensity [29,31]. So the effect of dye end capping is also investigated on a conjugated hyperbranched polyamine (HPo).

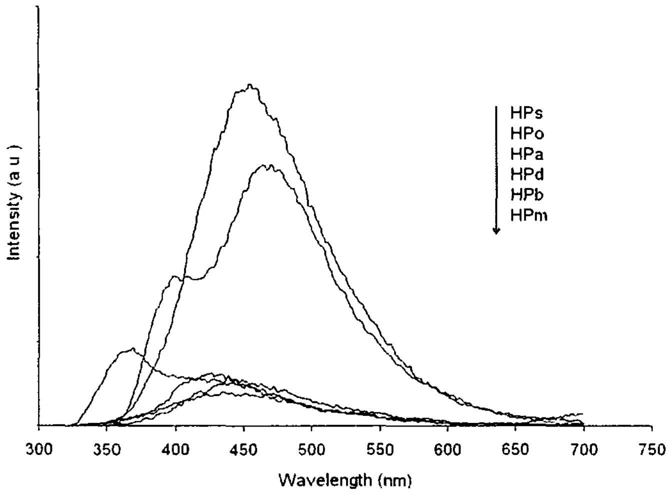

Figure 3.3. The fluorescence spectra of hyperbranched polyamines

Effect of concentration

The hyperbranched polyamine exhibits a general concentration 'self-quenching' effect with the increase of concentration of polymer (HPs) in DMSO solvent (Figure 3.4). Similar results have been reported by other researchers in case of hyperbranched poly(sulfone amine) and polyether [30,31]. The decrease of intensity with the increase of concentration of the polymer may be attributed by the quenching effect of amino groups present in the structure. Further this decrement via the self-association behaviors of polymers would change with concentration and hence the fluorescence behavior would also change with the same.

Effect of pH

As the hyperbarnched polyamine carries all three types of nitrogen atoms in its structure and energy migration is possible between chromophores, so the fluorescence intensity of the resultant polymer may depend on the pH of the solution. Figure 3.5 shows that the fluorescence intensity (at 450 nm) gradually increases with the increase of pH of the medium. It is well known that acidity of a solution always influence the

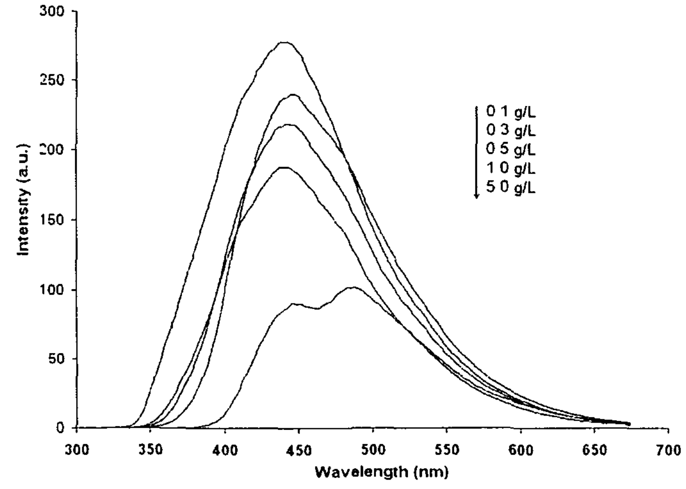

Figure 3.4. The fluorescence spectra of hyperbranched polyamine (HPs) with variation of concentration

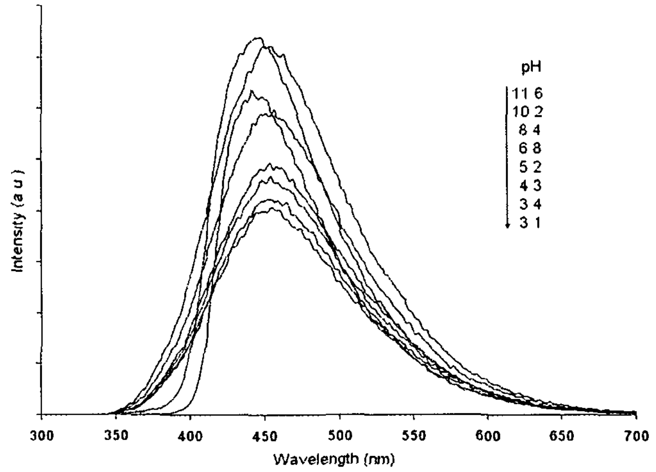

Figure 3.5. The fluorescence spectra of hyperbranched polyamine (HPs) with variation of pH

polarity, hydrogen bonding and the association state of polymer. The increase in fluorescence intensity with the increase of pH by addition of dilute alkali (NaOH) may be caused by weakening of association of hyperbranched polyamine. The decrease of intensity of fluorescence with the decrease of pH by addition of dilute acid (HCl) may be due to the formation of ammonium cation with decrease in pH. That is partial deformation of hydrogen bonds among inter- and intra- molecules in the presence of acid and also it behave as a polyelectrolyte [51]. In high pH amino groups remain deprotonated and association of the polymer is increased and hence intensity increases, this may be due to hydrogen bonding.

Effect of metal ion

Detection of metal ion by fluorescent chemosensor has been receiving much attention in recent years because of their potential application in clinical biochemistry and environment. However, fluorescent chemosensors for relative detection of transition metal ion, specially Cu^{2+}, which is third in abundance (next for iron and zinc) among the essential transition metals in the human body and plays an important role in various physiological processes. On the other hand, it is also known that copper ion despite being an essential element in biological system, has a toxic impact on the microorganism at even submicromolar concentrations. Thus it is highly desirable to design novel sensors for copper ions with high selectivity and sensitivity. There is, therefore the need of development on fluorescent sensors for detection of copper ion by using new fluorophores.

It is interesting that transition metal cation (such as Cu^{2+}) can quench the fluorescence of hyperbranched polyamine because of their branched architectures and presence of large number of coordinating sites, which help complexation with metal ions. Figure 3.6 shows an excellent selectivity for Cu^{2+} ion over other cations (Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}) by the hyperbranched polyamine (HPs). The quenching of fluorescence increases with the increase in concentration of Cu^{+2} ions (0.01-0.04%) but no such quenching in other cations is observed. The selectivity for Cu^{2+} might be interpreted to the geometrical difference between copper complex and other complexes as observed in other metal ligand complexes [51,52]. Due to Jahn –Teller effect copper complexes are characterized as square planar complexes but others generally form octahedral complexes [53,54]. Therefore hyperbranched polyamine can bind Cu^{2+} ion preferably over other metal ions. However, with addition of Cu^{2+} ion the fluorescence quenching became much more efficient as is evidenced from the plot of Stern-Volmer equation (Figure 3.7), which indicates better complexation. The quencher efficiency of Cu^{2+} ion can be measured by linear mathematical model, $F_O/F = 1 + kC_Q$, where F_O and F are the fluorescence intensity of the hyperbranched polyamine without any quencher and with a quencher at concentration of C_Q respectively and k is a constant.

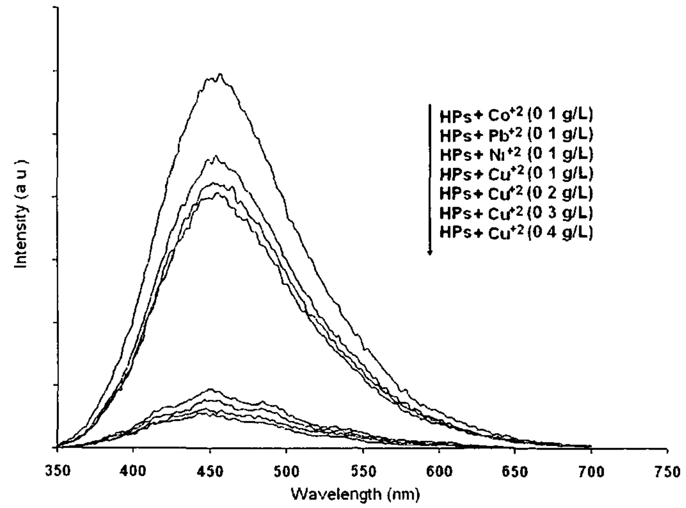

Figure 3.6. The fluorescence spectra of hyperbranched polyamine (HPs) and effect of metal ions

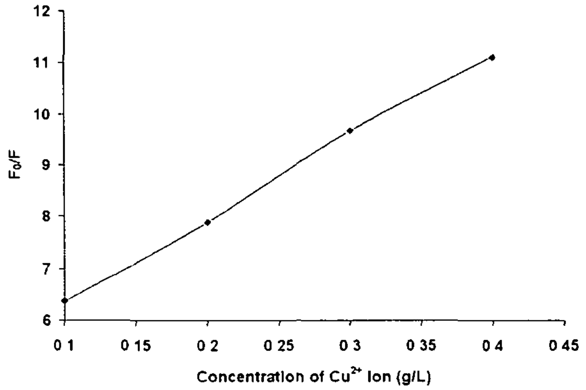

Figure 3.7. Quenching efficiency of Cu^{2+} ion at different concentrations on the fluorescence of hyperbranched polyamine (HPs) by Stern-Volmer plots.

End capping

The modification of large number of active functional groups of hyperbranched polyamine is of particular interest, and several research groups have successfully demonstrated this concept for a few hyperbranched polymer systems [52,55]. Here the organic compounds benzoyl chloride and 4-hydroxybenzaldehyde were used to modify the surface $-NH_2$ groups of hyperbranched polyamine (HPs) and the resulted end capped products are coded as E1 and E2 respectively. The fluorescence emissions of end capped hyperbranched polymers (0.1 g/L, in DMSO) were shown in Figure 3.8.

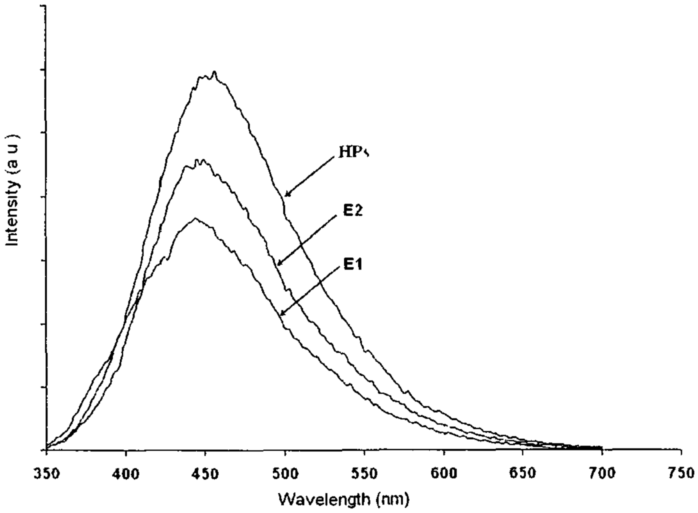

Figure 3.8. The fluorescence spectra of hyperbranched polyamine (HPs) and end capped hyperbranched polyamines (E1 and E2)

All these samples were excited at 285 nm wavelength of light and exhibit emission in the blue to yellow region from 350 to 650 nm with maxima at about 445-455 nm. From this figure it has been observed that intensity is decreased by endcapping of hyperbranched polyamine (HPs). It has also been seen that quenching effect is more prominent in E1 (benzoyl chloride end capped polyamine) than E2 (p-hydroxybenzaldehyde end capped polyamine). Therefore, it is confirmed that terminal electron donating groups such as –OH, -NH_2 enhance the intensity of fluorescence.

The fluorescence emission of dye (methyl red) end-capped hyperbranched polyamine (HPo) (E3, 0.1g/L, in DMSO) is shown in Figure 3.8. The sample was excited at 290 nm wavelength of light and exhibit emission in the blue to yellow region from 350 to 650 nm with maxima at about 455 nm and a shoulder at about 390 nm. From this result it has been observed (Figure 3.9) that end capping with methyl red dye enhanced the intensity of fluorescence significantly. This may be due to the facts that end capping prominently render the quenching process of energy and/ or electron transfer processes [29-31]. These processes otherwise could have been occurred between electron donating primary and/ or secondary amino groups and electron accepting aromatic and heterocyclic moieties present in the structure of the polymer. Further the dye molecule also enhances the conjugation and hence increases intensity.

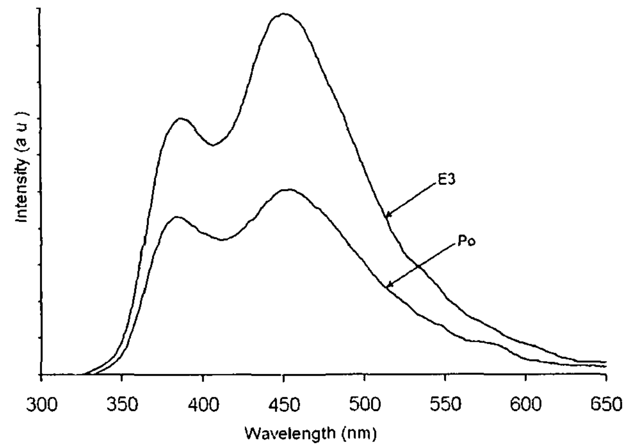

Figure 3.9. The fluorescence spectra of hyperbranched polyamine (HPo) and end capped hyperbranched polyamine (E3)

3.4. Conclusions

From this study, it can be concluded that the hyperbranched polyamines containing s-triazine ring show good thermostability under the nitrogen atmosphere, self-extinguishing characteristics and good solubility in highly polar solvents. The study shows that the fluorescence property of the polymers is influenced by variation of concentration, pH of the medium, end capping and the presence of Cu^{2+} ion. Thus, these hyperbranched polymers may find applications in compact laser devices, light harvesting/light emitting devices, copper ion and pH sensor.

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CHAPTER FOUR

Hyperbranched Polyamine as Multipurpose Polymeric Additives

4.1. Introduction

Virginity is not a virtue in case of polymers. The usefulness of polymers is obtained by adulteration and the way to adulterate them is very important for their ultimate performance [1]. For adulteration, it is necessary to incorporate some additives with appropriate amount to achieve desirable level of properties into the virgin polymer. Since most of the polymers suffer from attack by oxygen, light, ozone, high energy radiation, flammability, heat sensitivity, mechanical stress, etc. during process and service period. So generally antidegradant (0.2-1 phr, phr = parts per hundred), flame retardant (5-20 phr), heat stabilizer (1-4 phr), process aid (2-5 phr), etc. are necessary to incorporate into the virgin polymers [2]. Further, the strength properties of the polymers are generally low and hence it is necessary to incorporate some reinforcing fillers (20-60 phr) into the polymer matrix [2]. However, most of the conventional additives suffer from serious problems [3] like leaching, migration, volatility, etc. during service period as many of them are small molecular additives. Further, some of them are inorganic in nature, whereas polymers are generally organic in nature, so there is compatibility problem, in these cases. In addition to the above, the amount of conventional small molecular additives generally required is high to get the desired level of properties, which may adversely affect the other properties of the base polymers.

As already discussed in chapter one that highly branched macromolecules not only possess large number of surface functionalities but also they exhibit unique rheological properties like low melt or solution viscosity because of globular shape and

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Parts of this work have been published in Polym Degrad Stab, ***2007****, 92, 947-955 and Euas Chem Technol J,* ***2007****, 9, 29-38* non-entangled structure [4-7]. This unique architecture of these novel macromolecules makes them interesting candidate as one of the macromolecular additives with different commercial linear polymers along with many other applications.

Since these additives are macromolecular in nature, so they eliminate all the above problems, which are observed in the case of conventional small molecular additives. Further, because of large number of active functionalities on the surface of the dendritic polymers, the effectiveness will be very high. Thus these additives will be expected to act as a high performance polymeric additives for different base polymers. Many hyperbranched polymers viz. polyphenylene [8], polyesters [9-11], poly(ether amide) [12], polyamides [13], poly(amide ester) [14], etc. are utilized to improve desirable level of properties for different well-known linear polymers. Kim and Webster [9] used hyperbranched polyphenylene to improve processability and thermosatblity of polystyrene. Voit *et al.* reported the improvement of different properties of commercial linear polymers e.g. tensile strength and compression modulus of polycarbonate by blending with hyperbranched polyester [9], homogeneous distribution of dye molecules in polyolefin by modifying with polyester [10], processability of polyamide by mixing with hyperbranched poly(ether amide) [12], etc. Diao *et al.* used hyperbranched poly(amide ester) [14] as a compatibilizing agent in polypropylene/poly(vinyl chloride) blend.

Again as most of the polymers are organic in nature with often high hydrogen to carbon ratio, so they are combustible. For their various applications in the building, electrical, transportation, mining and other industries, they have to fulfill flame retardancy requirements as the mandatory regulations. Thus, the main objectives in development of flame retardant polymers are to increase ignition resistance and reduce rate of flame spread when incorporated in flammable polymers.

The halogenated compounds are good flame retardant additives for polyolefins, especially while used in combination with antimony trioxide, but they have serious disadvantages of emission of toxic gases and corrosive smokes [15]. To eliminate these problems, metal based compounds can be used. Here metallic hydroxide split off water and are environmental friendly. Again their low activity requires high concentration, which may adversely affect other desirable properties of the polymers [16]. Flame retardant containing only phosphorus as special element can produce its derivative with strong dehydration when oxygen is provided in the structure of the polymers and produces large amount of residue after combustion [17]. However, as there is no oxygen in polyolefins, so phosphorus containing flame retardants are not useful for these polymers. Recently, nitrogen containing flame retardant has great demand, especially in combination with phosphorus compound, because of their multifunctional advantages [18-21]. The main advantages of nitrogen based flame retardants are low toxicity, available in solid state, high efficiency and no need of presence of oxygen or any other particular element [22]. They are suitable for recycling as the nitrogen based compound has high decomposition temperature. In regard to waste disposal they are comparable with fertilizers as they posses the same elements of importance namely nitrogen and phosphorus [16,23,24]. Due to unique and unusual properties of special element containing hyperbranched polymer is an actual candidate as flame retardant additives. Further, design of hyperbranched polymers with s-triazine unit in the backbone, may offer high thermostability and flame retardancy [25,26].

In this chapter hyperbranched sulfone containing polyamine, HPs was utilized as a multipurpose polymeric additive and hyperbranched 1,4-diisopropyl group containing polyamine, HPa was used only as flame retardant additive with and without phosphorous compound for commercial linear polymers like low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC).

4.2. Experimental

4.2.1. Materials

Low density polyethylene (LDPE) [weight average molecular weight $1.0X10^5$ g/mol and density 0.91 g/c.c.] and plasticized poly(vinyl chloride) (PVC) [weight average molecular weight $1.2X10^5$ g/mol and density 1.27 g/c.c. with 25 (%) plasticizer dioctyl phthalate (DOP)] were obtained from local market and used as the base polymers. IPPD (N-isopropyl-N′-phenyl *p*-phenylenediamine), a well known commercial antidegradant was also obtained from the local market and used as received. Triphenylphosphine oxide (TPO) was obtained from SD fine Chem, India. Sodium hydroxide (NaOH) (Merck, India), hydrochloric acid (HCl) (Merck, India) and *N,N′*-dimethylacetamide (DMAc, SD fine Chem, India) were used as received. The technical specifications of these chemicals have already been given in the experimental section of chapter three, section 3.2.1.

The hyperbranched polyamines (HPs, HPa) were obtained by using the same methods as described in experimental section of chapter two, section 2.2.2. and the properties are described in chapter three in details.

4.2.2. Instruments and methods

4.2.2.1. Instruments

4.2.2.1.1. Brabender Plasticorder

The instrument is a S.C. Dey's & Co. made Brabender Plasticorder type instrument. It is used for compounding of polymeric materials with different additives. The cavity size of this instrument is 100 c.c. The screw rotational speed is variable (0-120 rpm) and can be heated from room temperature to 300 ^{O}C.

4.2.2.1.2. Compression Mold

The instrument is a S.C. Dey's & Co. made laboratory size Hydraulic Press with load capacity up to 15 tons. Area of the plate is 300 x 300 (mm^2) with temperature controller from room temperature to 300 ^{O}C.

4.2.2.1.3. Sample Cutter (Punture)

The instrument is a S.C. Dey's & Co. made manual sample cutter. The dimension of the die is as per the sample dimension of ASTM D 412-51 T.

4.2.2.1.4. Universal Testing Machine (UTM)

The instrument is a Zwick Z010 Universal Testing Machine (UTM) with crosshead speeds from 0.01 mm/min to 500 mm/min. Software used is Merlin (Win-98 platform). Load cells are 100 N and 10 kN with very high accuracy and wide range of materials can be tested.

4.2.2.1.5. Melt Flow Index (MFI) tester

The instrument is a S.C. Dey's & Co. made melt flow index tester. It is used to measure the processability of polymers and their blends. This instrument is a dead weight piston plastometer consisting of a thermostatically controlled heated stainless steel cylinder with a jet and the weighted piston operating within the cylinder. The cylinder having 30 mm diameter and 123 mm length with a smooth and straight hole of

0.95-1.0 mm diameter. It has a heater with digital temperature indicator cum controller, which maintains the temperature up to 300 ^{O}C with precision of ± 1 ^{O}C.

4.2.2.1.6. Hardness Tester

The instrument is a Durameter of shore A or shore D, made by S.C. Dey's & Co. and the instrument is as per the standard ASTM D 676-59.

4.2.2.1.7. *Limiting Oxygen Index (LOI) tester*

The instrument is a S.C. Dey's & Co. made limiting oxygen index tester and used to measure the limiting oxygen index (LOI) value for different self-supported and powder polymer samples. It can be used to measure the minimum volume of oxygen required to sustain a burn of a sample in an oxygen-nitrogen gas mixture as per the ASTM D 2863-77 standard method.

4.2.2.2. Methods

4.2.2.2.1. Compounding and molding

The hyperbranched polymers were processed at 145 ^{O}C for PVC and at 135 ^{O}C for LDPE in a Brabender plasticorder at dose level of 1, 5 and 7.5 phr (for HPs) and 5 phr (only for HPa) separately for both the cases. The linear polymer with the hyperbranched polyamine was mixed at screw speed of 60-65 rpm for 3-4 min in each case. Both the base polymers were also mixed with 5 phr of IPPD, 5 phr TPO and a combination of 2.5 phr hyperbranched polymer (HPa) with 2.5 phr TPO in the same way, separately. The pre-shaped sheets of compounded polymers were prepared in the two rolls laboratory size open mill followed by molding at 150 ^{O}C for 8 min for PVC and 10 min for LDPE respectively under a pressure of 5-6 tons in a laboratory size electrically heated two-platened compression mold. The sheets were kept for seven days at ambient condition for maturation before further studies.

4.2.2.2.2. Testing

To determine different properties at least three specimens per test were tested and the average values were reported. The processability of the compounds was measured using melt flow index (MFI) tester and by solution viscosity measurement. The MFI value was measured as the amount in gram of the material extruded by piston action through the standard orifice under the standard load in the plastimeter (S.C. Dey's & Co., Kolkata) at 190 ^{0}C for LDPE and 170 ^{0}C for PVC over a specified time period of 10 min. The solution viscosities of PVC and its compounds were measured by a suspended level Ubbelohde viscometer at (25±0.1) ^{0}C in DMAc of 0.5 g/dL concentration. On the other hand, the solution viscosity of LDPE compounds could not be measured due to the poor solubility of LDPE in common organic solvents at used experimental conditions.

Tensile strength (T.S.) and elongation at break (E.B.) were measured according to the standard ASTM D 412-51 T procedure using dumb-bell shape specimens (Figure 4.1.) at room temperature by Zwick Z010 Universal Testing Machine (UTM) with jaw separation speed of 50 mm/min. The hardness of all samples was measured by Shore A or Shore D type Durometer as per the standard ASTM D 676-59 T procedure.

Thermogravimetric (TG) analysis was carried out in Shimazdu TG 50 thermal analyzer using nitrogen flow rate of 30 mL/min and at the heat rate of 10 ^{0}C/min. The surface morphology of blends was studied by using SEM of SU-SEM probe analytical scanning microscope.

All dumb-bell shaped specimens were immersed for 10 days in water, for 72 h in aqueous 1% NaOH (w/v) and 2% HCl (v/v) solution at 30±1 ^{0}C for aging test. The heat aging test was carried out at 70 ^{0}C for 7 days in an electrically heated air-circulating oven as per the standard ASTM D 573 procedure.

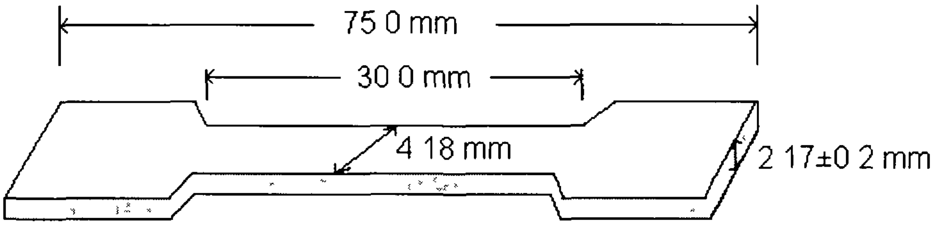

Figure 4.1. Diagram of dumb-bell shape specimen for tensile test

Flame retardancy test of the self-supported specimens was carried out by the measurement of LOI values as per the standard ASTM D 2863-77 procedure using following formula.

$$LOI = \{[O_2]/([N_2] + [O_2])\}x100$$

where $[N_2]$ = volume of nitrogen and $[O_2]$ = volume of oxygen in the oxygen-nitrogen gas mixture.

The specimen was clamped vertically in the center of the column in such a way so that the top of the specimen should be at least 100 mm below top end of the column. The dimension of self-supported polymer specimen for determination of LOI values is shown in Table 4.1. A mixture of nitrogen and oxygen gas was flown through the column in such a controlled rate that the total amount of gas mixture was 300 mL at each moment of the test. The amount of oxygen was initially low and it was increased after each trial for the same specimen until it reached the required amount. A pilot flame of 2.0±0.1 cm length was used to ignite the top of the specimen by touching it for 2 s and then it was removed. The burning of the specimen was noted at the minimum concentration of oxygen in the nitrogen-oxygen gas mixture, which supports flame of the specimen for at least 30 s after removal of the pilot flame.

Table 4.1. Specimen dimension (mm) for LOI test

Type	Width	Thickness	Length
Self-supported flexible polymer	6.5±0.5	2.0±0.25	70-150

4.3. Results and discussion

Since the hyperbranched polyamine (HPs) has a large number of active $-NH_2$ groups (degree of branching, DB = 0.56) and low solution viscosity (inherent viscosity, η_{inh} = 0.23 dL/g), so it is expected that this highly branched macromolecule will act as multipurpose polymeric additive. It has been experimentally observed that the physical property, mechanical property and processability of linear polymers can be improved by the incorporation of hyperbranched polymers [9-14].

The general chemical structures of the hyperbranched polyamines (HPs and HPa) are shown in Figure 4.2 and Figure 4.3. These structures indicate the presence of flame retardant special elements such as chlorine (4.05 % in HPs and 3.06 % in HPa) and nitrogen (19.17 % in HPs and 14.32 % in HPa), rigid and thermostable aromatic and triazine rings, and high carbon to hydrogen ratio (18.41 for HPs and 11.88 for HPa). All these structural features indicate that these hyperbranched polyamines might behave as flame retardant materials.

4.3.1. Morphology study

The morphology as observed from the fracture surfaces of PVC and LDPE molded samples exhibits a homogenous distribution of hyperbranched polyamine (HPs) (Figure 4.4) as well as hyperbranched polyamine (HPa) with TPO (Figure 4.5) in the base polymers. The homogeneous distribution of hyperbranched poly(ether amide) in polyamide-6 matrix was also observed by Huber *et al.* [12]. These results indicate that hyperbranched polymers have high capability to compatibilize with linear polymers. The mixing behavior of a linear polymer with the highly branched polymer at molecular level is expected to be quite different from the same between two linear polymers. This difference is mainly due to the conformational restrictions on the hyperbranched component [13]. Further, large number of functional groups of the hyperbranched polymer helps in mixing with linear polymer, as the sample is prepared either from solution or in the molten condition [27].

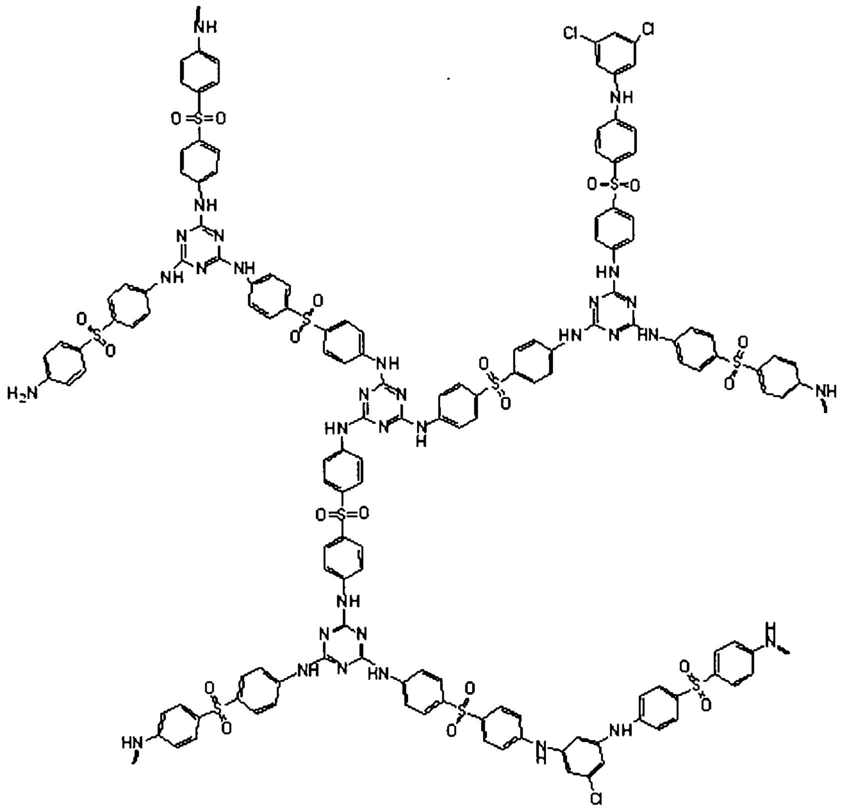

Figure 4.2. Structure of hyperbranched polyamine, HPs

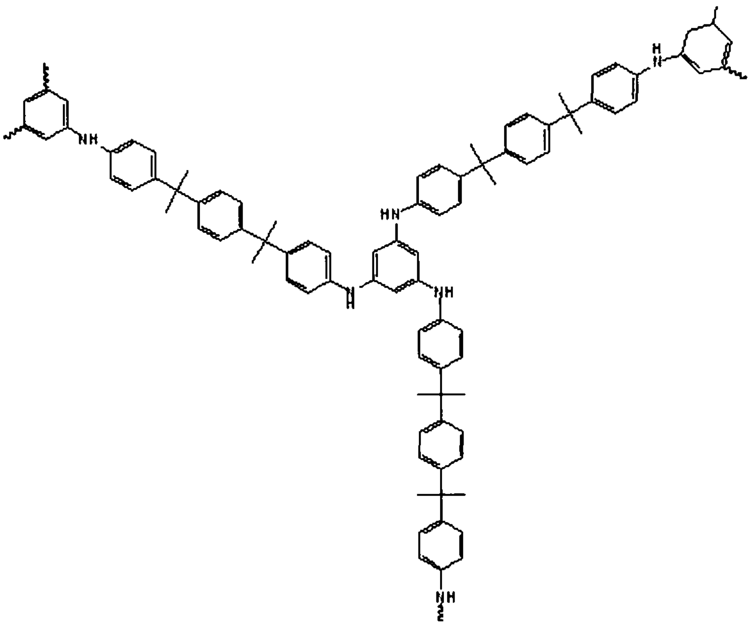

Figure 4.3. Structure of hyperbranched polyamine, HPa

The SEM micrographs of both polymers suggested that the minor phase domain sizes decrease on increase of the concentration of hyperbranched polyamine (HPs). This type of morphology is likely to improve the mechanical properties of the base polymer as the dose level increases, which may be due to uniform distribution of the components as well as better compatibilization at the polymer/polymer interface. Further, a significant change of surface morphology was observed even on mixing at low dose of hyperbranched polymer (HPs, 1 phr) for both the base polymers. However, from DSC study no conclusion is possible to draw, as there is no significant difference was noticed in the DSC curve for both the cases.

4.3.2. Processability study

Physical properties like solution viscosity, density, etc. of the compounded polymers are given in Table 4.2. The data show the decrease of the inherent viscosity of the PVC compounds with the increase of the concentration of hyperbranched polyamine (HPs). This may be due to the fact that the hyperbranched polyamine (HPs) has relatively lower viscosity (inherent viscosity 0.23 dL/g) than the linear base polymer, PVC (inherent viscosity 0.87 dL/g). Similar type of result was also reported in

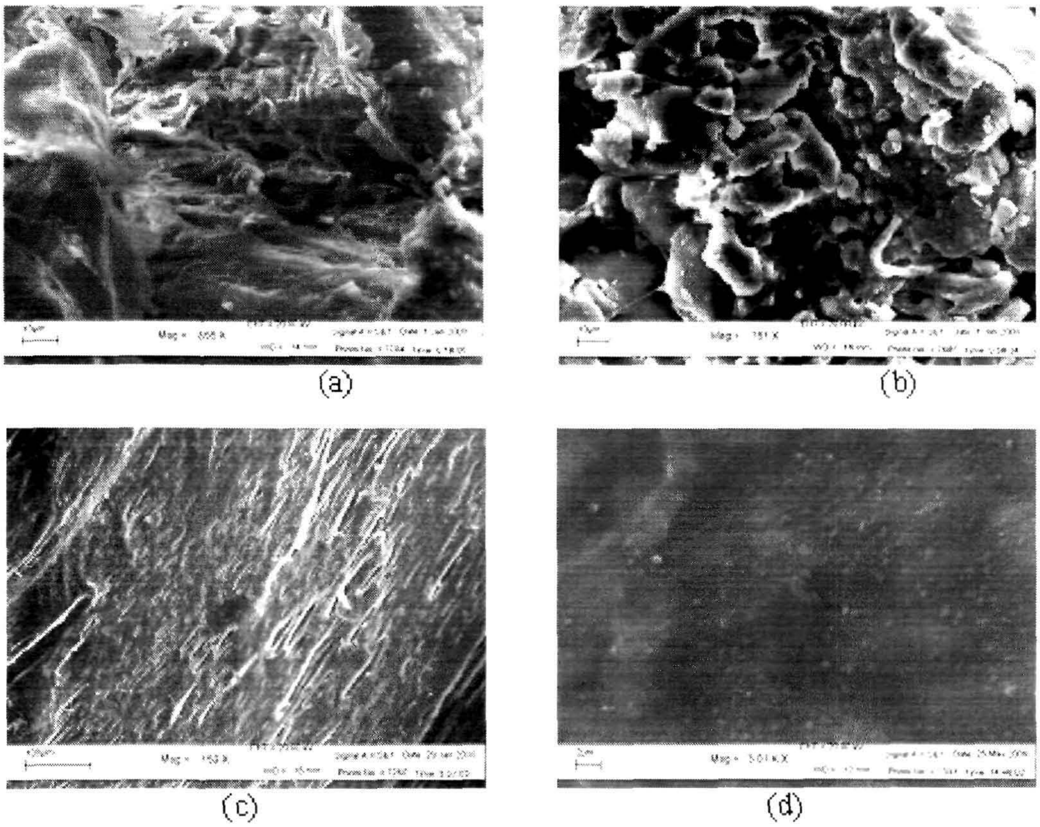

Figure 4.4. SEM micrographs of (a) LDPE with 5 phr hyperbranched polyamine (HPs), (b) 100% LDPE, (c) PVC with 5 phr hyperbranched polyamine (HPs) and (d) 100% PVC

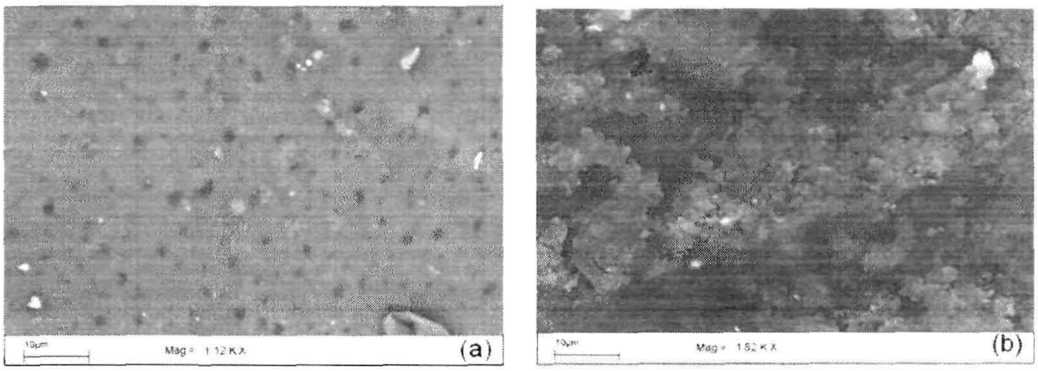

Figure 4.5. SEM micrographs for (a) PVC:HPa:TPO (100:2.5:2.5) and (b) LDPE:HPa:TPO (100:2.5:2.5)

case of linear polyamide-6 with hyperbranched poly(ether amide) compounds [12]. Thus the hyperbranched polyamine may act as a process aid. This has been further supported from MFI measurement (Figure 4.6) of the compounded polymers, where the MFI value of both PVC and LDPE compounds increases with the increase in hyperbranched polyamine content (HPs). These results indicate that this additive is acting as melt viscosity reducer. However, as the values are not significantly changing, so these results confirmed that there is no chemical reaction occurring between the base polymers and the hyperbranched additive. If there could have increased of molecular weight, both solution as well as melt viscosity should increased. However, the change of MFI of PVC based compounds is slightly higher than the LDPE based compounds at same dose level of hyperbranched polyamine. The higher value of MFI of PVC compounds may be due to the better compatibility of plasticized PVC with hyperbranched polymer as supported by SEM study (Figure 4.4). This better compatibility may be due to interaction of polar amine groups of hyperbranched polyamine with the polar chlorine atoms of PVC and ester groups of DOP plasticizer. In mixing process it has also been found that the initial rotational screw speed of the mixing equipment increased by 5 phr to 10 phr on addition of the hyperbranched polyamine for both the cases. The improvement of processability by incorporation of hyperbranched polymer is also reported in case of blends of linear polystyrene and hyperbranched polyester [28], which supports this result. On the other hand, in compounds of both PVC and LDPE with 5 phr of IPPD no significant change in the viscosity or screw speed was observed, which indicates that IPPD can not act as a process aid for those base polymers. This result confirmed that this hyperbranched polyamine could be employed to improve processability for linear polymer like LDPE or PVC.

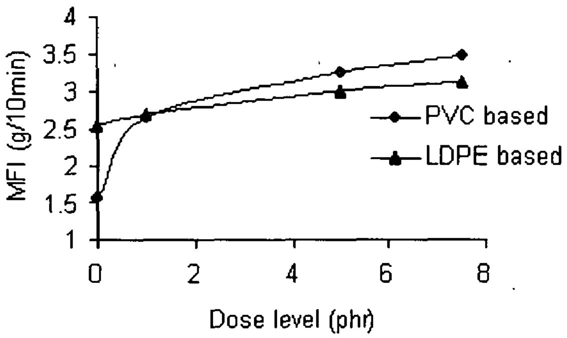

Figure 4.6. Melt flow index of PVC and LDPE based compounds

Table 4.2. Solution viscosity, density and melt flow index of PVC and LDPE samples

Physical Property	Sample code *							
	P0	P1	P5	P7.5	L0	L1	L5	L7.5
Viscosity(dL/g)	0.88	0.87	0.85	0.84	-	-	-	-
Density (g/mL)	1.27	1.275	1.28	1.28	0.89	0.90	0.93	0.94
MFI (g/10 min)	1.57	2.65	3.24	3.46	2.54	2.70	3.01	3.12

* digit indicates the amount of hyperbranched polymer incorporated in 100 parts of base polymer, and code P is for PVC and L is for LDPE.

4.3.3. Mechanical properties

The changes of mechanical properties of the polymers can be explained from the compatibility point of view. As the hydrogen atoms of amine of hyperbranched polyamine may interact with the -Cl group of the PVC or/and ester groups of DOP through H-bonding, so these interactions enhance the compatibility between this base polymer and the additive. Further, there is also polar-polar interaction between plasticized PVC and hyperbranched polyamine. However, such interactions are not possible in case of LDPE and hyperbranched polyamine. This is supported by SEM studies (Figure 4.4). This is also reflected in their mechanical properties (Table 4.3 and 4.4). Thus in case of PVC, the increment of tensile strength is relatively higher than that of LDPE based material with the increase of amount of hyperbranched additive. The tensile strength values decreases at high dose level (7.5 phr) in both the cases. Further the addition of higher dose than 7.5 was not studied because of commercial point of view. This is also due to the fact that a few earlier studies [10,28] showed that mechanical properties of the compounds of hyperbranched polymer with linear polymer decreases at high dose levels may be due to the globular non-entangled structure of the hyperbranched polymers. The higher tensile strength values were also observed for the samples in both the cases at dose level of 5 phr of hyperbranched polymer compared to the conventional antidegradent IPPD (Table 4.3 and 4.4). This may be due to the fact that hyperbranched additive has better compatibility than IPPD with both the base polymers. The retention of mechanical properties after heat aging and leaching in different chemical media (Table 4.5 and 4.6) for both the polymers indicate that the hyperbranched polyamine acts as antidegradant and also improves leaching properties. In this case, however, the polymer with IPPD also shows good retention after heat aging, though the retention after leaching was lower than hyperbranched additive containing polymer. These results indicate that even though IPPD is a good antidegradent, but it undergoes leaching problem may be due to small molecular size as well as lesser compatibility with the base polymers compared to hyperbranched polyamine. The better aging properties of the polymers by incorporation of polymeric additive was also reported by Karak and Maiti [29] in case of chloroprene and Natural rubber base polymers with antimony polyether. The hardness of both the polymers increases with the increase of amount of additive, which may be due to rigidity of triazine and aromatic moieties of hyperbranched additive as well as better compatibility. However, the change of hardness with IPPD can not be explained for both the cases. The elongation at break for PVC increases with the increase of hyperbranched polyamine dose level. Whereas in case of LDPE the reverse trend was observed (Table 4.3 and 4.4), which may be due to the fact that because of some interactions of PVC chain molecules with hyperbranched polyamine molecules, chains can be extended and as the dose level increases the extensibility also increases. Whereas in the case of LDPE as there is no interaction, so the additive could not help in chain extension rather LDPE remains as free particle, which may deteriorate the elongation capability of the base polymer.

Table 4.3. Mechanical properties of plasticized PVC with HPs before aging

Sample Code*	Tensile Strength (N/mm^2)	Elongation at Break (%)	Hardness (Shore-A)
P0	10.61±0.055	396±3.14	84±0.44
P1	12.47±0.068	452±4.38	85±0.00
P5	13.56±0.050	487±4.52	87±0.44
P7.5	12.91±0.112	532±4.59	88±0.00
PIPPD5	12.72±0.110	415±3.87	80±0.77

* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer, and code P is for PVC.

Table 4.4. Mechanical properties of LDPE with HPs before aging

Sample Code*	Tensile Strength (N/mm^2)	Elongation at Break (%)	Hardness (Shore-D)
L0	10.22±0.072	71±2.19	53±0.00
L1	10.49±0.104	51±1.78	55±0.44
L5	11.22±0.044	45±1.60	57±0.00
L7.5	10.98±0.105	41±1.26	58±0.77
LIPPD5	10.41±0.113	54±2.12	50±0.44

* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer and L is for LDPE

Table 4.5. Effect of leaching and heat aging in the mechanical properties of the PVC with HPs

Sample code*	Sample Treatment**	% Retention of Properties after Treatment		
		Tensile Strength	Elongation at Break	Hardness Shore-A
P0	HA	94±0.56	93±0.67	97±0.53
	WL	99±0.26	98±0.44	100±0.53
	BL	98±0.46	97±0.59	98±0.65
	AL	98±0.38	98±0.39	97±0.00
P1	HA	96±0.57	95±0.76	98±0.00
	WL	98±0.29	98±0.35	100±0.0
	BL	96±0.52	95±0.82	97±0.51
	AL	98±0.69	98±0.54	97±0.51
P5	HA	98±0.47	97±0.62	98±0.00
	WL	98±0.21	97±0.31	100±0.0
	BL	96±0.36	96±0.71	97±0.51
	AL	96±0.42	97±0.48	97±0.00
P7.5	HA	96±0.78	97±0.44	97±0.51
	WL	97±0.32	98±0.27	99±0.00
	BL	97±0.64	94±0.67	97±0.00
	AL	98±0.53	96±0.56	96±0.51
PIPPD5	HA	95±0.76	85±0.92	98±0.00
	WL	91±0.54	89±0.73	93±0.55
	BL	93±0.63	88±0.58	92±0.00
	AL	92±0.41	89±0.45	93±0.55

* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer, and code P is for PVC.

**HA- Heat aging for 7 days at 70 ^{o}C, WL- Leaching with water for 10 days at room temperature, BL- Leaching with 1% NaOH solution and AL- Leaching with 2% HCl solution for 3 days.

Table 4.6. Effect of leaching and heat aging in the mechanical properties of the LDPE with HPs

Sample code*	Sample Treatment**	% Retention of Properties after Treatment		
		Tensile Strength	Elongation at Break	Hardness Shore-D
L0	HA	96±0.72	92±0.67	96±0.84
	WL	98±0.51	97±0.45	98±0.00
	BL	94±0.56	93±0.71	94±0.78
	AL	96±0.47	96±0.86	94±0.00
L1	HA	98±0.42	94±0.47	98±0.00
	WL	99±0.21	98±0.61	98±0.00
	BL	97±0.39	96±0.72	97±0.81
	AL	99±0.19	96±0.59	96±0.00
L5	HA	98±0.44	97±0.48	98±0.00
	WL	99±0.37	98±0.45	98±0.00
	BL	98±0.53	97±0.63	99±0.79
	AL	99±0.39	98±0.54	98±0.00
L7.5	HA	97±0.68	95±0.57	98±0.80
	WL	99±0.42	95±0.56	96±0.00
	BL	98±0.49	96±0.71	98±0.00
	AL	99±0.32	97±0.63	96±0.00
LIPPD5	HA	97±0.67	94±0.83	97±0.81
	WL	96±0.55	94±0.77	98±0.00
	BL	95±0.70	93±0.69	98±0.00
	AL	92±0.83	92±0.75	98±0.80

* digit indicates the amount of hyperbranched polymer or IPPD additive incorporated in 100 parts of base polymer and L is for LDPE.

**HA- Heat aging for 7 days at 70 ^{O}C, WL- Leaching with water for 10 days at room temperature, BL- Leaching with 1% NaOH solution and AL- Leaching with 2% HCl solution for 3 days.

4.3.4. Flame retardancy study

The limiting oxygen index (LOI) values of the virgin hyperbranched polymers HPa and HPs were found to be 38 and 42 respectively, which indicate that both the hyperbranched polyamines exhibit self-extinguishing characteristics. It has already been reported [23] that triazine based polymers have very good flame retardant behavior for their excellent charring effect. This is mainly due to the presence of tertiary nitrogen in their ring structure. They also have other advantages like low toxicity, no corrosion, low smoke, good compatibility, etc. The LOI value may be used as an indicator to evaluate flame retardancy of a polymer. The hydrocarbon-based polymers with high hydrogen/carbon ratio like LDPE are highly susceptible to flame, whereas PVC is a self-extinguishing polymer. The formation of non-combustible HCl gas (major product, ~58%), and relatively low yield of organic degradation products (~38%) provides a reasonable explanation for the self-extinguishing characteristic of virgin rigid PVC [30]. But on addition of plasticizer like DOP, which is essential to make it soft for its different applications, the flame-retardant characteristic decreases proportionally to the amount of plasticizer. This is due to the fact that plasticizer is degraded to combustible gasses instead of 'boil off' during accidental over heating, which is first step of any burning process. A higher CO_2/CO ratio for plasticized PVC relative to virgin PVC probably reflects the greater flammability of plasticizer [30]. Again, the polyolefins like LDPE readily fragmented during accidental over heating, yielded highly volatile low molecular weight saturated and unsaturated hydrocarbons that are highly flammable [30]. Thus the flame-retardant properties of these polyolefines were examined by measuring the LOI values after blending with the hyperbranched flame retardant polyamines. The flame retardancy values of the blends of commercially available linear polymers such as plasticized PVC and LDPE with hyperbranched polyamines, commercial antidegradant IPPD and flame retardant TPO at different dose levels are shown in Tables 4.7. It has been observed that the LOI values of pure LDPE and plastisized PVC with no flame retardant additives are 17.5 and 33.7 respectively. From the present study, it has been observed that both the hyperbranched polyamines improve LOI values of the base polymers, plasticized PVC and LDPE (Table 4.7). As the amount of hyperbranched polyamine (HPs, Table 4.7) content in the blends increases the LOI value also increased for both the cases. This is quite obvious as with the increase of hyperbranched polymer content the concentration of special flame retardant elements increases, so the results. The high efficiency of hyperbranched polyamine may be due to the fact that it has some special elements such as –Cl, -N and –S in its structure, which are helping flame inhibition of the base polymers [31]. The LOI values at 5 phr dose level are much higher with hyperbranched polyamine for both the base polymers compared to the polymers with IPPD. However, the well-established antidegradant IPPD is not able to improve the flame retardancy of any of these linear base polymers. This result further proved that even though IPPD is a good antidegradant (section 4.3.3.) for plasticized PVC and LDPE but it can not be regarded as good flame retardant. While on addition of 5 phr of TPO, the values increased to 18.75 and 35.5 for LDPE and PVC respectively. This increment of LOI values is due to flame retardant characteristic of TPO. TPO has been used as flame retardant additive in many polymers and it is thought to act by directing decomposition towards production of less flammable gases and more carbonaceous char products. However, the exact action of phosphorus compounds as flame retardants in polyolefins is not well understood. It may be due to the formation of some polyphosphoric acids by the reaction with polymer melt and these polyacids may form a non-combustible coating over the polymer surface and thereby shielding the polymer matrix from the environmental oxygen. This may also be due to another action of phosphoric acid, which helps in release of HCl from the halogen bearing compounds (plasticized PVC and chlorine containing hyperbranched polyamine in this case). However, as already stated in the introduction section that phosphorus alone will not act effectively for polyolefins as there is no oxygen in the structure. Actually, phosphorus can produce its derivatives with strong dehydration, when oxygen is provided. The derivatives can dehydrogenate the substrate to increase the amount of char residue after combustion. Further, on addition of 5 phr of hyperbranched polyamine alone, the LOI values are higher than TPO based compounds with the same amount of flame-retardant additives (Tables 4.7). This may be due to the presence of nitrogen and chlorine in the structure of the hyperbranched polymer. These results prove the better flame retardancy characteristic of hyperbranched polyamine compared to commercial TPO flame retardant. Further, the LOI values increased to a significant extent when a combination of 2.5 phr of TPO with 2.5 phr of hyperbranched polyamine (HPa) was used for both the polymers (Tables 4.7). This result indicates that hyperbranched polyamine has synergistic flame-retardant effect with TPO in the above base polymers. This synergistic effect of nitrogen with phosphorus compounds was proved in several other reports. In a phenolic resin with 6 weight % of phosphorus has the same flame retardancy effect with a combination of 2 weight % phosphorus and 2 weight % nitrogen compounds [31]. The reason for these results is speculative, but perhaps these additives facilitate the formation of some ring structures, which provided more char residue and hence aid in flame retardancy. The observation in this study confirmed that the same phenomenon is also applicable for hyperbranched polyamine with TPO. Further a slight phosphorus-chlorine synergism may also occur here, as chlorine is available in the system [30].

Table 4.7. LOI values of LDPE and PVC based polymers with hyperbranched polyamines

Composition (phr)	LOI	Composition (phr)	LOI
LDPE (100)	17.5	PVC (100)	33.7
LDPE:HPs (100 :1)	18.75	PVC:HPs (100 :1)	35.0
LDPE:HPs (100 :5)	21.25	PVC:HPs (100 :5)	37.5
LDPE:HPs (100 :7.5)	22.5	PVC:HPs (100 :7.5)	38.5
LDPE:IPPD (100 :5)	18.25	PVC:IPPD (100 :5)	34.0
LDPE:HPa (100 :5)	21.0	PVC:HPa (100:5)	36.75
LDPE:TPO (100:5)	18.75	PVC:TPO (100:5)	35.5
LDPE:TPO:HPa (100:2.5:2.5)	26.0	PVC:TPO:HPa (100:2.5:2.5)	38.75

Evaluation of flammability by thermal analysis

TG is well suited to follow the vaporization and degradation profile of polymer systems. As the combustion process of polymeric materials has occur through four steps viz. (i) preheating, (ii) degradation, (iii) ignition, and (iv) combustion and propagation, so thermal analysis will definitely help in evaluation of flammability of such materials. However, TG can not detect unequivocally the exact mechanism, which dominates the inhibition process, though it can easily show whether the flame retardant undergoes char formation in an inert atmosphere at elevated temperature (above 500 ^{0}C) or not.

The TG analysis of PVC samples with 5 phr of hyperbranched polyamine and IPPD (Figures 4.7) indicates better thermostability by incorporation of hyperbranched polyamine, whereas thermostability decreases with IPPD in the nitrogen atmosphere. This further indicates that there are some interactions of hyperbranched polyamine with PVC and plasticizer molecules. As hyperbranched polymer has thermostable triazine and aromatic moiety, so the thermostability of the compounded PVC increased. Whereas thermostability of PVC with IPPD decreases may be due to fact that as there is no interaction with base polymer, so these molecules remain freely and during heating they are vibrating more easily causing higher heat building i.e. increasing kinetic energy in the system and thereby facilitate degradation of the polymer. Again in the case of LDPE (Figure 4.8), the thermostability of the base polymer increases by incorporation of hyperbranched polyamine as well as IPPD compared to the virgin base polymer. This high thermostability of LDPE on incorporation of additive may be due to the presence of thermostable triazine and aromatic moiety in hyperbranched polyamine and also aromatic moiety in IPPD.

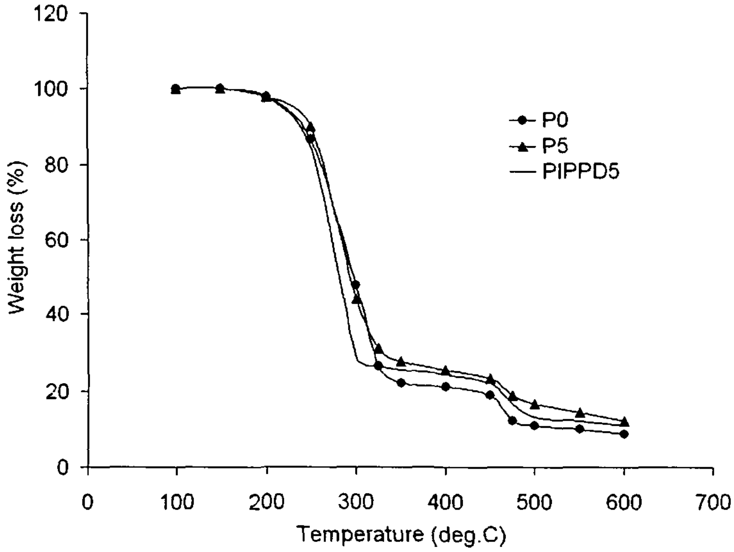

Figure 4.7. TG thermograms for PVC based polymeric materials (P0 = 100% PVC, P5 = 5 phr HPs with PVC, and PIPPD5 = 5 phr IPPD with PVC).

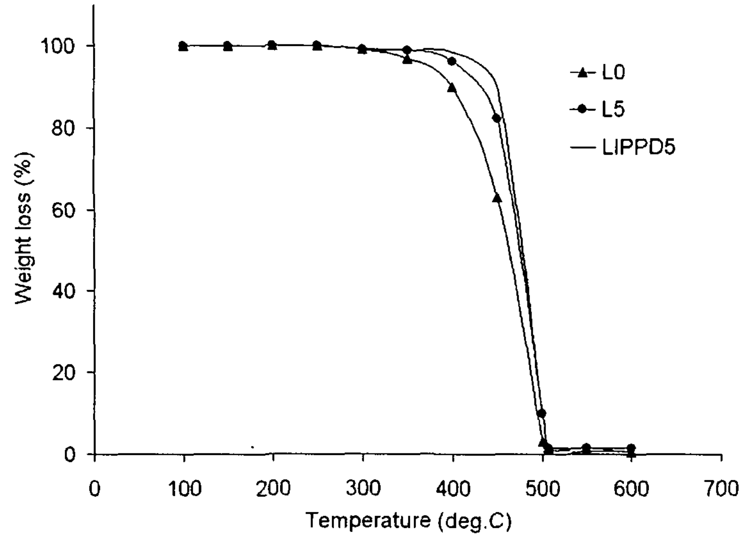

Figure 4.8. TG thermograms for LDPE based polymeric materials (L0 = 100% LDPE, L5 = 5 phr HPs with LDPE, and LIPPD5 = 5 phr IPPD with LDPE).

As the nitrogenated (triazine containing amino compound/material) flame retardants retard the flame by the formation of carbonaceous product, so higher char residues were observed in the TG curves (Figure 4.9 and 4.10) for the polymer systems with flame retardants such as hyperbranched polyamine (HPa) and a combination of hyperbranched polyamine (HPa) with triphenylphosphine oxide compared to the TG curves of respective base polymers in both the cases (Table 4.8). This high char formation reduces the amount of flammable fuel that the flammable polymer can create. This flame retardant can also act as an inert diluent as well as it retards the loss of other flame retardant, TPO that is present in the matrix [32] (Figure 4.9 and 4.10). A strong N-P synergistic effect was confirmed from the FT-IR spectra of the char compounds (discussed below), which was observed in LOI test, as discussed earlier. The difference of residue of the polymer systems with flame retardants minus the corresponding base polymer indicates the concentration of flame retardant in the systems was utilized in inhibition of flame by non-flammable product formation (Table 4.8). The thermostability of both the base polymers enhanced by the presence of only hyperbranched polymamine (HPa), as observed in TG thermograms and thus the rate of production of volatile components decreases, which improved the flame retardancy of the base polymers.

Table 4.8. The residual weight at 350 ^{O}C and at 600 ^{O}C for the polymer systems

Polymer composition (phr)	Residual weight (%) at 300 ^{O}C	Residue weight (%) at 600 ^{O}C
LDPE (100)	96.9	0.3
LDPE:HPa (100:5)	99.0	3.1
LDPE:HPa:TPO (100:2.5:2.5)	97.5	5.0
PVC (100)	22.2	8.89
PVC:HPa (100:5)	27.0	12
PVC:HPa:TPO (100:2.5:2.5)	28.0	14.6

These findings suggest that hyperbranched polyamine not only promotes some amounts of char formation (where heterocyclic moiety is mainly responsible) in the solid polymers, but it also improves the thermostability of the LDPE base polymer. Thus hyperbranched polyamine alone and a combination of this hyperbranched polyamine (HPa) with TPO act as very effective flame retardant, which was confirmed by LOI measurement as discussed earlier.

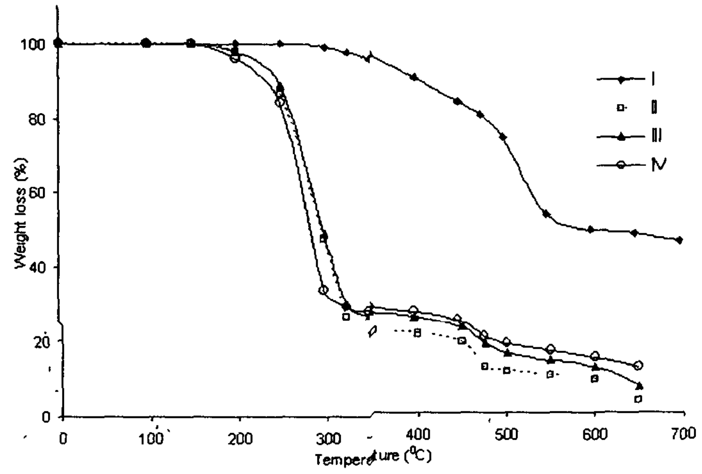

Figure 4.9. TG thermograms for I = HPa, II = 100% PVC, III = PVC with 5 phr HPa and IV = PVC with 2.5 phr HPa and 2.5 phr TPO

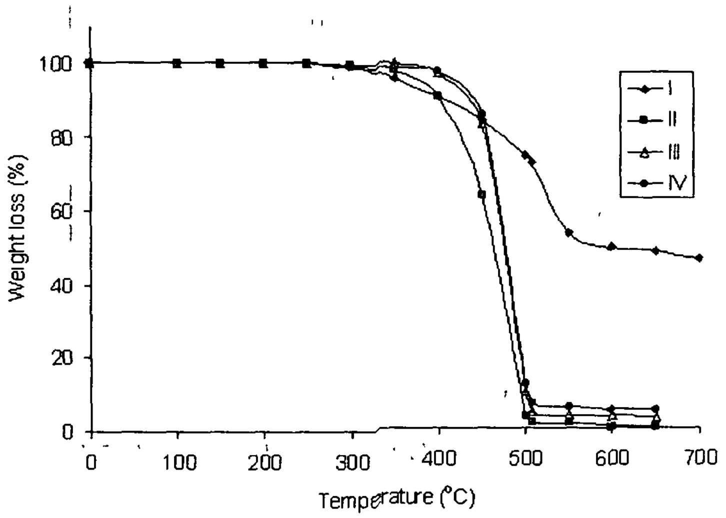

Figure 4.10. TG thermograms for I = HPa, II = 100% LDPE, III = LDPE with 5 phr HPa and IV = LDPE with 2.5 phr HPa and 2.5 phr TPO

The effects of heat aging and solvent leaching in different chemical media on LOI values have also been studied for all samples. It has been observed that there were no detectable changes of LOI values after heat aging and leaching in tested media.

FT-IR study for structural analysis of char residue

The FT-IR spectra of char residues of different samples are shown in Figure 4.11. This study is carried out to understand the synergistic effect of nitrogen with phosphorus compound. The spectra were taken from the char of the LOI tested sample

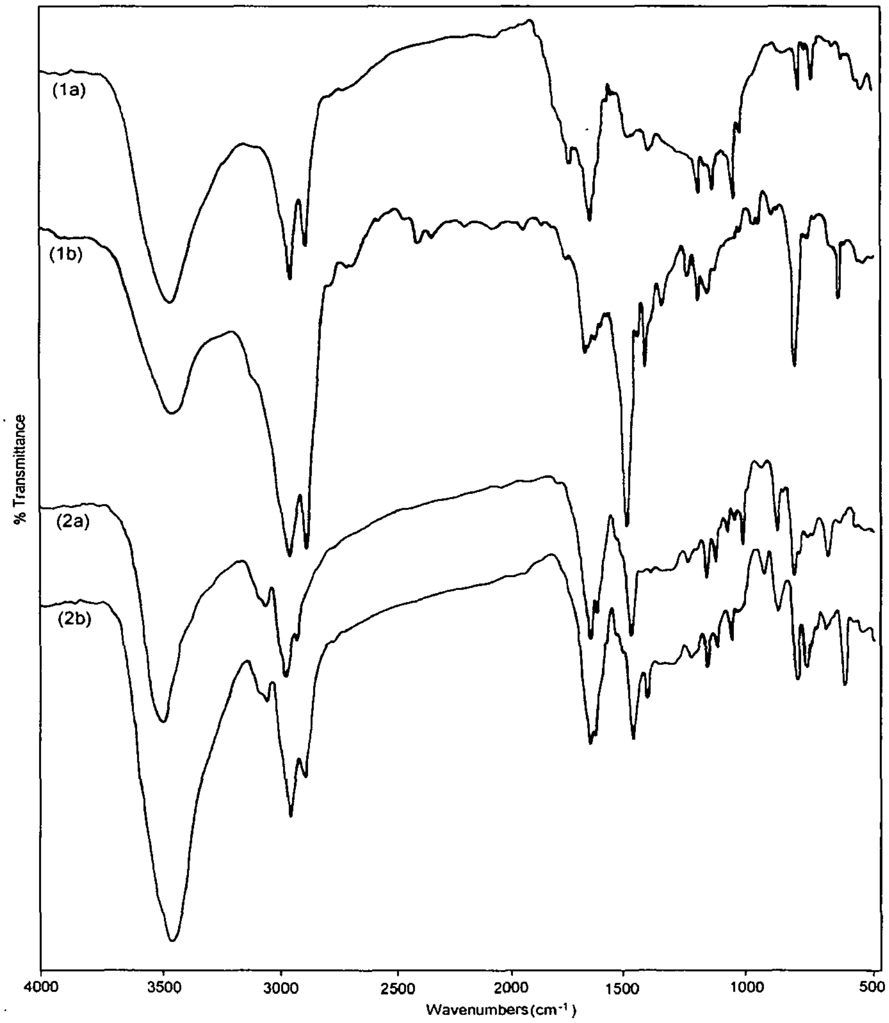

Figure 4.11. FT-IR spectra of residues of polymers with 2.5 phr HPa and 2.5 phr TPO after burnt in muffle furnace (1a for LDPE and 2a for PVC) and burnt from LOI test (1b for LDPE and 2b for PVC)

and by heating of samples in muffle furnace at 400 ^{O}C for 2h under open air. The spectra indicate some typical features of band with formation of $(PNC)_x$ complex by the presence of the following peaks. 3030-3426 cm^{-1} for NH stretching vibration, 2920 cm^{-1} and 2850 cm^{-1} for $-CH_2$ groups, 1630-1624 cm^{-1} for aromatic ring structure, 1206 cm^{-1} for stretching vibration of P-O-C structure in P-C complex [33], 1020-1080 cm^{-1} for skeleton vibration of triazine ring and symmetric vibration of P-O in P-O-C structure, 995 cm^{-1} for P(=O)-OH group and 912 cm^{-1} for P-O-P linkage in both cases. Thus FT-IR spectra confirm the chemical interaction between hyperbranched polyamine and TPO with the base polymers. Further, the presence of P-O-C and P-O-P linkages in the char residue was confirmed from the spectra. The band at 1060 cm^{-1} of muffle furnace samples is disappeared in the spectra of LOI tested char samples. While a new band appear at 1407 cm^{-1}. These further indicate the above chemical interaction. Hence it is confirmed that this combination of flame retardant additives is forming some carbonaceous char residues with the base polymer, which inhibit the flame and thereby increasing the flame retardancy.

4.4. Conclusions

From this study it has been found that hyperbranched aromatic polyamine (HPs) with s-triazine moiety can act as a multipurpose polymeric additive for the commercial linear polymers like plasticized PVC and LDPE. The hyperbranched polyamine has good compatibility with plasticized PVC and LDPE though the degree of compatibility with PVC is higher than LDPE. This hyperbranched polyamine improved the processability, mechanical properties and flame retardancy for both the base polymers. However, the improvement is higher in case of PVC than LDPE. The retention properties after heat aging as well as after leaching in different chemical media of the polymers were also improved. The hyperbranched polyamine has the better capability to prevent degradation, leaching and migration compared to the conventional antidegradant, IPPD.

This s-triazine based hyperbranched polyamine, HPa is a flame retardant additive for plasticized PVC and LDPE. The nitrogen-phosphorous synergistic effect is also observed for this hyperbranched polymer with commercial TPO flame retardant. Thus a combination of hyperbranched polyamine with TPO is a good flame retardant system for plasticized PVC and LDPE.

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CHAPTER FIVE

Hyperbranched Polyamines as Matrices for Preparation of Nanoparticles

5.1. Introduction

Metal particles such as silver, copper, etc. have been known as very effective antimicrobial agents since ancient times. Silver containing compounds and materials have been routinely used to prevent attack of a broad spectrum of microorganisms on prostheses [1], catheters [2], vascular grafts [3], human skin [4], arthroplasty [5], also used in medicine to reduce infection in burnt treatment [6,7], etc. Silver, in its different oxidation states (Ag^O, Ag^+, Ag^{2+}, and Ag^{3+}), has an inhibitory effect towards many bacterial strains and microorganisms. The papers published so far deal only with the study of the antibacterial properties of silver containing compounds/materials [8-12], as this metal exerts a stronger toxic action against prokaryotes (i.e., all types of bacteria) than eukaryotes (i.e., all other organisms, from fungi to human) [13,14]. However, eukaryotes especially fungi are also dangerous pathogenic microorganisms and hence the antifungal agents are also need to be studied. Fortunately, aqueous solutions based on copper ions [15] as well as copper complexes species [16-19] or copper-containing polymers [20,21] have often been used as effective antifungal agents. Further, both Ag and Cu ions as well as their compounds exhibit low toxicity to mammalian cells.

Metal particles in nanometer size have attracted considerable interest in recent years, as they have tremendous applications in area of biomedical, catalysis, optoelectronics, etc. [22-24] due to their unique size dependent properties. Among them, silver and copper colloids have been the major focus of interest toward their antimicrobial activity. In general, a wide variety of chemical synthesis of copper and silver nanoparticles with a narrow size distribution have been already reported by the use of photoreduction, radiolytic reduction, alcohol reduction, and reduction using various reducing agents in association with protective polymers and surfactants [25-

29]. However, preparations of copper nanopaticles are relatively difficult because they are easily oxidized [30-31]. Thus effort can be made to prepare stable nanoparticles of the above metals with control size in suitable matrices. The different matrices such as micelles [32], organic small molecules [33], linear polymers [34], mesoporous materials [35], dendritic polymers [8,36], etc. are used for this purpose, in general. Dendritic polymers particularly with polar terminal groups like amine, hydroxyl, amide, etc. are one of most useful class of matrices. This is due to fact that dendritic polymer fits perfectly with the definition of an ideal matrix, which stabilize the nanoparticles. This is due to the presence of large number of easily accessible terminal functional groups, high solubility in different solvents and low viscosity of the matrix [38]. In spite of these above favorable aspects, only a few attempts have been made so far to use such a matrix [8,36,38,39]. As poly(amido amine) dendrimer allows the formation of complexes with a wide variety of metal cations [40] that may form nanoparticles after reduction, so this dendritic polymer is already used as one of the important matrices for preparation of many metal nanoparticles [41]. Similarly, the studied hyperbranched polyamines with s-triazine units may also be used as an effective matrix for the same purpose.

In this chapter, therefore, the hyperbranched polyamines, HPd and HPb were utilized as matrices for synthesis of nanoparticles, which were used as an antimicrobial agent against particular microbes.

5.2. Experimental

5.2.1. Materials and methods

5.2.1.1. Materials

Cupric acetate monohydrate [$(CH_3COO)_2Cu.\ H_2O)$] was obtained from SD fine Chem, India. It was recrystallized from aqueous methanol before used and the technical specifications of these chemicals have already been given in experimental section of chapter three, section 3.2.1. Here it was used for preparation of Cu nanoparticles.

Silver nitrate ($AgNO_3$) was purchased from SD fine Chem, India. Its molecular weight (M_w) is 169.6 g/mol and minimum assay is 99.8 %. It was used as received and utilized for preparation of Ag nanoparticles.

Sodium borohydrate ($NaBH_4$) was collected from Merck, India. Its molecular weight (M_w) is 37.83 g/mol and minimum assay is 95%. Here it was used as reducing agent for metal ions.

N,N′-Dimethyl sulphoxide (DMSO) was purchased from Merck, India. Its technical specifications and purification has already been presented in experimental section of chapter three, section 3.2.1.

The hyperbranched polyamines (HPd and HPb) were obtained by using the same methods as described in experimental section of chapter two, section 2.2.2. They were used as matrices for nanoparticles.

Nutrient broth and nutrient agar (HIMEDIA, India) were used as received. The compositions of nutrient broth are pepetone -10 g/L, beef extract -10 g/L and sodium chloride -5 g/L and the agar are same compositions of nutrient broth and agar -12 g/L.

Bacillus Subtilis bacteria and *Candida albicans* fungus strains were collected from the Department of Molecular Biology and Biotechnology, Tezpur University, India.

5.2.1.2. Synthesis of nanoparticles

5.2.1.2.1. Synthesis of silver nanoparticles

1 g of hyperbranchred polyamine (HPd) with 10 mL DMSO was taken in a round bottom flask with constant stirring. 5 mL solution of 0.1 g of $AgNO_3$ in water was added dropwise into the polymer solution with vigorous stirring at room temperature (ca 27 ^{O}C). After completion of the addition the reaction mixture was stirred for another 20 min. Then 0.1 g of aqueous solution of $NaBH_4$ was added dropwise into the mixture. The reaction mixture was further stirred for another 20 min. The color of the resultant solution turns yellow to deep brown. This solution was kept for further studies.

5.2.1.2.2. Synthesis of copper nanoparticles

1 g of hyperbranched polyamine (HPb) with 10 mL DMSO was taken in a round bottom flask with constant stirring under N_2 purge. 5 mL solution of 0.1 g of copper acetate in water was added dropwise into the polymer solution with vigorous stirring at room temperature (ca 27 ^{O}C). After completion of addition the reaction mixture was stirred for another 30 min. Then 0.2 g of aqueous solution of $NaBH_4$ was

added dropwise into the mixture. The reaction mixture was further stirred for another 45 min. The color of the resultant solution turns from deep blue to yellow. This solution was kept for further studies.

5.2.2. Characterization and testing

FT-IR spectra for the compounds were recorded in a Nicolet (Impact 410, Madison, USA) FT-IR spectrophotometer by using KBr pellets. X-ray diffraction studies were made on the powder samples at room temperature (ca. 27 ^{O}C) on a Rigaku X-ray diffractometer (Miniflex, UK). The scanning rate used was 5.0 ^{O} min^{-1} over the range of 2θ = 10-90 ^{O} for the above study. UV spectra of samples were recorded in a Hitachi (U-2001, Tokyo, Japan) UV spectrophotometer by using 0.001% solution in DMSO:water (v:v, 1:1). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out in Shimazdu TG 50 and DSC 60 thermal analyzers respectively using the nitrogen flow rate of 30 mL/min and at the heat rate of 10 ^{O}C/min. The size and distribution of silver nanoparticles were studied by using JEOL, model noumber JEMCXII transmission electron microscope (TEM) at an operating voltage of 80 kV.

Preparation of culture media for incubation of microorganisms

1.3 g nutrient broth powder was dissolved in 100 mL water by gently boiling in a 250 mL conical flask stoppered by cotton plug. The broth was sterilized by autoclaving at 15 lbs pressure at 121 ^{O}C for 15 min. Then it was cooled in a laminar hood, which was disinfected beforehand by cleaning thoroughly with absolute alcohol followed by UV irradiation for 20 min. A disinfected wire loop size stock microorganism of *Bacillus Subtilis/Candida albicans* was transferred into the cold medium under laminar flow. After transferring the cultured microorganism, the conical flask was replugged and kept in an incubator oven for 24 h at 37 ^{O}C with constant shaking.

Testing of antibacterial activity

3.7 g of nutrient agar powder was dissolved in 100 mL of water by gently boiling in a conical flask. The agar solution was sterilized by autoclaving at 15 lbs pressure at 121 ^{O}C for 15 min. Then it was cooled to 40-45 ^{O}C in a laminar hood, which was disinfected beforehand following the same procedure as described earlier. 2 mL of the above culture broth medium was added into it, after taking all precautions to avoid any contamination, and mixed thoroughly by hand shaking. The content was then poured into four petri dishes with average equal agar thickness (2.5 mm). The dishes were cooled for sufficient time (25-35 min) to solidify the agar medium, then three grooves in each dish were made by a sterilized crock borer (5 mm diameter) and that medium was taken out from the dish by the help of a disinfected wire loop. 20 μL of each test solution of different concentrations was poured in each groove in three dishes. Each such dish contained polymer metal nanoparticles, polymer metal complex and pure polymer solution of same concentration. The 4th dish was used for control study by taking DMSO:water (v:v, 1:1) solvent only, without any test sample. The covered dishes were wrapped well by a paraffin film to seal them. The entire handling was done inside the laminar hood in front of a flame of a spirit lamp. Then the dishes were kept in an incubator oven at 37 ^{O}C for 24 h to test the antimicrobial activity of the polymer solution. After the test. inhibition zone diameter was measured from the clear zone of agar dish.

5.3. Results and discussion

5.3.1. Synthesis of nanoparticles

The metal nanoparticles are formed *in-situ* in the matrix of hyperbranched polyamines by reduction of metal ions in DMSO-water (v/v 1:1) mixed solvent. The polymeric matrix especially the hyperbranched polymer supports the stabilization of metal colloidal solution, prevents agglomeration and precipitation of the particles. As the used hyperbranched polyamines (Figure 5.1 and 5.2) have tertiary and secondary nitrogens in their structures along with large number of free active surface primary amine groups, so the metal ions are formed stable complexes and dispersed uniformly. The study shows that at particular ratio of Ag^+ to nitrogen, Ag^+ formed the most stable complex [42] in hyperbranched polyamine. Also Cu^{2+} ion has a strong tendency to form metal complexes with nitrogen [40]. Further, at this ratio it is believed that the copper nanoparticles formed are uniform in size and dispersion, which are the most desirable for such preparation. This is supported by UV-visible and TEM studies. Hence some of the challenging issues of nanoparticles formation are achieved to certain extent through this technique. The excess amount of reducing agent was used to ensure complete reduction of metal ions, this is confirmed by the change of reaction solution color from yellow to brown and blue to brown for silver and copper respectively and subsequent characterization of metal nanoparticles by different spectroscopic techniques. The colloidal silver nanoparticles do not precipitate or change in color even after five months of preparation and three months for copper in absence of oxygen. Further, there is no noticeable change in UV-visible absorption spectrum of silver colloid was observed during that period of study.

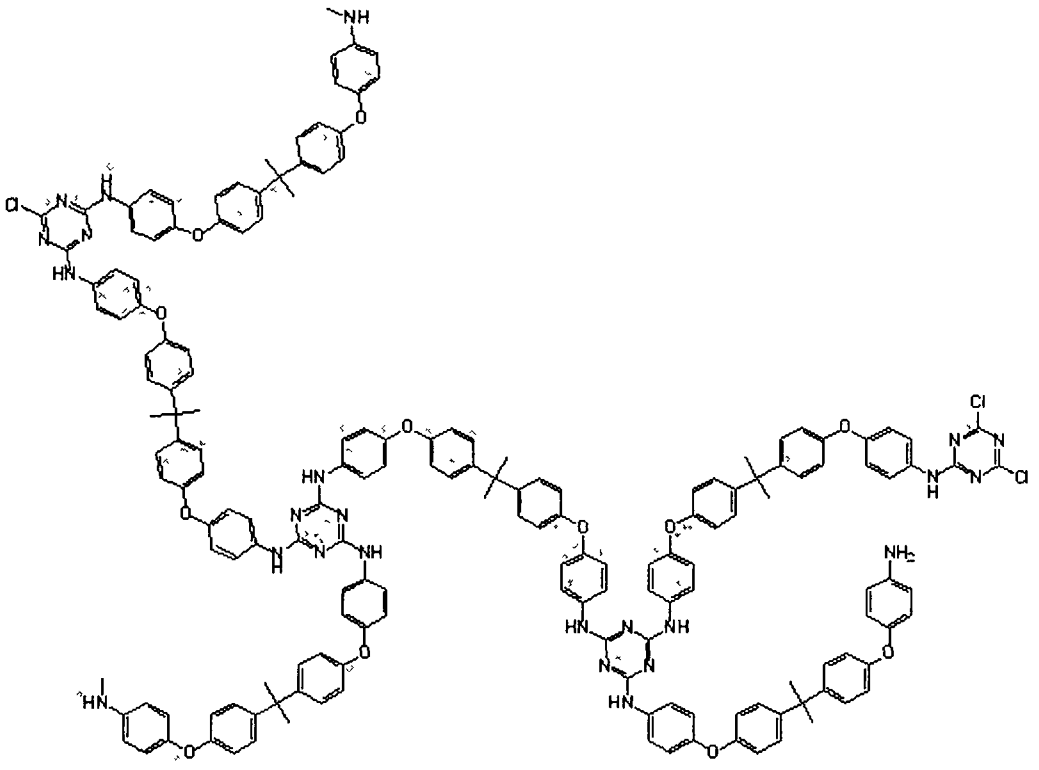

Figure 5.1. Structure of hyperbranched polyamine, HPd

5.3.2. Characterization

5.3.2.1 Characterization of silver nanoparticles

The formation of nanoparticle of silver in hyperbranched polymer matrix (HPd-Ag) is first observed by UV-visible absorption spectral studies. As no absorption peak was observed in UV-visible spectrum (Figure 5.3) of Ag^+ solution in polymer before reduction, except a little variation of absorption peak, which appears at about 295 nm instead of 287 nm of pure polymer solution This variation may be due to complex formation Ag$^+$ in hyperbranched matrix. The peak for Ag$^+$ was not observed here is due to its d^{10} configuration [6]. However a strong absorption at about 412 nm appeared after reduction of Ag$^+$ ions to Ag(0) (Figure 5.3). This peak is due to the surface plasmon absorption of silver metal of silver colloid, as Ag(0) nanoparticles are known to exhibit intense plasmon absorption bands in such visible region [43,44]. Further as the nature of the spectrum is almost symmetrical, so it is expected that the nanoparticles are well-dispersed and spherical shape, which are further supported by TEM studies. This is also supported by the fact that the formation of aggregation of nanoparticles resulted red-shift and broadened plasmon absorption and also formation of elongated nanoparticles leads to splitting of absorption peak into two, both of which are absent in UV spectrum of this study [28,45].

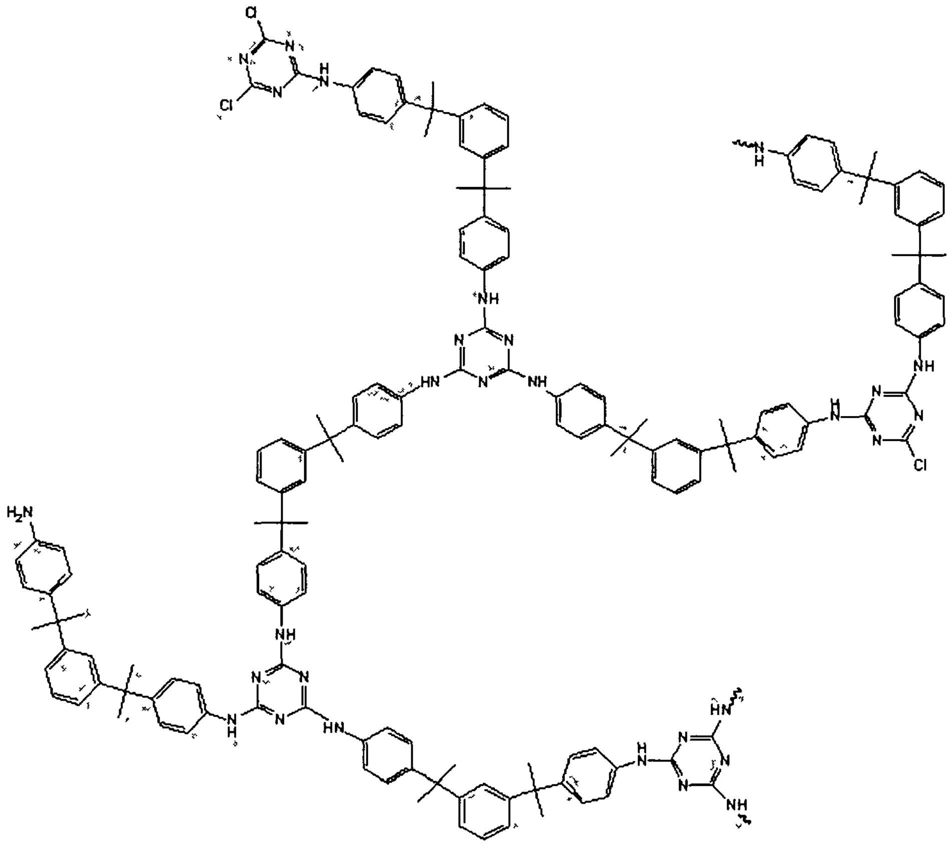

Figure 5 2. Structure of hyperbranched polyamine, HPb

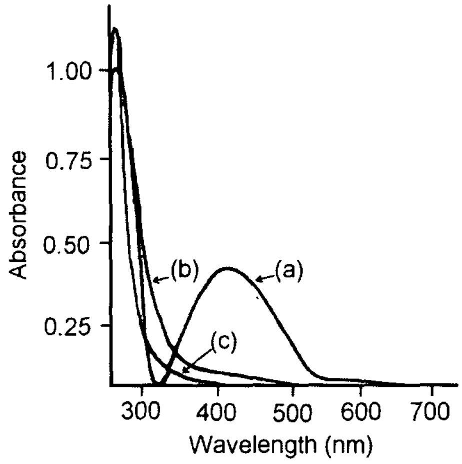

Figure 5.3. UV spectra of (a) HPd-Ag, (b) silver based HPd complex and (c) HPd

Figure 5.4 shows the infrared spectra for the pure hyperbranched polymer (HPd) and polymer in the presence silver nanoparticles (HPd-Ag). The analysis showed that the spectral features of HPd and HPd-Ag samples are quite different. The $-CH_2$ symmetric and asymmetric stretching bands appeared at 2870 and 2965 cm^{-1} respectively for HPd and corresponding bands are observed at 2862 and 2960 cm^{-1} for HPd-Ag respectively. It is well known that the peak positions for symmetric and asymmetric $-CH_2$ stretching vibration can be used as the sensitive indicator of the alkyl chains [46]. This decrease in wave number is characteristic of highly ordered conformation. Further, all the amines viz. primary, secondary and tertiary vibration frequencies showed large shifts in the ranges of 3420 -3300 cm^{-1} for stretching, 1585-1560 cm^{-1} and 1487 cm^{-1} for bending vibration and increase in transmittance of the bands in presence of silver nanoparticles compared to the pure polymer. The result indicates a strong interaction between amines and Ag nanoparticles.

TEM (Figure 5.5) studies confirmed that Ag nanoparticles are not agglomerated, well-dispersed and almost spherical shape with particles size 3 nm to 15 nm. The size distribution of the particles is also found to be narrow (Figure 5.6).

The X-ray diffractrogram (Figure 5.7) of the powder sample is well agreement with the literature values [47]. All the prominent peaks at 2θ values of about 38^O, 44.2^O, 64.4^O, 77.6^O, 81.6^O representing the 111, 200, 220, 311 and 222 Bragg's reflections of 'fcc' structure of silver. The Scherrer's equation was used to estimate the crystalline domain size (D):

$$D = k\lambda/\beta\cos\theta$$

Where $k = 0.9$ is for the Ag cubic structure, $\lambda = 1.541$ Å is the X-ray wavelength, β is the angular width and θ is the diffraction angle. The average crystalline domain size was found to be 6.5 nm and this result is in agreement with average diameter of Ag nanoparticles estimated by TEM.

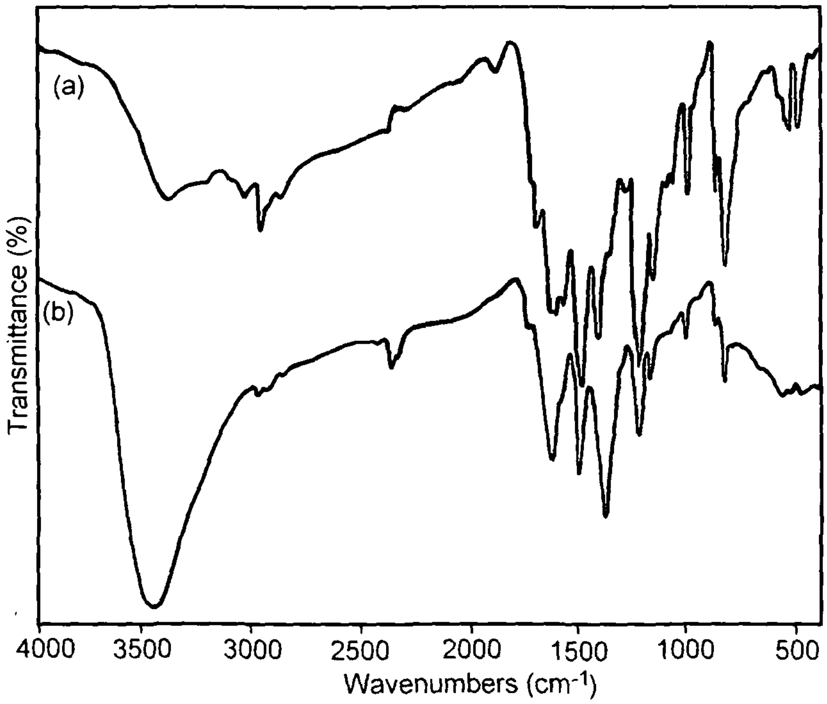

Figure 5.4. FT-IR spectra of (a) HPd and (b) HPd-Ag

The thermogravimatric analysis of the polymers viz. HPd and HPd-Ag (Figure 5.8) showed that the initial degradation temperature increased about 40 ^{0}C, from 260 ^{0}C to 300 ^{0}C. This may be due to the presence of silver nanoparticles, which restricted the mobility of the chains in the polymer compared to pure polymer. The overall thermostability of the polymer is also improved for the same reason.

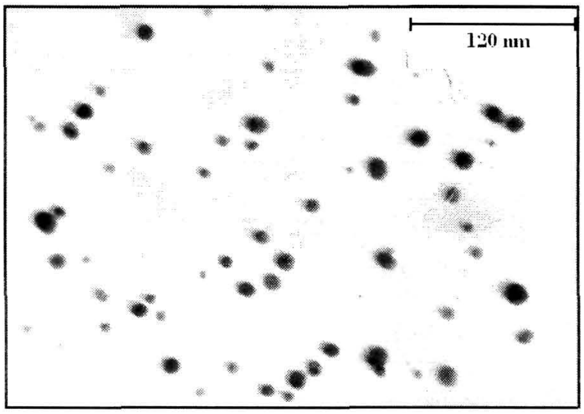

Figure 5.5. TEM micrograph of silver nanoparticles

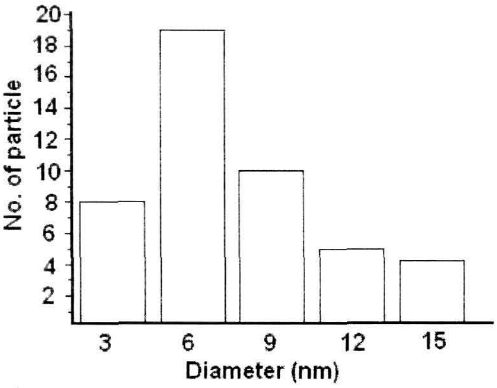

Figure 5.6. Histogram for size distribution of silver nanoparticles

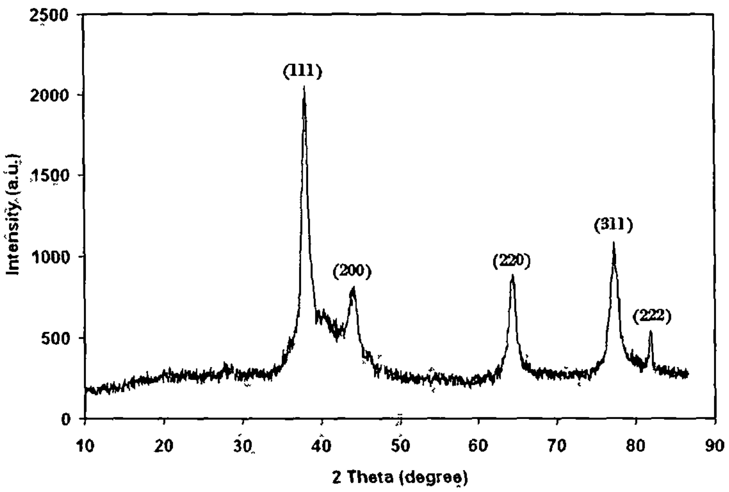

Figure 5. 7. X-ray diffractogram of HPd-Ag

The structural confindness of the polymer by the presence of nanoparticles is also supported by the increase of glass transition temperature of the polymer from 240 °C to 274 °C, as measured from DSC curves.

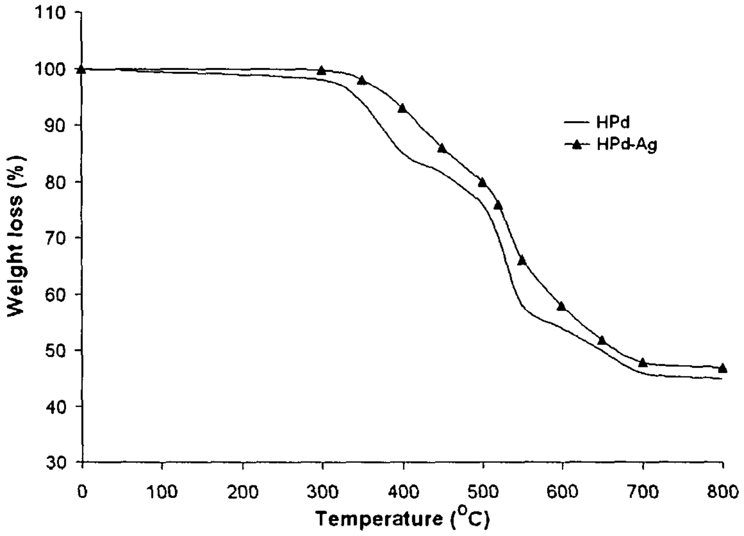

Figure 5.8. TG thermograms for HPd and HPd-Ag

5.3.2.2. Characterization of copper nanoparticles

The formation of copper nanoparticle in hyperbranched polymer matrix (HPb-Cu) is first observed by UV-visible absorption spectral studies. Chemical reduction of Cu^{2+}-loaded hyperbranched polyamine with excess of $NaBH_4$ results in intra-hyperbranched-Cu nanoparticles [40]. Evidence for this comes from the immediate change in solution color from blue to golden brown. The absorbance band in UV spectrum shows a monotonic decrease from about 300 nm to 590 nm of nearly exponential slope (Figure 5.9). The measured onset of this transition at 590 nm agrees with the accepted value [48], which strongly suggests that the presence of separated copper nanoparticles, which is further supported by TEM studies.

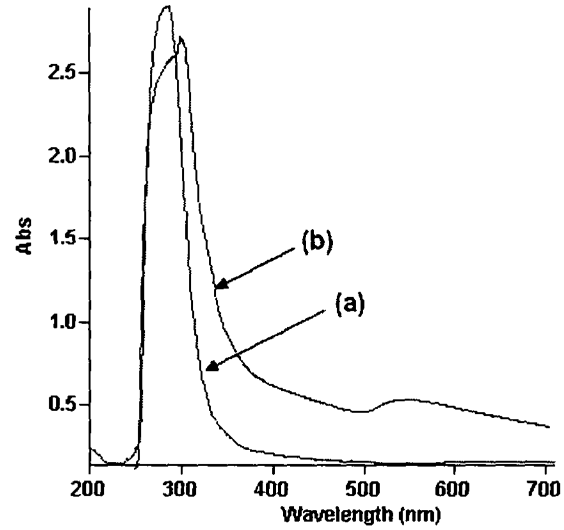

Figure 5.9. UV spectra of (a) HPb and (b) HPb-Cu

Figure 5.10 shows the infrared spectra for the pure hyperbranched polymer (HPb) and polymer in the presence copper nanoparticles (HPb-Cu). The analysis showed that the spectral features of HPb and HPb-Cu samples are quite different. All the amines viz. primary, secondary and tertiary vibration frequencies showed shifts in the ranges of 3420-3300 cm^{-1} for stretching, 1585-1560 cm^{-1} and 1487-1472 cm^{-1} for bending vibration and decrease in transmittance of the bands in presence of copper nanoparticles compared to the pure polymer. The result indicates a strong interaction between amines and Cu nanoparticles [49].

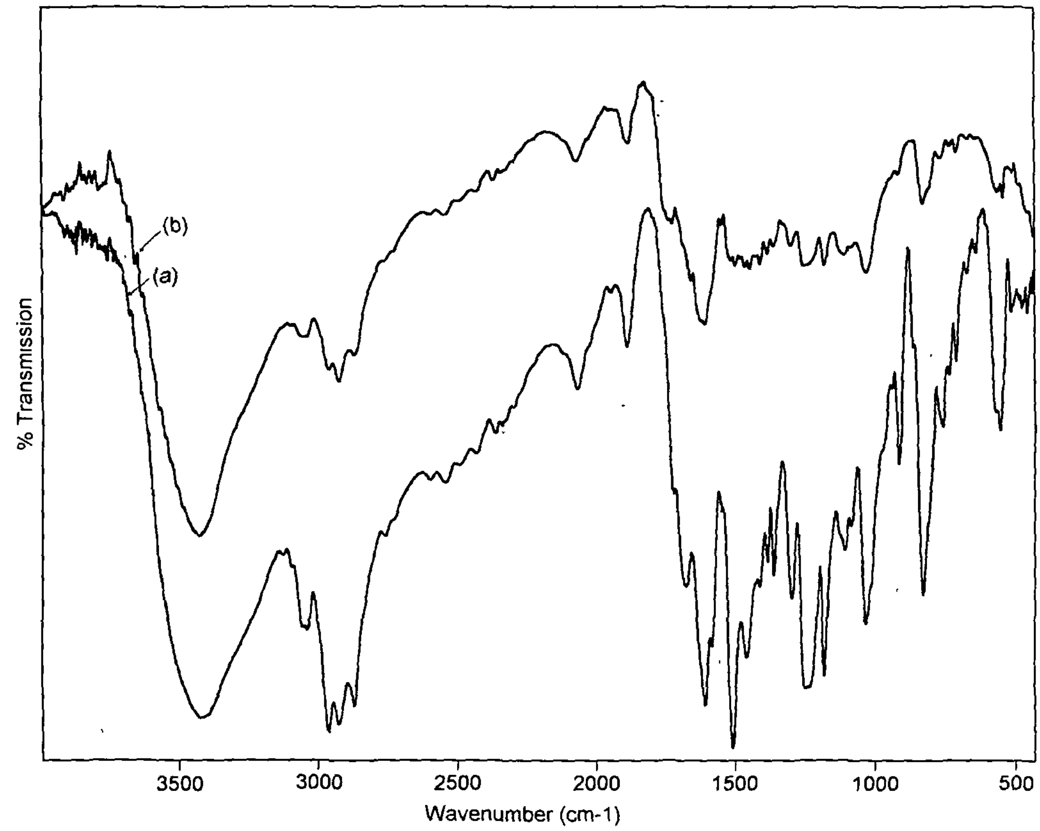

Figure 5.10. FT-IR spectra of (a) HPb and (b) HPb-Cu

TEM (Figure 5.11) studies confirmed that Cu-nanoparticles are not agglomerated, well-dispersed and almost spherical shape with particles size 3 nm to 15 nm. The size distribution of the particles is also found to be narrow (Figure 5.12). These results are similar to Ag-nanoparticles in earlier case.

The X-ray diffractrogram (Figure 5.13) of the powder sample is well agreed with the literature values [50]. All the reflection peaks at 2θ values of about 43.5 ^{O}, 50.7 ^{O} and 70.2 ^{O} are representing the 111, 200 and 220 Bragg's reflections of cubic structure of copper. The Scherrer's equation was also used here to estimate the crystalline domain size (D). The average crystalline domain size was found to be 8.5 nm and this result is in agreement with average diameter of Cu nanoparticles estimated by TEM.

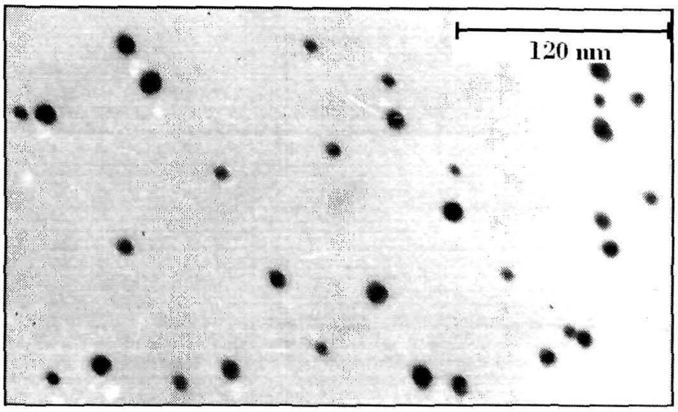

Figure 5.11. TEM micrograph of copper nanoparticles

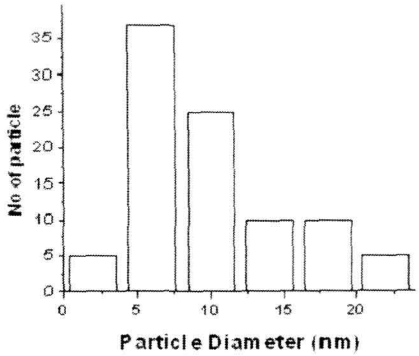

Figure 5.12. Histogram for size distribution of copper nanoparticles

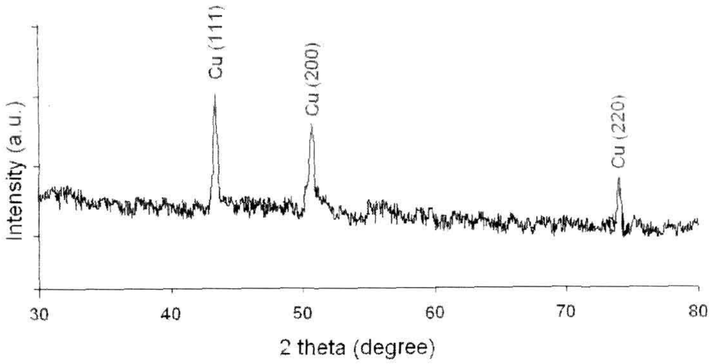

Figure 5.13. X-ray diffractogram of HPb-Cu

5.3.3.1. Biological activity of nanoparticles

5.3.3.1. Biological activity of silver nanoparticles

The antimicrobial property of silver is found to be the best among different metals in the following order Ag > Hg > Cu > Cd > Cr > Pb> Co >Au > Zn > Fe > Mn > Mo > Sn [22]. Further, the increase of bacterial resistance to various antimicrobial agents generates a serious problem in the treatment of infectious diseases as well as in epidemiological practice [51]. Thus the development of new antimicrobial substances is very much significant. The inhibition zone diameter against the concentration of the HPd-Ag is plotted in Figure 5.14. The results of this study clearly demonstrated (Figure 5.14) that the colloidal silver nanoparticles inhibited the growth of the tested bacteria viz. *Bacillus Subtilis* even at very low total concentrations of silver (1.2 g/100L).

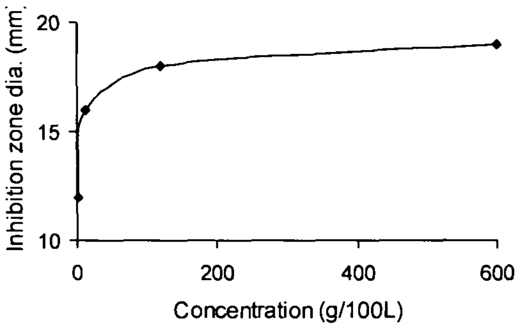

Figure 5.14. Variation of inhibition zone diameter with concentration of HPd-Ag solution for *Bacillus Subtilis* bacteria

However, the mechanism of the bactericidal effect of silver colloid particles against the bacteria is not very well understood. Silver nanoparticles may attach to the surface of the cell membrane and disturb its power function such as permeability and respiration [52]. It is reasonable to state that the binding of the active agent to the bacteria depends on the surface area available for such interactions. Smaller particles have the larger surface area and hence interactions will be more than the larger particles of active agent. The studies reported that the silver nanoparticles are not only at the present surface of cell membrane, but they also present inside the bacteria [53]. Hence there is a possibility that the silver nanoparticles may also interact inside the bacteria, which may also cause damage of the cells by interacting with phosphorus- and sulfur-containing DNA [54].

5.3.3.2. Biological activity of copper nanoparticles

In the field of biomedical polymeric materials, infections associated with the biomaterials represent a significant challenge to develop antimicrobial surfaces for more wide spread applications of medical implants. In this context, Cu nanomaterials exhibit effective antifungal properties [55]. In this report, the results of antifungal studies clearly demonstrated (Fig 5.15) that the colloidal copper nanoparticles inhibited the growth of the tested fungus, *Candida albicans* even at very low concentrations of copper (1.4 g/100L). It is reasonable to state that the binding of the active agent to the fungus depends on the surface area available for such interactions. The extremely small size of copper nanoparticles exhibit enhanced properties compared to bulk copper. As the smaller particles have larger surface area and hence interactions will be more than the larger particles of active agent. This allows them to easily interact with other particles and increases their antifungal efficiency [58].

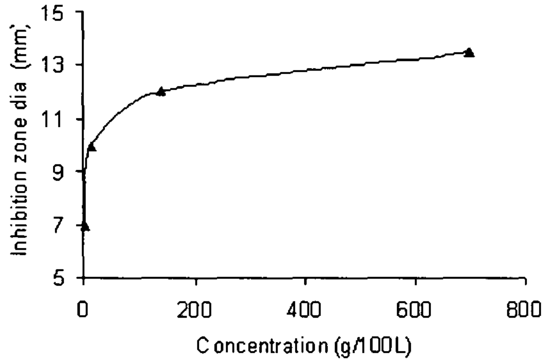

Figure 5.15. Variation of inhibition zone diameter with concentration of HPb-Cu solution for *Candida albicans* fungus

5.4. Conclusions

From this study, it can be concluded that well-dispersed, fine and stable silver and copper nanoparticles have been prepared by using hyperbranched polyamines as the matrices. These nanoparticles were well characterized by using different spectroscopic and analytical techniques. The study shows that the thermo-stability of silver nanoparticles containing hyperbranched polyamines is better than the corresponding pure polymer. These metal nanoparticles (Ag/Cu) act as effective antimicrobial agents against the particular bacteria or fungus.

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CHAPTER SIX

Hyperbranched Polyamine as a Potential Agent for Thermosetting Resins

6.1. Introduction

Thermosetting resins need to be formulated with a few additives to crosslink and to obtain desirable level of performance characteristics for their different applications [1]. Among these additives, the crosslinking agent is the most important. The resins based on vegetable oil are conventionally cured by transition metal catalyzed peroxide systems such as Co-/Mn-octate/napthate with methyl ethyl ketone peroxide (MEKP) in the presence of styrene as a reactive diluent [2]. However, this system requires long time to achieve optimum level of crosslinking, especially for the resins obtained from non-drying vegetable oils and resulted relatively rigid network [3]. Thus there is a need of an effective crosslinking agent for this type of resins.

As the uses of renewable resources in different fields of applications of polymers have been increasing tremendously because of worldwide improved environmental concerns and depletion of world oil pool, scientists are trying to utilize such resources for their products. The vegetable oils are a class of such resources used to prepare different kinds of industrial resins. As poly(ester amide) improves the film characteristics compared to the conventional low cost vegetable oil based polyester resins in terms of drying time, hardness, chemical resistance, etc. [4-5], so an attempt has been made to synthesize poly(ester amide) resin in the present investigation. This resin has been used in different fields of applications [6-8] such as paint, coating, adhesives, binder for composites, etc. Nahar (*Masua ferrea L.*) is a plant available in India, especially in North-East region of the country, produces exceptionally high oil content seeds (70%) and hence is utilized as a local vegetable oil [9].

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*Parts of this work have been published in Prog Org Coat, **2004**, 51, 103-108.*
*and Prog Org Coat, **2007**, 60, 328-334.*

Again, epoxy resin is one of the most important thermosetting industrial materials, because of it's many excellent properties like high thermal stabilities, good adhesion, superior mechanical and electrical properties. Thus it is widely utilized in the field of coatings, adhesives, binder for composites, etc. [10-12]. However, epoxy resin is rather brittle as it is cured by large amount of aliphatic or aromatic amine, amides, dicarboxilic acids or anhydrides, etc., in most of the cases. This is because of its highly crosslinked structure, which rigidifies the molecular network, decreases deformability and increases process induced shrinkage [13,14]. Thus there is also need of other improved crosslinking agent for this resin.

Now, as it is observed that hyperbranched polymer has a high potential as additive and modifier in polymeric materials, so it may be used for the crosslinking of the above resins. This is also due to it's unique chemical and physical structure, which induce unusual properties (discussed in chapter one) that can solve the problems related to processability, compatibility, and hence may made it suitable as a crosslinker [15-17] in epoxy and vegetable oil based poly(ester amide) resins.

Further, one of the main drawbacks of epoxy and vegetable oil based poly(ester amide) resins like many other organic polymers is their flammability, which limits there use in many applications like electronic, high performance adhesives, coatings, etc. [18-19]. A considerable attention has been paid, therefore, to control the flammability of such resins. The use of nitrogenous macromolecular hyperbranched polyamine flame retardant eliminates all the drawbacks of conventional small molecular flame-retardant additives as well as it will act as reactive types additive, which is very effective as it may chemically attach with the resin system [18-23].

In addition to the above, advanced antifungal epoxy coating materials are very important innovations for a number of biotechnological applications [24]. Copper/ polymer nanocomposites can be a valid option for such purposes because of the highly dispersed nature of the metal releasing clusters and large nanoparticle-polymer interfaces that ensures a high reactivity [24,25] as well as toxicity of copper nanoparticles towards fungi. All this calls for exploring alternative materials for efficient antifungal coatings.

In the present investigation, it is therefore expected that the hyperbranched reactive polyamine with thermostable s-triazine ring may effectively function as crosslinking agent, reactive flame retardant, heat stabilizer, viscosity reducer as well as improve to chemical resistance in many chemical media. The hyperbranched polyamine/Cu nanoparticles cured epoxy may also act as antifungal materials in addition to the above.

In this chapter, therefore, the hyperbranched polyamine (HPb) was utilized as potential agents for thermosetting resins such as vegetable oil based poly(ester amide) and commercially available bisphenol A based epoxy resins.

6.2. Experimental

6.2.1. Materials and methods

6.2.1.1. Materials

Nahar *(Mesua ferrea* L.) seeds were collected from Jorhat, Assam, India. The oil is brown in color, pungent and slightly viscous liquid. The oil was extracted from the matured seeds, purified by alkali process and dried under vacuum [26]. This oil possesses oleic (52.3%) and linoleic (22.3%) acids as unsaturated fatty acids and palmitic (15.9%) and stearic acids (9.5%) as saturated fatty acids [27].

Adipic acid (AA) was obtained from SRL, India. The compound has melting point (m.p.) 151-153 ^{O}C, minimum assay 99.0%, maximum sulfated ash 0.005%, and molecular weight (M_w) 146.14 g/mol. It was used as received for preparation of resin.

Maleic anhydride (MA) obtained from Merck, India. The compound has melting point (m.p.) 51-53 ^{O}C, minimum assay 99.0%, maximum sulfated ash 0.005%, and molecular weight (M_w) 98.06 g/mol. It was used as received for preparation of resin.

Phthalic anhydride (PA) obtained from S. D. Fine Chem. Ltd., India. The compound has melting point (m.p.) 131-133 ^{O}C, minimum assay 99.0%, maximum sulfated ash 0.005% and molecular weight (M_w) 148.12 g/mol. It was used as received for preparation of resin.

Diethanolamine was obtained from Merck, India. The compound has melting point (m.p.) 25-28 ^{O}C, minimum assay 98.0%, water 0.5%, and molecular weight (M_w) 105.14 g/mol. It was used as received.

Methyl-ethyl ketone peroxide (MEKP) and cobalt octate were obtained from Kumud enterprise, Kharagpur. MEKP is a clear liquid with density of 1.053 g/mL and cobalt octate is 2% solution of cobalt octate in cyclohexanone.

Diethyl ether was obtained from Merck, India. It has formula weight (F_w) 74.12 g/mol, purity ≥ 98%, density at 20 ^oC, 0.713-0.716 g/c.c. It was used as received.

Lead mono-oxide obtained from Loba Chemie, India with minimum assay 99%, maximum limit of impurities chloride 0.02%, copper 0.005 % and iron 0.01%. It was used as received.

Anhydrous sodium sulfate (Na_2SO_4) was obtained from Merck, India. It has molecular weight (M_w) 142.04 g/mol and purity 99% with chloride (0.01%), nitrate (0.01 %), potassium (0.01%) and iron (0.01%) as impurities. It was used as received.

Magnesium turning (Mg-turning) was purchased from SRL, India. It has atomic weight (A_w) 24.31 g/mol and purity 99.8% with maximum 0.05% iron as impurity. It was purified by thorough washing with dilute HCl followed by washing with distilled water. The process is repeated for several times until the turning became shining. Finally it was washed with acetone and dried under vacuum at 45 ^oC for 4-5 h. The dried turnings were used in the same day.

Methanol (CH_3OH) was obtained from Merck, India. It has formula weight (F_w) 58.0 g/mol, purity ≥ 99.5%, density 0. 971 g/mL and boiling point (b.p.) 56-57 ^oC. It is used as a solvent and also as a reagent to prepare sodium methoxide. Super dry methanol was used for this purpose, which was obtained as follows. An amount of about 4 g of purified dry Mg-turnings was taken in a 1000 mL single neck round bottom flask. A pinch of iodine was added into it and heated for 2-3 min. About 50 mL of distilled methanol was added into the above mixture. The flask was then fitted with a reflux condenser along with a guard tube containing anhydrous calcium chloride. The mixture was refluxed until the color of the iodine disappeared. Then about 600 mL of distilled methanol was added in the flask and it was refluxed until the color of the solution became milky white. This was then distilled. The distillate obtained was the super dry methanol and kept in an amber bottle using 4A type molecular sieves.

Nutrient broth and nutrient agar (HIMEDIA, India) were used as received and the technical specifications of these chemicals have already been given in experimental section of chapter five, section 5.2.1.

Styrene was obtained from Merck, Germany with density 0.906 g/ml, minimum assay ≥ 99%. It contained tertiary butyl catecol as inhibitor. Styrene was used after removal of the inhibitor by washing with 4% alkali solution followed by washing with distilled water and then dried by vacuum distillation.

Sodium metal (Na) was obtained from Merck, Germany. It has atomic weight (A_w) 22.9 g/mol and purity 98.8% with chloride (0.01%), silica (0.002%), calcium (0.1%) and iron (0.01%) as impurities. It was kept in paraffin oil and used as received after cutting into small pieces.

Tetrahydrofuran (THF) from Merck, India was used as received. It has formula weight (F_w) 72.11 g/mol, purity ≥ 99.0%, density at 20 ^{O}C 0.89 g/c.c. and boiling point (b.p.) 66 ^{O}C.

Xylene from Merck, India was used as received. It has formula weight (F_w) 106.17 g/mol, purity ≥ 98.0%, density at 20 ^{O}C 0.86 g/c.c. and boiling point (b.p.) 137-143 ^{O}C.

p-Tolune sulfonic acid (PTSA) was obtained from Loba Chemie, India. The compound has melting point (m.p.) 100-105 ^{O}C, minimum assay 98.0%, maximum sulfated ash 0.2%, and molecular weight (M_w) 190.21 g/mol. It was used as received.

The hyperbranched polyamine (HPb) was obtained by using the same methods as described in experimental section of chapter two, section 2.2.2. Here it was used as crosslinker for thermosetting resins.

The copper nanoparticle based hyperbranched polyamine (HPb-cu) was obtained by using the same methods as described in experimental section of chapter five, section 5.2.2. Here it was used as crosslinker for thermosetting resins.

Bisphenol-A based epoxy resin, Araldite LY 250 and poly(amido amine) based hardener, HY 840 were obtained from Hindustan Ciba Geigy *Ltd.* and used as received.

Candida albicans fungus strain was collected from the Department of Molecular Biology and Biotechnology, Tezpur University, India.

6.2.1.2. Synthesis of poly(ester amide) resin from Nahar seeds oil

6.2.1.2.1. Preparation of sodium methoxide

Sodium methoxide was obtained by the reaction of supper dry methanol with metallic sodium by the standard procedure [28]. The white powder of sodium methoxide was stored in a desiccator for further used.

6.2.1.2.2. Preparation of methyl esters of the oil

25 g of oil in 50 mL super dry methanol and 0.5 % sodium methoxide of oil were refluxed for three hours in 250 mL round bottom flask under the nitrogen

atmosphere. The content of flask were then cooled to room temperature and kept overnight. The excess methanol was removed by distillation and the methyl esters were extracted by petroleum ether (b.p. 60-80) °C, washed with 15% aqueous NaCl solution and dried over anhydrous sodium sulfate. The methyl esters of the mixed fatty acids were purified from ether by distillation. The product obtained was in quantitative yield.

6.2.1.2.3. Preparation of diethanol amide from the methyl ester of the oil

A three necked round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a dropping funnel was used for the preparation for the diethanol amide of the esters. 3.45 g diethanol amine and 0.5% sodium methoxide of ester were taken in the flask with constant stirring under the nitrogen atmosphere and heated to (110-115) °C, then 8.42 g methyl esters of the oil was added into the reaction mixture drop wise over a period of one hour. The heating was continued for another three hours with constant stirring. Then the reaction mixture was cooled to room temperature, dissolved in petroleum ether, washed with 15 % aqueous NaCl solution and dried over anhydrous sodium sulfate. The petroleum ether was removed by distillation to yield, N,N′-bis(2-hydroxyethyl) Nahar oil amide (diethanol amide of the fatty acids). The yield was ≈ 80 %.

6.2.1.2.4. Preparation of poly(ester amide) resin

0.08 mole (29.1 g) of the amides of the fatty acids and 0.05 % of PbO of amide were taken in a three necked round bottom flask with the same arrangement as described earlier. The mixture was heated to (120-125) °C and 0.08 mole of powder anhydride or diacid [13.28 g for phthalic anhydride (PA), 7.84 g for maleic anhydride (MA) and 11.68 g for adipic acid (AA)] was added into the mixture with 20 mL xylene to facilitate the mixing of the reactants. Then it was heated to (180-190) °C for 2.5 h to 3.5 h and cooled to room temperature. The reaction was monitored by acid value determination of the viscous product. The yield was found to be high (90 %).

6.2.1.3. Curing of poly(ester amide) resin

A homogenous mixture of poly(ester amide) resin with 30 phr (parts per hundred gram of resin) of styrene as the reactive diluent, 4 phr of MEKP as the initiator and 2 phr of cobalt octate as the accelerator without, and with 5.0, 7.5 and 10.0 phr of hyperbranched polyamine (HPb) as 20% solution in THF along with 0.01 phr of PTSA was prepared separately in a glass beaker at room temperature by hand stirring for 5-7 min. Samples containing the poly(ester amide) resin with only hyperbranched polyamine in the presence of 0.01 phr PTSA at dose levels of 2.5, 5 and 10 phr were also prepared. Then the mixtures were uniformly coated on mild steel plates (150 mm X 50 mm X 1.60 mm), tin plates (150 mm X 50 mm X 0.40 mm.) and glass plates (75 mm X 25 mm X 1.75 mm) and allowed to cure at specified temperatures for the different time period.

6.2.1.4. Curing of epoxy resin

A homogenous mixture of epoxy resin with 10, 15, 20 and 25 phr of hyperbranched polyamine (HPb) as 20% solution in THF along with and without 25 phr of poly(amido amine) hardener was prepared separately in a glass beaker at room temperature by hand stirring for 5-7 min. Samples containing the epoxy resin with 15 phr HPb-Cu and 25 phr hardener and with only 50 phr poly(amido amine) hardener were also prepared. Then the mixtures were uniformly coated on mild steel plates, tin plates and glass plates as above and allowed to cure at specified temperatures for the different time period.

6.2.2. Characterization and testing

FT-IR spectra for the compounds were recorded in a Nicolet (Impact 410, Madison, USA) FT-IR spectrophotometer by using KBr pellet. ^{1}H-NMR and ^{13}C-NMR spectra of the compounds were recorded with 400MHz NMR (Varian, USA) spectrometer by using d_6-DMSO as the solvent and TMS as an internal standard. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out in Shimadzu TG 50 and DSC 60 thermal analyzers respectively using the nitrogen flow rate of 30 mL/min and at the heating rate of 10 ^{O}C/min. The flame retardancy test of all samples were carried out by measurement of limiting oxygen index (LOI) value by a flammability tester (S.C. Dey Co., Kolkata) as per the standard ASTM D 2863-77 procedure for self-supported samples. The inherent viscosity of the polymer was measured with 0.5% (w/v) solution in DMAc at 27±0.1 ^{O}C by using an Ubbelohde suspended level viscometer. The other physical properties of the resins such as acid value, iodine value, saponification value, and density were determined by standard methods, as reported earlier [29]. The coating performance of the cured films was evaluated by determination of pencil hardness using pencils of different grades ranging from 6B to 6H, impact resistance by falling weight (ball) method and adhesion (cross-cut) by using commercial cello tape [30-31]. The morphology of the blends was studied by the scanning electron microscopy (SEM) analysis using JSM 35CF (JEOL) after gold coating.

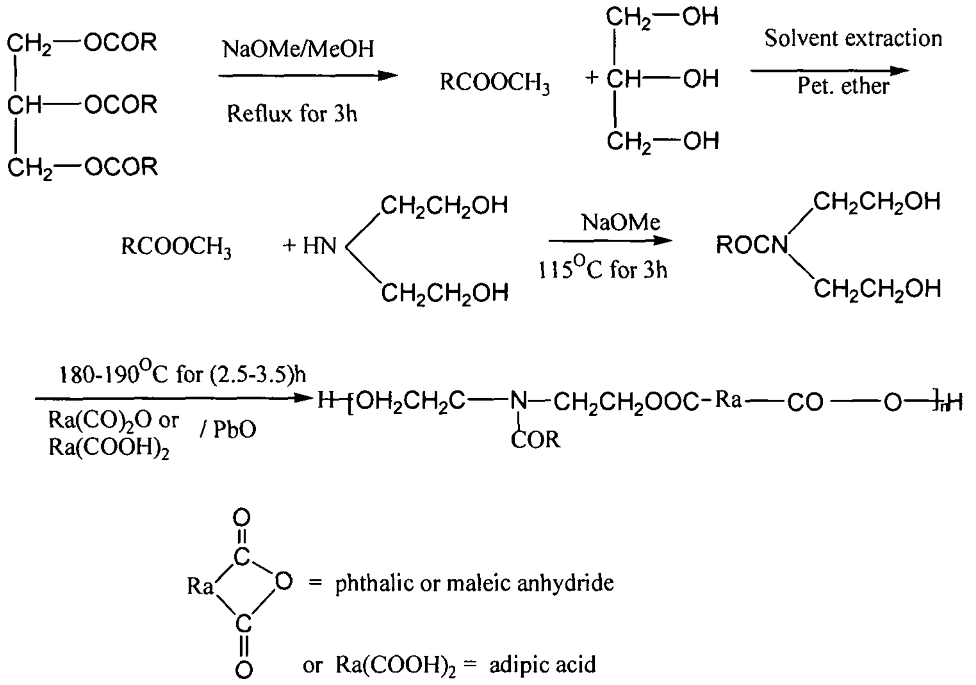
Preparation of culture media and testing of antibacterial activity

100 ml of both potato dextrose broth and agar was prepared and sterilization was done. The fungal broth was incubated for 2 days in the 30 ^{O}C to get 1X10^{6} population per mL of the media. An aliquot (1.0 mL) of the fungal broth was poured into each plates coated by different epoxy films. In the first step, the broth was brought into contact with bioactive coating for 24 h. In the second step, a plate counter agar solid culture medium was poured into the plates that were subsequently incubated for 48 h at 37 ^{O}C so that the vital cells eventually presents, could grow into colonies. The same procedure was performed on specimens prepared for control and blank experiments. The microorganism colony presence was then evaluated, by counting the colony forming units per petri plate (CFU/mL).

6.3. Results and discussion

6.3.1. Resinification of Nahar oil

The poly(ester amide) resins were synthesized by three-step reaction procedure using anhydride or diacid as the dibasic acid as shown in scheme 1. Sodium methoxide and PbO were used as the catalysts for the first two steps and last step of the reaction, respectively (Scheme 1). Even though in most of the reports [32] the azeotropic technique was used but it has been found that by our technique, the resin was formed very easily with lesser time with good yield. This may be due to use of metal oxide catalyst in the resinification reaction. The xylene used during resinification reaction was automatically removed from the product by evaporation under reaction conditions, as the solid content of the resin was found to be ~100%.



Scheme 6.1. Synthesis of poly(ester amide) resins

6.3.2 Characterization of intermediate products and the resins

The intermediates like methyl ester of the fatty acids and oil fatty amide, and the synthesized resins were characterized by FT-IR and ^{1}H-NMR spectroscopic techniques. The important peaks in IR spectra of methyl ester of the fatty acid appeared at 1772 cm^{-1} (C=O stretching frequency of ester), 1617 cm^{-1} (C=C stretching frequency of fatty acid), diethanol amide of the fatty acids appeared at 3380 cm^{-1} (OH stretching frequency), 1622 cm^{-1} (C=O stretching frequency of amide carbonyl) and poly(ester amide) of the oil appeared at 1642-1653 cm^{-1} (C=O stretching frequency of amide carbonyl) and 1736-1745 cm^{-1} (C=O stretching frequency of ester carbonyl) are also shown in (Figure 6.1). The peaks in IR spectra indicate [33] the formation of the products as expected, which were further supported by ^{1}H-NMR studies. The peaks at $\delta = 0.80\text{-}0.88$ ppm for terminal methyl group of the fatty acids chains, and $\delta = 1.50\text{-}1.61$ ppm may be due to the protons of -CH$_2$- group attached next to the above terminal methyl group. The peaks at $\delta = 1.18 - 1.30$ ppm for the protons of all the internal -CH$_2$- groups present in the fatty acids chains. The peaks for protons of unsaturated carbons appear at $\delta = 5.2 - 5.3$ ppm. The -CH$_2$- protons attached with the double bonds found at δ = 1.9 – 2.0 ppm, whereas the protons for –CH_2- attached with ester groups was observed at δ = 2.2-2.3 ppm for all the intermediates that is methyl ester and amide derivatives of the oil and the resins. The peak for the protons of methoxy group of

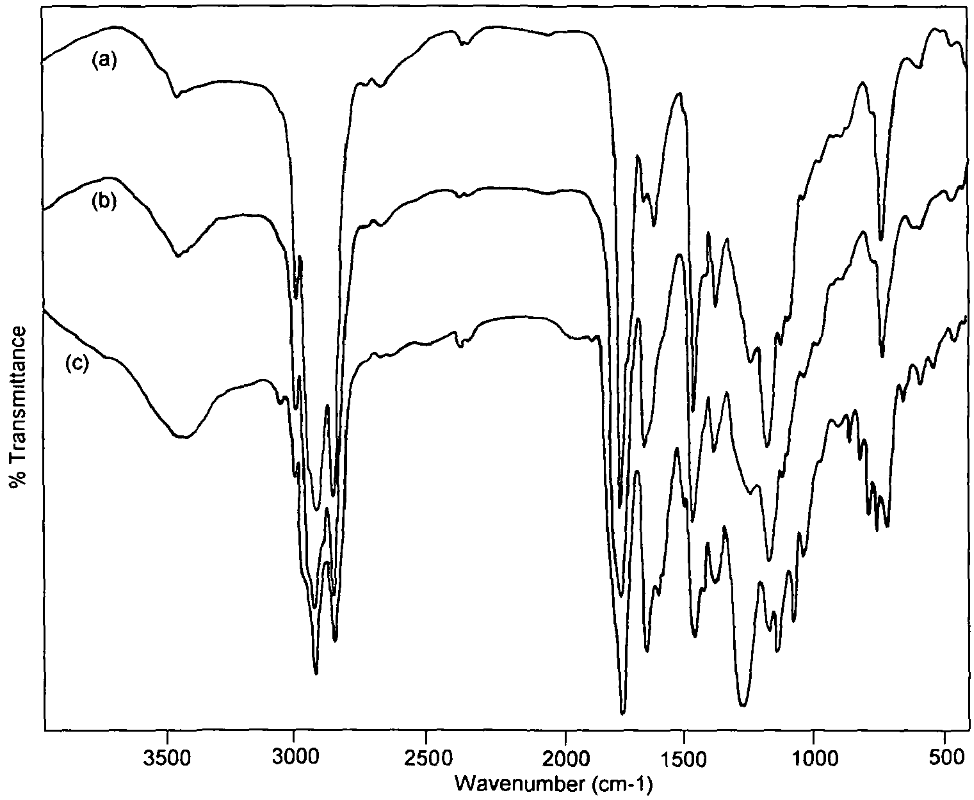


Figure 6.1. FT-IR spectra of poly(ester amide) resins [(a) = AA based, (b) = MA based and (c) = PA based]

methyl ester derivative appears at δ = 4.1-4.3 ppm. The peaks at δ = 3.4-3.5 and δ = 3.6 was found for -CH_2- protons of amide derivatives attached directly with tertiary nitrogen and –OH group, respectively. The phthalic anhydride containing resin (Figure 6.2) show peaks at δ = 7.3 – 7.5 ppm for aromatic protons, δ = 2.75-2.78 for -CH_2- attached ester group containing aromatic moiety and δ = 3.6 for -CH_2- attached with amide nitrogen. Whereas maleic anhydride containing resin (Figure 6.3) show peaks at δ = 4.1– 4.3 ppm for -CH_2- attached with double bond containing ester of maleic anhydride moiety and amide nitrogen. In case of adipic acid containing resin (Figure 6.4) the peaks at δ = 3.6 ppm and δ = 4.2 ppm for –CH_2- attached with amide nitrogen and $-CH_2-$ present in between ester and amide groups. The formation of poly(ester amide)s is supported by the characteristic peaks in IR spectra, which indicates the presence of amide and ester groups. The resin formation was confirmed by the viscosity measurement.

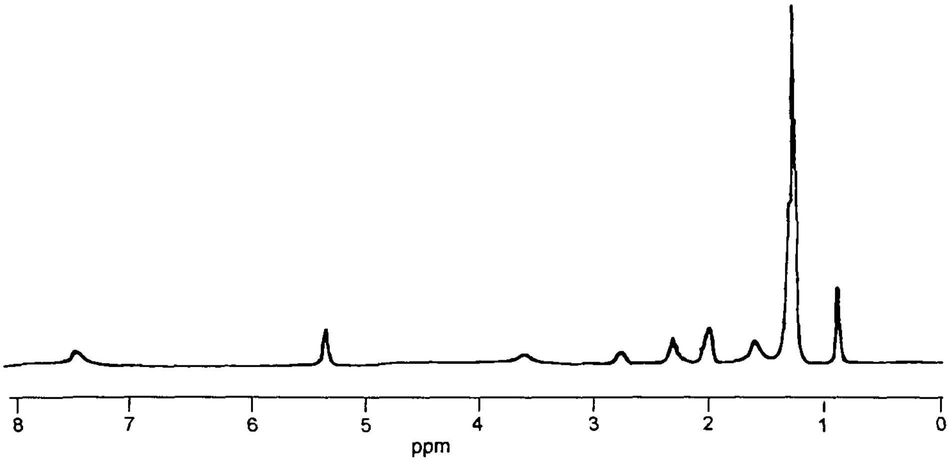


Figure 6.2. ^{1}H-NMR spectra of PA based poly(ester amide) resin

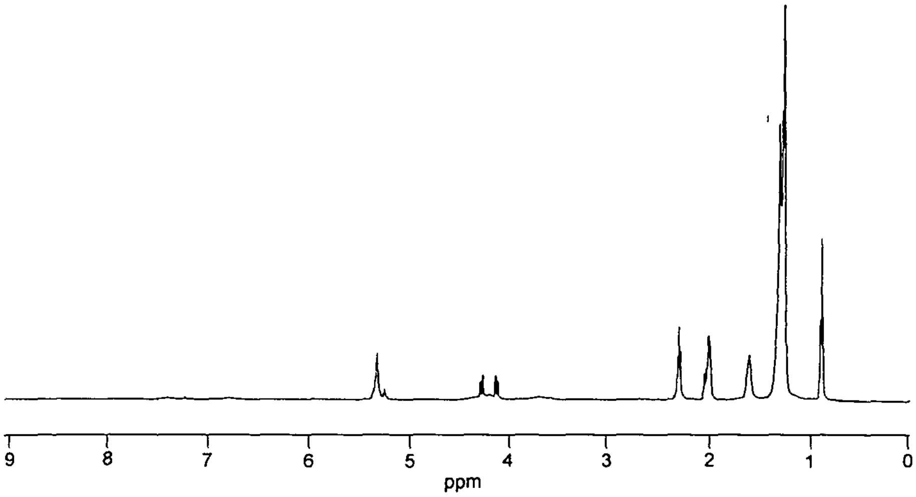


Figure 6.3. ^{1}H-NMR spectra of MA based poly(ester amide) resin

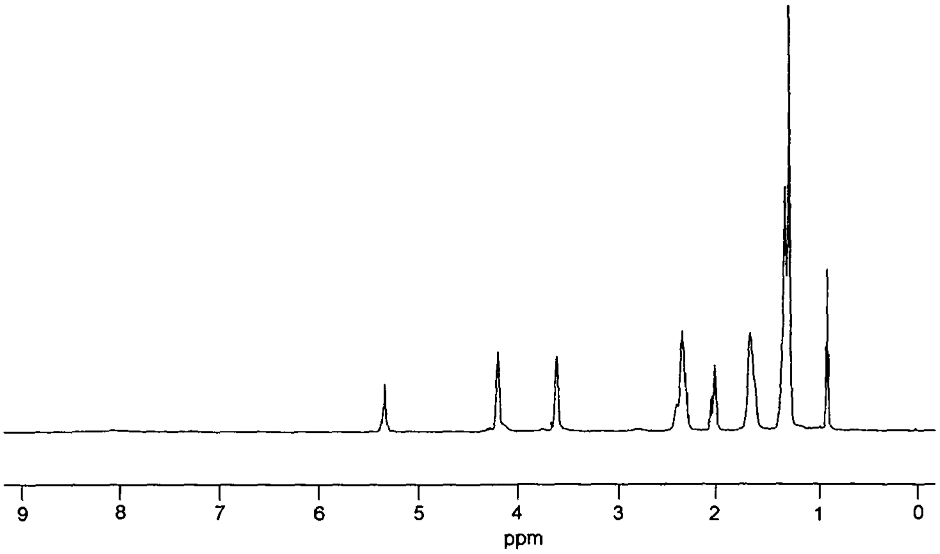


Figure 6.4. ^{1}H-NMR spectra of AA based poly(ester amide) resin

The physical properties like color, acid value, iodine value, saponification value, viscosity, etc. for the resins were determined and shown in the Table 6.1.

Table 6.1.The physical properties of the poly(ester amide) resins

Property	Resin (PA based)	Resin (MA based)	Resin (AA based)
Color	Dark brown	Dark brown	Dark brown
Acid Value (mg KOH /g)	17.45	10.47	39.27
Iodine Value (g I_2 /100 g)	59.72	72.12	54.36
Saponification Value (mg KOH /g)	263	273	320
Specific Gravity	0.89	1.01	0.97
Viscosity (η_{inh}, 0.5% DMAc at 27 ^{0}C)	0.81	0.92	0.74

The moderate acid and iodine value indicated that the resin could be used for coating and paint applications. This will also help the resin to be used as matrix for reinforced composites, especially for the polar cellulosic fiber such as bamboo fiber [34].

However, phathalic anihidide based poly(ester amide) resin shows best properties among the three resins. So this resin is used for further studies.

6.3.3. Curing study of the resins

6.3.3.1. Curing study of the poly(ester amide) resin

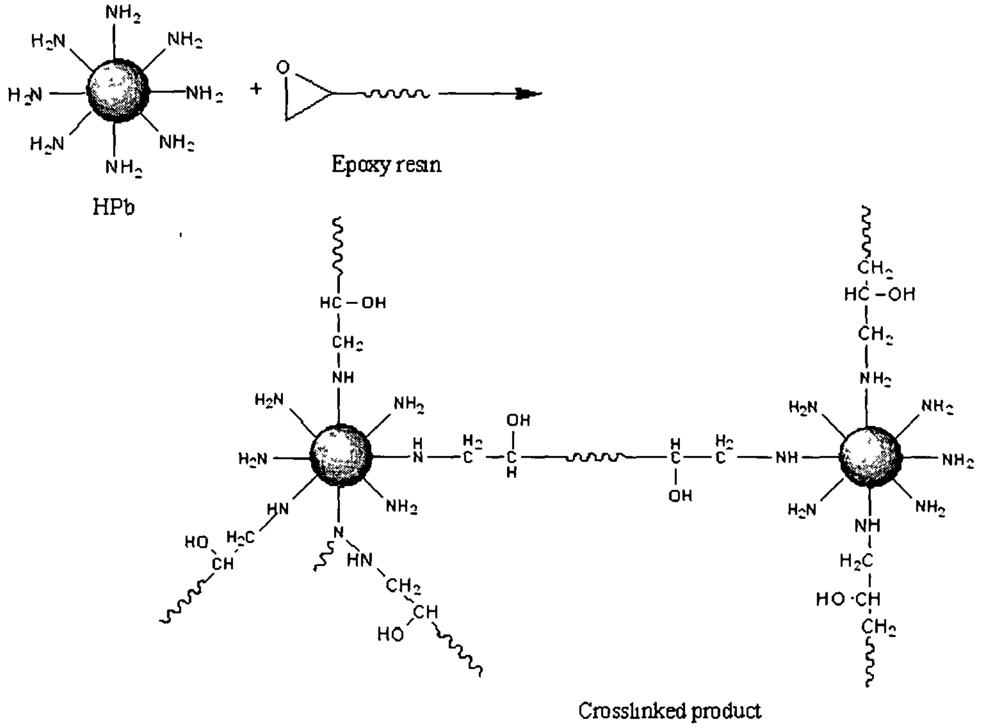
The resin was not cured at room temperature or even at high temperature without curing agent. However, the same was cured by using a combination of curing agents such as styrene, MEKP and cobalt octate at 175 ^{O}C for 4 h. But when hyperbranched polyamine in the presence of PTSA was used with the above system, it was found that the curing time decreases with the increase of dose of hyperbranched polymer (Table 6.2). Further, using hyperbranched polyamine alone as the curing agent, it can be cured at 175 °C for 7 to 4 h at dose level of 2.5 to 10 phr. This is due to the presence of large numbers of free reactive surface amino groups in the structure of the hyperbranched polyamine, which may react with the ester, free acid, hydroxyl groups, unsaturated moiety, etc. of the polyester resin. The higher dose than 10 phr was not studied because of commercial point of view as well as due to the fact that the cured resin became rather brittle even at dose level of 10 phr of hyperbranched polymer. This may be due to the presence of rigid structure of the hyperbranched polymer.

Table 6.2. Drying time of poly(ester amide) resin

Resin code	Curing system (phr)	Time (h)
PEA-CV	30:4:2:: styrene:MEKP:Co-octate	4
PEA-CV-2.5PA	30:4:2:2.5:: styrene:MEKP:Co-octate:HPb	3.5
PEA-CV-5PA	30:4:2:5:: styrene:MEKP:Co-octate:HPb	3
PEA-CV-7.5PA	30:4:2:7.5:: styrene:MEKP:Co-octate:HPb	2.5
PEA-2.5PA	2.5 ::HPb	7
PEA -5PA	5 ::HPb	6
PEA-10PA	10 ::HPb	4

6.3.3.2. Curing study of the epoxy resin

The curing or cross-linking of epoxy resin is done through the epoxy / hydroxyl groups. The curing agents commonly termed as hardeners are diamines and polyamines or acids and anhydrides. The bisphenol A based epoxy resin was cured by using commercial poly(amido amine) hardener (50 phr) at 100 ^{0}C for 30 min. However, the same was also cured by using a combination of above hardener (25 phr) and HPb (15 phr) at same time and temperature. Also hyperbranched/Cu nonoparticles (HPb-Cu) system with poly(amido amine) hardener can cure the resin at same time and dose as hyperbranched polymer alone can. But when hyperbranched polyamine (HPb) was used alone with the above resin, it has been found that the epoxy can be cured at 100 ^{0}C for 40 to 20 min at dose level of 10 to 30 phr (Table 6.3). This is due to the presence of large numbers of free reactive surface primary and secondary amino groups in the structure of the hyperbranched polyamine, which may react with epoxy group of the epoxy resin (Scheme 6.2). The dose higher than 30 phr was not studied because of commercial point of view as well as due to the fact that the cured resin became rather brittle even at dose level of 30 phr of hyperbranched polymer. This may be due the presence of rigid structure of the hyperbranched polymer.



Scheme 6.2. Possible crosslinking reactions in epoxy resin

Table 6.3. Drying time of epoxy resin

Resin code	Curing system (phr)	Time (min)
ER-HD	100:50:: Epoxy:Hardener	30
ER-15PA	100:15:: Epoxy: HPb	45
ER-20PA	100:20:: Epoxy: HPb	35
ER-30PA	100:30:: Epoxy: HPb	25
ER-HD-10PA	100:25:10:: Epoxy:Hardener: HPb	35
ER-HD-15PA	100:25:15:: Epoxy:Hardener: HPb	30
ER-HD-20PA	100:25:20:: Epoxy:Hardener:HPb	25
ER-HD-15PA/Cu	100:25:15:: Epoxy:Hardener: HPb -Cu	30

6.3.4. Coating performance of the resins

6.3.4.1. Coating performance of the poly(ester amide) resin

The performance of the poly(ester amide) resin was studied by the measurement of drying time, pencil hardness, impact resistance, adhesive strength, thermal stability, and chemical resistance in different chemical media for the resins with conventional drying system compared to conventional drier system with 5 phr of hyperbranched polyamine. The miscibility of the hyperbranched polymer with the resin system was studied by SEM (Figure 6.5) and it has been observed that there is no distinct phase separation in both the cases.

Physical properties

The drying of resin means the conversion from the liquid state to solid state by crosslinking reaction, which forms a three dimensional network structure. In this case the crosslinking is mainly from radical reaction of resin initiated by peroxide or aerial oxidation by absorbing oxygen from the atmosphere at high temperature in the presence of conventional drier system (PEA-CV). As the oil is non-drying, the resin requires a long time to dry [2]. Whereas in case of drying of resin with hyperbranched polyamine (PEA-CV-5PA) the time required is less (Table 6.2), which is due to the various crosslinking reactions as mentioned above (section 6.3.3.1) along with the radical reaction. The pencil hardness (Table 6.4) value for the PEA-CV-5PA is higher than the PEA-CV due to higher crosslinking density, the presence of rigid aromatic moieties and greater H-bonding in the former than the latter. Swelling test and FT-IR study also supports this fact. The FT-IR spectrum of PEA-CV-5PA indicates the presence of broad band for extended H-bonded >C=O groups at 1695 cm^{-1}. The adhesion characteristic for both the resin systems is very good, which is due to the presence of different polar groups. A little improvement in falling ball impact resistance in case of PEA-CV-5PA compared with PEA-CV indicates that hyperbranched polyamine can also act as impact modifier. This result is also supported by other results [35]. All the results indicated that PEA-CV-5PA is a better material than PEA-CV for surface coating applications.

Thermal study

From the thermogravimetric (TG) analysis of the resin systems it has been found that the thermostability of the resin was enhanced a little by the presence of hyperbranched polyamine (Figure 6.6.). The residual weight with the HPb is much higher than that without hyperbranched polymer at 600 ^{o}C (Table 3). These findings suggest that hyperbranched polyamine not only promotes some amounts of char formation (where heterocyclic moiety is mainly responsible) in the solid polymers, but it also helps the thermostability of the resin, which is due to chemical crosslinking, formation of H-bonding, enhanced compatibility, etc.

6.4. Coating performance of poly(ester amide) resin

Property	PEA-CV	PEA-CV-5PA
Drying time (h)	4.0	3.0
Pencil hardness	2H pass	3H pass
Adhesion (%)	100	100
Impact resistance (cm)	10-12	14-15
Specific gravity	0.89	0.91
Swelling (%)	12.87	4.76
LOI	21	25
Char residue (%)	4.6	11.2

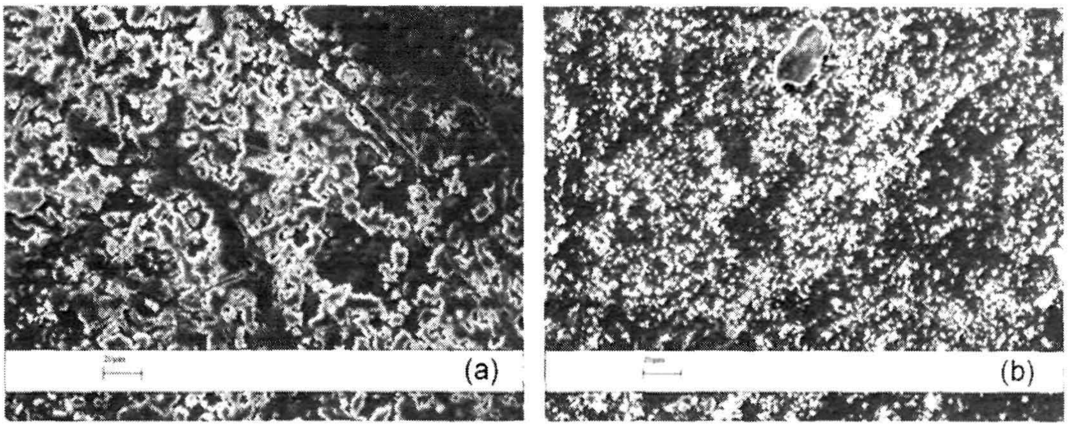


Figure 6.5. SEM micrographs for (a) = PEA-CV and (b) = PEA-CV-5PA

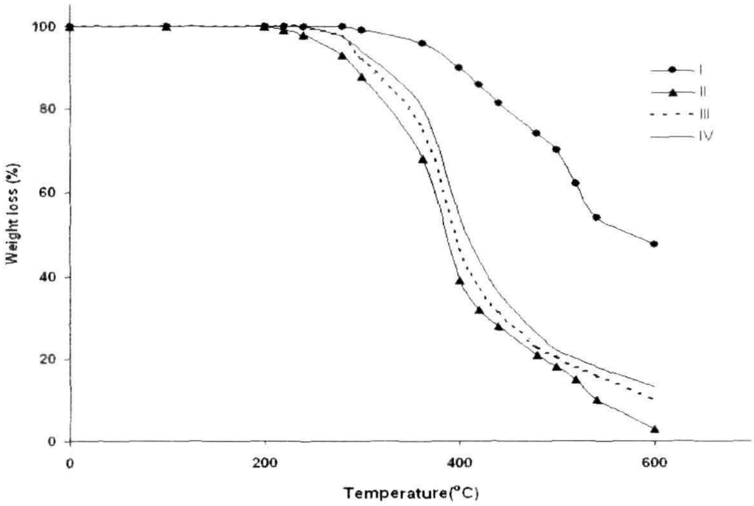


Figure 6.6. TG thermograms for I = HPb, II = PEA-CV, III = PEA-5PA and IV = PEA-CV-5PA

Chemical resistance

The results for the cured resin systems (Table 6.5) indicate that they have excellent chemical resistance in all tested media except dilute aqueous NaOH solution. In alkali solution the loss of adhesion was observed in both the cases, though the loss of weight in case of PEA-CV is little higher than PEA-CV-5PA system. This small improvement of alkali resistance may be due to the higher crosslinking density, the presence of rigid aromatic moieties and greater H-bonding in the former than the latter.

Table 6.5. Chemical resistance of cured poly(ester amide) resin

Medium	Weight loss (%)	
	PEA-CV	PEA-CV-5PA
Distilled water	-0.01	0.01
10 wt % aqueous NaCl	0.01	0.00
5 wt % aqueous HCl	0.02	0.01
3 wt % aqueous NaOH	0.20	0.12

6.3.4.2. Coating performance of the epoxy resin

The performance of the epoxy resin was also studied by the measurement of above performance characteristics like the earlier resin system. The results were compared for the poly(amido amine) hardener (ER-HD) curing system to the combination system of ER-HD with 15 phr of hyperbranched polyamine/Cu-nanoparticles (ER-HD-15PA/Cu). The SEM (Figure 6.7) studies indicate that there is no distinct phase separation in the latter case.

Physical Properties

In the drying of this resin the crosslinking is mainly from the reaction of active hydrogen atoms of primary and secondary amine groups with epoxy groups (Scheme 1). However, aliphatic di/poly-amines are highly reactive and offer fast curing even at room temperatures but they are toxic and skin sensitive compared to aromatic diamine. Whereas drying of resin with aromatic hyperbranched polyamine the time required is less (Table 6.4), which is due to the various crosslinking reactions with large number of functional groups presents in their structure. The pencil hardness (Table 6.6) value for the ER-HD-15PA/Cu is higher than the ER-HD is due to higher crosslinking density, the presence of rigid aromatic and triazine moieties and more number of H-bonding in the former than the latter. Swelling test and FT-IR study also supports this fact. The FT-IR spectrum of ER-HD-15PA/Cu indicates the presence of broad band for extended H-bonded OH groups at 3333 cm^{-1}. The adhesion characteristic for both the resin systems is very good, which is due to the presence of different polar groups. These results indicated that ER-HD-15PA/Cu is better material than ER-HD for surface coating applications.

Table 6.6. Coating performance of epoxy resin

Property	ER-HD	ER-HD-15PA/Cu
Drying time (min)	30	30
Pencil hardness	3H pass	4H pass
Adhesion (%)	100	100
Swelling (%)	10.71	3.69
LOI	21	26
Char residue (%) at 800 ^{O}C	4.1	14.8

Thermal study

From the thermogravimetric (TG) analysis of the resin systems it has been found that the thermostability of the resin was enhanced by the presence of hyperbranched polyamine (Figure 6.8) like earlier case. The char residue with the HPb is much higher than that without hyperbranched polymer at 800 ^{O}C (Table 6.6). Again, thermostability of the resin was further enhanced a little in the presence of Cu nanoparticles. These findings suggest that hyperbranched polyamine promotes the amount of char formation as well as thermostability of the resin, which is due to chemical crosslinking, formation of H-bonding, enhanced compatibility, etc.

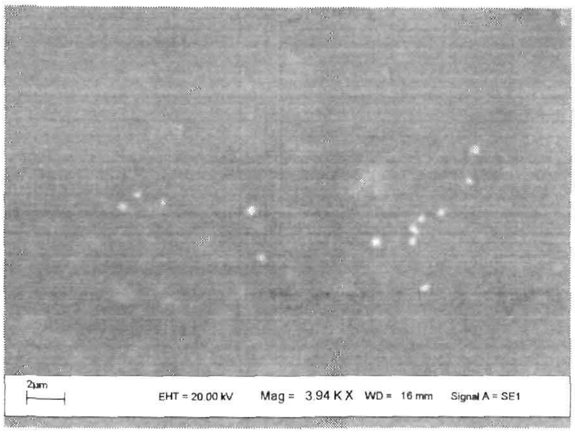


Figure 6.7. SEM micrographs for ER-HD-15PA/Cu

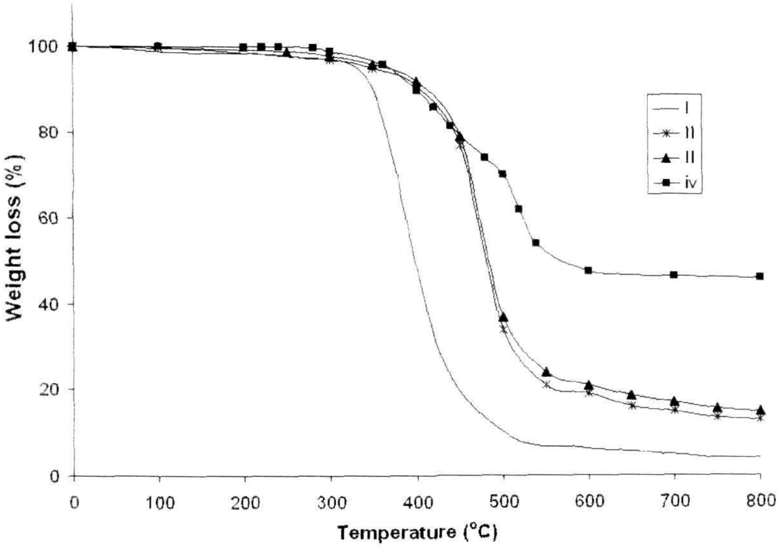


Figure 6.8. TG thermograms for I = EP-HD, II = EP-HD-15PA, III = ER-HD-15PA/Cu and IV = HPb

Chemical resistance

The chemical resistance results (Table 6.7) indicate that the epoxy resins have excellent chemical resistance in all tested media except dilute aqueous NaOH solution similar to earlier tested resin. In alkali solution the loss of adhesion was observed in both the cases, though the loss of weight in case of EP-HD is little higher than ER-HD-15PA/Cu system. This little improvement of alkali resistance may be due to the higher crosslinking density, the presence of rigid aromatic moieties and greater H-bonding in the former than the latter like earlier.

Table 6.7. Chemical resistance of cured epoxy resin

Medium	Weight loss (%)	
	ER-HD	ER-HD-15PA/Cu
Distilled water	0.01	-0.01
10 wt % aqueous NaCl	0.01	0.00
5 wt % aqueous HCl	0.03	0.01
3 wt % aqueous NaOH	0.22	0.10

Biological activity

The screening of the bioactivity of the nanocomposite was performed *in-vitro* against the *Candida albicans* fungus. The control experiment was performed by just pouring the culture broth with the living cells into a sterilite plate. The blank experiment was aimed to exclude that any biological activity could be ascribable to the sole polymer matrix. The inhibition of ER-HD-15PA/Cu with respect to ER-HD was 40 CFU/mL.

6.3.5. Flame retardancy study

As already stated in the introduction, the polymeric nature and hyperbranched architecture make these types of polymers very much compatible with the other polymeric systems, it is expected and also found from SEM studies that hyperbranched polyamine and poly(ester amide) or epoxy resin formed a miscible system (Figure 6.5 and 6.7). This result also indicates that the hyperbranched polyamine has good compatibilizing capability with the resin systems.

It has already been reported [36] and found in this study that triazine based polymers have very good flame retardant behavior for their excellent char forming effect. The LOI value may be used as an indicator to evaluate flame retardancy of a polymer. The hydrocarbon-based polymers with high hydrogen/carbon ratio like poly(ester amide) and epoxy resins are highly susceptible to flame. Thus the flame-retardant behavior of these resin systems was examined by the LOI test. The results are tabulated in Table 6.4 and Table 6.6. From the table, It has been observed that the LOI value of poly(ester amide) resin without flame retardant additive is lower than that with 5 phr of hyperbranched polyamine. Again LOI value of epoxy resin without flame retardant additive (ER-HD) is lower than that with 15 phr of hyperbranched polyamine/Cu nanoparticle system (ER-HD-15PA/Cu). This increment of LOI value is due to flame retardant characteristic of HPb as it has nitrogen and chlorine as the special elements in its structure.

6.4. Conclusions

From this study it can be concluded that the renewable Nahar seed oil is utilized successfully for the synthesis of the industrially important poly(ester amide) resins. The resins were successfully characterized by the determination of physical properties and spectroscopic studies. This hyperbranched polymer was used successfully as a potential agent for *Mesua ferrea* l. seed oil based poly(ester amide) resin and commercially available bisphenol A based epoxy resins. The performance characteristics like rate of curing, hardness, impact resistance, thermostability, flame retardancy, chemical resistance, etc. of the resins are improved by the addition of the hyperbranched polyamine at relatively low dose level. This hyperbranched polyamine-Cu nanoparticles system acts as effective antifungal activity against *Candida albicans* fungus.

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CHAPTER SEVEN

Conclusions and Future Scope

7.1. Summary and conclusions

The present thesis works on synthesis, characterization and applications of six hyperbranched polyamines with s-triazine moiety in their structures. The whole thesis is divided into three components. The first component of the thesis mainly describes a brief literature review, which reports on concept, importance, general techniques of preparation, characterization, properties and applications of hyperbranched polyamines. In this chapter the limitation of earlier works, scope and objectives, and plan of work for the present investigation are also presented. The whole technical work of the present investigation is divided into five different parts, which is the second component of the thesis.

In the first part of the second component, the synthesis and characterization of six hyperbranched aromatic polyamines with s-triazine moiety in the main chain are discussed. These polymers have been synthesized by a simple nucleophilic displacement polymerization technique using relatively low cost monomers via an A_2 + B_3 approach. The synthesized polymers were characterized by the conventional techniques such as FT-IR, UV, NMR, etc. spectroscopies and elemental analysis.

In the second part, the physical, thermal and fluorescence properties of these hyperbranched polyamines are described. The hyperbranched polyamines show low viscosity, high solubility and good thermostability. The study shows that the fluorescence of the polymers exhibit emission in the blue to yellow region and the intensity of fluorescence are influenced by the variation of concentration of polymer, pH of the medium, presence of metal ions and nature of end groups.

The third part of the technical work is the studies on improvement of performance characteristics of two commercial linear polymers before and after aging by blending with a representative hyperbranched polyamine. This hyperbranched polymer is acting here as a multipurpose polymeric additive for both the base polymers. This part also describes the use of hyperbranched polyamines as polymeric flame retardant additives for above commercial linear polymers.

The fourth part of the technical work is on synthesis of metal nanoparticles such as silver and copper by using hyperbranched polyamine as a matrix. It has been shown that metal nanoparticles are highly stable and well dispersed in these matrices.

The fifth part of the technical work involves the use of hyperbranched polyamine as a crosslinker for thermosetting resins such as vegetable oil based poly(ester amide) and commercially available bisphenol A based epoxy resins. The studies show that the hyperbranched polyamine enhances the rate of crosslinking reaction as well as improves many desirable performance characteristics. The present investigation is, therefore, worked according to the plans that were described in chapter one. The objectives of the investigation are also fulfilled by this study.

The third component of the thesis is this chapter, which mainly highlights the whole work of the present investigation. From the present investigation following conclusions can be drawn.

i) Triazine based six hyperbranched polyamines have been synthesized from commercially available relatively low cost monomers by an $A_2 + B_3$ approach for the first time. The gel formation was avoided by high dilution and slow addition of the reactants.

ii) The synthesized polyamines were characterized successfully by the conventional analytical and spectroscopic techniques.

iii) The physical, thermal and optical properties of these hyperbranched polyamines were studied. The results indicate that hyperbranched polymers exhibit some very useful properties like high solubility, low viscosity, high thermostability, blue to yellow fluorescence, etc.

iv) The synthesized polyamine was used as multipurpose polymeric additive for commercially available linear polymers such as plasticized PVC and LDPE for the first time. The retention properties of the base polymers after heat aging and leaching in different media are found to be very good.

v) The flame retardancy of the hyperbranched polymers was studied by the measurement of limiting oxygen index values and the polymers were found to be self extinguishing in nature.

vi) Hyperbranched polyamines showed their effectiveness as polymeric flame retardants for linear polymers like plasticized PVC and LDPE at different dose levels. They also exhibit synergistic effect with the commercial flame retardant additive, triphenylphosphine oxide.

vii) Hyperbranched polyamines used as matrices for preparation of highly stable, well-dispersed and biologically active metals such as silver and copper nanoparticles.

viii) The hyperbranched polyamine was used as a promising material for thermosetting resins such as vegetable oil based poly(ester amide) and commercially available bisphenol A based epoxy resins.

Thus the overall major achievement of the present investigation is development of hyperbranched aromatic polyamines with s-triazine unit in their structures as multipurpose polymeric additives for industrially useful linear polymers, crosslinkers for thermosets, matrices for nanoparticles by simple method and using easily available monomers.

7.2. Future scope

As this is the first comprehensive and systematic study on s-triazine based hyperbranched aromatic polyamines using directly cyanuric chloride as one of the monomers, so there are some of future scopes for further studies on this subject. A few of these are -

i) the comprehensive studies of such aromatic hyperbranched polyamines as flame retardant for linear polymers, crosslinker for thermosetting resins and as matrix for preparation of nanoparticles,

ii) development of flame retardant s-triazine based hyperbranched polyamines with phosphorous element in the structures to verify the nitrogen-phosporous synergistic effect,

iii) development of conducting hyperbranched polyamine by proper choice of diamine component.

etc.

List of Publications

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7. Mahapatra S.S. and Karak N., “Hyperbranched polyamine: A promising curing agent for a vegetable oil based poly(ester-amide) resin”, Prog. Org. Coat. **2007**, 60, 328-334.
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Conferences Presentation (Published as Proceeding):

1. Dutta N., Mahapatra S.S., Karak N., and Dolui S.K., "Development of polyester and poly(ester amide) from Nahar oil." National Workshop on Science and Technology for regional development: case for North-East India, IIT Guwahati, February **2004.**
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3. Karak N., Dutta N., Mahapatra S.S. and Dutta S., "Development of resins from Nahar seed oil for surface coating applications." International Conference on Surface Coatings 2004, Mumbai, October **2004**.
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5. Mahapatra S.S. and Karak N., "Highly branched polymeric additives for commercial polyolefines," CMDAYS'06, Tezpur University, August **2006.**
6. Mahapatra S.S., Borah J. and Karak N., "Hyperbranched Polymers – Multipurpose Polymeric Additives," International Conference on Polymer Processing (ICPP 2007), BUCT, Beijing, China, May **2007.**
7. Mahapatra S.S. and Karak N., "Hyperbranched Polyamines: Synthesis, Characterization and Prospect," International Seminar on Frontiers in Polymer Science and Technology (POLY-2007), Guwahati, November **2007**.
8. Mahapatra S.S. and Karak N., "Hyperbranched Polyamines: Promising Materials," International Conference on Rubber and Rubber like Materials 2008 (ICRRM08), IIT Kharagpur, January **2008.**
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