# Preparation of Hyperbranched Aromatic Polyimides via $A_{2}+B_{3}\ \mbox{Approach}$

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ABSTRACT: Two novel B<sub>3</sub> 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-phenylenediamine  $(A_2)$  and tri(phthalic anhydride)  $(B_3)$  (method A) and (b) 1,4-phenylenediamine  $(A_2)$  and tri-(phthalic acid methyl ester) (B<sub>3</sub>) (method B) in a 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 the  $A_2 + B_3$  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 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 <sup>1</sup>H 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 to that of their linear analogues.

## Introduction

Dendrimers and hyperbranched polymers, which are termed as "dendritic macromolecules", have received much attention in recent years.<sup>1-6</sup> 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;<sup>7</sup> 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 toward 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 1,2,7,8diepoxyoctane (A2) and 1,1,1-tris(hydroxymethyl) ethane (B<sub>3</sub>). Fang and Okamoto<sup>10</sup> also reported the synthesis of hyperbranched polyimides from dianhydrides (A2) and tris(4-aminophenyl)amine (B<sub>3</sub>). More recently, Yan et al.11 reported a new strategy for synthesis of the hyperbranched polymers by combination of an unsymmetrical BB'<sub>2</sub> monomer and an A<sub>2</sub> monomer, for which in situ AB'2 intermediate formation during polymerization was suggested to resemble the AB<sub>2</sub> polymerization.

Although the  $A_2 + B_3$  polymerization approach shows many advantages (such as facile preparation and scaling up, easy to tailor structure, etc.) over the AB<sub>2</sub> polymerization approach, it has an intrinsic problem that gelation is unavoidable over a certain conversion in a 1:1 molar monomer feed ratio, as pointed out by Flory over 50 years ago.<sup>12</sup> 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,<sup>12</sup> 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 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 the common knowledge that the hyperbranched polymers are usually thought to be low in inherent viscosity. The reason for the phenomenon that hyperbranched polymers by the  $A_2 + B_3$  approach often show high inherent viscosity is unclear yet, and the correlation of this with macromolecular structures is also lacking elucidation.

Hyperbranched polyimides were mainly prepared from  $AB_x$  monomers.<sup>13–16</sup> Little research was reported about preparation through the  $A_2 + B_3$  approach.<sup>10</sup> In this work, a nonideal  $A_2 + B_3$  polymerization strategy was employed for the preparation of hyperbranched polyimides, for which new monomers tri(phthalic acid methyl ester) (B<sub>3</sub>) and 1,4-phenylenediamine (A<sub>2</sub>) were allowed to polycondense directly in the presence of condensation agent (method B). As a comparison, the polymerization of tri(phthalic anhydride) (B<sub>3</sub>) and the diamine (A<sub>2</sub>) (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 a flexible aromatic ether linkage. The corresponding tri(phthalic acid methyl ester) isomers (B<sub>3</sub>) were also prepared from the tri-(phthalic anhydride). As shown in eq 1, 1,3,5-benzene-



triol and 4-nitrophthalonitrile 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(3,4dicarboxylphenoxy)benzene (2). Subsequent dehydration reaction of (2) afforded 1,3,5-tri(1,3-dioxo-1,3-dihydroisobenzofuran-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.<sup>17</sup> The new monomers were characterized by <sup>1</sup>H NMR, <sup>13</sup>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 an isomeric mixture of *p*- and *m*-methyl esters (p-p-p-, p-p-m-, p-m-m-, m-m-m-). As shown in Figure 1, the aromatic protons connected with p- and m-methyl esters can be distinguished at peak a". The integration of peak "a" suggests that the overall ratio of *m*- and *p*-methyl esters is about 3:1.

**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-phenylenediamine (A<sub>2</sub>) 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-phenylenediamine, which affords a poly(amic acid) (PAA) precursor, and method B denotes the polymerization of the isomeric tri-(phthalic acid methyl ester) (4) and 1,4-phenylenediamine which gives the poly(amic acid methyl ester) (PAAME) precursor. The PAA and PAAME precursors



Figure 1.  ${}^{1}H$  NMR spectra of trianhydride (3) and tri(phthalic acid methyl ester)s (4).

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 endcapped 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 method. The high reaction temperature, simultaneous addition, and high polymerization concentration often afforded a 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 (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  $\times$  10<sup>4</sup>). The molecular weight distribution reaches 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 as high as  $3 \times 10^5$  shows such a low inherent viscosity. Thus, we guess that the high molecular weight part in TEPI is indeed slightly cross-linked 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 method  $^{18}$  under mild conditions, was employed. Using the diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phospho-

nate (DBOP) as condensation agent, the polymerization was carried out at room temperature through a "one-step" procedure.<sup>18</sup> Gelation could be avoided when the polymerization was conducted at a concentration lower

Table 1. Polymerization Conditions and Results for the Synthesis of Hyperbranched Poly(amic acid) (PAA) and<br/>Poly(amic acid methyl ester) (PAAME) via A2 + B3 Polymerization Approach

method	entry	concn <sup>c</sup> (g/mL)	temp (°C)	feed method	yield, %	$ \eta_{\rm inh}^e$ (dL/g)	$M_{ m w}{}^f$	$M_{\rm w}/M_{\rm n}^{f}$
$\mathbf{A}^{a}$	1	0.025	rt	one portion		gel		
	2	0.017	0	one portion		gel		
	3	0.017	0	dropwise	91	0.21		
	4	0.017	$0/rt^d$	dropwise	95	0.28	$3.02  imes 10^5$	23.0
	5	0.012	0	dropwise	92	0.18		
$\mathbf{B}^{b}$	1	0.19	rt	one portion		gel		
	2	0.11	rt	one portion		gel		
	3	0.097	rt	one portion	97	0.97	$1.25 imes10^5$	2.63
	4	0.073	rt	one portion	90	0.25	$6.74 imes10^4$	2.08
	5	0.058	rt	one portion	86	0.23	$3.76 imes10^4$	1.84
	6	0.032	rt	one portion	78	0.17	$3.36  imes 10^4$	2.17

<sup>*a*</sup> Method A, polyaddition of trianhydride (B<sub>3</sub>) and 1,4-phenylenediamine (A<sub>2</sub>) in DMAc. For the dropwise addition method, the addition time was 30 min. <sup>*b*</sup> Method B, direct polycondensation of tri(phthalic acid methyl ester) (B<sub>3</sub>) and 1,4-phenylenediamine (A<sub>2</sub>) in NMP with DBOP as condensation agent. <sup>*c*</sup> Calculated by (the total mass of A<sub>2</sub> and B<sub>3</sub> monomers)/ (the volume of the solvent). <sup>*d*</sup> During the period of dropwise addition, the temperature was kept as 0 °C. Then the temperature was elevated to room temperature (rt). <sup>*e*</sup> Measured at a concentration of 0.5 g/dL at 30 °C in DMAc for method A and NMP for method B. <sup>*f*</sup> 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 (d*n*/d*c*) were 0.150 mL/g for **B3**, 0.172 mL/g for **B4**, 0.188 mL/g for **B5**, 0.196 mL/g for **B6**, and 0.1278 mL/g for **A4**.

than the critical concentration of 0.1 g/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.<sup>18</sup> As shown in eq 2, the polymerization 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 existing byproduct (5) to form an active intermediate II (reaction c); (iii) the reaction of the active intermediate II with an amine nucleophile to yield an amide product (reaction d). Apparently, reactions 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



**Figure 2.** Influence of polymerization concentration on the inherent viscosity ( $\eta_{inh}$ ) and weight-average molecular weight ( $\overline{M}_w$ ) for method B.

B is a nonideal  $A_2 + B_3$  polymerization. It is assumed that a macromolecular structure with a low branching density would be formed at the early polymerization stage. Afterward, the later appearing active intermediate IIs would further react with the rest of the amine nucleophiles to develop a hyperbranched structure. Thus, formation of the three-dimension network is avoided. This may be the reason the polymerization by method B can achieve high molecular weight without gelation. However the tri(phthalic anhydride) (B<sub>3</sub>) for method A has three high reactive functional groups with equal reactivity, whose polymerization is a typical ideal  $A_2 + B_3$  polymerization toward gelation. Therefore, the  $A_2 + B_3$  polymerization by method A often leads to gelation, even if the addition of the  $A_2$  monomer is controlled to drip into the B<sub>3</sub> monomer.

As shown in Figure 2, it is interesting to observe that there exists a dramatic inherent viscosity increase for **TE-PAAMEs** by method B over the polymerization concentration of 0.08 g/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 0.08 g/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 work<sup>16</sup> with that of the present one. The hyperbranched poly(amic acid methyl ester) precursors

Table 2. Solubility of Hyperbranched Polymers<sup>a</sup>

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

 $^a\,{\rm Key:}\,$  ++, soluble at room temperature; +, soluble upon heating;  $\pm,$  partially soluble; –, insoluble.

were previously prepared from AB<sub>2</sub> monomer<sup>16</sup> under the same polymerization condition as the present one, and their chemical structures are similar to that in this work. One of the previous precursors (ref 16, Table 1, polymer 9) shows a molecular weight as large as that of the present work (method B, entry 3), but its inherent viscosity is only 0.27 dL/g, much lower than that of present work (0.97 dL/g). Thus, we assume that it is the structure difference, instead of the molecular weight difference, that mainly causes a sharp rise of the inherent viscosity over a concentration of 0.08 g/mL. The observation of a dramatic rise in inherent viscosity suggests the possible onset of the cross-linking reaction and an architectural change above a concentration of 0.08 g/mL. To elucidate this phenomenon, the fine hyperbranched structure of as-prepared polymers needs to be characterized.

Table 2 lists solubility of polymers. For method A, **PAA**, **TE-PAA**, and **TEPI** are hardly soluble in organic solvent at room temperature but are soluble upon heating in aprotic polar solvents. When the temperature is decreased to room temperature again, the solutions are still homogeneous. For 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 a filter with 0.2  $\mu$ m diameter mesh, and no gel is observed.

**Characterization of the Hyperbranched Struc**ture. Generally, hyperbranched polymers are composed of three kinds of repeating units: dendritic, linear, and terminal units depending on the number of unreacted functional groups. The macromolecular structure of a hyperbranched polymer is indeed a block construction of three units. In this work, the dendritic, linear, and terminal units are distinguished by considering how many functional groups in the B<sub>3</sub> monomer are consumed, similar to the case for hyperbranched polymers prepared from AB<sub>2</sub> monomers. The linear and terminal units have one and two unreacted B functional groups, respectively, whereas the dendritic unit has no unreacted B group. With the aid of <sup>1</sup>H NMR measurement, it was found that the aromatic protons derived from the central aromatic ring of the B<sub>3</sub> monomers are sensitive to the number of B functional groups, which is capable of assigning the three units. The precursors are not suitable for structural determination because of the presence of isomeric structures. TEPIs are also not suitable for structure determination because all central aromatic protons in dendritic, linear, and terminal units have the same chemical environment. However ATPIs gave a clear difference between dendritic, linear, and terminal units in the chemical environment, as shown in Scheme 1. Figure 3 shows the <sup>1</sup>H NMR spectra of ATPIs. The peaks of the central aromatic protons were separated into three peaks. To assign each peak, den-



**Figure 3.** <sup>1</sup>H NMR spectra of anhydride terminated hyperbranched polyimides (**ATPI**s) and model compounds. Key: D, dendritic unit; L, linear unit; T, terminal unit.

dritic and terminal model compounds were synthesized. As given in eq 3, the dendritic model compound was



prepared from tri(phthalic anhydride) (**3**) and 4-toluidine in toluene/DMSO mixture. The terminal model compound was prepared by a multistep synthesis as illustrated in eq 4. The peak assigned to the central aromatic protons on the dendritic model compound was observed at lower magnetic field than that on the terminal model compound. Comparing the <sup>1</sup>H NMR spectra of **ATPIs** with those of model compounds, one can clearly assign the peaks due to dendritic and terminal units in the **ATPIs**. The peak attributed to the linear unit can be deduced by excluding the dendritic and terminal peaks.

On the basis of the integration of the deconvoluted peaks assigned to different units, the molecular fractions of dendritic ( $X_d$ ), linear ( $X_L$ ) and terminal unit ( $X_t$ ) have been calculated, as shown in Table 3. It is apparent that the **ATPI-A4** shows higher dendritic and lower terminal content in comparison with **ATPI-B5**. Since **ATPI-A4** contains many oligomers, the structural feature of high dendritic content seems to suggest the existence of an intramolecular cross-linking, which leads to the formation of microgels. This may be the reason



hyperbranched **PAAs** by method A show low solution viscosity but poor solubility. It is interesting that the distribution of dendritic, linear, and terminal contents of **ATPI-A4** is observed to be seriously deviated from the statistically value (0.25:0.50:0.25) predicted from AB<sub>2</sub> hyperbranched polymers. Although the reason for this is complicated, it is reasonable that a characteristic of A<sub>2</sub> + B<sub>3</sub> polymerization is responsible for this. In an A<sub>2</sub> + B<sub>3</sub> polymerization, the first step reaction among A<sub>2</sub> and B<sub>3</sub> monomers forms a complicated A<sub>x</sub>B<sub>y</sub> intermediate, which does not contribute to the formation of dendritic, linear, and terminal units. However in an AB<sub>2</sub> polymerization, every step reaction among AB<sub>2</sub> monomers does contribute to the formation of one of the three units. This may be the deviation reason.

For **ATPIs** by method B, the comparison of the molecular fractions  $X_d$ ,  $X_L$ , and  $X_t$  reveals that the distribution of dendritic, linear, and terminal contents is dependent on polymerization concentration. The distribution of dendritic, linear, and terminal contents also deviates from the statistical value (0.25:0.50:0.25) based on AB<sub>2</sub> polymerization. Different from method A, the dendritic contents of **ATPIs** by method B are lower than the statistical value (0.25) when the polymerization

Table 3. Fraction of Dendritic, Linear, and Terminal Units in the Hyperbranched Polyimides

			•		
code	$\eta_{\mathrm{inh}}{}^{a}$ (dL/g)	$X_{d}^{b}$	$X_{\rm L}$	Xt	$DB^{c}$
ATPI-A4 <sup><math>d</math></sup>	0.28	0.33	0.46	0.21	0.54
ATPI–B3 ATPI–B4 ATPI–B5 ATPI–B6	0.97 0.25 0.23 0.17	0.29 0.23 0.20 0.18	0.45 0.44 0.47 0.48	0.26 0.33 0.33 0.34	0.55 0.56 0.53 0.52

<sup>*a*</sup> The corresponding precursor inherent viscosity. <sup>*b*</sup> X<sub>d</sub>, dendritic unit fraction; X<sub>L</sub>, linear unit fraction; X<sub>b</sub> terminal unit fraction. The three unit fractions are calculated from the integration of the three deconvoluted peaks assigned to the central aromatic ring of the B<sub>3</sub> monomer in the NMR spectra. <sup>*c*</sup> Degree of branching, calculated by DB =  $(X_d + X_l)/(X_d + X_L + X_l)$ . <sup>*d*</sup> ATPI, anhydride terminated hyperbranched polyimide; A, method A; 4, the entry code in Table 1.



**Figure 4.** Relationships of the dendritic unit content (or terminal unit content) as a function of polymerization concentration.

concentration is lower than 0.08 g/mL. This seems to be caused by the polymerization feature of method B, in which a low branching density structure is formed at the early polymerization stage. Despite the reason mentioned for method A, the unique polymerization feature in method B also contributes to the deviation of the three units distribution from the statistical value.

Figure 4 exhibits the change of dendritic content and terminal content as a function of polymerization concentration. The dendritic content of **ATPI**s shows an apparent rise above the polymerization concentration of 0.08 g/mL; moreover, the terminal content exhibits a sharp decrease. However the variation of dendritic content and terminal content below the concentration of 0.08 g/mL is not so dramatic. The obvious difference in hyperbranched structure after the concentration of 0.08 g/mL suggests the onset of cross-linking reaction, which should be responsible for the sharp rise of inherent viscosity.

**Properties of Hyperbranched Polyimides by** Chemical Imidization. The thermal properties of hyperbranched polyimides by chemical imidization are summarized in Table 4. TEPI by method A shows slightly higher glass transition temperature than that by method B. The glass transition temperatures of **TEPI**s 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  $T_{gs}$  are in the range of 212-235 °C, which are higher than that (186 °C) of hyperbranched polyimide analogues from AB<sub>2</sub> monomer.<sup>16</sup> The 5% weight loss temperatures of **TEPI**s by method B are in the range of 480-505 °C. TEPI-A4 by method A shows a 5% weight loss at 500 °C, close to that of TEPI-B3. The 5% weight loss temperatures of **TEPI**s by  $A_2 + B_3$  polymerization approach surpasses that by AB<sub>2</sub> polymerization approach (455 °C),<sup>16</sup> although both have a similar chemical structure.

**Preparation and Properties of Hyperbranched Polyimide Films.** Hyperbranched polymers from the AB<sub>2</sub> monomers are considered to be unsuitable for the preparation of self-standing films due to lack of chain entanglements.<sup>6,19,20</sup> To cope with this problem, Moore et al.<sup>19</sup> suggested an effective method of lowering the degree of branching (DB) in hyperbranched polyimides, for which an AB monomer was used to copolymerize with the AB<sub>2</sub> monomer. Our laboratory has also attempted this method and obtained hyperbranched polyamide films with good mechanical properties.<sup>20</sup> More recently, Fang and Okamoto<sup>21</sup> reported the preparation of self-standing films from the A<sub>2</sub> + B<sub>3</sub> hyperbranched polyimides by introducing an end-cross-linking agent.

Table 4. Thermal and Mechanical Properties of Hyperbranched Polyimides (TEPIs)

		hyperbranched polyimide					
sample type	property	$A4^a$	B6	B5	B4	B3	
polyimides by chemical imidization	$T_{g}(^{\circ}C)^{b}$ $T_{5}/T_{10} (^{\circ}C)^{c}$	235 500/535	212 485/535	219 480/525	223 480/520	230 505/545	
polyimide films by thermal imidization	$\begin{array}{c} {\rm T_{S}(^{\circ}{\rm C})^{d}} \\ {\rm T_{g}(^{\circ}{\rm C})^{b}} \\ {\rm T_{5}/T_{10}} \ (^{\circ}{\rm C})^{c} \\ {\rm T_{g}(^{\circ}{\rm C})^{e}} \\ {\rm T_{g}(^{\circ}{\rm C})^{f}} \\ {\rm E}' \ ({\rm GPa})^{g} \end{array}$	231 236 500/535 266 245 3.2	215 214 505/545 245 217 3.1	222 221 495/550 251 226 3.3	223 225 505/555 257 231 3.5	229 230 510/560 261 236 4.0	

<sup>*a*</sup> A, polymerization by method A; 4, the entry code in Table 1. <sup>*b*</sup> Glass transition temperature ( $T_g$ ) measured by DSC under nitrogen, heating rate 10 °C/min. <sup>*c*</sup> 5% and 10% weight loss temperature measured by TGA under nitrogen, heating rate 10 °C/min. <sup>*d*</sup> Softening point, measured by TMA at a heating rate of 5 °C/min. <sup>*e*</sup> Glass transition temperature obtained from tan  $\delta$  curve of DMA at a heating rate of 5 °C/min. <sup>*f*</sup> Glass transition temperature obtained from tan  $\delta$  curve of DMA.



**Figure 5.** Dynamic mechanical analysis (DMA) spectra of hyperbranched polyimide (**TEPI**) films. Key: A, storage modulus; B, loss modulus; C, loss tangent  $\delta$ .

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 cannot be dissolved in organic solvents any more, which is similar to 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 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 with a transparent yellow appearance. It is remarkable that **TE-PAAMEs** with relatively low inherent viscosities can also afford flexible self-standing films.

The thermal and dynamic mechanical properties of the films are also summarized in Table 4. Their glass transition temperatures show the same varying tendency as that by chemical imidization. The softening points ( $T_{\rm s}$ s) by TMA measurement range from 215 to 231 °C for **TEPI** films, similar to their glass transition temperatures. The 5% weight loss temperatures for the films are located in the range 495–510 °C, slightly higher than those by chemical imidization.

Figure 5 shows the DMA curves of **TEPI** films. The glass transition temperatures obtained by both loss modulus and tangent  $\delta$  are higher than that obtained by DSC measurement, indicating that the mechanical

response is slower than the thermal equilibrium response. The storage modulus of TEPI films by method B ranged from 3.1 to 4.0 GPa, similar to that of their linear analogues. The high storage modulus suggests the existence of a good chain entanglement in the films, implying a topological structure different from that observed for  $AB_2$  self-polymerization.

The appearance of entanglement in the films by method B may be due to two factors: (1) the  $A_2 + B_3$ polymerization feature, which is different from the AB<sub>2</sub> 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 cross-linking reaction should be the third factor for the formation of the self-standing films. The fact that asprepared films do not soluble in organic solvents demonstrates the occurrence of the cross-linking reaction. However, this seems not to be the main reason for selfstanding films, because the cross-linking reaction can also appear in the polyimide film from an AB<sub>2</sub> precursor and it does not help to form a self-standing film. For example, hyperbranched poly(amic acid methyl ester) from an AB<sub>2</sub> monomer cannot afford a self-standing film, although the cross-linking reaction occurred in the film and afforded a insoluble film after 300 °C annealing.<sup>16</sup> In conclusion, the successful film preparation suggests a feasible approach toward obtaining the self-standing films from hyperbranched polymers with a high DB by employing the nonideal  $A_2 + B_3$  polymerization approach.

## Conclusion

Hyperbranched polyimides were successfully synthesized via the  $A_2 + B_3$  polymerization, and their selfstanding 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 toward high molecular weight for  $A_2 + B_3$  polymerization. The hyperbranched polymers obtained by the nonideal  $A_2 + B_3$  polymerization approach (method B) are suitable for smooth, flexible, and self-standing film preparation.

## **Experimental Section**

**Materials.** *N*-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were purified by vacuum distillation over calcium hydride. Pyridine and triethylamine were purified by distillation over calcium hydride. 1,4-Phenylenediamine was purified by sublimation under vacuum before use. Diphenyl (2,3-dihydro-2-thioxo-3benzoxazolyl)phosphonate (DBOP) is a regent grade product of Tokyo Chemical Industry Co., Ltd., and was used as received. All other chemicals are regent grade and were used as received unless otherwise stated.

Monomer Preparation. Synthesis of 1,3,5-Tri(3, 4-dicyanophenoxy)benzene (1). To a completely dry flask, 1.26 g (0.01 mol) of 1,3,5-benzenetriol and 5.19 g (0.03 mol) of 4-nitrophthalonitrile were dissolved in 60 mL of DMF. Then 8.28 g (0.06 mol) of potassium carbonate was added into the flask, and the mixture was stirred at room temperature for 48 h. The reaction mixture was poured into 1000 mL of water. The crude product was collected by filtration, washed with water, and dried under vacuum. After refluxing in methanol twice, the product was filtrated and washed using cold methanol for three times. The white powdery product was dried under vacuum, affording 4.08 g of 1,3,5-tri(3, 4-dicyanophenoxy)benzene (1). Yield: 76%. <sup>1</sup>H NMR ( $\delta$ , ppm): 8.15-8.12 (d, 3H); 7.97–7.96 (d, 3H); 7.65–7.61(q, 3H); 7.05 (s, 3H). <sup>13</sup>C NMR (δ, ppm): 160.1; 159.6; 136.1; 123.0; 122.9; 116.7; 115.3; 115.2; 109.5; 108.9. IR (KBr, cm<sup>-1</sup>): 2230, 1621, 1586, 1566, 1487, 1454, 1413, 1306, 1280, 1249, 1196, 1170, 1135, 1121, 1088, 1007, 951, 898, 849, 526. Anal. Calcd for C<sub>30</sub>H<sub>12</sub>O<sub>3</sub>N<sub>6</sub>: C, 71.43; H, 2.40; N, 16.66. Found: C, 71.23; H, 2.79; N, 16.66.

Synthesis of 1,3,5-Tri(3, 4-dicarboxylphenoxy)benzene (2). In a 200 mL flask, 6.56 g (0.013 mol) of (1) and 13.83 g (0.25 mol) of potassium hydroxide were dissolved in 120 mL of water/ethylene glycol (1:1 volume) mixed solvent. The mixture was refluxed for 4 h until the evolution of byproduct ammonia was ceased. The yellow clear solution was poured into 300 mL of water and the pH of solution was adjusted to be 3–4. The white precipitate was collected by filtration and washed with dilute hydrochloric acid and then water. After recrystallization from aqueous acetic acid, 8.0 g of 1,3,5-tri(3, 4-dicarboxylphenoxy)benzene (2) was obtained as a white crystal. Yield: 90%. <sup>1</sup>H NMR (δ, ppm): 8.02–7.99 (d, 3H); 7.56 (s, 3H); 7.22-7.19(q, 3H); 6.66 (s, 3H). <sup>13</sup>C NMR (δ, ppm): 167.4; 167.1; 157.8; 157.5; 146.6; 143.2; 138.3; 137.2; 119.5; 106.2. IR (KBr, cm<sup>-1</sup>): 3600-2250, 1717, 1593, 1578, 1496, 1456, 1417, 1377, 1266, 1221, 1120, 1065, 1008, 898, 880, 845, 793, 775, 656. Anal. Calcd for C<sub>30</sub>H<sub>18</sub>O<sub>15</sub>: C, 58.26; H, 2.90. Found: C, 58.02; H, 2.98.

Synthesis of 1,3,5-Tri(1,3-dioxo-1,3-dihydroisobenzofuran-5-yloxy) benzene (3). In a 50 mL flask, 0.5 g of (2) was dissolved in 2 mL of acetic anhydride and 20 mL of acetic acid. The solution was kept at reflux for 1 h under nitrogen, and a white crystal was formed. The crystal was isolated by filtration to give 0.42 g of 1,3,5-tri(1,3-dioxo-1,3-dihydroisobenzofuran-5-yloxy)benzene (3). Yield: 92.0%. <sup>1</sup>H NMR ( $\delta$ , ppm): 8.10–8.07 (d, 3H); 7.79 (s, 3H); 7.72–7.69 (d, 3H); 6.96 (s, 3H). <sup>13</sup>C NMR ( $\delta$ , ppm): 162.6; 162.4; 157.2; 157.1; 134.0; 127.7; 125.7; 114.1; 108.5; 107.8. IR (KBr, cm<sup>-1</sup>): 1848, 1773, 1597, 1482, 1464, 1445, 1349, 1276, 1217, 1166, 1122, 1077, 1007, 932, 890, 849, 739, 670. Anal. Calcd for C<sub>30</sub>H<sub>12</sub>O<sub>12</sub>: C, 63.84; H, 2.14; N. Found: C, 63.60; H, 2.27.

Synthesis of 1,3,5-Tri[(3-methyloxycarbonyl-4-carboxyl)phenoxy]benzene and Isomers (4). To a 100 mL flask was added 2.5 g of 3 and 50 mL of methanol. The mixture was refluxed for 24 h, and the solid was completely dissolved in the solution. The resulting solution was poured into ice– water and the isomeric mixture (4) was collected as a white powder. Yield: 92%. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.79–7.76 (d, 2.2H); 7.67, 7.64 (d, 0.80H); 7.27–7.20 (m, 6H); 6.74 (s, 3H); 3.71 (s, 9H). <sup>13</sup>C NMR ( $\delta$ , ppm): 167.7; 167.6; 166.9; 166.7; 158.7; 158.3; 157.6; 157.5; 135.9; 135.5; 131.8; 131.0; 126.2; 125.7; 120.0; 119.5; 117.9; 117.2; 107.6; 107.5; 52.5; 52.4. IR (KBr, cm<sup>-1</sup>): 3300, 2951, 1728, 1593, 1578, 1496, 1456, 1439, 1290, 1215, 1124, 1066, 1010, 846, 789. Anal. Calcd for C<sub>33</sub>H<sub>24</sub>O<sub>15</sub>: C, 60.00; H, 3.66. Found: C, 60.16; H, 3.69.

**Model Compound Preparation. Synthesis of Dendritic** Model Compound. In a dry flask purged with nitrogen, 0.137 g of 3 and 0.078 g of p-toluidine were dissolved in 2 mL of dry DMAc. The reaction solution was stirred for 3 h, and then 0.22 mL of pyridine and 0.35 mL of acetic anhydride were added. The temperature was elevated to 115 °C and kept there overnight. After cooling to room temperature, the reaction mixture was poured into a large amount of water to precipitate the product. After filtration, the precipitate was washed with 100 mL of methanol for three times and dried under vacuum. Yield: 96%. <sup>1</sup>H NMR (δ, ppm): 7.98 (d, 3H); 7.65–7.59 (t, 6H); 7.29-7.28 (d, 12H); 6.86 (s, 3H). <sup>13</sup>C NMR (δ, ppm): 161.2, 157.8, 137.5, 129.2, 129.1, 126.9, 126.3, 125.6, 123.9, 113.1, 113.0, 107.1, 20.6. IR (KBr, cm<sup>-1</sup>): 1776, 1724, 1599, 1516, 1479, 1450, 1441, 1375, 1267, 1236, 1197, 1165, 1120, 1091, 1003, 858, 819, 792, 779, 746, 696, 671. Anal. Calcd for C<sub>51</sub>H<sub>33</sub>O<sub>9</sub>N<sub>3</sub>: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.36; H, 4.23; N, 5.11.

**Synthesis of Terminal Model Compound.** The terminal model was prepared by a multistep synthesis (eq 4) and will be published elsewhere. <sup>1</sup>H NMR ( $\delta$ , ppm): 8.18–8.13 (m, 2H); 7.86–7.78 (m, 3H); 7.59–7.57 (m, 2H); 7.48–7.35 (m, 6H); 6.72–6.69 (t, 3H). <sup>13</sup>C NMR ( $\delta$ , ppm): 168.6, 168.1, 167.4, 166.0, 162.6, 161.6, 157.8, 157.2, 156.3, 146.1, 137.6, 136.4, 134.2, 131.4, 127.8, 127.5, 126.3, 125.7, 124.1, 119.9, 117.7, 114.1, 113.3, 110.6, 110.3, 100.0. IR (KBr, cm<sup>-1</sup>): 3086, 1851, 1782, 1724, 1597, 1523, 1498, 1481, 1456, 1444, 1371, 1346, 1267, 1199, 1120, 1076, 1001, 933, 889, 852, 837, 752, 740.

Polymer Preparation. Method A. Synthesis of 4-Toluidine End-Capped Poly(amic acid) (TE-PAA). To a solution of 0.253 g of tri(phthalic anhydride)(3) in 10 mL of dry DMAc was added a solution of 0.048 g of 1,4-phenylenediamine in 7.5 mL of DMAc dropwise within 30 min. The reaction temperature was kept at 0 °C. After the addition, the reaction mixture was stirred for 2 h at room temperature, and then, 0.048 g of *p*-toluidine was added. The reaction was allowed to continue for additional 6 h. The resulting clear solution was poured into methanol containing 1% LiCl to precipitate the product. After being washed with methanol several times, the product was dried at room temperature under reduced pressure. A pale-yellow powdery TE-PAA was obtained. Yield: 95%. <sup>1</sup>H NMR (δ, ppm): 9.97–9.91 (d, 1H); 7.92–7.90 (d, 1.1H); 7.57-7.50 (d, 4.6H); 7.34-7.30 (m, 1.3H); 7.22-7.19 (d, 1.8H); 7.11-7.08 (d, 1.1H); 6.70-6.51 (m, 2.3H); 2.26 (s, 1.8H). IR (KBr, cm<sup>-1</sup>): 3600-2000, 1776, 1720, 1595, 1516, 1479, 1454, 1408, 1375, 1321, 1263, 1207, 1118, 1007, 949, 891, 835, 796, 748, 698 524.  $\eta_{\rm inh} = 0.28$  dL/g.

Synthesis of Anhydride Terminated Polyimide (ATPI). To a solution of 0.253 g of tri(phthalic anhydride) (3) in 10 mL of dry DMAc was added dropwise a solution of 0.048 g of 1,4-phenylenediamine in 7.5 mL of DMAc within 30 min at 0 °C. After the addition, the reaction mixture was stirred for 2 h at room temperature. Then 6 mL of acetic anhydride and 4 mL of pyridine were added to the reaction mixture, and the solution was stirred at room temperature for additional 5 h. Then the reaction temperature was elevated to 115 °C and kept overnight. After precipitation in dry toluene, the product was collected by filtration and dried under vacuum. Yield: 97%. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.96–7.95 (m, 1.7H); 7.58–7.22 (m, 7.5H); 6.83–6.69 (t, 1H). IR (KBr, cm<sup>-1</sup>): 1853, 1780, 1720, 1593, 1516, 1477, 1437, 1358, 1261, 1236, 1192, 1118, 1074, 995, 887, 827, 787, 740, 690, 671, 628, 524.

Synthesis of 4-Toluidine End-Capped Polyimide by Chemical Imidization (TEPI). To a solution of 0.1 g of TE-PAA in 20 mL of DMAc were added 3 mL of acetic anhydride and 2 mL of pyridine. The solution was heated at 100 °C overnight. After cooling to room temperature, the solution was poured into methanol to precipitate the product. A yellow powdery **TEPI** was collected and dried under vacuum. Yield: 100%. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.88–7.84 (d, 2.6H); 7.54–7.48 (m, 4.9H); 7.21 (s, 3.8H); 6.75 (s, 1H); 2.29 (s, 0.95 H). IR (KBr, cm<sup>-1</sup>): 1778, 1724, 1597,1516, 1479, 1456, 1439, 1363, 1263, 1236, 1196, 1163, 1120, 1078, 999, 943, 837, 789, 744, 694, 669, 528, 509.

Method B. Synthesis of Poly(amic acid methyl ester) (PAAME) in Different Concentrations. In a three-neck flask under N<sub>2</sub>, 0.5 g of 4, 0.082 g of 1,4-phenylenediamine, and 0.2 mL of triethylamine were dissolved in NMP to afford solutions with different concentrations (as shown in Table 1). Then 0.697 g of DBOP was added to the solution. The reaction mixture was stirred at room temperature for 2 h and then was poured into methanol containing 1% LiCl to precipitate the polymers. After the isolation by filtration and washing with methanol several times, a white powdery polymer was obtained. PAAME-B3: yield, 97%. PAAME-B4: yield, 90%. PAAME-B5: yield, 86%. PAAME-B6: yield, 78%. <sup>1</sup>H NMR  $(\delta, ppm)$ : 10.12 (s, 1H); 7.65–7.59 (m, 1.1H); 7.38 (s, 3.1H); 7.24-7.17 (m, 2.6H); 7.02 (s, 2.9H); 6.56-6.46 (m, 1.9H); 3.53, 3.49 (d, 5.6H). IR (KBr, cm<sup>-1</sup>): 3200, 2953, 1724, 1666, 1593, 1576, 1516, 1489, 1456, 1437, 1406, 1358, 1302, 1277, 1211, 1120, 1066, 1010, 951, 837, 785, 756.

Synthesis of Anhydride Terminated Polyimide (ATPI). To a solution of 0.1 g of poly(amic acid methyl ester) (PAAME) in 3 mL of NMP were added 1 mL of acetic anhydride and 0.5 mL of pyridine. The reaction was kept overnight at 115 °C. Then polymer was precipitated via pouring reaction mixture into dry toluene. After filtration and drying in a vacuum oven at 100 °C overnight, **ATPI** was obtained in high yield. **ATPI-B3**: yield, 100%. **ATPI-B4**: yield, 98%. **ATPI-B5**: yield, 100%. **ATPI-B6**: yield, 92%. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.64–7.47 (m, 1.4H); 7.26 (s, 3H); 7.02–6.88 (m, 1H); 6.52–6.38 (t, 1H). IR (KBr, cm<sup>-1</sup>): 1851, 1778, 1720, 1597, 1516, 1479, 1456, 1441, 1368, 1265, 1238, 1197, 1120, 1078, 1005, 891, 837, 789, 744, 694, 671.

Synthesis of 4-Toluidine End-Capped Poly(amic acid methyl ester) (TE-PAAME). In a three-necked flask under N<sub>2</sub>, 0.3 g of **PT-PAAME** and 0.082 g of *p*-toluidine were dissolved in 10 mL of NMP. To this solution were added 0.697 g of DBOP and 0.21 mL of triethylamine. The reaction mixture was stirred overnight at room temperature, and then it was poured into methanol to precipitate the polymer. After isolation by filtration, washing with methanol for several times and drying under vacuum, a yellowish-white powdery TE-PAAME was obtained in high yield. TE-PAAME-B3: yield, 99%. TE-PAAME-B4: yield, 95%. TE-PAAME-B5: yield, 95%. TE-**PAAME-B6**: yield, 93%. <sup>1</sup>H NMR (δ, ppm): 10.34–10.26 (d, 1H); 7.94 (m, 2.4H); 7.73-7.41 (m, 11.5H); 7.18 (m, 15.6H); 7.06-7.05 (m, 3.9H); 6.80-6.78 (m, 3.8H); 3.71 (s, 5.9H); 2.21 (s, 4.2H). IR (KBr, cm<sup>-1</sup>): 2951, 1724, 1595, 1516, 1454, 1439, 1360, 1317, 1302, 1271, 1238, 1209, 1122, 1091, 1068, 1008, 947, 837, 746, 690.

**Synthesis of 4-Toluidine End-Capped Polyimide** (**TEPI**). To a solution of 0.1 g of **TE-PAAME** in 3 mL of NMP were added 1 mL of acetic anhydride and 0.5 mL of pyridine. The reaction mixture was stirred at 115 °C overnight and then was poured into water to precipitate the polymer. After isolation by filtration, the polymer was washed by water several times and dried at 40 °C under vacuum overnight. A yellowish-brown powdery **TEPI** was obtained in high yield. **TEPI-B3**: yield, 100%. **TEPI-B4**: yield, 96%. **TEPI-B5**: yield, 98%. **TEPI-B6**: yield, 95%. <sup>1</sup>H NMR ( $\partial$ , ppm): 7.90–7.81 (bd, 2.1H); 7.50(bs, 6.3H); 7.23 (s, 5.7H); 6.82(bs, 1H); 2.29 (s, 1.1H). IR (KBr, cm<sup>-1</sup>): 2951, 1780, 1720, 1595, 1516, 1477, 1456, 1437, 1360, 1261, 1232, 1192, 1163, 1116, 1072, 995, 831, 787, 742, 690, 665.

Film Preparation. (1) Film Preparation from TE-PAA Precursor. The polymerization solution of **TE-PAA** was condensed gradually under reduced pressure at room temperature. The solution volume was reduced to  $^{1}/_{5}$  of the original one. After filtration with a 0.5  $\mu$ m filter, the solution was cast onto a glass plate and heated according to following procedure: 100 °C/1 h, 200 °C/1 h, and 300 °C/1 h. A pale-yellow film was peeled from the glass plate in boiling water. (2) Film Preparation from TE-PAAME Precursors. A solution of 0.2 g of TE-PAAME in 1.5 mL of DMAc was prepared. After filtration with a 0.5  $\mu$ m filter, the solution was cast on a glass plate. The following operation was the same as the film preparation from TE-PAA precursor. IR (KBr, cm<sup>-1</sup>): 3073, 1778, 1728, 1599, 1516, 1479, 1456, 1441, 1363, 1267, 1238, 1197, 1165, 1122, 1080, 1003, 943, 839, 790, 744, 694, 671, 528, 511.

Measurements. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 Fourier transform infrared spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-AL 300 MHz spectrometer. Thermogravimetric analysis (TGA) was carried out with a Seiko TG/DTA 6200 at a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 6200 using a heating rate of 10 °C/min under nitrogen. Thermal mechanical analysis (TMA) was conducted on a Seiko TMA/SS6000 in a penetration mode with 10 g load and 5 °C/min heating rate. Dynamic mechanical thermal analysis (DMA) was performed on a dynamic mechanical analyzer DVA-200S in tension mode at a heating rate of 5 °C/min and a frequency of 10 Hz. Gel permeation chromatography (GPC) was performed on a JAS-CO HPLC 880PU fitted with polystyrene-divinylbenzene columns (two Shodex KD806MS and KD802.5) and a Shodex RI-71 refractive index detector. DMF containing 0.01 mol Lof lithium bromides was used as an eluent. The molecular weights were determined by laser light scattering measurement using a mini DAWN apparatus (Wyatt Technology Co.). Specific refractive increments (dn/dc) of polymers were measured in DMF at 690 nm by using an Optilab 903 apparatus (Wyatt Technology Co.). Inherent viscosity of TE-PAA and TE-**PAAME** was measured in DMAc and NMP at a concentration of 0.5 g dL<sup>-1</sup> at 30 °C, respectively.

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