

Synthesis and properties of hyperbranched polyimides with various comonomer ratios

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Polymers with highly branched, globular macromolecular structures have attracted increasing attention in recent years because they are expected to have unique properties when compared to their linear analogues. Hyperbranched polyimides (HBPIs) possess the combination property of hyperbranched polymers and polyimides, with higher glass transition temperatures and superior solubility. Hyperbranched polyimides can be prepared from different types of monomers, such as AB_2 , A_2+B_3 , and $A_2+B'B_2$ monomers.^[1-16] But the methods of AB_2 monomers and A_2+B_3 monomers are unpractical to prepare hyperbranched polyimides in a large scale because of the requirement of special AB_2 monomers for the former methods, and the stringent polymerization conditions for the latter to avoid gel formation, for example, low monomer concentrations, strictly controlled slow addition rates, and molar ratios of monomers.

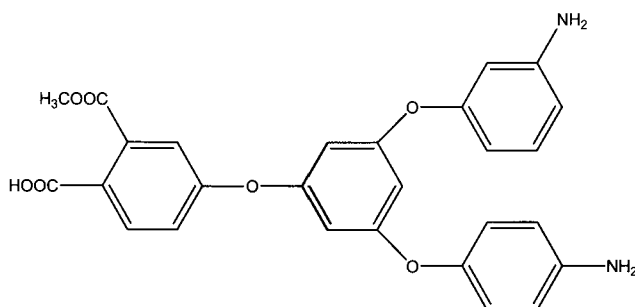


Fig. 1 AB_2 -type monomer for hyperbranched polyimide^[5-6]

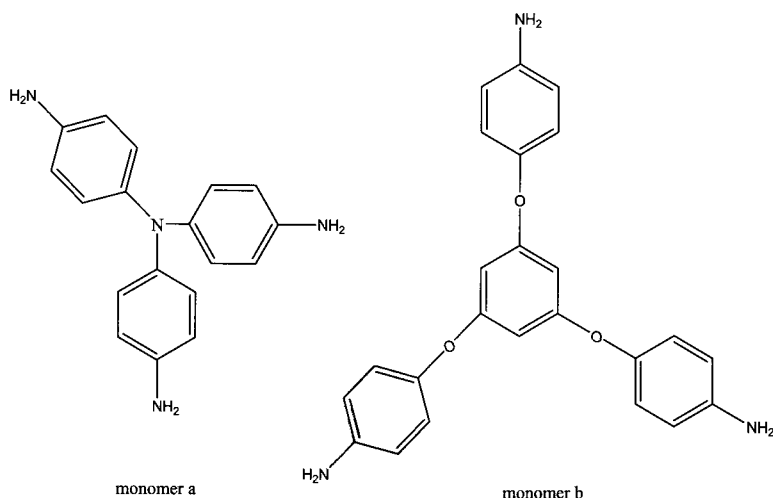


Fig. 2 B_3 -type monomer for hyperbranched polyimides^[8-10]

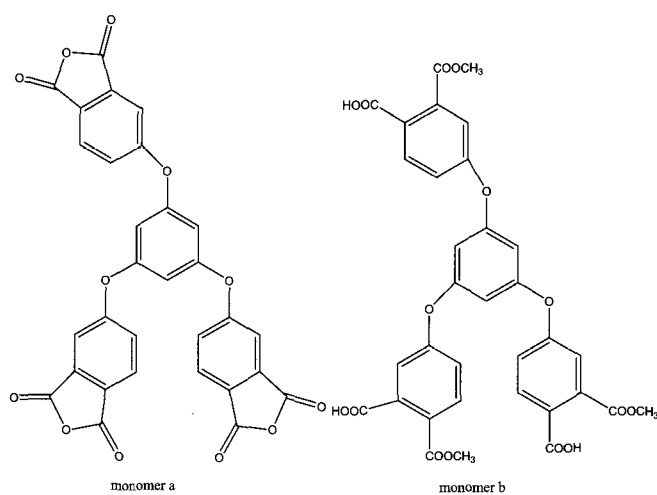


Fig. 3 B₃-type monomer for hyperbranched polyimides^[16]

Flory's theory of gelation formation in the polymerization of A₂+B₃ monomers is based on the following assumptions: (1) the equal reactivity of all A groups, as well as B groups, in both monomers and the growing polymers; (2) the exclusive reactivity of A groups with B groups; and (3) no intramolecular cyclization and chain termination in the process.^[17] If one of the assumptions is disobeyed, that is, the discriminably different reactivity of the functional groups, the theory will be invalid, and so the relaxation of such strictures on the polymerization process have been sought. So, A₂+B'B₂ approach have drawn much attention because it can avoid gelation during the preparation of hyperbranched polyimides to use monomers containing the same functional groups but with different reactivities.^[18-23]

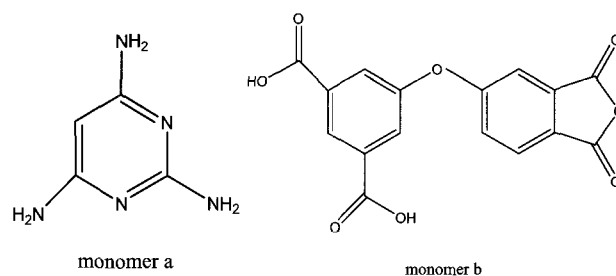


Fig. 4 B'B₂-type monomer for hyperbranched polyimides

In our work, we adopted 2,4,6-triaminopyrimidine(TAP) as a B'B₂ monomer for the preparation of hyperbranched polyimides, aiming to make the polymerization process facile and shed light on the relationships between the gel formation and the different reactivities of functional groups. But in contrast to the linear analogues, HBPIs exhibit poor mechanical properties and heat resisting property due to a considerably lower number of physical entanglements between the macromolecules. In accord with this fact, we tried to improve heat resisting property of HBPIs by incorporation of difunctional B₂ comonomer into the polymer structure. As such B₂ comonomer we used difunctional 4,4'-oxydianiline(ODA). This approach could be described as A₂+ B'B₂+B₃ or more simply A₂+B₃+B₂ copolymerization (if we suppose the same B functional group reactivity).

1. Synthesis of BPDA-TAP hyperbranched polyimides

A typical polymerization procedure follows. Measurable BPDA and TAP were mixed in NMP under stirring and argon at ambient temperature. About 24h later, measurable m-xylene were added, and the solution was heated at 180°C to remove water evolved for 8 h. After cooling to ambient temperature, the

solution was precipitated in ethanol. The powdery products were obtained by filtration followed by drying at 200°C under vacuum for 24 h.

Table1. the addition for synthesis of BPDA-TAP hyperbranched polyimide

	TAP/g	BPDA/g	NMP/g
PI-1	2.5	5.88	49
PI-2	2.5	8.82	66
PI-3	2.5	11.76	84

Results and discussion

In our work, three molar ratios of BPDA to TAP ---2:1,1:1, and 3:2---were adopted to prepare anhydride, amino, and anhydride- and amino-terminated hyperbranched polymers respectively. The typical FTIR spectra of the products, as shown in Figure 5, reflect the full imidization of poly(amic acid)s as demonstrated by no existence of the characteristic peaks of poly(amic acid) around 1660 cm^{-1} . Through all the polymerization processes, no precipitation or gel appeared.

The hyperbranched polyimides exhibited good solubility in NMP and DMSO. It's performance was shown in table 2. The glass-transition temperature(T_g) of the products decreased with DB increasing, which was attributed to the increased free volume and mobility of the molecules because the end-group contents of hyperbranched polymers increased with the molecular weights. The different end group type may also contribute to the changes in T_g .

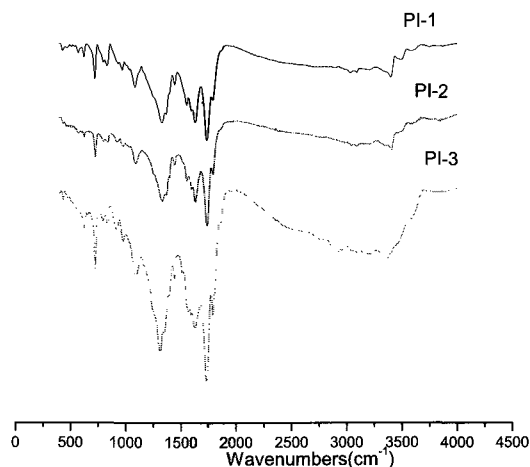


Fig.5 FTIR spectra of PI-1, PI-2 and PI-3.

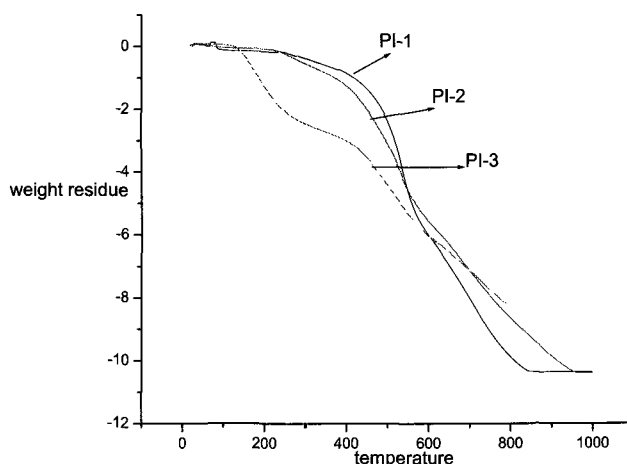


Fig. 6 Thermogravimetric curves of hyperbranched polyimides in nitrogen

Table 2. Properties of the Obtained Hyperbranched Polyimides

Sample	TAP:BPDA	DB(%)	Mn	Tg(°C)	10% Weight Loss(°C)
PI-1	1:1	25	6,900	222	420
PI-2	2:3	54	9,900	210	383
PI-3	1:2	71	13,200	190	188

2. Synthesis of amine-terminated BPDA-TAP-ODA hyperbranched polyimides

A series of hyperbranched polyimides were prepared with different molar ratios between TAP and ODA. The molar ratio between anhydride and the total amount of amines was kept 1:1. Mensurable ODA and TAP were mixed in NMP under stirring and argon at ambient temperature for 0.5 h. Then ODPA was added to this solution. About 24h later, mensurable m-xylene were added, and the solution was heated at 180°C to remove water evolved for 8 h. After cooling to ambient temperature, the solution was precipitated in ethanol. The powdery products were obtained by filtration followed by drying at 200°C under vacuum for 24 h.

Table 3. The addition for synthesis of amine-terminated BPDA-TAP-ODA hyperbranched polyimides

	TAP/g	ODA/g	BPDA/g	NMP/g
PI-11	0.625	4.5	5.88	65
PI-12	1.25	3.0	5.88	60
PI-13	1.875	1.5	5.88	55

3. Synthesis of anhydride-terminated BPDA-TAP-ODA hyperbranched polyimides

The above procedure was followed except that the molar ratio anhydride/amines was kept 2:1.

Table 4. The addition for synthesis of anhydride-terminated BPDA-TAP-ODA hyperbranched polyimides

	TAP/g	ODA/g	BPDA/g	NMP/g
PI-21	0.625	4.5	11.76	99
PI-22	1.25	3.0	11.76	94
PI-23	1.875	1.5	11.76	89

Results and discussion

The performance of BPDA-TAP-ODA hyperbranched polyimides was shown in table 5. They have very good thermal stability, which increased with higher content of ODA comonomer for amine-terminated BPDA-TAP-ODA hyperbranched polyimides and decreased for anhydride-terminated BPDA-TAP-ODA hyperbranched polyimides. Amine-terminated hyperbranched polyimides generally exhibited higher thermal stability than anhydride-terminated hyperbranched polyimides. And the BPDA-TAP-ODA hyperbranched polyimides exhibited higher thermal stability than BPDA-TAP hyperbranched polyimides.

Table 5. Properties of the Obtained Hyperbranched Polyimides

	PI-11	PI-12	PI-13	PI-21	PI-22	PI-23
Tg(°C)	255	238	227	218	208	199
10% Weight Loss(°C)	595	530	412	524	487	398

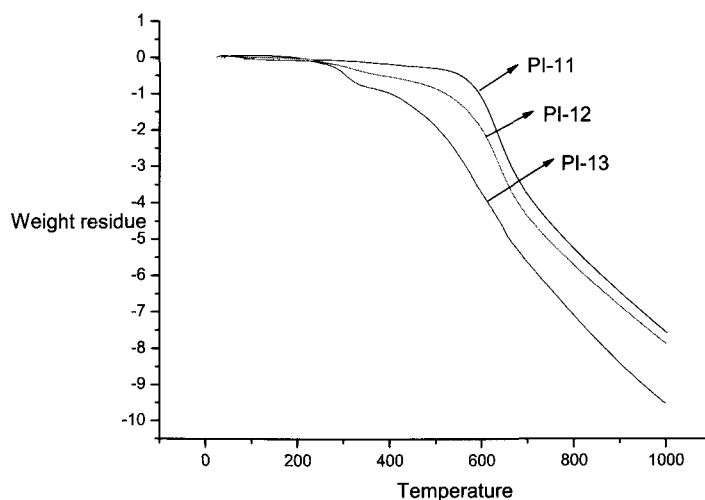


Fig.7 Thermogravimetric curves of amine-terminated BPDA-TAP-ODA hyperbranched polyimides

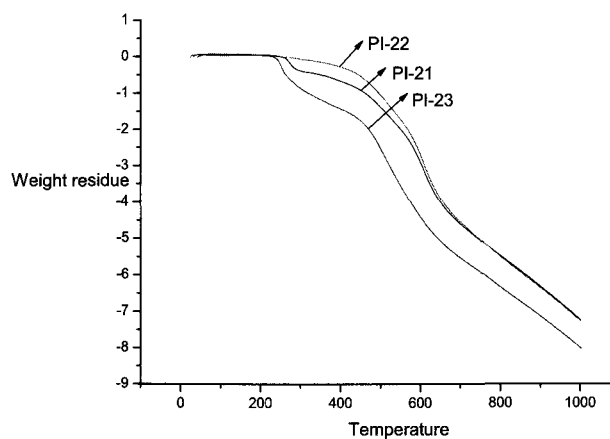


Fig. 8 Thermogravimetric curves of anhydride-terminated BPDA-TAP-ODA hyperbranched polyimides

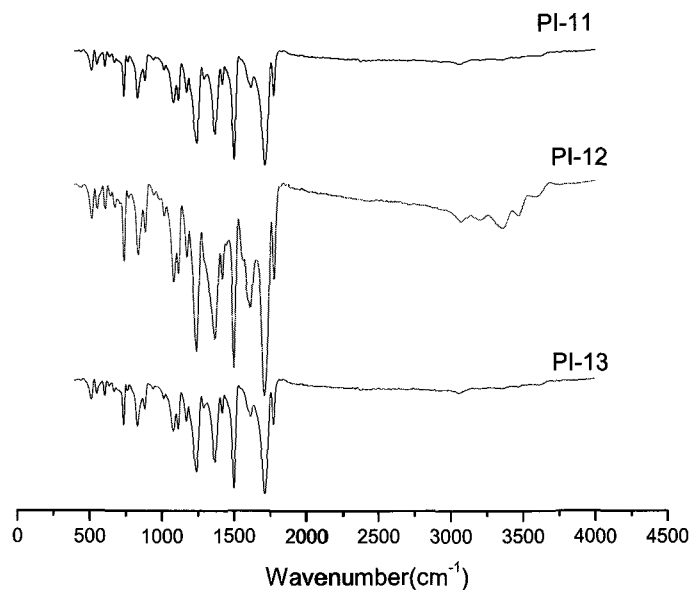


Fig. 9 FTIR spectra of PI-11, PI-12 and PI-13.

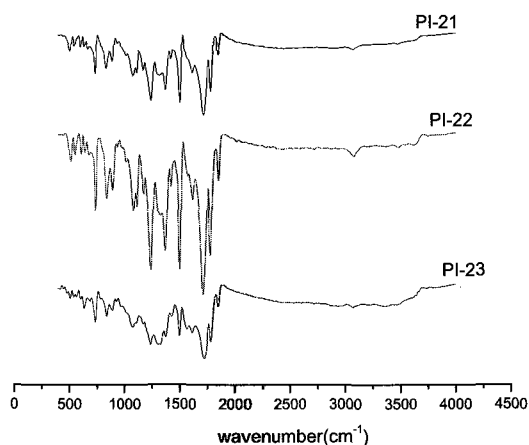


Fig. 10 FTIR spectra of PI-21, PI-22 and PI-23.

Hyperbranched polyimides is a new research field, with the emerging of new synthetic methods, optimization of the testing means and more functional ways, it will be widely used in aerospace, microelectronics, coatings, membranes, molding compounds and laminated composite material through the modification of the end group, crosslinking, copolymerization and blending.

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(More Refs see p181)