

Hyperbranched Aromatic Polyamines with *s*-Triazine Rings

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ABSTRACT: Two aromatic hyperbranched polyamines with *s*-triazine rings were synthesized from A₂ (4,4'-sulfonyl dianiline or 4,4'-methylene dianiline) and B₃ (2,4,6-trichloro-*s*-triazine) types of monomers by a single-step nucleophilic displacement polymerization technique in the presence of diisopropyl ethyl amine as the base. The hyperbranched polyamines were obtained in high yields (~82–90%) with this technique. The polymers were characterized through solubility testing, measurements of the inherent viscosity, Fourier transform infrared, ultraviolet, ¹H-NMR, and ¹³C-NMR spectroscopy, and X-ray diffraction studies. The inherent viscosities of the polymers were in the range of 0.23–0.42 dL/g in 0.5% (w/v) *N,N'*-dimethylacetamide at 27 ± 0.1°C. They were soluble only in highly polar solvents such as *N,N'*-dimethylacetamide, dimethylformamide, di-

methyl sulfoxide, and *N*-methylpyrrolidone. The thermal behavior of the polymers was investigated with thermogravimetric analysis and differential scanning calorimetry studies. The flame-retardant characteristics of the polymers were tested through the measurement of the limiting oxygen index. In the thermogravimetric analysis of these hyperbranched polyamines, no weight loss was observed below 250°C under a nitrogen atmosphere, whereas differential scanning calorimetry showed that the glass-transition temperatures were about 240 and 230°C for the polymers with sulfonyl and methylene groups, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 95–102, 2007

Key words: flame retardance; hyperbranched; polyamines; structure; synthesis; thermal properties

INTRODUCTION

Polymers with heterocyclic moieties show important physical, chemical, and thermal properties. Seeking to improve the solubility and processability of heterocyclic polymers while maintaining the thermal stability, some have published reports describing the synthesis and properties of heterocyclic polymers with *s*-triazine moieties, such as polyesters,¹ poly(amide imide)s,² polyazomethines,³ polyureas,⁴ polycyanurates,⁵ polyamides,⁶ polyamines,⁷ and polyethers.⁸ All these reports are based on linear polymers only. Recently, dendritic polymers have attracted considerable global attention because of their improved physical and chemical properties, which are generated from their unique architectural features.⁹ Dendritic polymers include both dendrimers and hyperbranched polymers. Dendrimers are monodisperse and perfectly regularly branched structures, whereas

hyperbranched polymers are polydisperse and less regular and have more defective branched structures.^{10,11} However, the synthesis of dendrimers needs more stringent reaction conditions and a time-consuming and laborious process. Hence, their large-scale production is very difficult. On the other hand, the synthesis of hyperbranched polymers is much easier, involves only a single step, has no need of any purification, and thus can be performed on a larger scale without any great difficulty. Thus, research on hyperbranched polymers is very important for different value-added applications.^{12,13} Hyperbranched polymers are generally synthesized from AB_{*m*}-type (*m* ≥ 2) monomers, but the availability of such monomers is limited. For the synthesis of those monomers, very tedious and cumbersome organic synthetic routes are also required.^{14,15} To overcome these problems, recently we attempted a simple and useful A₂ + B₃ approach to the synthesis of hyperbranched aromatic polyethers¹⁶ with a nucleophilic displacement polymerization technique. A similar type of approach was used by Frechet et al.¹⁷ for the synthesis of hyperbranched aliphatic polyethers by employing a proton-transfer polymerization technique. Other researchers have used the same A₂ + B₃ approach to the synthesis of hyperbranched polyimides.^{18–20} Like any other approach, this approach has its own merits and demerits. Here the polymerization process is very easy and simple and offers a high yield and

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often a tailored structure. However, experience has revealed that gelation is a very common problem in this kind of approach and leads to useless products, except in the case of adhesives. The ideal conditions for gelation in this case, as described by Flory,²¹ are based on the following assumptions: (1) the equal reactivity of an A or B group at every moment of this reaction, (2) no intermolecular cyclization, and (3) the restriction of the reaction between A and B groups. If these can be avoided, gelation will not occur. In this investigation, every attempt was made to avoid gelation by the use of a high-dilution technique and the slow addition of the monomer along with the control of other reaction parameters. To the best of our knowledge, this is the first successful report on the synthesis of triazine-containing hyperbranched aromatic polyamines with an A₂ + B₃ approach without any gel formation.

This investigation involved the synthesis of two aromatic, heterocyclic hyperbranched polyamines with *s*-triazine rings. Furthermore, as it has been reported^{22,23} that sulfide groups increase the thermooxidative resistance and refractive index while reducing the water-absorbing capacity, a sulfonyl-group-containing aromatic diamine was chosen for this study. A methylene-containing aromatic diamine was also used to synthesize another hyperbranched polyamine to compare all the results with those of the hyperbranched polyamine containing sulfonyl groups.

Therefore, we report here the successful synthesis and characterization of two hyperbranched aromatic polyamines with triazine moieties obtained from A₂- and B₃-type monomers through the use of the nucleophilic displacement polymerization technique for the first time. The solution and thermal behaviors of the synthesized polymers are also discussed here.

EXPERIMENTAL

Materials

N,N'-Dimethylacetamide (DMAc; Merck, Bombay, India) was used after purification by vacuum distillation over calcium oxide. 2,4,6-Trichloro-*s*-triazine (CYC) and diisopropyl ethyl amine (DIPEA; Merck, Schuchardt, Germany) were used as received. 4,4'-Sulfonyl dianiline (SDA) and 4,4'-methylene dianiline (MDA; Merck) were used after recrystallization from aqueous ethanol. All other chemicals were reagent-grade and were used as received unless otherwise stated.

Instruments and methods

Fourier transform infrared (FTIR) spectra for the polymers were recorded with a Nicolet (Madison, WI) Impact 410 FTIR spectrophotometer with KBr pellets.

¹H-NMR and ¹³C-NMR spectra of the polymers were recorded with an AMX (Michigan, USA) 400-MHz NMR spectrometer with dimethyl sulfoxide-*d*₆ as the solvent and tetramethylsilane (TMS) as the internal standard. Ultraviolet (UV) spectra of the hyperbranched polyamines were recorded with a Hitachi (Tokyo, Japan) U-2001 UV spectrophotometer with a 0.001% solution in DMAc. The inherent viscosity of the polymers was measured with a 0.5% (w/v) solution of each polymer in DMAc at 27 ± 0.1°C with an Ubbelohde suspended-level viscometer. X-ray diffraction (XRD) studies were made of the powders of the hyperbranched polyamines at room temperature (ca. 25°C) on a Phillips (Leeds, United Kingdom) X-ray diffractometer (operating at 40 kV and 40 mV) with nickel-filtered Cu K α radiation (λ = 1.5418 nm). The scanning rate was 1.0°/min over the range of 2 θ = 0–50° for the study. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were performed with PerkinElmer (Boston, MA) Pyris-6 and Pyris-1 thermal analyzers, respectively, under a nitrogen atmosphere (at a flow rate of 20 mL/min) at a heating rate of 10°C/min. The limiting oxygen index (LOI) of each polymer powder was determined with a modified version of ASTM Standard D 2863-77. Each dry, ground powder sample was placed in a glass cup with a diameter of 1.0 cm and a height of 1.01 cm attached to a glass rod of 80 cm, which was clamped by the sample holder. The remaining procedure was the same as the ASTM method. The LOI values obtained by this technique were the averages of at least three tests for each sample. The densities of the polymers were determined with a pycnometer (Kolkata, India) in dry toluene at room temperature (ca. 25°C) by the conventional liquid-displacement method. The solubility of the polymers was observed in different solvents after 2 days at room temperature with a 0.01-g sample in 1.0 mL of a solvent. The chlorine and sulfur contents of the polymers were determined by the standard Schoniger oxygen combustion method.

Synthesis of the first polymer (Ps)

To a dry 250-mL, three-necked, round-bottom flask, 3.20 g (0.0129 mol) of SDA, 1.11 g (0.0086 mol) of DIPEA, and 20 mL of DMAc were added under an N₂ purge. When the chemicals were dissolved completely, 1.58 g (0.0086 mol) of a CYC solution in 28 mL of DMAc was added dropwise for about 1 h at 0–5°C with constant stirring. After the completion of the addition, the reaction mixture was stirred for another 1 h under the same conditions, and this was followed by an increase in the temperature to 40–45°C. At this temperature, again 1.11 g of DIPEA was added to the reaction mixture, and stirring was

continued for another 2 h. Then, the temperature was again raised to 85–90°C, and another 1.11 g of DIPEA was added. The reaction was continued for another 6 h under the same conditions. Then, it was cooled and poured slowly with constant stirring into 1 L of ice-cold water. The precipitate that formed was collected by filtration and washed several times, at first with methanol and then with acetone, to remove the unreacted reagents. The product was dried under a vacuum at 45–50°C for 3 days to obtain a dry powder of the polymer.

Yield: 82%. Inherent viscosity: 0.23 dL/g. ¹H-NMR (δ, ppm): 10.86, 9.93–9.89 and 9.87–9.62 (–NH), 3.60 (–NH₂), 5.98–8.01 (aromatic). ¹³C-NMR (δ, ppm): 163.99, 153.42, 126.27–129.18, 113.11, 120.23–121.06. FTIR (KBr, cm⁻¹): 3370–3399, 1406–1409, 1014–1050, 690.

Synthesis of the second polymer (Pm)

Pm was synthesized with exactly the same procedure described for Ps, except that MDA was used in place of SDA.

Yield: 90%. Inherent viscosity: 0.42 dL/g. ¹H-NMR (δ, ppm): 11.17, 9.12 and 9.09 (–NH), 3.61 (–NH₂), 6.66–8.93 (aromatic), 3.85–3.75 (aliphatic CH₂). ¹³C-NMR (δ, ppm): 164.17, 135.27–137.78, 119.38–121.51, 128.29–129.19, 115.90, 53.57. FTIR (KBr, cm⁻¹): 3370–3399, 1406–1409, 1014.

RESULTS AND DISCUSSION

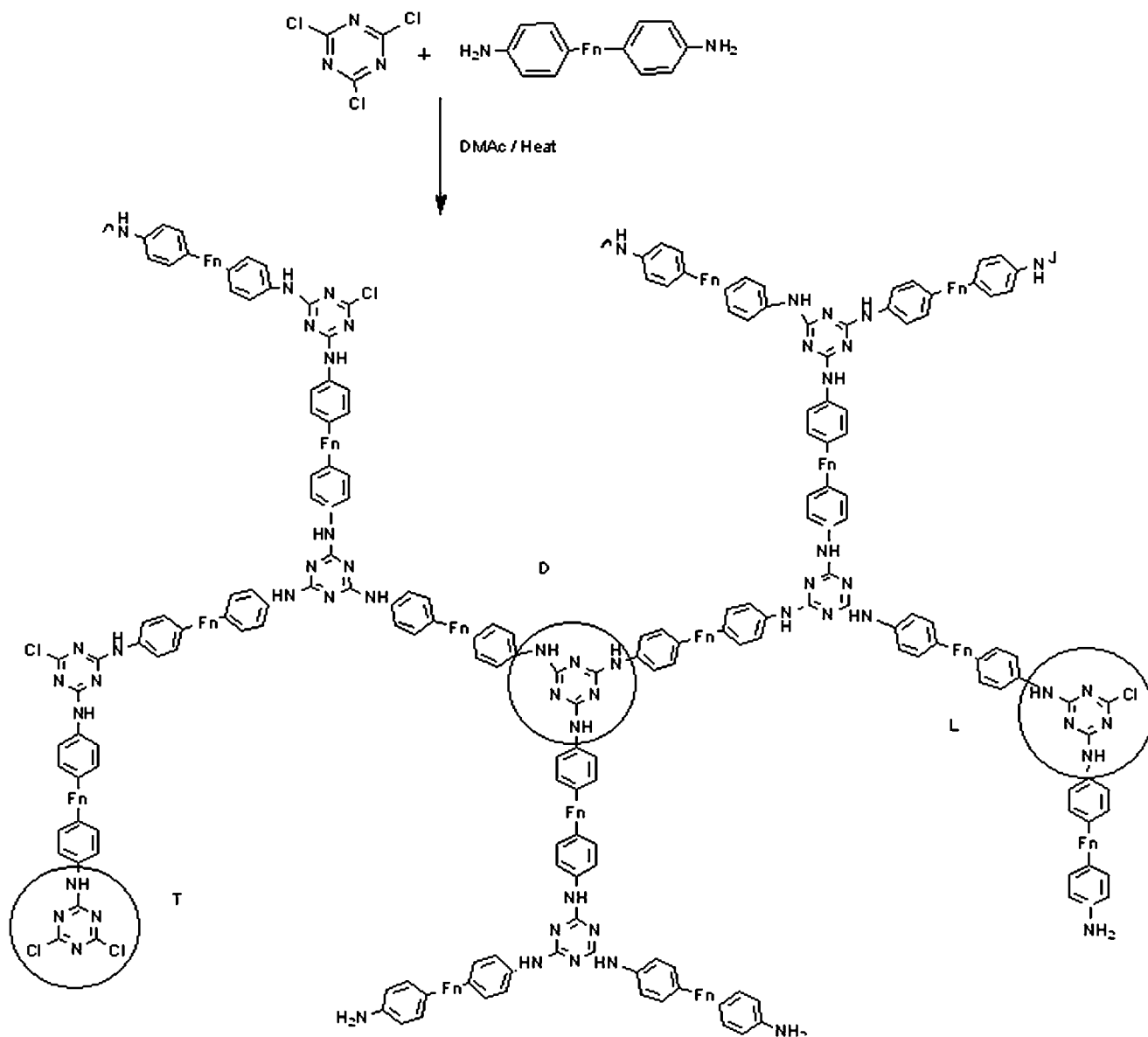
Polymer synthesis

Hyperbranched polymers Ps and Pm were synthesized by a nucleophilic displacement polymerization reaction from the corresponding aromatic diamine (A₂) and CYC (B₃) in a molar ratio of 3 : 2 in the presence of DIPEA, as shown in Scheme 1. This polycondensation reaction is a three-step reaction as the reactivity of the three chlorine atoms of the triazine moiety is different. This was reported by previous workers for the nucleophilic substitution of chlorine atoms in CYC by different amine compounds.^{24,25} The polymerization conditions and the results are summarized in Table I. The reaction was carried out at three different temperatures in a stagewise manner in both cases. This stagewise condensation reaction prevented gel formation in the synthesized hyperbranched polymers, as no gel was observed under the reaction conditions of this polymerization process. This was confirmed by the solubility test in each case. Moreover, when the temperature of the reaction was higher than the temperature at any stage, a large quantity of fumes was generated, and the reaction happened to be uncontrolled. Even a two-stage or single-stage reaction resulted in a gel product. The

high-temperature single-stage reaction with simultaneous addition and a high concentration of the reactants often afforded a gel, and this indicated that the polymerization was uncontrollable. This was due to the high rate of reaction between the chlorine atoms of the triazine unit and the amine-functional groups of the aromatic diamine. The use of a high reaction concentration (20%) led to gel formation and a low yield. The use of another molar ratio (1 : 1) of the reactants resulted in a low yield and viscosity (70% yield and 0.18 dL/g inherent viscosity for the Ps polymer). Even in solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), the yield and viscosity of the Ps polymer were not so good. Thus, the success of this approach is dependent of the following factors: the concentration and ratio of the reactants, the solvent, the purity of the reactants, and the reaction time and temperature. This type of approach has otherwise proved to be difficult to control, and a hyperbranched polymer is often obtained with a high molecular weight.^{26,27} The dilute solution viscosities of these polymers were relatively low, and this may have been due to the globular-type structure, as supported by other reports.^{14,15} The higher viscosity and higher yield of Pm versus those of Ps may have been due to the fact that the steric hindrance of Ps was higher than that of Pm. This was due to the large size of the sulfonyl group in comparison with the methylene group. Furthermore, the nucleophilicity of SDA is lower than that of MDA, and this hindered the polycondensation reaction in the case of Ps versus Pm; hence, a low yield was obtained for Ps.

Characterization of the polymers

The densities were 1.24 g/cc for Ps and 1.29 g/cc for Pm, and both Ps and Pm were light brown. The moderate density values for both polymers may have been due to the presence of a rigid aromatic triazine moiety and polar and hydrogen-bonding interactions, which increased the compactness of the polymers. The presence of hydrogen bonding was confirmed by FTIR spectra (discussed later). Furthermore, the compactness of the polymers was not so high because the polymers were amorphous in nature, as confirmed by the XRD study. Thus, the two opposing effects resulted in moderate densities for the polymers. The relatively high softening points were quite obvious as they possessed large amounts of rigid triazine and other aromatic moieties, but at the same time, the polymers were amorphous in nature, so the values were not very high. However, the softening points for the two polymers were not very well determined, as they were not observed in DSC curves under a nitrogen atmosphere (discussed later).



Scheme 1 Synthesis of the hyperbranched polyamines with the A₂ + B₃ approach.

The maximum wavelengths of polymers Ps and Pm in DMAc solutions were observed at 310 (abs. 1.582) and 300 nm (abs. 1.909), respectively, which

indicated the presence of aromatic moieties with conjugation. For both polymers, two more peaks with similar intensities were also observed [320 nm

TABLE I
Polymerization Conditions and Results for the Synthesis of the Hyperbranched Polyamines via the A₂ + B₃ Approach

| Polymer | Temperature (°C) ^a | Time (h) ^a | Concentration (%) ^b | Yield (%) | η_{inh} (dL/g) ^c | DB ^d |
|---------|-------------------------------|-----------------------|--------------------------------|-----------|----------------------------------|-----------------|
| Ps | 0–5/40–45/85–90 | 2/2/6 | 10 | 82 | 0.23 | 0.64 (0.56) |
| Pm | 0–5/40–45/85–90 | 2/2/7 | 10 | 90 | 0.42 | 0.68 (0.60) |

^a The same batch of reactions was carried out in three stages: 0–5°C for 2 h, 40–45°C for 2 h, and 85–90°C for 6 h for Ps and for 7 h for Pm.

^b The weight-to-volume ratio of the reactants to the solvent.

^c Inherent viscosity of the hyperbranched polyamines measured at a concentration of 0.5 g/dL in DMAc at 27 ± 0.1°C.

^d The DB values inside and outside parentheses were calculated with eqs. (1) and (2), respectively.

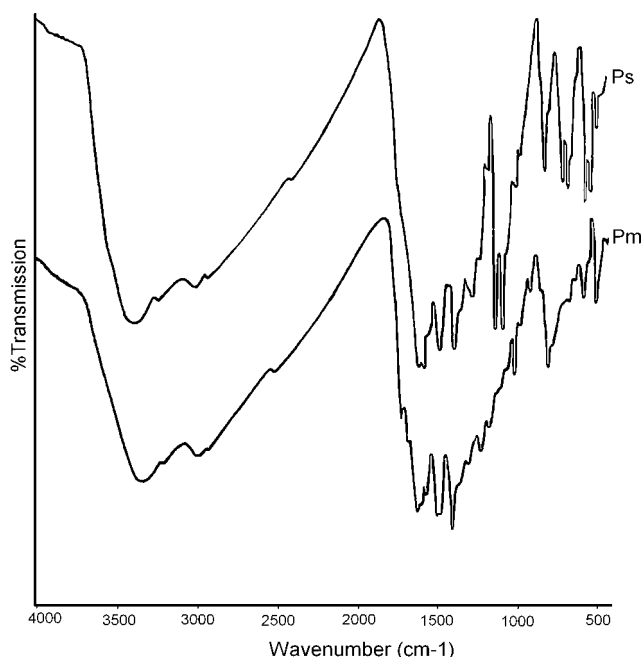


Figure 1 FTIR spectra of the hyperbranched polyamines.

(abs. 1.532) and 300 nm (abs. 1.441) for Ps and 310.5 (abs. 1.875) and 290 nm (abs. 1.866) for Pm]. These three peaks may have been due to the presence of three different types of units in the hyperbranched polyamines: dendritic, linear, and terminal units. The higher maximum wavelength of Ps versus that of Pm was due to higher conjugation in the former than in the later, as the sulfonyl group took part in conjugation in Ps. The FTIR spectra of the polymers (Fig. 1) indicated the presence of an aromatic amine linkage, N—H (primary or secondary), at 3370–3399 cm^{-1} . The peak nature in both cases was mainly due to associated N—H bonds as these were weak but sharp peaks.²⁸ The N—H bending vibrations for primary and secondary aromatic amines for both polymers were found separately at 1572–1594 and 1496–1511 cm^{-1} , respectively. The marginal shift of these absorption values may have been due to the presence of hydrogen bonding.²⁸ The presence of these

TABLE II
Elemental Analysis Data of the Hyperbranched Polyamines

| Polymer | | C | H | N | S ^b | Cl ^b |
|---------|-------------------------|-------|------|-------|----------------|-----------------|
| Ps | Calculated ^a | 56.32 | 3.35 | 18.77 | 10.73 | — |
| | Found | 54.86 | 2.98 | 19.17 | 8.00 | 4.05 |
| Pm | Calculated ^a | 72.52 | 4.80 | 22.56 | — | — |
| | Found | 69.26 | 4.20 | 21.87 | — | 3.50 |

^a Calculated with an ideal dendritic structure with no chlorine atom.

^b Estimated by the Schoniger oxygen combustion method.

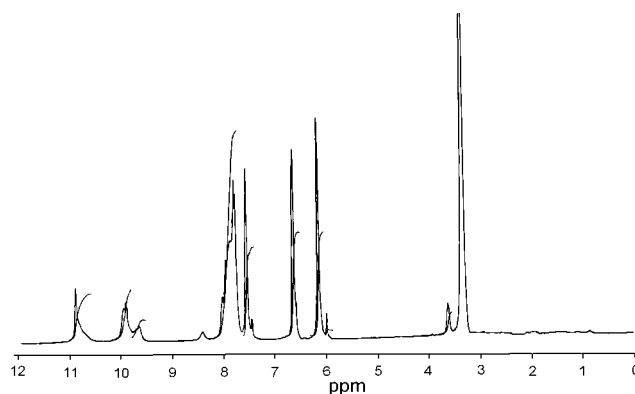


Figure 2 $^1\text{H-NMR}$ spectrum of the sulfonyl-group-containing hyperbranched polyamine (Ps).

peaks in the polymers confirmed the occurrence of a nucleophilic displacement polymerization reaction with the formation of a secondary amine bond. The C=N bond of the triazine moiety appeared at 1406–1409 cm^{-1} in the IR spectra for both polymers. The aromatic C—Cl bond was observed at 1014–1050 cm^{-1} for both cases, and this indicates that the displacement reaction was not completed. This was confirmed by a quantitative estimation of chlorine by the Schoniger oxygen combustion method (Table II). The structures of the polymers were further supported by NMR studies. The $^1\text{H-NMR}$ spectra (Figs. 2 and 3) of the polymers indicated the presence of important peaks for the different types of protons.²⁸ Three different peaks appeared for the secondary N—H protons of the polymers, and this confirmed the presence of three different units: dendritic, linear, and terminal units. The peaks at $\delta = 10.86$ ppm, $\delta = 9.93$ – 9.89 ppm, and $\delta = 9.87$ – 9.62 ppm were due to N—H protons attached to the terminal triazine unit (triazine with two unsubstituted chlorine atoms), to the linear unit (triazine with one unsubstituted chlorine atom), and to the dendritic unit (triazine with no chlorine atom) for the Ps hyperbranched polyamine. The peaks at $\delta = 11.17$ ppm, $\delta = 9.12$ ppm, and $\delta = 9.09$ ppm were due to the pro-

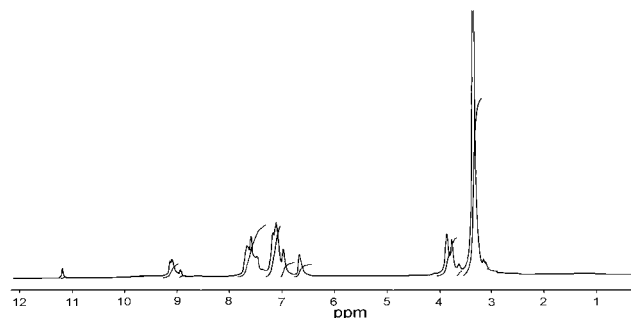


Figure 3 $^1\text{H-NMR}$ spectrum of the methylene-group-containing hyperbranched polyamine (Pm).

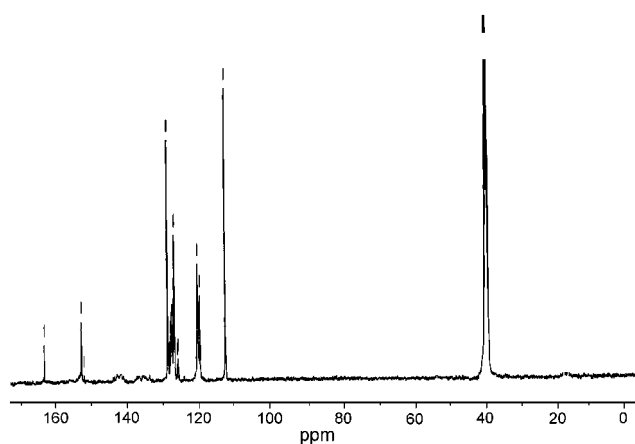


Figure 4 ^{13}C -NMR spectrum of the sulfonyl-group-containing hyperbranched polyamine (Ps).

tions of N—H, which were attached to the terminal triazine unit, to the linear unit, and to the dendritic unit, respectively, for Pm. The peaks for the NH_2 protons appeared at $\delta = 3.60$ ppm for Ps and at $\delta = 3.61$ ppm for Pm. The aliphatic CH_2 protons of the Pm hyperbranched polyamine appeared at $\delta = 3.85$ – 3.75 ppm. The protons for the aromatic moieties appeared at $\delta = 5.98$ – 8.01 ppm for Ps and at $\delta = 6.66$ – 8.93 ppm for Pm as a multiplet, perhaps because of the presence of different types of chemical environments as a large number of conformations were possible for both polymers. The ^{13}C -NMR spectra (Figs. 4 and 5) further support the structures of the polymers shown in Scheme 1. All the important peaks could be observed in these spectra.²⁸ The peaks at $\delta = 163.99$ ppm and $\delta = 164.17$ ppm were due to the carbon atoms present in the dendritic triazine units for polyamines Ps and Pm, respectively. The peaks at $\delta = 153.42$ ppm, $\delta = 126.27$ – 129.18 ppm, $\delta = 113.11$ ppm, and $\delta = 120.23$ – 121.06 ppm may have been due to the carbons attached to secondary N—H groups and ortho, meta, and directly attached to sulfonyl groups, respectively, for the Ps polymer. The peaks at $\delta = 135.27$ – 137.78 ppm, $\delta = 119.38$ – 121.51 ppm, $\delta = 128.29$ – 129.19 ppm, and $\delta = 115.90$ ppm may have been due to the carbons attached to the secondary N—H groups and ortho, meta, and directly attached to methylene groups, respectively, for the Pm polymer. The peak for the CH_2 carbon appeared at $\delta = 53.57$ ppm for the Pm polymer. Thus, ^{13}C -NMR spectroscopy was not able to detect the carbon of the triazine units with one or two chlorine atoms, as there was no peak at about $\delta = 172$ ppm or higher.²⁸ The elemental analysis data of the polymers (Table II) also support the structures of the polymers shown in Scheme 1. The variation of the elemental analysis values from the ideal dendritic structure (calculated) was quite obvious as the hyperbranched structure had large structural defects

and was complex in nature. Thus, it was very difficult to assign the exact structure of the hyperbranched polymers.

Degree of branching (DB)

The structural perfection of hyperbranched polymers is usually characterized by the determination of their DB. This was determined here according to Frechet et al.²⁹ [eq. (1)] and Frey et al.³⁰ [eq. (2)]:

$$\text{DB} = (D + T)/(D + T + L) \quad (1)$$

$$\text{DB} = (2D)/(2D + L) \quad (2)$$

where D, T, and L refer to the number of dendritic, terminal, and linear units in the structure of the polymer, respectively. Experimentally, DB is generally determined from NMR spectroscopy through a comparison of the integration of the peaks for the respective units in a hyperbranched polymer.²⁹ The structure of a hyperbranched polymer is indeed a block construction of the three units. In this work, the dendritic, terminal, and linear units were distinguished by the consideration of how many functional groups in the B_3 monomer (CYC) were consumed; this is similar to the case for hyperbranched polymers from AB_2 monomers. The linear and terminal units had one and two unreacted B functional groups (chlorine atoms), respectively. With the help of ^1H -NMR measurements, we found that the secondary N—H linkages derived from the central aromatic (triazine) ring of the B_3 monomers were sensitive to the number of B functional groups, which were capable of assigning the three units (Figs. 2 and 3). The relative amounts of the aforementioned units were calculated by the respective integration of the ^1H -NMR peaks. The peaks for the different units were assigned as discussed in the section on characterization. The values of DB for both polymers were calculated from the integration of ^1H -NMR peaks

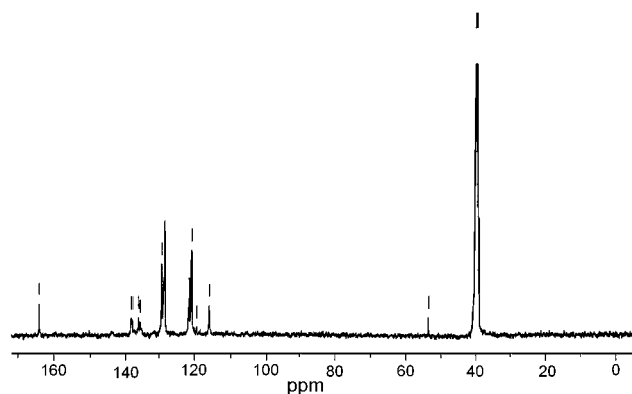


Figure 5 ^{13}C -NMR spectrum of the methylene-group-containing hyperbranched polyamine (Pm).

TABLE III
Thermal Characteristics and Solubility Behavior of the Hyperbranched Polyamines

| Polymer | T_5 (°C) ^a | LOI | CR ₈₀₀ (%) ^b | T_g ^c | Solubility ^d | | | | | |
|---------|-------------------------|-----|------------------------------------|--------------------|-------------------------|-----|------|-----|-----|---------|
| | | | | | DMAc | DMF | DMSO | NMP | THF | Toluene |
| Ps | 305 | 42 | 55 | 240 | + | + | + | + | – | – |
| Pm | 250 | 32 | 48 | 230 | + | + | + | + | – | – |

^a Temperature at 5% weight loss.

^b Char residue at 800°C obtained from a TGA curve at a heating rate of 10°C/min under a nitrogen atmosphere.

^c Glass-transition temperature.

^d + = soluble; – = insoluble.

and are given in Table I. The DB values obtained with the two equations were almost equal, although Frey et al.'s equation resulted in somewhat higher values for both hyperbranched polymers. These DB values indicated that both polymers exhibited a nearly ideal hyperbranched structure (DB close to 0.5) rather than a more linear (DB close to zero) or dendritic structure (DB close to unity).

Properties of the polymers

The thermal properties and solubility characteristics of the resulting hyperbranched polymers are summarized in Table III. The first 3–4% weight loss may have been due to the loss of moisture and volatile organic solvents present in the polymer in both cases (Fig. 6). This was confirmed by isothermal heating at about 200°C for 1 h. A two-stage degradation pattern was observed for the degradation of both polymers up to 800°C. In the first stage from 300 to 430°C, a weight loss of ~ 14% was observed, perhaps because of the loss of sulfonyl groups and unsubstituted chlorine (3.50% as HCl) for the Ps polymer. For the Pm polymer, it occurred from 250 to 550°C with a weight loss of ~ 28%, which was mainly due to a loss of unsubstituted (4.05%) chlorine as HCl and methylene (–CH₂–) moieties of the aromatic amine part. The second stage of degradation occurred from 520 to 700°C with a weight loss of ~ 20% for the Ps polymer and from 570 to 730°C with a weight loss of ~ 14% for the Pm polymer, perhaps because of the elimination of terminal amine groups and the degraded products of the aromatic moieties. The char residue at 800°C was mainly due to the nondegradable triazine and aromatic moieties. TGA confirmed that both hyperbranched polymers exhibited good thermostability and that the Ps polymer was more thermostable than the Pm polymer; this was obvious as the former had more thermostable sulfonyl groups versus thermolabile methylene linkages in the latter. The high thermostability of polymers with triazine moieties has also been reported by other researchers.³¹

However, the flame retardancy test indicated that the Pm polyamine had a lower LOI value than Ps

(Table III). This may have been due to the presence of a thermolabile –CH₂– moiety, which may have formed flammable CH₄, CH₃–CH₃, and other molecules for the Pm polymer. However, Ps did not possess such a flammable moiety but had nonflammable sulfur as a special element. The presence of the methylene moiety in the Pm polymer chain made it more flexible than Ps, as determined by the measurement of the glass-transition temperature from DSC studies (Table III). In the DSC studies, no melting or crystallization peak was observed for the polymers, and this indicated that these hyperbranched polymers were amorphous in nature. This was further supported by the XRD study. The solubility studies showed that the polymers were soluble only in highly polar solvents such as DMAc, DMF, DMSO, and *N*-methylpyrrolidone (NMP) but were insoluble in most other solvents such as hydrocarbon solvents, water, and chlorinated common organic solvents. This may have been due to the presence of polar

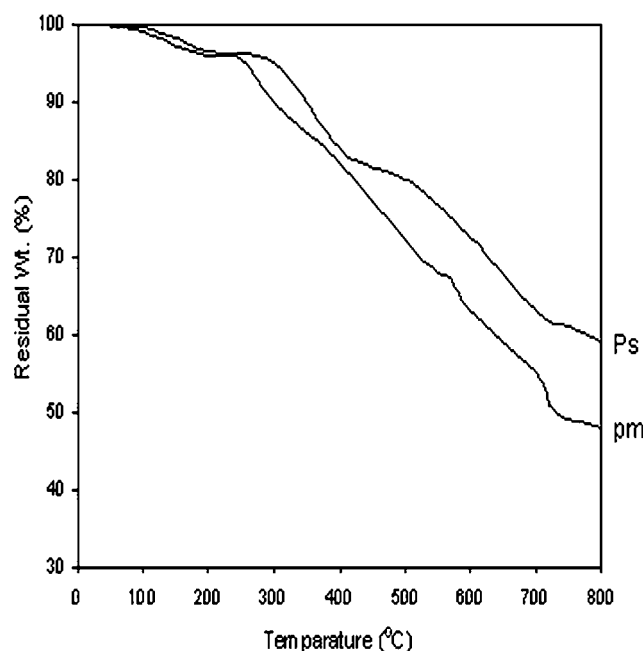


Figure 6 TGA thermograms for the sulfonyl- and methylene-group-containing hyperbranched polyamines (Ps and Pm).

—NH— groups, rigid triazine units, and aromatic moieties in the polymer structures. However, this solubility behavior was superior to that of a similar type of aromatic linear polyamine,⁷ and this may have been due to the presence of a large number of surface groups and the globular structure of the hyperbranched polymers. This high solubility not only supported the formation of the hyperbranched structure but also confirmed that the polymers were not crosslinked gel products.

CONCLUSIONS

From this study, it could be concluded that hyperbranched polyamines containing *s*-triazine rings were synthesized successfully with an A₂ + B₃ approach. The synthesized polyamines were well characterized with different spectroscopic and analytical techniques. The DB values of the hyperbranched polyamines indicated that the structures of the polymers were more hyperbranched than linear or dendritic. The polymers also showed good thermostability under a nitrogen atmosphere and good solubility in highly polar solvents.

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