

Preparation of Hyperbranched Aromatic Polyimides via A_2+B_3 Approach

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ABSTRACT: Two novel B_3 monomers, tri(phthalic anhydride) and tri(phthalic acid methyl ester), were synthesized. Hyperbranched polyimides were prepared by A_2+B_3 polymerizations of: (a) 1,4-phenylene diamine (A_2) and tri(phthalic anhydride) (B_3) (method A); and (b) 1,4-phenylene diamine (A_2) and tri(phthalic acid methyl ester) (B_3) (method B) in 1:1 molecular ratio. Gelation was effectively avoided in the A_2+B_3 polymerization by method B and a dramatic inherent viscosity increase at the critical polymerization concentration was observed. The high viscosity phenomena, generally observed in the preparation of hyperbranched polymers through A_2+B_3 approach, are elucidated by the hyperbranched structure (dendritic, linear and terminal content) characterization for polyimides with different viscosities. The self-standing films were successfully prepared from the hyperbranched precursors by the casting method. The results indicate that the weight average molecular weight of hyperbranched precursors are ranged from 33,600 to 125,000 g/mol and their inherent viscosities are varied from 0.17 to 0.97 dL/g. The degree of branching (DB) of hyperbranched polyimides is estimated to be 0.52-0.56 by ^1H NMR measurement. Their glass transition temperatures measured by differential scanning calorimetry (DSC) range from 212 to 236°C. The 5% weight loss temperatures of films, measured by thermogravimetric analysis (TGA), are around 500°C. Their tensile storage modulus by dynamic mechanical thermal analysis (DMA) attains 4.0 Gpa, similar with that of their linear analogues.

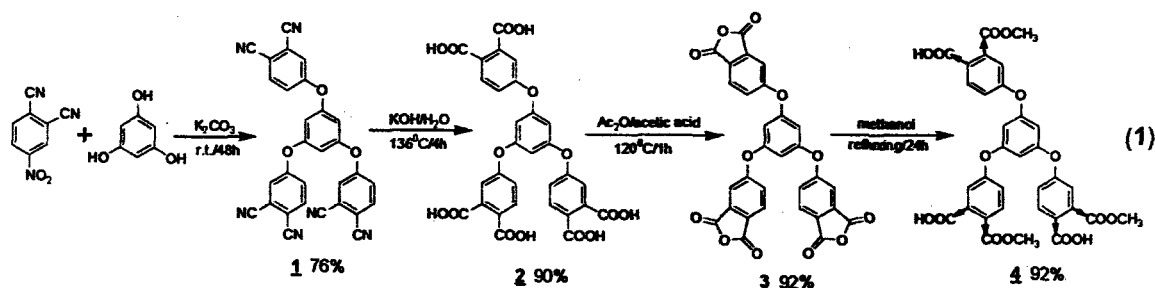
Introduction

Dendrimers and hyperbranched polymers, which are termed as 'dendritic macromolecules', have received much attention in recent years.¹⁻⁶ Because of their unique architecture, these polymers show attractive properties such as low viscosity and excellent solubility in organic solvents. Hyperbranched polymers are generally prepared by facile one-pot self-polymerization of AB_x monomers,⁷ however their monomers are not always commercially available and access to them sometimes involves in tedious multistep organic synthesis. To overcome this drawback, recently we have attempted a facile A_2+B_3 approach towards hyperbranched aromatic polyamides.⁸ Moreover Fréchet et al.⁹ synthesized hyperbranched aliphatic polyethers via A_2+B_3 approach by employing proton transfer polymerization of 1,2,7,8-diepoxyoctane (A_2) and 1,1,1-tris(hydroxymethyl) ethane (B_3). Fang and Okamoto¹⁰ also reported the synthesis of hyperbranched polyimides from dianhydrides (A_2) and tris(4-aminophenyl) amine (B_3). More recently, Yan et al.¹¹ reported a new strategy for synthesis of the hyperbranched polymers by combination of an unsymmetrical BB'_2 monomer and an A_2 monomer, of which in-situ AB'_2 intermediate formation during polymerization was suggested to resemble the AB_2 polymerization.

Although A_2+B_3 polymerization approach shows many advantages (such as facile preparation and scaling up, easy to tailor structure) over AB_2 polymerization approach, it has an intrinsic problem that the gelation is unavoidable over a certain conversion in 1:1 mol monomer feed ratio, as pointed out by Flory over 50 years ago.¹² Thus the major concern of the A_2+B_3 polymerization focuses on how to avoid the gelation. An ideal A_2+B_3 polymerization system toward gelation, as described by Flory,¹² is based on three assumptions: (1) equal reactivity of all A or B groups at any given stage of the reaction, (2) the neglect of intramolecular cyclization, and (3) the condensation being restricted to the reaction between an A and a B group. However, if an A_2+B_3 polymerization did not obey these assumptions, gelation would be probably avoided. From the viewpoint of avoiding gelation in A_2+B_3 polymerization, the polymerization strategy, which deviates from the ideal A_2+B_3 polymerization, merits attempting.

In addition, it is intriguing to observe that the hyperbranched polymers by A_2+B_3 approach often show a relatively high inherent viscosity. This fact gives rise to a little confusion about common knowledge that the hyperbranched polymers are usually thought to be low in inherent viscosity. The reason why hyperbranched polymers via A_2+B_3 approach often show high inherent viscosity is unclear yet, and the correlation of this phenomenon with macromolecular structures is also lack of elucidation.

Hyperbranched polyimides were mainly prepared from AB_x monomers.¹³⁻¹⁶ Few research was reported about the preparation through A_2+B_3 approach.¹⁰ In this work, a non-ideal A_2+B_3 polymerization strategy was employed for the preparation of hyperbranched polyimides, of which new monomer tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) were allowed to take direct polycondensation in the presence of condensation agent (method B). As a comparison, the polymerization of tri(phthalic anhydride) (B_3) and the diamine (A_2) (method A) was also investigated. Polymerization behavior was studied from the viewpoint of avoiding gelation and affording a polymer with high molecular weight. Self-standing films were successfully obtained from the hyperbranched precursors by thermal imidization.

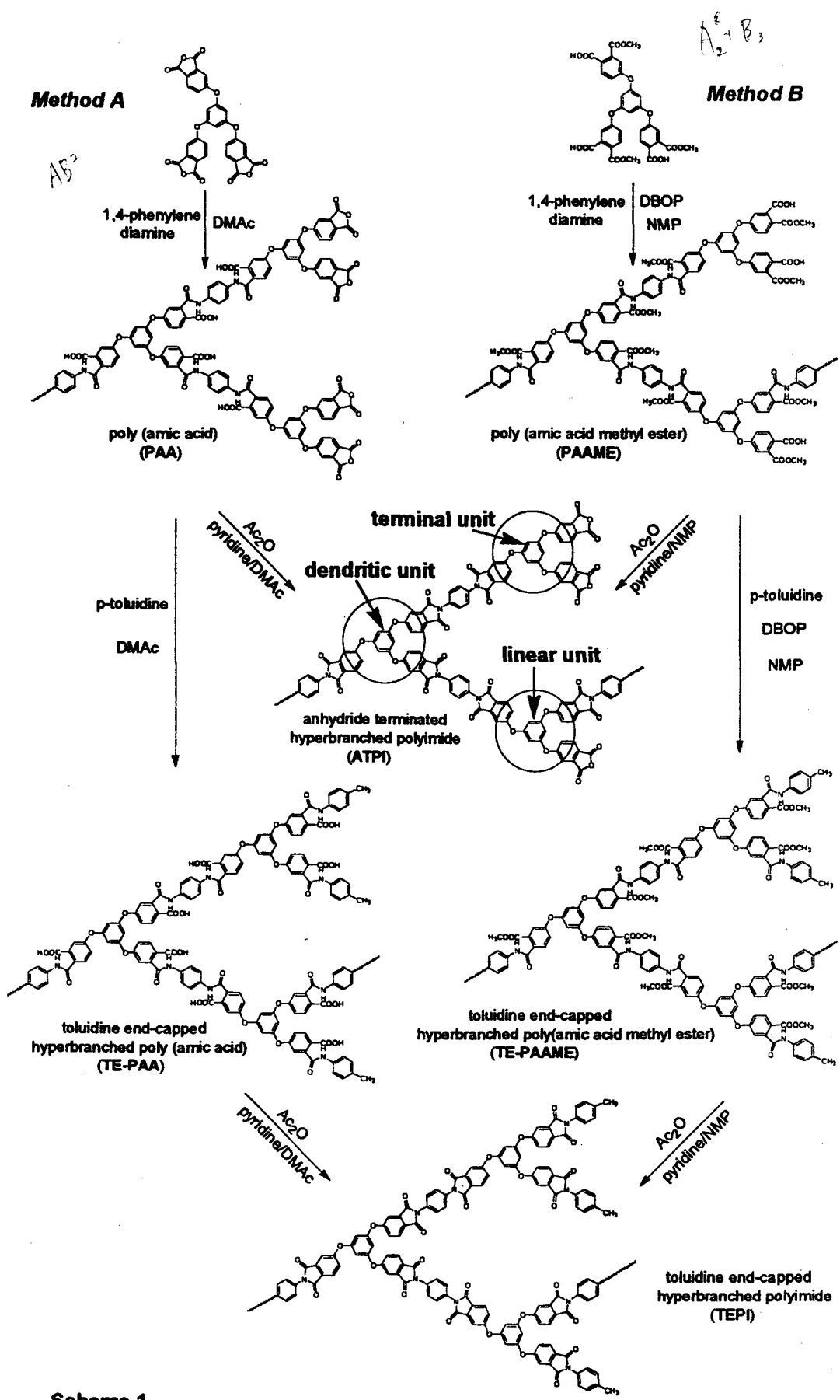


Results and Discussions

Synthesis of Monomers. Considering both thermal stability and solubility, we have designed a new tri(phthalic anhydride) bearing flexible aromatic ether linkage. The corresponding tri(phthalic acid methyl ester) isomers (B_3) were also prepared from the tri(phthalic anhydride). As shown in Eq. 1, 1,3,5-benzenetriol and 4-nitrobenzonitrile were allowed to react through nucleophilic substitution in the presence of potassium carbonate to give 1,3,5-tri(3,4-dicyanophenoxy)benzene (1). Then a basic hydrolysis reaction successfully converted the compound (1) to 1,3,5-tri(3,4-dicarboxyphenoxy)benzene (2). Subsequent dehydration reaction of (2) afforded 1,3,5-tri(1,3-dioxo-1,3-dihydro-isobenzofuran-5-yloxy)benzene (3) as a new tri(phthalic anhydride). To employ direct polycondensation, the tri(phthalic anhydride) (3) was converted into 1,3,5-tri[(3-methyloxycarbonyl-4-carboxyl)phenoxy]benzene and its isomers (4) by refluxing in methanol. The esterification of the tri(phthalic anhydride) is believed to enhance the polymer precursor's solubility.¹⁷ The new monomers were characterized by ^1H NMR, ^{13}C NMR, IR and elemental analysis. When monomer (3) was reacted with methanol, an ester linkage could be formed at para and meta position to the ether bond. Therefore, monomer (4) is isomeric mixture of *p*- and *m*-methyl esters (*p-p-p*-, *p-p-m*-, *p-m-m*-, *m-m-m*-).

Synthesis of Polymers. As shown in Scheme 1, hyperbranched polyimides were synthesized from both B_3 monomers, (tri(phthalic anhydride) (3) and tri(phthalic acid methyl ester) (4)), and 1,4-phenylene diamine (A_2) in molecular ratio of 1:1, respectively. In this paper, method A refers to the polymerization of the tri(phthalic anhydride) (3) and 1,4-phenylene diamine, which affords poly(amic acid) (PAA) precursor, and method B denotes to the polymerization of the isomeric tri(phthalic acid methyl ester) (4) and 1,4-phenylene diamine which gives poly(amic acid methyl ester) (PAAME) precursor. The PAA and PAAME precursors were end-capped with 4-toluidine by adopting the same reaction conditions as the precursor synthesis. The 4-toluidine end-capped poly(amic acid) (TE-PAA) and 4-toluidine end-capped poly(amic acid methyl ester) (TE-PAAME) were then converted into 4-toluidine end-capped polyimides (TEPI) by cyclodehydration in the presence of acetic anhydride and pyridine. The molecular weight was determined from TEPI for method A and TE-PAAME for method B by GPC measurements. The anhydride-terminated polyimides (ATPI) were also prepared from PAA and PAAME under the same reaction conditions as TEPI synthesis.

The polymerization conditions and results are summarized in Table 1. As shown in Table 1, the polymerization by method A was accomplished at 0°C by employing a dropwise addition way. The high reaction temperature, simultaneous addition and high polymerization concentration often afforded gel, indicating that the polymerization is uncontrollable due to high reactivity between anhydride and amine functional groups. All PAA precursors show low inherent viscosity and poor solubility in organic solvents at room temperature. The PAA with the highest inherent viscosity



Scheme 1

Table 1 The Polymerization Conditions and Results for the Synthesis of Hyperbranched Poly(amic acid) (PAA) and Poly(amic acid methyl ester) (PAAME) via A_2+B_3 Polymerization Approach

metho d	entry	concentratio n ^c (g/ml)	temperatu re (°C)	feed way	yield %	η_{inh}^e (dL/g)	M_w^f	M_w/M_n^f
	1	0.025	r.t.	one portion		gel		
	2	0.017	0	one portion		gel		
A ^a	3	0.017	0	dropwise	91	0.21		
A ₂	4	0.017	0/r.t. ^d	dropwise	95	0.28	3.02x10 ⁵	23.0
	5	0.012	0	dropwise	92	0.18		
	1	0.19	r.t.	one portion		gel		
	2	0.11	r.t.	one portion		gel		
B ^b	3	0.097	r.t.	one portion	97	0.97	1.25x10 ⁵	2.63
A ₂ +B ₃	4	0.073	r.t.	one portion	90	0.25	6.74x10 ⁴	2.08
	5	0.058	r.t.	one portion	86	0.23	3.76x10 ⁴	1.84
	6	0.032	r.t.	one portion	78	0.17	3.36x10 ⁴	2.17

^a Method A, polyaddition of trianhydride (B_3) and 1,4-phenylene diamine (A_2) in DMAc. For the dropwise addition way, the addition time was 30min. ^b Method B, direct polycondensation of tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) in NMP with DBOP as condensation agent. ^c calculated by (the total mass of A_2 and B_3 monomers) (the volume of the solvent). ^d During period of dropwise addition, the temperature was kept as 0°C. Then the temperature was elevated to room temperature. ^e Measured at a concentration of 0.5g/dL at 30°C in DMAc for method A and NMP for method B. ^f Determined by GPC measurement with a laser light scattering detector in DMF containing lithium bromide (0.01 mol/L) as an eluent. The samples for GPC determination were 4-toluidine end-capped polyimide (TEPI) for method A and 4-toluidine end-capped poly(amic acid methyl ester)s (TE-PAAMEs) for method B. The specific refractive increments (dn/dc) were 0.150 mL/g for B3, 0.172mL/g for B4, 0.188mL/g for B5, 0.196mL/g for B6 and 0.1278mL/g for A4.

(entry 4, method A) is converted to TEPI, which also exhibits poor solubility in organic solvent at room temperature. However, both PAA and TEPI are soluble in organic solvents upon heating. It is noted that the weight-average molecular weight of the TEPI is unexpectedly high, but its number-average molecular weight is much low (1.31×10^4 g/mol). The molecular weight distribution attains 23, indicating that the TEPI is a mixture of oligomers and high molecular weight polymers. It is hard to believe that TEPI with a weight-average molecular weight high up to 3×10^5 shows such low an inherent viscosity. Thus we guess that the high molecular weight part in TEPI is indeed slightly crosslinked microgel formed at the stage of PAA preparation, which causes poor solubility for both PAA and TEPI. The microgels do not entangle well one other, resulting in a low inherent viscosity.

Since the polymerization by method A was difficult to control, method B, a direct polycondensation method¹⁸ under mild conditions, was employed. Using the diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP) as condensation agent, the polymerization was carried out at room temperature through a 'one-step' procedure.¹⁸ Gelation could be avoided when the polymerization was conducted at a concentration lower than the critical concentration of 0.1g/ml. Hyperbranched TE-PAAME precursors with high molecular weight were prepared by this method.

The success in avoiding the gelation for A_2+B_3 polymerization by method B may be due to its polymerization characteristic. The polymerization by method B was carried out via a 'one-step' procedure, of which the DBOP was added into the solution of monomers mixture in the presence of triethylamine.¹⁸ As shown in eq.2, the polymerization is proceeded as follows: (i) *in-situ* activation of the carboxylic acid of B_3 monomer by DBOP to form an active intermediate I (reaction (a)); (ii) the reactions of active intermediate I either with an amine nucleophile to produce an amide product (reaction (b)), or with an existed by-product (5) to form an active intermediate II (reaction (c)); and (iii) the reaction of the active intermediate II with an amine

nucleophile to yield an amide product (reaction (d)). Apparently, the reaction (b) and (c) are competitive reactions, which prevents all active intermediate Is from reacting with the amine nucleophiles at the early polymerization stage. Since the active intermediate Is (B_3) are not constrained to react only with amines (A_2) at the initial polymerization stage, the polymerization by the method B is a non-ideal A_2+B_3 polymerization. It is assumed that a macromolecular structure with a low branching density would be formed at the early polymerization stage. Afterwards, the later appeared active intermediate IIs would further react with the rest amine nucleophiles to develop a hyperbranched structure. Thus the three-dimension network is avoided to form. This may be the reason why the polymerization by the method B can achieve high molecular weight without gelation. However the tri(phthalic anhydride) (B_3) for method A has three high reactive functional groups with equal reactivity, which is a typical ideal A_2+B_3 polymerization towards gelation. Therefore the A_2+B_3 polymerization by method A often leads to gelation, even if the A_2 monomer is controlled to add dropwise into B_3 monomer.

As shown in Fig. 1, it is interesting to observe that there exists a dramatic inherent viscosity increase for TE-PAAMEs by method B over the polymerization concentration of 0.08g/ml. Although the molecular weight has influence on inherent viscosity, the increase of molecular weight is not so dramatic as that of inherent viscosity below and above the polymerization concentration of 0.08g/ml. This implies that the molecular weight rise seems not to be the only reason for the sharp rise of inherent viscosity, although it really has influence on the inherent viscosity. Such a conclusion can also be drawn after comparing the results of our previous work¹⁶ with that of present one. The hyperbranched poly(amic acid methyl ester) precursors were previously prepared from AB_2 monomer¹⁶ at the same polymerization condition as present one, and their chemical structure is similar with that in this work. One of the previous precursors (ref. 16, Table 1, polymer 9) shows a molecular weight the same high as that of present work (method B, entry 3), but its inherent viscosity is only 0.27dL/g, much lower than that of present work (0.97dL/g). Thus we assume that it is the structure difference, other than molecular weight difference, that mainly causes a sharp rise of the inherent viscosity over the concentration of 0.08g/ml. The observation of dramatic rise in inherent viscosity suggests the possible onset of the crosslinking reaction and an architectural change above the concentration of 0.08g/ml. To elucidate this phenomenon, the fine hyperbranched structure of as-prepared polymers needs characterization.

Table 2 lists solubility of polymers. For the method A, PAA, TE-PAA and TEPI are hardly soluble in organic solvent at room temperature, but soluble upon heating in aprotic polar solvents. When the temperature is decreased to room temperature again, the solutions are still homogeneous. For the method B, PAAMEs, TE-PAAMEs and TEPIs are soluble in DMAc, DMF, DMSO and NMP at room temperature. The solutions of TE-PAAMEs in NMP or DMAc can pass the filter with 0.2 μ m diameter mesh and no gel is observed.

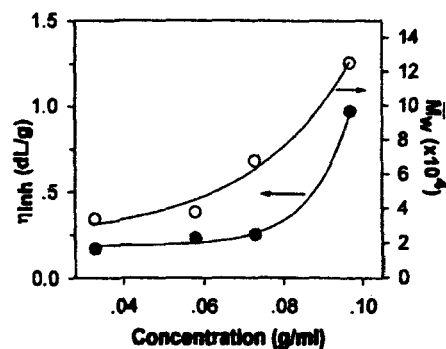
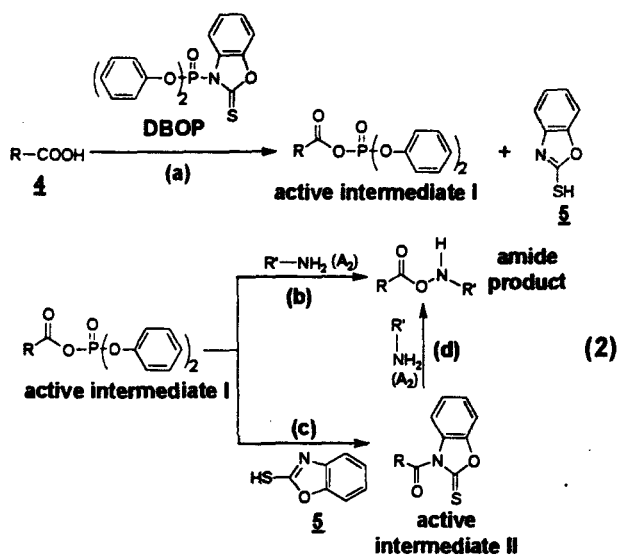


Fig. 1 The influence of polymerization concentration on the inherent viscosity (η_{inh}) and weight average molecular weight (\bar{M}_w) for method B

Table 2 The Solubility of Hyperbranched Polymers

method	polymer	solvent					
		NMP	DMF	DMSO	DMAc	THF	acetone
A	PAA	+	+	+	+	-	-
	TE-PAA	+	+	+	+	-	-
	TEPI	+	+	+	+	-	-
B	PAAME	++	++	++	++	±	-
	TE-PAAME	++	++	++	++	+	-
	TEPI	++	++	++	++	-	-

++, soluble at room temperature. +, soluble upon heating. ±, partially soluble. -, insoluble.

Table 3 Thermal and Mechanical Properties of Hyperbranched Polyimides (TEPIs) A_2+B_3

sample type	property	hyperbranched polyimide				
		A4 ^a	B6	B5	B4	B3
polyimides	$T_g(^{\circ}\text{C})^b$	235	212	219	223	230
by chemical imidization	$T_5/T_{10} (^{\circ}\text{C})^c$	500/535	485/535	480/525	480/520	505/545
	$T_s(^{\circ}\text{C})^d$	231	215	222	223	229
polyimide	$T_g(^{\circ}\text{C})^b$	236	214	221	225	230
films by	$T_5/T_{10} (^{\circ}\text{C})^c$	500/535	505/545	495/550	505/555	510/560
thermal	$T_g(^{\circ}\text{C})^e$	266	245	251	257	261
imidization	$T_g(^{\circ}\text{C})^f$	245	217	226	231	236
	$E' (\text{Gpa})^g$	3.2	3.1	3.3	3.5	4.0

^a A, polymerization by method A; 4, the entry code in Table 1. ^b Glass transition temperature (T_g) measured by DSC under nitrogen, heating rate $10^{\circ}\text{C}/\text{min}$; ^c 5% and 10% weight loss temperature measured by TGA under nitrogen, heating rate $10^{\circ}\text{C}/\text{min}$; ^d Softening point, measured by TMA at a heating rate of $5^{\circ}\text{C}/\text{min}$; ^e Glass transition temperature obtained from $\tan\delta$ curve of DMA at a heating rate of $5^{\circ}\text{C}/\text{min}$; ^f Glass transition temperature obtained from loss modulus curve of DMA; ^g Tensile storage modulus measured by DMA

Properties of Hyperbranched Polyimides by Chemical Imidization. The thermal properties of hyperbranched polyimides by chemical imidization are summarized in Table 3. TEPI by method A shows slightly higher glass transition temperature than that by method B. The glass transition temperatures of TEPIs by method B increase with the polymerization concentration. This variation tendency may be a combination effect of both molecular weight and hyperbranched structure features. Their T_g s are in the range of $212\text{--}235^{\circ}\text{C}$, which are higher than that (186°C) of hyperbranched polyimide analogues from AB_2 monomer.¹⁶ The 5% weight loss temperatures of TEPIs by method B were in the range of $480\text{--}505^{\circ}\text{C}$. TEPI-A4 by method A showed a 5% weight loss at 500°C , close to that of TEPI-B3. The 5% weight loss temperatures of TEPIs by A_2+B_3 polymerization approach surpasses that by AB_2 polymerization approach (455°C),¹⁶ although both have a similar chemical structure.

Preparation and Properties of Hyperbranched Polyimide Films. Hyperbranched polymers from the AB_2 monomers are considered to be unsuitable for the preparation of self-standing films due to lack of chain entanglements.^{6, 12, 13} To cope with this problem, Moore et al.¹⁹ suggested an

effective method of lowering the degree of branching (DB) in hyperbranched polyimides, of which an AB monomer was used to copolymerize with the AB₂ monomer. Our laboratory has also attempted this method and obtained hyperbranched polyamide films with good mechanical properties.²⁰ More recently, Fang and Okamoto²¹ reported the preparation of self-standing films from the A₂+B₃ hyperbranched polyimides by introducing an end-crosslinking agent.

In this work, hyperbranched polyimide films from TE-PAAMEs and TE-PAA precursors were successfully prepared by casting their DMAc solutions onto glass plates upon heating. Films from either TE-PAAMEs or TE-PAA precursors by a thermal imidization at 300°C can not be dissolved in organic solvents any more, which is similar with their linear analogues. Film from TE-PAA was prepared directly from a condensed original reaction solution due to poor solubility of TE-PAA precursor after precipitation. As-prepared film is heterogeneous and rough despite of its flexibility, suggesting existence of microgels. The formation of a self-standing film by method A may be due to the chain extension reaction among the oligomers. However films from TE-PAAMEs are flexible and smooth in transparent yellow appearance. It is remarkable that TE-PAAMEs with relatively low inherent viscosity can also afford flexible self-standing films.

The thermal and dynamic mechanical properties of the films are also summarized in Table 3. Their glass transition temperatures show the same varying tendency as that by chemical imidization. The softening points (T_s) by TMA measurement are ranged from 215 to 231°C for TEPI films, similar with their glass transition temperatures. The 5% weight loss temperatures for the films are located in range of 495~510°C, slightly higher than those by chemical imidization.

Fig.2 shows the DMA curves of TEPI films. The glass transition temperatures by both loss modulus and tangent δ are higher than that by DSC measurement, indicating that the mechanical response is slower than thermal equilibrium response. The storage modulus of TEPI films by method B is ranged from 3.1 to 4.0 Gpa, similar with that of their linear analogues. The high storage modulus suggests existence of a good chain entanglement in the films, implying their different topological structure from that by AB₂ self-polymerization.

The appearance of entanglement in the films by method B may be due to two factors: (1) the A₂+B₃ polymerization feature, which is different from the AB₂ self-polymerization, and (2) the unique polymerization characteristic of method B, of which a low branching density structure would be formed at the early polymerization stage. Both factors would provide the contributions to the formation of a low branching density structure at the early polymerization stage. Although the polymerization at the later stage afforded a hyperbranched structure with a high DB, the low branching density topology would be still remained. A low branching density topology, in combination with a high molecular weight, causes a favorable molecular interpenetration, leading to the formation of entanglement. Despite of the chain entanglement, the intermolecular crosslinking reaction should be the third factor for the formation of the self-standing films. The fact that as-prepared films do not soluble in organic solvents demonstrates the occurrence of the crosslinking reaction. However, this seems not to be the main reason for self-standing films, because the crosslinking reaction can also appear in the polyimide film from an AB₂ precursor and it does not help to form a self-standing film. For example, hyperbranched poly(amic acid methyl ester) from an AB₂ monomer can not afford self-standing film, although the crosslinking reaction occurred in the film and afforded a insoluble film after 300°C annealing.¹⁶ In conclusion, the successful film preparation suggests a feasible approach toward the self-standing films from the hyperbranched polymers with a high DB by employing the

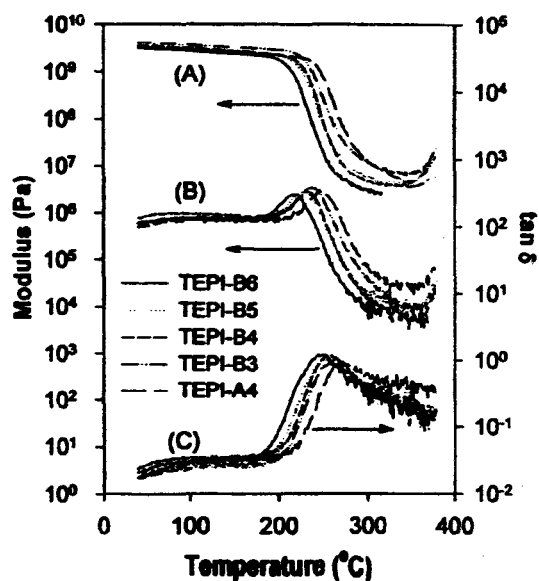


Fig.2 The dynamic mechanical analysis (DMA) spectra of hyperbranched polyimide (TEPI) films. Where: A, storage modulus; B, loss modulus; C, loss tangent δ

non-ideal A_2+B_3 polymerization approach.

Conclusion

Hyperbranched polyimides were successfully synthesized via the A_2+B_3 polymerization and their self-standing films were also successfully obtained. The macromolecular structure of hyperbranched polyimides is dependent on polymerization concentration, monomer reactivity and polymerization method. The comparison of two polymerization methods (method A and B) provides useful information in avoiding the gelation and towards high molecular weight for A_2+B_3 polymerization. The hyperbranched polymers by the non-ideal A_2+B_3 polymerization approach (method B) are suitable for smooth, flexible and self-standing film preparation.

References and Notes

- 1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. III. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 138.
- 2) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1176.
- 3) Voit, B. I. *Acta Polym.* 1995, 46, 87.
- 4) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci.-Pure Appl. Chem.* 1996, 33, 1399.
- 5) Malmström, E.; Hult, A. *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* 1997, C37, 555.
- 6) Voit, B. *J. Polym. Sci.: Part A: Polym. Chem.* 2000, 38, 2505
- 7) (a) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* 1990, 112, 4592. (b) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* 1991, 113, 4583. (c) Kim, Y. H.; Webster, O. W. *Macromolecules* 1992, 25, 5561. (d) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* 1995, 269, 1080. (e) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* 1998, 36, 1685. (f) Yang, G.; Jikei, M.; Kakimoto, M. *Macromolecules* 1999, 32, 2215.
- 8) Jikei, M.; Chon, S.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* 1999, 32, 2061
- 9) Emrick, T.; Chang, H.; Fréchet, J. M. J. *Macromolecules* 1999, 32, 6380.
- 10) Fang, J.; Kita, H.; Okamoto, K. *Macromolecules* 2000, 33, 4639.
- 11) (a) Yan, D.; Gao, C. *Macromolecules* 2000, 33, 7693. (b) Gao, C.; Yan D. *Macromolecules* 2001, 34, 156-161
- 12) Flory P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 9
- 13) Harrison, R. M.; Feast, W. J. *Polym. Mater. Sci. Eng.* 1997, 77, 162.
- 14) Kricheldorf, H. R.; Bolender, O.; Wollheim, T. *High Perform. Polym.* 1998, 10, 217.
- 15) Maier, G.; Zech, C.; Voit, B. Komber, H. *Macromol. Chem. Phys.* 1998, 199, 2655.
- 16) (a) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* 2000, 33, 1111. (b) Yamanaka, K.; Jikei, M.; Kakimoto, M. *Macromolecules* 2000, 33, 6937.
- 17) Nishizaki, S.; Moriwaki, T. *Kogyo Kagaku Zasshi* 1970, 73, 1873.
- 18) (a) Ueda, M.; Kameyama, A.; Hashimoto, K. *Macromolecules* 1988, 21, 19. (b) Ueda, M.; Mori, H. *Macromol. Chem.* 1993, 194, 511. (c) Ueda, M.; Mori, H. *Bull. Chem. Soc. Japan.* 1992, 65(6), 1636.
- 19) Markoski, L. J.; Thompson, J. L.; Moore, J. S. *Macromolecules* 2000, 33, 5315
- 20) Jikei, M.; Fujii, K.; Yang, G.; Kakimoto, M. *Macromolecules* 2000, 33, 6228.
- 21) Fang, J.; Kita, H.; Okamoto, K. *J. Membrane Sci.* 2001, 182, 245.