# Synthesis and Comparison of Hyperbranched Aromatic Polyimides Having the Same Repeating Unit by $AB_2$ Self-Polymerization and $A_2 + B_3$ Polymerization

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ABSTRACT: A new AB<sub>2</sub> monomer, designed from a template of the repeating unit of the hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization, was successfully prepared via a multistep synthesis. Hyperbranched polyimides, having the same repeating unit as that by nonideal  $A_2 + B_3$  polymerization, were prepared from this new AB<sub>2</sub> monomer by direct self-polycondensation in the presence of diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP). Hyperbranched polyimides, with a molecular weight of  $1.11 \times 10^4$  to  $1.73 \times 10^5$  and an inherent viscosity of 0.12-0.17 dL/g, were obtained. As-prepared hyperbranched polyimides were soluble in DMF, DMAc, DMSO and NMP. By <sup>1</sup>H NMR analysis, the degree of branching (DB) of the prepared hyperbranched polyimides was estimated to be around 0.50. By thermogravimetric analysis (TGÅ) and differential scanning calorimetry (DSC) measurement, their 5% weight loss temperatures and glass transition temperatures were found to be in the ranges 445-460and 155-161 °C, respectively. A comparison between the hyperbranched polyimides by AB<sub>2</sub> selfpolymerization and nonideal A2 + B3 polymerization reveals that their physical properties, such as viscosity, thermal stability, and glass transition temperature, etc., are different from each other. Especially, a comparison between the plots of intrinsic viscosity  $[\eta]$  vs molecular weight  $M_w$  elucidates that their molecular shapes are also different each other. The examination of the chain entanglement and intermolecular interaction by employing a freeze-extracting technique reveals that hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization have a certain extent of chain entanglement and intermolecular interaction. A comprehensive analysis finally suggests that hyperbranched polyimides by AB<sub>2</sub> self-polymerization have a compact highly branching structure, while that by nonideal  $A_2 + B_3$ polymerization have a low branching density topology.

## Introduction

Hyperbranched polymers have received considerable attention for the past decade.<sup>1-16</sup> These polymers have a treelike randomly branched topology with a branchon-branch structure, which affords a compact, globular molecule in combination with a number of terminal groups. Hyperbranched polymers resemble dendrimers in many physical properties such as high solubility, low solution viscosity, and absence of entanglement etc.; however, their preparation is more facile and easier to scale-up than dendrimers. Hyperbranched polymers are generally prepared by one-pot self-polymerization of the  $AB_m$  monomers.<sup>1–16</sup> Since the  $AB_m$  monomers are not always commercially available and their preparation sometimes involves in synthetic effort, a facile  $A_2 + B_3$ approach was put forward recently.<sup>17a</sup> Hyperbranched polymers, such as polyamide,<sup>17</sup> polyether,<sup>18</sup> polyimide<sup>19</sup> and poly(sulfone-amine),<sup>20</sup> etc., have been successfully prepared by this approach.

In our previous paper,<sup>21</sup> we reported a new strategy for preparing hyperbranched polyimides by employing a nonideal  $A_2 + B_3$  polymerization. The unique  $A_2 + B_3$ direct polycondensation by using the DBOP as a condensation agent was found to deviate from the ideal  $A_2$ +  $B_3$  polymerization—a well-known gelation system addressed by Flory over 50 years ago.<sup>22</sup> Therefore, gelation was effectively avoided, and high molecular weight polymers were successfully obtained. It is re-

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markable that as-prepared hyperbranched polymers could afford tough and self-standing films. Since hyperbranched polymers are not suitable for self-standing film preparation due to lack of a sufficient chain entanglement,<sup>9,11,16</sup> this unexpected result motivates our interest in elucidating whether hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization have a different molecular topology from that by  $AB_2$  self-polymerization.

It is worthy of noting that the attempts to compare  $AB_2$  self-polymerization and  $A_2 + B_3$  polymerization were addressed in hyperbranched polyether<sup>18b</sup> and polyaramide<sup>17c</sup> preparations. Especially, a comparison in the structure and properties between polyaramides by two polymerization methods was dealt with.<sup>17c</sup> It was concluded that the distributions of dendritic, linear and terminal unit of both hyperbranched polyaramides were different each other.  $^{\rm 17c}$  The hyperbranched polyaramide by  $A_2 + B_3$  polymerization was found to have a high dendritic content and a denser packing structure with a low solution viscosity,<sup>17c</sup> whose features are rather similar to the hyperbranched polyimides by ideal  $A_2$  + B<sub>3</sub> polymerization as reported in our previous work.<sup>21</sup> Unfortunately, the comparison of the structure and properties between both polyaramides was based on noncomparable molecular weight, since high molecular weight could not be achieved without gelation for polyaramides by  $A_2 + B_3$  polymerization. Different from the above work, this work focuses on comparison between hyperbranched polyimides by nonideal  $A_2 + B_3$ polymerization and AB<sub>2</sub> self-polymerization with com-

#### Scheme 1



parable high molecular weight. In particular, we are interested in their molecular topology difference and the topology feature cause.

In this work, we describe the synthesis of a new AB<sub>2</sub> monomer, which is designed from the repeating unit of the hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization. Hyperbranched polyimides derived from this new AB<sub>2</sub> monomer were prepared by employing the same direct polycondensation as that in nonideal  $A_2 + B_3$  polymerization. The differences in structure and physical properties between both hyperbranched polyimides are compared and discussed.

#### **Results and Discussions**

Monomer Synthesis. An isomeric mixture of monomer 6 was prepared by a multistep synthetic procedure, as shown in Scheme 1. At first, a nucleophilic nitro displacement reaction in 4-nitrophthalonitrile by phloroglucinol in the presence of potassium carbonate afforded compound 1, which was a disubstituted compound of phloroglucinol. Compound 1 was then hydrolyzed to form compound **2** in the presence of potassium hydroxide. Compound 2 was allowed to take a nucleophilic substitution reaction with 4-fluoro-N-(4-nitrophenyl) phthalimide to give compound 3. Subsequent dehydration reaction of compound 3 in (1) acetic acid, pyridine, and acetic anhydride and (2) acetic acid and anhydride afforded compound 4. Compound 4 was methylated in refluxing methanol to give compound 5, which was finally turned into  $AB_2$  monomer **6** by hydrogenation of nitro group in the presence of Pd/C catalyst. The new AB<sub>2</sub> monomer was characterized by using <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectra and elemental analysis. Figure 1 depicts its <sup>1</sup>H NMR spectrum. It is interesting that the imide ring in compound 4 was also ring-opened by methylation, which was confirmed by the disappearance of the IR peak at 1770 cm<sup>-1</sup> assigned to the imide structure and the appearance of a <sup>1</sup>H NMR peak around 10 ppm due to the amide structure. Since peaks in the <sup>1</sup>H NMR spectrum overlapped seriously due to the existence of many isomers for monomer 6, it



Figure 1. <sup>1</sup>H NMR spectrum of AB<sub>2</sub> monomer 6.

was difficult to calculate the ratio of *p*- and *m*-methyl substitution.

**Polymer Synthesis.** Scheme 2 illustrates the synthesis of hyperbranched polymers from monomer **6**. As a reference, the nonideal  $A_2 + B_3$  polymerization as reported in previous work<sup>21</sup> was also presented in Scheme 2. It is apparent that hyperbranched polymers by both AB<sub>2</sub> and nonideal  $A_2 + B_3$  methods have the same repeating unit at every synthetic stage of **PAAMEs**, **TE—PAAMEs**, **ATPIs**, and **TEPIs**. The self-polymerization of **6** was carried out in the presence of DBOP. As-prepared poly(amic acid methyl ester) (**PAAME**) precursors were end-capped with *p*-toluidine by adopt-

Scheme 2



ing the same reaction conditions as the precursor synthesis. The *p*-toluidine end-capped poly(amic acid methyl ester)s (**TE—PAAMEs**) were then converted into *p*-toluidine end-capped polyimides (**TEPI**) by cyclodehydration in the presence of acetic anhydride and pyridine. The anhydride-terminated polyimides (**ATPI**) were prepared from **PAAME** under the same reaction conditions as **TEPI** synthesis.

The conditions and results for AB<sub>2</sub> self-polymerization are summarized in Table 1. As a comparison, the conditions and results of the nonideal A<sub>2</sub> + B<sub>3</sub> polymerization are also listed. As seen in Table 1, the selfpolymerization of **6** was carried out through a "one-step" procedure as literature mentioned,<sup>23</sup> which is the same as that in the nonideal A<sub>2</sub> + B<sub>3</sub> polymerization. However the self-polymerization at a room temperature together with a dilute concentration (AB<sub>2</sub>, entry 1 and 2) could only afford low molecular oligomers with a molecular weight around  $1.1 \times 10^4$ . Thus, measures such as elevating solution concentration and polymerization temperature were taken to ensure the formation of high molecular weight polymer. It is observed that the polymerization at 50 °C could afford a polymer with a molecular weight up to  $1.73 \times 10^5$ . However increasing the polymerization concentration showed a limited increase of polymer molecular weight (AB<sub>2</sub>, entry 3). This suggests that the temperature is a crucial condition for such an AB<sub>2</sub> self-polymerization. Gelation was not observed under the given conditions listed in Table 1.

It is worth to note that the inherent viscosities of **TE—PAAMEs** by  $AB_2$  self-polymerization shows an obvious different from that by nonideal  $A_2 + B_3$  polymerization. The **TE—PAAMEs** by  $AB_2$  self-polymerization shows lower inherent viscosity than that by nonideal  $A_2 + B_3$  polymerization. Especially, the inherent viscosities are distinct between the high molecular

 Table 1. Polymerization Conditions and Results for the

 Synthesis of Hyperbranched Polyimides via AB2

 Self-Polymerization and A2 + B3 Polymerization<sup>a</sup>

method	entry	concn <sup>b</sup> (g/mL)	temp (°C)	yield <sup>c</sup> (%)	$\eta_{\mathrm{inh}}^{d}$ (dL/g)	$M_{ m w}{}^e$	$M_{\rm w}/M_{\rm n}$
AB <sub>2</sub>	1	0.06	room temp	70	0.12	$1.14  imes 10^4$	1.2
	2	0.16	room temp	71	0.12	$1.11  imes 10^4$	1.3
	3	0.32	room temp	75	0.13	$2.55  imes 10^4$	1.5
	4	0.06	50	82	0.15	$5.13 imes10^4$	1.9
	5	0.08	50	94	0.17	$1.73  imes 10^5$	2.3
$A_2 + B_3$	3	0.097	room temp	97	0.97	$1.25  imes 10^5$	2.63
	4	0.073	room temp	90	0.25	$6.74  imes 10^4$	2.08
	5	0.058	room temp	86	0.23	$3.76  imes 10^4$	1.84
	6	0.032	room temp	78	0.17	$3.36  imes 10^4$	2.17

<sup>*a*</sup> Direct polycondensation in NMP with DBOP as condensation agent. <sup>*b*</sup> Calculated by (the total mass of  $A_2$  and  $B_3$  monomers)/ (the volume of the solvent). <sup>*c*</sup> The yield of precursors before endcapping. <sup>*d*</sup> Inherent viscosity of end-capped precursors measured at a concentration of 0.5 g/dL at 30 °C in NMP. <sup>*c*</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 dertermination were 4-toluidine end-capped poly(amic acid methyl ester)s (**TE—PAAMEs**). The specific refractive increments (d*n*/d*c*) of AB<sub>2</sub> samples were 0.139 mL/g for 1, 0.143 mL/g for 2, 0.136 mL/g for 3, 0.140 mL/g for 4, and 0.143 mL/g for 5; that of  $A_2$ + $B_3$  samples were 0.150 mL/g for 3, 0.172 mL/g for 4, 0.188 mL/g for 5, and 0.196 mL/g for 6.



**Figure 2.** Relationships between log  $[\eta]$  vs log  $M_w$  of toluidine end-capped hyperbranched poly(amic acid methyl ester)s: ( $\bullet$ ) AB<sub>2</sub> self-polymerization; ( $\bigcirc$ ) nonideal A<sub>2</sub> + B<sub>3</sub> polymerization. The  $\alpha$  values are obtained from the slope of relationship lines.

weight samples by AB<sub>2</sub> self-polymerization and nonideal  $A_2 + B_3$  polymerization. The **TE—PAAME-A<sub>2</sub>+B<sub>3</sub>-3** (A<sub>2</sub> + B<sub>3</sub>, entry 3) with a molecular weight of  $1.25 \times 10^5$  showed an inherent viscosity as high as 0.97dL/g, while the **TE—PAAME-AB<sub>2</sub>-5** showed a inherent viscosity of 0.17dL/g despite of its molecular weight of  $1.73 \times 10^5$ . This phenomenon implies the difference between both polymers in chain entanglement and intermolecular interaction, which is presumably caused by the different molecular topology, as their chemical structures of repeating unit are same each other.

Relationship between weight-average molecular weight  $M_w$  and intrinsic viscosity  $[\eta]$  for both **TE—PAAMEs** by AB<sub>2</sub> self-polymerization and nonideal A<sub>2</sub> + B<sub>3</sub> polymerization is shown in Figure 2. Comparison of the intrinsic viscosities between both **TE—PAAMEs** reveals that the hyperbranched polymer by AB<sub>2</sub> self-polymerization exhibits a lower  $[\eta]$  than that by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization. The intrinsic viscosity for high molecular weight **TE—PAAME** by AB<sub>2</sub> self-polymerization is rather lower than that by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization, even if its molecular weight is higher than the later. Since the intrinsic viscosity is related to the hydrodynamic volume of the polymer coil in a dilute solution, the above result suggests that **TE—PAAMEs** 

by AB<sub>2</sub> self-polymerization have a more compact structure than that by nonideal  $A_2 + B_3$  polymerization. From the Figure 2, a shape factor  $\alpha$ , which is defined by the Mark–Houwink equation  $([\eta] = KM^{\alpha})$ , can be calculated from the slope of the log  $[\eta] - \log M_w$  line through the least-squares method. It is found that the  $\alpha$  values are 0.31 for AB<sub>2</sub> self-polymerization and 0.44 for nonideal  $A_2 + B_3$  polymerization. Usually, the  $\alpha$ value lies between 0.5 and 1.0 for randomly coiled linear polymers. The  $\alpha$  value of **TE-PAAMEs** by AB<sub>2</sub> selfpolymerization is noticeably lower than 0.5, indicating that the molecular shape of such hyperbranched polymers is distinct from that of linear ones. However, the  $\alpha$  value of **TE—PAAMEs** by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization is near to 0.5, implying that the molecular shape of these hyperbranched polymers is close to that of linear ones to a certain extent.

The degree of branching (DB) of hyperbranched polymers is defined as the ratio of the sum of dendritic (D) and terminal units (T) vs total sum of dendritic, linear (*L*) and terminal units, e.g. DB = (D + T)/(D + T)+ L), as first introduced by Fréchet et al.<sup>24a</sup> It was pointed out that such a definition was only valid for high molecular weight hyperbranched polymers based on AB2 monomers.<sup>24b</sup> Thus, Frey et al. introduced a general expression for DB without molecular weight limitation based on hyperbranched polymers from AB<sub>m</sub> monomers, e.g. DB = 2D/(2D + L).<sup>24b</sup> It was suggested that neither the Fréchet definition nor the Frey definition was sufficient in the description of the topological feature of a hyperbranched polymer.<sup>11</sup> Furthermore, both definitions seem unsuitable for  $A_2 + B_3$  polymerization, because they are based on AB<sub>2</sub> self-polymerization and  $AB_m$  self-polymerization, respectively. An  $AB_2$  selfpolymerization (or AB<sub>m</sub> self-polymerization) would afford the single focal point in each macromolecule, while an  $A_2 + B_3$  polymerization would perhaps result in the multi focal points in a macromolecule. Although both DB definitions are insufficient in describing the molecular topological feature, the determination of DB can give clear information on the molecular ratio of the dendritic, linear and terminal units in a macromolecule.<sup>17–21</sup> At least, the determination of DB can provide the information on the structural feature difference between hyperbranched polymers by AB<sub>2</sub> self-polymerization and  $A_2 + B_3$  polymerization, as addressed in the literature.<sup>17c</sup>

In previous work,<sup>21</sup> it was found that **ATPI**s gave a clear difference in chemical environment among dendritic, linear and terminal units, as shown in Scheme 2. The aromatic protons of the central aromatic ring in a given unit can be clearly distinguished with the aid of <sup>1</sup>H NMR measurement. In this work, the same method as the previous work was employed to investigate the distribution of dendritic, linear, and terminal units in as-prepared hyperbranched polyimides. Thus, ATPI from PAAME-AB<sub>2</sub>-5 was prepared for <sup>1</sup>H NMR measurement and its spectrum is depicted in Figure 3. As a comparison, the <sup>1</sup>H NMR spectrum of an **ATPI** by nonideal  $A_2 + B_3$  polymerization is also added in Figure 3. It is clear that both <sup>1</sup>H NMR spectra fit very well each other, demonstrating that both polymers have the same chemical structure. Like that in the previous work, the peaks of the central aromatic protons in <sup>1</sup>H NMR spectrum of ATPI by AB2 self-polymerization were separated into three peaks. By employing the same dendritic and terminal model as the previous work,<sup>21</sup>



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

Гable 2. Solubilitv	y of Hy	perbranched	Polymers <sup>a</sup>

	solvent					
polymer	NMP	DMF	DMSO	DMAc	THF	acetone
PAAME	+	+	+	+	±	_
TE-PAAME	+	+	+	+	+	-
TEPI	+	+	+	+	_	_

 $^a$  Key: +, soluble at room temperature; ±, partially soluble; –, insoluble.

Table 3. Thermal Properties of HyperbranchedPolyimides by AB2 Self-Polymerization

		hyperbranched polyimides					
properties	1 <sup>a</sup>	2	3	4	5		
$\frac{T_{g} (^{\circ}C)^{b}}{T_{5}/T_{10} (^{\circ}C)^{c}}$	155 450/500	155 445/510	156 455/510	160 450/510	161 460/520		

<sup>*a*</sup> 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.

the assignments of three peaks were confirmed. The integration of the deconvoluted peaks assigned to different units was calculated to be 1.0, 2.0, and 0.99 for the dendritic, linear and terminal units, respectively. This distribution is consistent with the statistical prediction based on AB<sub>2</sub> self-polymerization,<sup>24b</sup> e.g. D:L:T = 1:2:1. It is worthy of mentioning that the molecular ratio of three units for **ATPIs** by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization deviates from 1:2:1, providing clear information in structural difference between **AT-PIs** by AB<sub>2</sub> self-polymerization and nonideal A<sub>2</sub> + B<sub>3</sub> polymerization.

**Polymer Properties.** The solubility of hyperbranched polymers by AB<sub>2</sub> self-polymerization at every synthetic stage is summarized in Table 2. **PAAMEs**, **TE—PAAMEs**, and **TEPIs** obtained by AB<sub>2</sub> self-polymerization are soluble in DMAc, DMF, DMSO, and NMP at room temperature, similar to that obtained by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization. The solutions of **TE—PAAMEs** in NMP could pass the filter with 0.2  $\mu$ m diameter mesh and no gel was observed.

The thermal stability and glass transition temperatures of hyperbranched polyimides by chemical imidization are summarized in Table 3. The 5% weight loss temperatures of **TEPI**s obtained by AB<sub>2</sub> self-polymerization are in the range 450-460 °C, lower than that  $(480-505 \text{ °C})^{21}$  obtained by nonideal  $A_2 + B_3$  polymerization. However these data are close to that (455 °C)<sup>25</sup> of a hyperbranched polyimide from another AB<sub>2</sub> monomer. The glass transition temperatures of **TEPI**s by AB<sub>2</sub> self-polymerization are in a range of 155-161 °C, which are also lower than those (212-230 °C)<sup>21</sup> by nonideal  $A_2 + B_3$  polymerization. It is remarkable that the thermal stability and glass transition temperatures of both **TEPI**s show such a big difference, although both **TEPIs** have the same repeating unit and a close molecular weight. The difference in the thermal stability and glass transition temperatures between both TEPIs is assumed to be caused by their different molecular topology. As mentioned above, **TEPIs** by AB<sub>2</sub> selfpolymerization has a compact structure. The compact molecular structure would resist the molecular globules from penetrating one another, leading to lack of chain entanglement. In addition, the less molecular penetration would also result in poor intermolecular interaction derived from both van der Waals force and chargetransfer complex interaction, the later was demonstrated to be an important interaction in polyimides.<sup>26</sup> It is reasonable to think that the intermolecular interaction among TEPI molecules by AB2 self-polymerization would be only the van der Waals force among the methyl end groups on the molecular globule periphery. The poor intermolecular interaction, together with lack of chain entanglement, would lead to a low glass transition temperature. However, TEPIs by nonideal  $A_2 + B_3$  polymerization could penetrate one another to form a certain extent of chain entanglement and strong intermolecular interaction, giving rise to a high glass transition temperature. As to the thermal stability, the weight loss temperature of **TEPI**s at the early degradation stage is assumed to be mainly associated with the peripheral chemical structure of the molecular globules because of an unbalance temperature field from the molecular periphery to core during heating procedure. The peripheral chemical structure of the **TEPI** molecular globules by AB<sub>2</sub> self-polymerization is composed of methyl end groups due to the compact molecular structure, while that by nonideal  $A_2 + B_3$  polymerization consists of both methyl end groups and imide backbone owing to the loose packing structure. Undoubtedly, the later should be more thermally stable than the former at the early thermal degradation stage.

Transparent yellow films from both **TE—PAAME**s by AB<sub>2</sub> self-polymerization and nonideal  $A_2 + B_3$  polymerization were prepared by solution casting method in DMAc upon heating. All resulting films by AB<sub>2</sub> selfpolymerization were brittle, fragile, and not self-standing. The failure for film preparation from TE-PAAME-1, -2, and -3 by AB<sub>2</sub> self-polymerization was perhaps due to their low molecular weight. However for **TE—PAAME-4** and **-5** obtained by AB<sub>2</sub> self-polymerization, this should be caused by the lack of chain entanglement and intermolecular interaction in films. The films prepared from **TE—PAAME**s by nonideal A<sub>2</sub> + B<sub>3</sub> polymerization were tough and self-standing.<sup>21</sup> Table 4 shows the mechanical properties of hyperbranched polyimide films obtained by  $A_2 + B_3$  polymerization. The tensile strength and elongation at break of these films are about 18-29 MPa and 1%, respectively. Their tensile moduli can attain 3.2 GPa. The tensile strength of these hyperbranched polyimide films is much lower than that of their linear analogues,

Table 4. Mechanical Properties of HyperbranchedPolyimides by A2 + B3 Polymerization

	<b>TEPI</b> <sup>a</sup>				
properties	<b>3</b> <sup>b</sup>	4	5	6	
tensile strength (MPa) <sup>c</sup>	$29\pm1$	$27\pm2$	$21\pm4$	$18\pm2$	
elongation at break (%)	$0.9\pm0.2$	$1.1\pm0.1$	$0.9\pm0.1$	$0.8\pm0.1$	
tensile modulus $(GPa)^d$	3.2	2.6	2.3	2.3	

<sup>*a*</sup> **TEPI**, toluidine end-capped hyperbranched polyimide. <sup>*b*</sup> **3**, the code of samples by  $A_2 + B_3$  polymerization in Table 1. <sup>*c*</sup> Tensile test was carried out at room temperature with a film specimen at a dimension of  $40 \times 5 \times 0.02$  mm. The tensile rate is 4 mm/min. <sup>*d*</sup> Calculated from dividing the average tensile strength by the average elongation at break.

demonstrating that the chain entanglement and intermolecular interaction in the films are limited due to hyperbranched structure.

**Examination of the Existence of Chain Entangle**ment and Intermolecular Interaction in TEPIs. The physical properties of the partially disentangled TEPIs (freeze-extracted samples) and the original TE-**PIs** (samples without freeze-extracting treatment) were examined to elucidate the existence of chain entanglement and intermolecular interaction. It has been well established that a disentangled single- or pauci-chain particle of macromolecule can be obtained through a socalled "freeze-drying" technique.<sup>27</sup> The basic idea approaching a disentangled polymer by freeze-drying technique is that the disentangled status of polymer chains in a very dilute solution remains unchangeable after a rapid freezing of the polymer solution in the fraction of a second. Then the frozen solvent is removed by sublimation, leading to the disentangled polymers in which individual polymer chains are collapsed to globular particles rather than being intertwined. A disentangled single-chain polymer, as compared with the original polymer, usually exhibits an obvious difference in physical properties, such as nonradiative energy transfer behavior,<sup>27a-c</sup> crystallization kinetic,<sup>27d,e</sup> and glass transition temperature<sup>27j,k</sup> etc. Since the freeze-drying technique has to employ a solvent with a low boiling point temperature so as to remove it easily by sublimation, such a technique is not suitable for polymers that can only dissolved in the polar solvents with a high boiling point temperature. To overcome this problem, recently Xue et al. developed a freeze-extracting technique<sup>28</sup> in which a frozen polymer solution was extracted by another solvent to afford a partially disentangled polymer. Because TEPIs can only dissolved in the polar solvents, partially disentangled **TEPIs** by the freeze-extracting technique were prepared using NMP as a solvent.

The DSC curves of a freeze-extracted **TEPI** (AB<sub>2</sub>, entry 5) by AB<sub>2</sub> self-polymerization, together with its original sample, are illustrated in Figure 4. Both samples were subjected to heating scans up to 300 °C for four times at a heating rate of 10 °C/min. Obviously, the glass transition temperature between the freezeextracted sample and the original one does not show an apparent difference. This suggests that the hyperbranched polymers by AB<sub>2</sub> self-polymerization do not have sufficient chain entanglement and strong intermolecular interaction at their original status, leading to an unchangeable glass transition temperature after the freeze-extracting treatment.

The DSC measurements are also carried out for both freeze-extracted **TEPI** ( $A_2 + B_3$ , entry 3) and its original



**Figure 4.** DSC curves of freeze-extracted **TEPI-AB<sub>2</sub>-5** by AB<sub>2</sub> self-polymerization and its original sample.



**Figure 5.** DSC curves of freeze-extracted **TEPI-A<sub>2</sub>+B<sub>3</sub>-3** by nonideal  $A_2 + B_3$  polymerization and its original sample.

sample by nonideal  $A_2 + B_3$  polymerization, as shown in Figure 5 under the same scanning procedure as mentioned above. The glass transition temperature shows an observable difference between both samples. The glass transition temperature for the original sample is about 230 °C, while it decreases to 217 °C after freezeextracted treatment. It is interesting that the glass transition temperature of freeze-extracted **TEPI** tends to increase gradually from 217 to 223 °C with the scan times. However even after the fourth scan with a temperature up to 300 °C, its glass transition temperature is still lower than that of the original sample. These evidences strongly suggest the existence of chain entanglement and intermolecular interaction in TEPI by nonideal  $A_2 + B_3$  polymerization. The existence of chain entanglement and intermolecular interaction usually restricts the mobility of the segments in a polymer chain. Disentanglement and elimination of intermolecular interaction by freeze-extracting treatment can help to enhance the mobility of the segments, resulting in a decrease of the glass transition temperature.

An Attempt to Elucidate the Molecular Topology. The conclusion from freeze-extracting experiment provides useful information on elucidating the molecular topology for **TEPI**s by nonideal  $A_2 + B_3$  polymerization and  $AB_2$  self-polymerization. It is well-known that the branching chain length between two affinity branching points play an important role in forming good chain entanglement and strong intermolecular interaction.<sup>9</sup>



hyperbranched polyimide by AB<sub>2</sub> self-polymerization

**Figure 6.** Comprehensive analysis for the molecular topology of hyperbranched polyimides by AB<sub>2</sub> self-polymerization.



hyperbranched polyimide by A<sub>2</sub>+B<sub>3</sub> polymerization

Figure 7. Comprehensive analysis for the molecular topology of hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization.

If the branching chain length were less than the critical molecular weight for forming the penetrable macromolecules, none of the chain entanglement and strong intermolecular interactions would be formed among the macromolecules.<sup>9</sup> On the contrary, the opposite conclusion would be drawn. Thus, it is assumed that the hyperbranched polyimides obtained by nonideal  $A_2$  + B<sub>3</sub> polymerization should have sufficiently long linear chain between two affinity branching points. Undoubtedly, the hyperbranched polyimides by AB<sub>2</sub> self-polymerization should only have short chain between two affinity branching points. In combination of the conclusion from freeze-extracting experiment and the result from intrinsic viscosity vs molecular weight relationship, a comprehensive analysis for the possible molecular topologies of both hyperbranched polyimides was summarized in Figures 6 and 7, respectively.

However it is difficult to imagine that the hyperbranched polyimides by nonideal  $A_2 + B_3$  polymerization could have sufficiently long linear chain for forming well chain entanglement and strong intermolecular interaction, since its linear unit content (below 50% mol)<sup>21</sup> is even lower than that by AB<sub>2</sub> self-polymerization. It is reasonable to guess that the dendritic and terminal units would also take part in constructing the long linear chains and form the short pendent segments alone the long linear chains. Thus, the possible topologies for molecules by nonideal  $A_2 + B_3$  polymerization and AB<sub>2</sub> self-polymerization are deduced, as shown in Figure 8. Obviously, the molecular topology by nonideal  $A_2 + B_3$  polymerization is loose packing low branching



Figure 8. Imaginary molecular topologies of hyperbranched polyimides by  $AB_2$  self-polymerization and nonideal  $A_2 + B_3$  polymerization.

density structure bearing long linear chains, while that by  $AB_2$  self-polymerization is highly compact branchon-branch structure without long linear chains.

The occurrence of low branching density topology in nonideal  $A_2 + B_3$  polymerization should be related to its polymerization features, as mentioned in previous work.<sup>21</sup> The sequential reaction of B groups due to DBOP activation feature would slow the dendritic unit formation. The  $A_2 + B_3$  polymerization feature, for which the  $A_x B_y$  intermediates would form at the early polymerization stage and contribute nothing to any dendritic, linear and terminal unit formation, would also delay the dendritic unit formation. Thus, it is easy to imagine that the linear oligomers or polymers bearing short pendant segments would be formed at the early stage of the nonideal  $A_2 + B_3$  polymerization, as illustrated in Figure 8. The later stage polymerization among these oligomers or polymers would develop a branching structure, leading to a loose packing low branching density topology.

## Conclusion

Hyperbranched polyimides, having the same repeating unit as that by nonideal  $A_2 + B_3$  polymerization, were successfully prepared from a new AB<sub>2</sub> monomer by self-polymerization. Hyperbranched polyimides obtained by AB<sub>2</sub> self-polymerization have a compact highly branching structure, while those obtained by  $A_2 + B_3$ polymerization have a loose-packing, low branching density topology. Hyperbranched polyimides obtained by  $AB_2$  self-polymerization are different from that obtained by nonideal  $A_2 + B_3$  polymerization in many physical properties, such as solution viscosity, thermal stability, and glass transition temperature. Hyperbranched polymers obtained by AB<sub>2</sub> self-polymerization are not suitable for self-standing film preparation, while that by nonideal  $A_2 + B_3$  polymerization can afford tough self-standing films. The underlying reason, elucidated by the freeze-extracting experiment, is the difference in chain entanglement and intermolecular interaction.

## **Experimental Section**

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

Monomer Preparation. Synthesis of 4-Fluoro-N-(4nitrophenyl)phthalimide. To a three-neck flask equipped with water segregator were added 5.0 g (0.03 mol) of 4-fluorophthalic anhydride, 4.16 g (0.03 mol) of p-nitroaniline, and 10 mL of DMF. The solution was stirred for 1 h at room temperature, and then 50 mL of toluene and 0.42 g of 4-toluenesulfonic acid were added. The solution was allowed to reflux for overnight, and the byproduct water was separated in segregator. After the reaction solution was cooled to room temperature, a pale yellow needle crystal was appeared. The crystal product was isolated by filtration, washed three times with every 200 mL of toluene and dried at 60 °C under reduced pressure. Yield: 88%. <sup>1</sup>H NMR (δ, ppm): 8.71-8.67 (m, 1H), 8.63–8.62 (t, 1H), 8.45–8.41 (m, 2H), 8.27–8.24 (d, 1H), 7.82-7.78 (d, 2H). <sup>13</sup>C NMR (δ, ppm): 167.7, 165.2, 165.1, 164.3, 146.2, 137.6, 134.6, 127.7, 126.5, 124.2, 122.0, 111.6. IR (KBr, cm<sup>-1</sup>): 3109, 1776, 1732, 1612, 1594, 1524, 1487, 1443, 1373, 1346, 1271, 1242, 1172, 1120, 1087, 1010, 948, 890, 853, 837, 797, 749, 736, 724, 685, 666, 647, 627, 581, 529.

Synthesis of Compound 1. To a 100 mL completely dry flask under N2 purge were added 2.52 g (0.02 mol) of phloroglucinol, 2.77 g (0.016 mol) of 4-nitrophthalonitrile, and 50 mL of DMF. After the chemicals were dissolved, 8.28 g (0.06 mol) of potassium carbonate was added into the flask. The mixture was stirred vigorously at room temperature for 15 h, and the resulting mixture was poured into 1000 mL of dilute HCl solution. The precipitate was collected by filtration. After recrystallization from water/methanol (50:50 in volume) mixed solvents, pure product 1 was obtained as yellow crystal. Yield: 53%. <sup>1</sup>H NMR ( $\delta$ , ppm): 10.3(s, 1H), 8.11–8.08 (d, 2H), 7.90–7.89 (d, 1H), 7.56–7.52 (t, 2H), 6.48–6.45 (t, 3H). <sup>13</sup>C NMR (*d*, ppm): 160.6, 156.0, 136.2, 122.9, 122.6, 116.7, 115.8, 115.3, 108.6, 104.7, 103.0. IR (KBr, cm<sup>-1</sup>): 3357, 3081, 2234, 1621, 1593, 1567, 1484, 1463, 1424, 1412, 1346, 1276, 1249, 1198, 1169, 1141, 1127, 1088, 1010, 889, 850, 831, 722, 668, 610, 524, 442.

Synthesis of Compound 2. To a 100 mL flask were added 6.3 g (0.0167 mol) of 1, 17.8 g of KOH, and 65 mL of water.

The solution was allowed to reflux overnight until the evolution of the byproduct ammonia ceased. The yellow clear solution was poured into 160 mL of water, and the pH of solution was adjusted to be 3–4. A white precipitate appeared and collected by filtration and washed with dilute hydrochloric acid and then pure water. After recrystallization from aqueous acetic acid, product **2** was obtained as a white crystal. Yield: 95%. <sup>1</sup>H NMR ( $\delta$ , ppm): 10.0 (s, 1H), 7.99–7.96 (d, 2H), 7.45 (s, 2H), 7.19–7.16 (t, 2H), 6.29–6.24 (t, 3H). <sup>13</sup>C NMR ( $\delta$ , ppm): 167.7, 167.3, 160.0, 158.1, 157.6, 137.0, 133.3, 128.1, 119.7, 119.4, 102.4, 101.6. IR (KBr, cm<sup>-1</sup>): 3240, 1725, 1703, 1624, 1598,1573, 1493, 1461, 1419, 1371, 1272, 1233, 1146, 1124, 1068, 1010, 932, 898, 841, 793, 761, 708, 678, 652, 607, 574, 448.

Synthesis of Compound 4. To a completely dry flask purged with N<sub>2</sub> were added 3.75 g (0.00825 mol) 2, 11.4 g of  $K_2CO_3$ , and 60 mL of DMSO. The mixture was heated at 100 °C for half an hour, then 60 mL of toluene was added, and a water segregator was installed. The mixture was allowed to reflux for 1 h and the toluene was driven off by elevating temperature to 140 °C. At this time, 2.36 g (0.00825 mol) of 4-fluoro-*N*-(4-nitrophenyl)phthalimide was added, and the reaction was carried out at 155 °C for 5 h. Then DMSO was driven off under reduced pressure, and the resulting residue as a pale yellow powder was dissolved in 100 mL of pure water. A dilute HCl solution (5 wt %) was added dropwise to the solution to adjust the pH value to be 4. Then the water was evaporated off under reduced pressure, and a residue obtained as a yellow powder was collected and extracted with acetone at room temperature for 24 h. After filtration, a clear yellow filtrate was collected. After distilling off the acetone under vacuum at room temperature, a yellow powder was obtained and dried at 136 °C under reduced pressure for overnight. The product 3 was obtained as a fluffy yellow powder.

To a 100 mL completely dry flask were added above product 3, 120 mL of acetic acid, 16 mL of pyridine and 24 mL of acetic anhydride. The solution was heated at 115 °C overnight, and then was filtrated at room temperature. The filtrate was collected, and the solvents were driven off under vacuum. The residue was dried at room temperature under reduced pressure for overnight. The resulting yellow powder was then dissolved in 120 mL of acetic acid and 24 mL of acetic anhydride again. The solution was heated at 120 °C for 1 h, and then the solvents were driven off under vacuum. The residue was dried at 100 °C under reduced pressure for overnight and product 4 was collected as a yellow powder. Yield: 67%. <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.

Synthesis of Compound (5). To a completely dry flask were added 1 g (0.00146 mol) of 4 and 40 mL of methanol. The mixture was refluxed and gradually turned into a clear solution. The refluxing was continued overnight, and then filtrated after the temperature was lowered to room temperature. A clear yellow solution was obtained and was condensed to one-third of its original volume at room temperature under vacuum. The solution was poured to 500 mL of water to precipitate the product. After isolation by filtration, washing with water, and drying under vacuum at room temperature, the product **5** was obtained as a fluffy white powder. Yield: 92%. <sup>1</sup>H NMR (δ, ppm): 10.9 (s, 1H), 8.40-8.37 (d, 0.4H), 8.26-8.23 (d, 1.6H), 7.92-7.53 (m, 6.3H), 7.37-7.26 (m, 4.6H), 6.77-6.71 (m, 3H), 3.77 (s, 5.5H), 3.74-3.73 (d, 3.4H). <sup>13</sup>C NMR (*d*, ppm): 168.2, 168.1, 167.5, 167.4, 167.3, 167.2, 166.5, 166.1, 165.8, 159.8, 159.2, 158.8, 158.2, 158.1, 158.0, 157.4, 146.7, 145.8, 145.7, 142.9, 136.4, 136.0, 133.7, 132.4, 131.6, 130.9, 128.1, 126.3, 126.2, 125.5, 124.7, 120.1, 119.7, 119.3, 117.8, 107.9, 53.2, 53.1, 52.9. IR (KBr, cm<sup>-1</sup>): 3331, 3084, 2956, 1726, 1594, 1573, 1509, 1437, 1409, 1331, 1304, 1277, 1213, 1120, 1066, 1009, 851, 785, 752, 707, 690, 503.

Synthesis of Compound 6. Into a 90 mL autoclave were added 2 g (0.00266 mol) of 5, 40 mL of THF, 10 mL of methanol, and 0.2 g of 10% Pd/C catalyst. The mixture was stirred under 20 atm of hydrogen at room temperature for 48 h and then filtered with Celite to get a clear yellow filtrate. The filtrate was condensed to one-fourth of its original volume and poured into water to precipitate the product. The precipitate was collected by filtration and dried under vacuum at room temperature for 24 h and at 40 °C for 2 h. Compound 6 was obtained as a white fluffy powder. Yield: 89%. <sup>1</sup>H NMR  $(\delta, ppm)$ : 9.93 (s, 1H), 7.85–7.82 (d, 2H), 7.72–7.70 (d, 0.5H), 7.64-7.61 (d, 0.5H), 7.54-7.50 (d, 0.46H), 7.42-7.40 (d, 0.6H), 7.26 (s, 7H), 6.75 (s, 3H), 6.63-6.60 (d, 0.46H), 6.55-6.52 (d, 2.5H), 3.77 (s, 5.3H), 3.72 (s, 3.6H). <sup>13</sup>C NMR (δ, ppm): 167.7, 167.6, 166.9, 166.8, 166.5, 166.0, 165.0, 159.3, 158.7, 158.3, 157.7, 157.6, 156.3, 145.3, 144.6, 141.5, 135.9, 135.6, 134.1, 131.1, 130.2, 128.6, 128.2, 125.8, 122.8, 121.4, 119.6, 118.8, 117.3, 116.2, 113.9, 113.5, 52.6, 52.5, 52.4, 52.3. IR (KBr, cm<sup>-1</sup>): 3446, 3378, 3073, 2956, 2605, 1723, 1593, 1573, 1515, 1491, 1454, 1436, 1278, 1213, 1121, 1067, 1009, 889, 837, 788, 705, 518. Anal. Calcd for C<sub>39</sub>H<sub>30</sub>O<sub>14</sub>N<sub>2</sub>: C, 62.40; H, 4.03; N, 3.73. Found: C, 62.10; H, 4.09; N, 3.62.

**Polymer Preparation. Synthesis of Poly(amic acid methyl ester) (PAAME).** A typical procedure for synthesis of **PAAME** is described as follows. To a completely dry flask under N<sub>2</sub> were added 0.5 g of **6**, 0.21 mL of triethylamine, and 6 mL of NMP. Then 0.697 g of DBOP was added to the solution. The reaction solution was stirred at 50 °C for 24 h. Then the solution was poured into methanol containing 1% LiCl to precipitate the polymer. After the isolation by filtration and washing with methanol for several times, a white powdery polymer was obtained. **PAAME-AB<sub>2</sub>-5**. Yield: 94%. <sup>1</sup>H NMR ( $\delta$ , ppm): 10.55 (s, 0.5H), 10.19 (m, 0.5H), 7.99–7.58 (m, 3.8H), 7.47 (m, 7.9H), 7.30 (m, 3.6H), 7.19 (m, 1.3H), 6.81 (m, 3.0H), 3.77–3.70 (d, 4.5H). IR (KBr, cm<sup>-1</sup>): 3482, 3073, 2956, 1778, 1725, 1594, 1515, 1477, 1438, 1358, 1268, 1198, 1119, 1006, 971, 949, 838, 785, 746, 692, 671, 528.

Synthesis of Anhydride-Terminated Polyimide (ATPI). To a solution of 0.12 g of PAAME in 6 mL of NMP were added 2.3 mL of acetic anhydride and 1.7 mL of pyridine. The reaction was carried out at 115 °C under N<sub>2</sub> overnight. Then polymer was precipitated via pouring the reaction solution into dry toluene. After isolation by filtration and drying under vacuum at 60 °C overnight, **ATPI** was obtained in a brown powder. **ATPI-AB<sub>2</sub>-5.** Yield: 94%. <sup>1</sup>H NMR ( $\delta$ , ppm): 7.94–7.82 (m, 2.4H), 7.57 (bs, 6.9H), 7.35–7.25 (m, 4.1H), 6.84–6.71 (t, 3.0H). IR (KBr, cm<sup>-1</sup>): 3071, 1777, 1724, 1596, 1514, 1479, 1437, 1365, 1238, 1196, 1080, 1006, 838, 794, 746, 693, 671, 595, 528.

Synthesis of *p*-Toluidine End-capped Poly(amic acid methyl ester) (TE-PAAME). To a completely empty flask under N<sub>2</sub> were added 0.5 g of **PAAME**, 0.37 g of *p*-toluidine, and 15 mL of NMP. To this solution were added 0.697 g of DBOP and 0.21 mL of triethylamine. The reaction solution was stirred overnight at room temperature and then 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 powder of TE-PAAME was obtained. **TE—PAAME-AB<sub>2</sub>-5**. Yield: 95%.  $\eta_{inh} = 0.17 dL/g$ . <sup>1</sup>H NMR (δ, ppm): 10.49 (s, 0.1H), 10.19 (s, 0.4H), 10,06 (s, 0.2H), 7.94 (m, 2.4H), 7.57 (bs, 5.6H), 7.28 (bs, 4.9H), 7.12 (s, 1.3H), 6.81 (m, 3.0H), 3.78 (s, 2.7H), 2.36 (s, 2.6H). IR (KBr,  $cm^{-1}$ ): 3074, 2951, 2882, 1778, 1722, 1594, 1514, 1475, 1455, 1438, 1412, 1357, 1301, 1269, 1208, 1137, 1119, 1090, 1065, 1009, 971, 949, 844, 781, 748, 693, 671, 616, 512, 426.

**Synthesis of** *p***-Toluidine End-Capped Polyimide** (**TEPI**). To a solution of 0.39 g of **TE—PAAME** in 16 mL of NMP were added 7 mL of acetic anhydride and 5 mL of pyridine. The reaction solution 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 powder of **TEPI** was obtained. **TEPI-AB<sub>2</sub>-5**. Yield: 97%. <sup>1</sup>H NMR (δ, ppm): 7.95–7.83 (m, 2.7H), 7.56 (bs, 6.8H), 7.29 (bs, 5.7H), 6.83 (bs, 3.0H), 2.35 (s, 2.4H). IR (KBr,  $\rm cm^{-1}$ ): 3073, 2945, 1778, 1725, 1595, 1515, 1479, 1438, 1362, 1267, 1197, 1120, 1004, 837, 789, 745, 695, 670, 593, 529, 419.

**Freeze-Extracted Sample Preparation.** The freezeextracted samples were prepared by dissolving a certain amount of **TEPI** in NMP to afford a solution with a concentration of 0.5 g/L. The solution was then rapidly frozen by immersion of a vigorously shaken flask in a dry ice-acetone bath. Then the frozen solution was poured into a large amount of cold methanol at -20 °C. The powdery **TEPI** was collected by filtration, washed with methanol for several times and dried under vacuum at room temperature. A fluffy powder of **TEPI** was obtained and stored at  $-20^{\circ}$  for DSC measurement. Prior to DSC measurement, the sample was dried again under vacuum at 40 °C for 2 h.

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 a 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 L<sup>-1</sup> of 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-PAAMEs was measured at a concentration of 0.5g  $\dot{d}L^{-1}$  in NMP at 30 °C by using an Ostwald viscometer. Intrinsic viscosity of TE-PAAMEs was measured in DMF at 30 °C by utilizing an Ubbelohde viscometer.

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