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Hyperbranched Polyimides Prepared by Ideal A_2+B_3 Polymerization, Non-Ideal A_2+B_3 Polymerization and AB_2 Self-Polymerization

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Summary: In this paper, hyperbranched polyimides having the same repeating unit were synthesized by employing ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization methods. The polymerization behavior, polymer properties were compared for three methods. Hyperbranched polyimides by ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization methods show apparent difference in many physical properties, such as inherent viscosity, glass transition temperature, and film formation behavior etc. The hyperbranched polymers by the non-ideal A_2+B_3 polymerization are suitable for smooth, flexible and self-standing film preparation, which provides useful information for hyperbranched polymers toward self-standing materials.

Keywords: A_2+B_3 polymerization, film, hyperbranched, polyimides, preparation

Introduction

Hyperbranched polymers have received considerable attention for ten more years.[1-7] Hyperbranched polymers are generally prepared by one-pot self-polymerization of the AB_x monomers.[1-7] Since the AB_x 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.[8] Hyperbranched polymers, such as polyamide,[8] polyether,[9] polyimide[10] and poly (sulfone-amine)[11] etc., were successfully prepared by this approach.

An A_2+B_3 polymerization has many advantages over AB_2 self-polymerization, such as: (1) monomers are commercially available and easy to obtain; (2) polymerization is convenient to scale up; and (3) the polymer structure is easy to tailor due to various choice of monomers for a certain polymerization. However, it must be noted that A_2+B_3 polymerization has an intrinsic problem, i.e. the gelation is unavoidable over a certain conversation in 1:1 mol monomer feed ratio, as pointed out by Flory over 50 years ago.[12] Thus the major concern of the A_2+B_3 polymerization focuses on how to avoid the gelation. An ideal A_2+B_3 polymerization system toward gelation, as described by Flory,[12] is based on three

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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.

In our previous paper,[13] a new strategy for preparing hyperbranched polyimides by employing a non-ideal A_2+B_3 polymerization has been reported. 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. Therefore gelation was effectively avoided and soluble hyperbranched polyimides with high molecular weight were successfully prepared. In this paper, hyperbranched polyimides having the same repeating unit were synthesized by employing ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization methods. The polymerization behavior, polymer properties were compared for three methods.

Results and Discussions

In this paper, two novel B_3 monomers, i.e. tri(phthalic anhydride) and tri(phthalic acid methyl ester), were employed to carry out A_2+B_3 polymerization. The molecular design of two B_3 monomers was aimed at high thermal stability, good solubility and equal reactivity of each functinal group. As shown in Fig.1, each B_3 monomer is designed to have three independant functional groups with the same reactivity. To carry out AB_2 self-polymerization, a new AB_2 monomer was designed from a template of a repeating unit of the hyperbranched polyimides by A_2+B_3 polymerization.

Hyperbranched polyimides were synthesized by A_2+B_3 polymerization from both B_3 monomers (tri(phthalic anhydride) and tri(phthalic acid methyl ester)), and 1,4-phenylene diamine (A_2) in molecular ratio of 1:1, respectively. The ideal A_2+B_3 polymerization of the tri(phthalic anhydride) and 1,4-phenylene diamine afforded poly(amic acid) (**PAA**) precursor, and the non-ideal A_2+B_3 polymerization of the tri(phthalic acid methyl ester) and 1,4-phenylene diamine gave poly(amic acid methyl ester) (**PAAME**) precursor. The **PAA** and **PAAME** precursors were end-capped with 4-toluidine by adopting the same reaction conditions as the precursor synthesis. The 4-toluidine end-capped poly (amic acid) (**TE-PAA**) and 4-toluidine end-capped poly (amic acid methyl ester) (**TE-PAAME**) were then converted into 4-toluidine end-capped polyimides (**TEPI**) by cyclodehydration in the presence of acetic anhydride and pyridine. The anhydride-terminated polyimides (**ATPI**) were also prepared

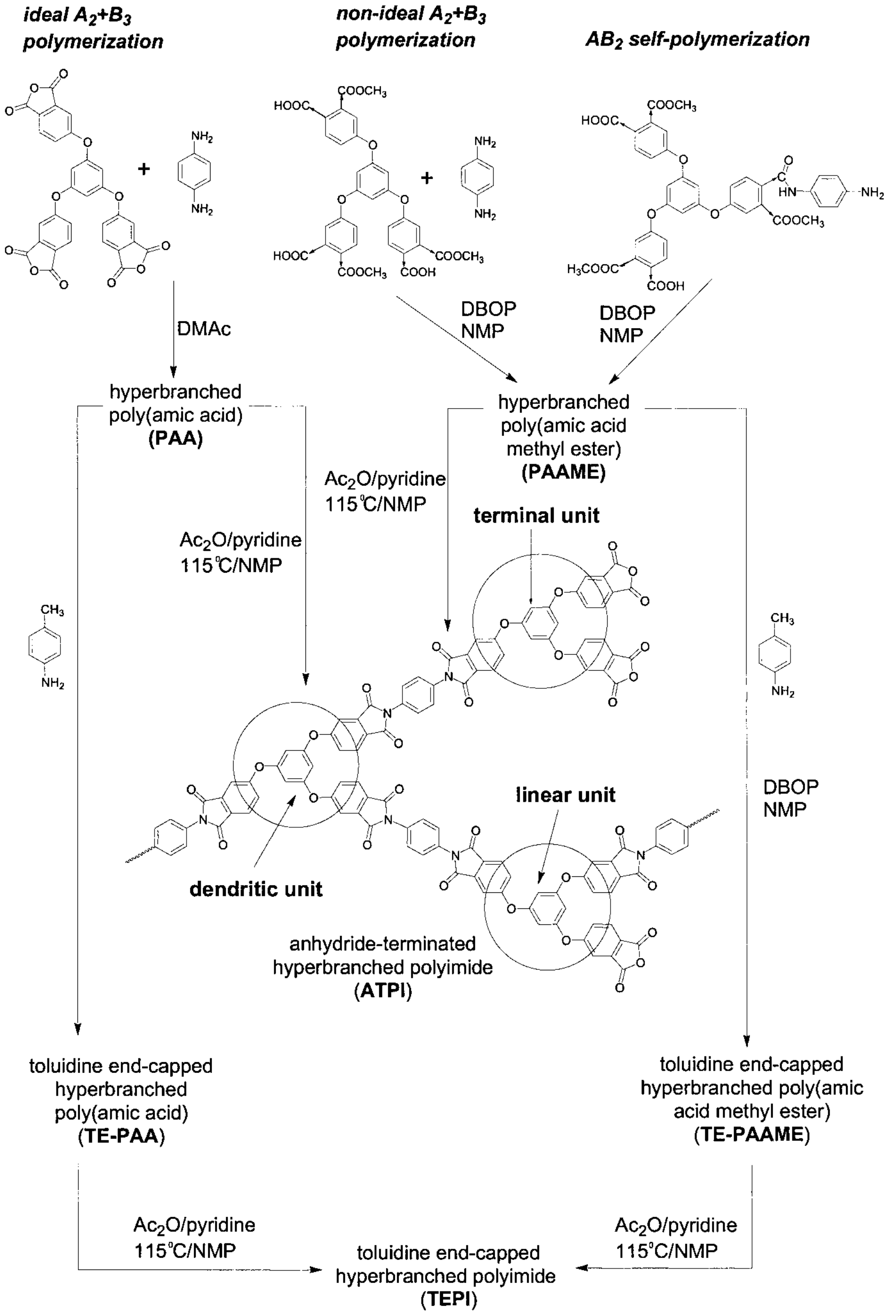
ideal A2+B3 polymerization
non-ideal A2+B3 polymerization
AB2 self-polymerization
COOCH3
HOOC
NH2
HN
H3COOC
COOH
DMAc
DBOP
NMP
hyperbranched poly(amic acid) (PAA)
hyperbranched poly(amic acid methyl ester) (PAAME)
Ac2O/pyridine 115°C/NMP
terminal unit
CH3
linear unit
dendritic unit
anhydride-terminated hyperbranched polyimide (ATPI)
toluidine end-capped hyperbranched poly(amic acid) (TE-PAA)
toluidine end-capped hyperbranched poly(amic acid methyl ester) (TE-PAAME)
toluidine end-capped hyperbranched polyimide (TEPI)

Figure 1

from **PAA** and **PAAME** under the same reaction conditions as **TEPI** synthesis. It can be seen that **TEPIs** and **ATPIs** by both A_2+B_3 polymerizations show the same chemical structure in the repeating unit. On the other hand, hyperbranched polyimides were prepared by self-polymerization of the new AB_2 monomer. As-prepared poly(amic acid methyl ester) (**PAAME**) precursors were end-capped with 4-toluidine by adopting the same reaction conditions as the precursor synthesis. The 4-toluidine end-capped poly(amic acid methyl ester)s (**TE-PAAMEs**) were then converted into 4-toluidine end-capped polyimides (**TEPI**) by cyclodehydration in the presence of acetic anhydride and pyridine. The anhydride-terminated polyimides (**ATPI**) were also prepared from **PAAME** under the same reaction conditions as **TEPI** synthesis. It is apparent that hyperbranched polymers by both AB_2 self-polymerization and non-ideal A_2+B_3 polymerization have the same chemical structure for the repeating unit at every synthetic stage of **PAAMEs**, **TE-PAAMEs**, **ATPIs** and **TEPIs**.

The polymerization conditions and results are summarized in Table 1. It is clear that A_2+B_3 polymerization of the tri(phthalic anhydride) and 1,4-phenylene diamine is a typical ideal A_2+B_3 polymerization, which always causes gelation. Thus, a dropwise addition way by dripping A_2 monomer into B_3 monomer was employed (see table 1, ideal A_2+B_3 polymerization, entry 3). It is noted that the weight-average molecular weight of the **TEPI** is unexpectedly high, but its number-average molecular weight is much low ($1.31X10^4$ g/mol). The molecular weight distribution attains 23, indicating that the **TEPI** is a mixture of oligomers and high molecular weight polymers. Since the **PAA** and **TEPI** are only soluble in organic solvents upon heating, their poor solubility demonstrate that the high molecular part of the **PAA** and **TEPI** is indeed a slightly crosslinking microgel.

The A_2+B_3 polymerization of tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) was carried out through a 'one-step' procedure as literature mentioned, [14] which can successfully achieve the high molecular weight and soluble polymers. A weight-average molecular weight ranging from 33,600 to 125,000 is achieved for this polymerization approach. It was pointed by Flory that, the A_2+B_3 polymerization in 1:1 mol generally results in gelation over a certain conversation of functional groups.[12] This prediction is based on the exclusive reactivity between functional group A and B. However in our case, the functional group B is not restricted to react only with functional group A. The *in-situ* activation of carboxyl groups in a B_3 monomer by DBOP affords an intermediate functional group B′ at first. Moreover a by-product from DBOP is also formed. The B′ can either react with a functional group A to carry out a step of polymerization, or react with a by-product (as

Table 1. Polymerization conditions and results for the synthesis of hyperbranched polyimide precusors via ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization.

method	entry	concent. [a] (g/ml)	temp. [b] (^{0}C)	yield %	η_{inh} [c] (dL/g)	M_w [d]	M_w/M_n [d]
ideal A_2+B_3 polymerization	1	0.025	r.t.		gel		
	2	0.017	0		gel		
	3	0.017	0/r.t.[f]	95	0.28	3.02×10^5	23.0
non-ideal A_2+B_3 polymerization	1	0.19	r.t.		gel		
	2	0.11	r.t.		gel		
	3	0.097	r.t.	97	0.97	1.25×10^5	2.63
	4	0.073	r.t.	90	0.25	6.74×10^4	2.08
	5	0.058	r.t.	86	0.23	3.76×10^4	1.84
	6	0.032	r.t.	78	0.17	3.36×10^4	2.17
AB_2 self-polymerization	1	0.06	r.t.	70	0.12	1.14×10^4	1.2
	2	0.16	r.t	71	0.12	1.11×10^4	1.3
	3	0.32	r.t	75	0.13	2.55×10^4	1.5
	4	0.06	50	82	0.15	5.13×10^4	1.9
	5	0.08	50	94	0.17	1.73×10^5	2.3

[a] Concentration, calculated by (the total mass monomers)/ (the volume of the solvent).

[b] Temperature.

[c] Inherent viscosity measured at a concentration of 0.5g/dL at 30^{0}C.

[d] 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 polyimide (**TEPI**) for ideal A_2+B_3 polymerization and 4-toluidine end-capped poly (amic acid methyl ester)s (**TE-PAAME**s) for non-ideal A_2+B_3 polymerization as well as AB_2 self-polymerization. The specific refractive increments (d*n*/d*c*) were 0.1278mL/g for entry 3 of ideal A_2+B_3 polymerization; 0.150, 0.172, 0.188 and 0.196 for entry 3, 4, 5 and 6 of non-ideal A_2+B_3 polymerization; 0.139, 0.143, 0.136, 0.140 and 0.143 mL/g for entry 1, 2, 3, 4 and 5 of AB_2 self-polymerization.

mentioned above) to result in an intermediate functional group B″. Although B″ can also react with an A to carry out a step of polymerization, the competition between B′/A reaction and B′/by-product reaction prevents B′ from reacting with A entirely. Such an A_2+B_3 polymerization in 1:1 mol deviates from Flory's ideal A_2+B_3 polymerization toward gelation. Thus the A_2+B_3 polymerization of tri(phthalic acid methyl ester) (B_3) and 1,4-phenylene diamine (A_2) is a non-ideal A_2+B_3 polymerization. This may be the main cause for avoiding the gelation. Due to such a unique polymerization characteristic, it is assumed that a macromolecular structure with a low branching density would be formed at the early polymerization stage, whose topology was retained at the later polymerization stage.

The self-polymerization of the new AB_2 monomer was also carried out through a 'one-step' procedure,[14] which is the same as that in the non-ideal A_2+B_3 polymerization. However low molecular oligomers with a molecular weight around 1.1×10^4 g/mol were obtained at room temperature. It is observed that the polymerization at 50^0C could afford a polymer with a molecular weight high up to 1.7×10^5 g/ml. Gelation was not observed under the given conditions listed in Table 1.

As seen in Table 1, a comparision of the inherent viscosities for as-prepared hyperbranched polyimide precursors reveals that polymers by non-ideal A_2+B_3 polymerization show the highest inherent viscosity, indicating the existence of stronger chain-entanglement. The formation of chain-entanglement is due to the intermolecular penetration, which is resulted from the low branching density topology of polymers by non-ideal A_2+B_3 polymerization. Apparently, hyperbranched polymers by AB_2 self-polymerization is lack of chain-entanglement, resulting in a low inherent viscosity despite of high molecular weight (table 1, AB_2 self-polymerization, entry 5). Just like the general hyperbranched polymers by AB_2 self-polymerization, as-prepared hyperbranched polyimide precursors have a compact highly branching structure, leading to a impenetrable molecule. In addition, hyperbranched polyimide precursors by ideal A_2+B_3 polymerization also exhibit a low inherent viscosity. This is perhaps due to its slightly crosslinking structure, preventing the molecules from penetration one another.

The degree of branching (DB) of hyperbranched polymer was defined as the ratio of the sum of dendritic and terminal units vs total units (dendritic, linear and terminal units). It was found that **ATPI**s gave a clear difference in chemical environment among dendritic, linear and terminal units, as shown in Fig. 1. The aromatic protons of the central aromatic ring in a given unit can be clearly distinguished with the aid of ^{1}H NMR measurement. Thus the DBs for hyperbranched polyimides by ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization were estimated to be 0.54, 0.52-0.55 and 0.50, respectively. The DB for hyperbranched polyimides by ideal A_2+B_3 polymerization and non-ideal A_2+B_3 polymerization is seriously deviated from the statistically predication value (0.50), which is different from that by AB_2 self-polymerization.

The thermal properties of hyperbranched polyimides by chemical imidization are summarized in Table 2. **TEPI** by ideal A_2+B_3 polymerization shows slightly higher glass transition temperature than that by non-ideal A_2+B_3 polymerization. The glass transition temperatures of **TEPI**s by non-ideal A_2+B_3 polymerization are in the range of 212-235^0C, which are far higher than that (160^0C) of hyperbranched polyimide by AB_2 self-polymerization. The big difference

Table 2. Thermal properties of hyperbranched polyimide via ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization.

method	entry [a]	T_g (^{0}C) [b]	T_5 (^{0}C) [c]	T_{10} (^{0}C) [c]
ideal A_2+B_3 polymerization	3	235	500	535
non-ideal A_2+B_3 polymerization	3	230	505	545
	4	223	480	520
	5	219	480	525
	6	212	485	535
AB_2 self- polymerization	4	160	450	510
	5	161	460	520

a) The entry code in Table 1.

b) Glass transition temperature (T_g) measured by DSC under nitrogen, heating rate 10^{0}C/min

c) 5% and 10% weight loss temperature measured by TGA under nitrogen, heating rate 10^{0}C/min

in glass transition temperatures was caused by the different molecular structure, i.e. the slightly crosslinking structure for ideal A_2+B_3 polymerization, the low branching density topology for non-ideal A_2+B_3 polymerization and the compact highly branching structure for AB_2 self-polymerization. As given in Table 2, the thermal stability for hyperbranched polyimides are also different for three polymerization methods. The 5% weight loss temperatures of **TEPIs** by non-ideal A_2+B_3 polymerization were in the range of 480~505^{0}C. **TEPI** by ideal A_2+B_3 polymerization showed a 5% weight loss at 500^{0}C, close to one of **TEPIs** (entry 3) by non-ideal A_2+B_3 polymerization. The 5% weight loss temperatures of **TEPIs** by A_2+B_3 polymerization methods surpasses that by AB_2 self-polymerization method (450-460^{0}C), although both have the same chemical structure for the repeating unit. This may be caused by the different structure topology. By the way, the residue trace unreacted amine group in hyperbranched polyimides by AB_2 self-polymerization, of which at least one unreacted amine group was theoretically existed in every molecules, should be another reason. Hyperbranched polymers are generally unsuitable for the preparation of self-standing films due to lack of chain entanglements. The film preparation was attempted for hyperbranched polyimide precursors by three polymerization methods. Hyperbranched polyimide films from three kinds of precursors were successfully prepared by casting the DMAc solutions onto glass plates upon heating. Film from **TE-PAA** by ideal A_2+B_3 polymerization was prepared directly from a condensed original reaction solution due to poor solubility of **TE-PAA** precursor after precipitation. The films from **TE-PAAMEs** by non-ideal A_2+B_3 polymerization and **TE-PAA** by ideal A_2+B_3 polymerization were self-standing, while that from **TE-PAAMEs** by AB_2 self-polymerization were brittle, fragile and not self-standing. The different film formation behavior is related to their molecular structure. The formation of a self-standing film by ideal A_2+B_3 polymerization may be due to the chain extension reaction among the oligomers, and that by non-ideal A_2+B_3 polymerization should be caused by chain-entanglement due to their low branching density structure. The failure in self-standing film formation for **TE-PAAMEs** by AB_2 self-polymerization should be resulted from chain-entanglement lack due to the compact impenetrable moleculr structure. The film from **TE-PAA** by ideal A_2+B_3 polymerization is heterogeneous and rough despite of its flexibility, suggesting existence of microgels. However films from **TE-PAAMEs** by non-ideal A_2+B_3 polymerization are flexible and smooth in transparent yellow appearance. The mechanical properties of as-prepared polyimide films are listed in Table 3. The hyperbranched polyimide film by non-ideal A_2+B_3 polymerization (N-3), whose precursor has the highest inherent viscosity, showed the highest tensile strength. This suggests the existence of the strongest chain-entanglement in this film. Although the chain extension reaction among the oligomers affoded a self-standing film, the tensile strength of the film by ideal A_2+B_3 polymerization was the lowest one. This indicates that the chain extension reaction is limited in enhancing the mechanical properties. As-prepared films showed a elongation at break around 1.0%. Their tensile modulus are above 2.3 GPa, which is close to their linear analogues.

Table 3. Mechanical properties of hyperbranched polyimide films by A_2+B_3 polymerization.

properties	AEPI				
	I-3 [a]	N-3 [b]	N-4	N-5	N-6
tensile strength (MPa) [c]	18 ± 2	29 ± 1	27 ± 2	21 ± 4	18 ± 2
elongation at break (%)	0.8 ± 0.1	0.9 ± 0.2	1.1 ± 0.1	0.9 ± 0.1	0.8 ± 0.1
tensile modulus (GPa) [d]	2.3	3.2	2.6	2.3	2.3

[a] I, ideal A_2+B_3 polymerization; 3, entry code in table 1.

[b] N, non-ideal A_2+B_3 polymerization; 3, entry code in table 1.

[c] Tensile test was carried out at room temperature with a film specimen at a dimension of 40 × 5 × 0.02 mm. The tensile rate is 4 mm/min.

[d] Calculated from dividing the average tensile strength by the average elongation at break

Conclusions

The hyperbranched polyimides by ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization, and AB_2 self-polymerization have different topological structure one another, although they have the same repeating unit. The polyimides by ideal A_2+B_3 polymerization have a three-dimensional network (crosslinking) structure, and that by AB_2 self-polymerization have a compact highly branching architecture without chain-entanglement. However the polyimides by non-ideal A_2+B_3 polymerization have a low branching density topology with apparent chain-entanglement, although they are hyperbranched polymers with a *DB* above 0.5. Due to their difference in topological structure, hyperbranched polyimides by ideal A_2+B_3 polymerization, non-ideal A_2+B_3 polymerization and AB_2 self-polymerization methods show apparent difference in many physical properties, such as inherent viscosity, intrinsic viscosity, glass transition temperature, and film formation behavior etc. The hyperbranched polymers by the non-ideal A_2+B_3 polymerization are suitable for smooth, flexible and self-standing film preparation, which provides useful information for hyperbranched polymers toward self-standing materials.

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