Notes

Eliminating Variations in Elemental Composition in Studies on the Physical Properties of Linear to Hyperbranched Etherimide Copolymers

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Introduction

It has long been known that molecular architecture can be used as a tool to modify the rheological and material properties of polymeric materials. Most of the work in this area has focused on one of two branching extremes: either molecules with relatively small branching density (e.g., LDPE, HDPE, LLDPE) or highly branched polymers (dendrimers and hyperbranched polymers). However, systematic studies on the sole effect of branching, from highly branched to linear, on material properties are lacking in the literature. In our previous publications we reported on the syntheses and properties study of randomly branched poly(etherimide) (PEI) AB/AB_2 copolymers with various degrees of branching.[1,2] By varying the ratio of AB (linear) and AB_2 (branched) monomers, PEI AB/AB_2 copolymers of nearly constant weight-average molecular weight, M_w, ranging in molecular structure from fully hyperbranched (HBP) to linear were synthesized. However, by increasing the ratio of AB to AB_2 monomers, in addition to decreasing the branching density, the number of unreacted B end groups that affect the elemental composition decrease as well, making it difficult to decouple the two effects on material and rheological properties.

It has been shown in both dendrimers and hyperbranched polymers that end group composition and concentration can have a significant effect on *intra*molecular and *inter*molecular interactions, which are manifested in solubility, thermal, and rheological properties.[3,4] To isolate the effects of branching on properties, we synthesized appropriate terminating groups (A′) and devised a synthetic scheme, $((aAB_2 + bAB) + aA')$, that maintains constant elemental composition as a function of branching (see Scheme 1). In this paper we present the synthesis and properties study of the PEI AB_2/AB/A′ copolymers with constant elemental composition and branching ranging from hyperbranched to linear. Comparisons with the previously characterized PEI AB/AB_2 copolymer series are presented as well.

Synthetic Procedures

Typical Synthetic Procedure ($\mathbf{x}_{AB} = 0.40$): One Step Solid Addition of A′. For higher amounts of AB_2 ($x_{AB} \leq 0.67$) the polycondensation was performed by by quickly immersing a polymerization vessel containing monomers **1** (4.70 g, 9.38 mmol) and **2** (2.32 g, 6.25 mmol), a catalytic amount of cesium fluoride (35 mg, 2 mol %), and 15 mL of DMAc into a preheated 150 °C silicon oil bath. Upon stirring under a nitrogen atmosphere, the solid reagents dissolved quickly, forming a slightly yellow solution. Within about 30 s after complete dissolution, the reaction mixture began bubbling vigorously, and TBDMS fluoride evolution was observed. After the mixture was mechanically stirred for the designated time (10 min following dissolution of solids), **3** (2.70 g, 9.38 mmol) was added as a solid in one portion, and the sides of the vessel were rinsed with an additional 7 mL of DMAc via a syringe (total, 22 mL of DMAc). The mixture was then mechanically stirred for an additional 10 min (20 min total) and then removed from heat. While still hot, the viscous reddish solution was poured into a blender with 500 mL of absolute ethanol, followed by rapid blending. The polymer quickly precipitated, leaving a white slurry. The product was then filtered on a 2 L coarse, glass sintered funnel and washed with an additional 500 mL of ethanol and allowed to air-dry. The polymer was then dried overnight in a high-vacuum oven at 100 °C to yield 5.451 g of an off-white powder (92% isolated yield). Thermal analysis showed the material to contain 3−4 wt % volatiles (solvent or water). ^1H NMR (d_6-DMF) showed that the termination step was 95+% complete as evidenced by the absence of residual resonances from TBDMS groups, and only aromatic proton resonances were observed which were consistent with the assigned structure.[5]

Typical Synthetic Procedure ($\mathbf{x}_{AB} = 0.67$): One Step Solution Addition of A′. For lower amounts of AB_2 ($x_{AB} \geq 0.67$) the polycondensation was performed by quickly immersing a polymerization vessel containing monomers **1** (1.567 g, 3.125 mmol) and **2** (6.965 g, 18.75 mmol), a catalytic amount of cesium fluoride (35 mg, 2 mol %), and 15 mL of DMAc into a preheated 150 °C silicon oil bath. Upon stirring under a nitrogen atmosphere, the solid reagents dissolved quickly, forming a slightly yellow solution. Within about 30 s after complete dissolution, the reaction mixture began bubbling vigorously, and TBDMS fluoride evolution was observed. After the mixture was mechanically stirred for the designated time (10 min following dissolution of solids), **3** (0.754 g, 3.125 mmol), which was previously dissolved in 5 mL of DMAc, was added in one portion via a syringe, and the syringe and sides of the vessel were rinsed with an additional 2 mL of DMAc via the same syringe (total, 22 mL of DMAc). The mixture was then mechanically stirred for an additional 10 min (20 min total) and then removed from heat. While still hot, the viscous reddish solution was poured into a blender with 500 mL of absolute ethanol, followed by rapid blending. The polymer quickly precipitated, leaving a white slurry. The product was then filtered on a 2 L coarse, glass sintered funnel and washed with an additional 500 mL of ethanol and allowed to air-dry. The polymer was then dried overnight in a high-vacuum oven at 100 °C to yield 5.619 g of an off-white powder (95% isolated yield). Thermal analysis showed the material to contain 3−4

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Scheme 1. Reaction Scheme for Constant Molecular Compositon HBP with DB = 0−1: (1) 1 + 2, DMAc, 150 °C, cat. CsF, 5 min; (2) 3, DMAc, 150 °C, 10 min

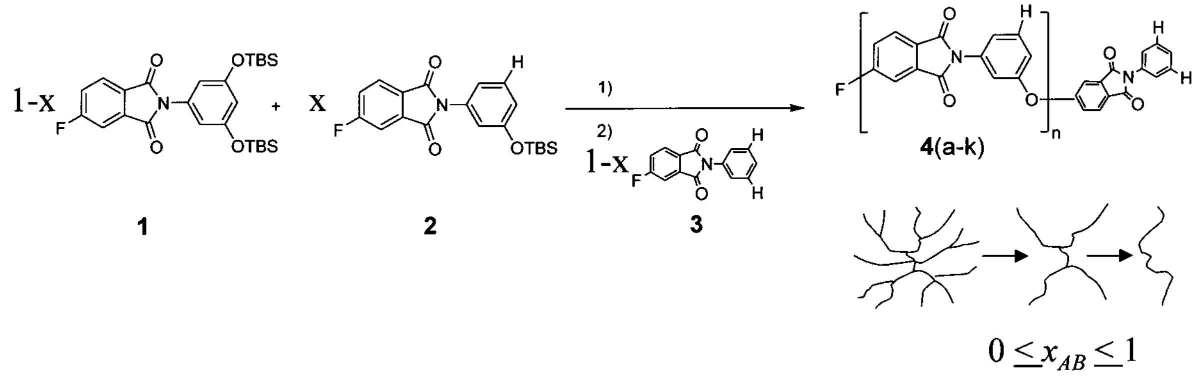

Table 1. Molecular Weight and Physical Properties of AB/AB$_2$/A′ PEI Copolymers

AB/AB$_2$/A′ PEI copolymers[3]	x_{AB}	M_n[a]	M_w[a]	PDI[a]	T_g (°C)	10 wt % loss (°C)	[η] (dL/g)[a]	a[a]	yield[b]	film formation[e]
4a[c]	0.00	37 000	56 800	1.54	219	431	0.108	0.43	89	−
4b[c]	0.40	38 300	68 700	1.79	205	485	0.117	0.44	95	−
4c[c]	0.67	37 300	70 370	1.89	201	456	0.135	0.47	92	−
4d[d]	0.86	38 730	118 100	3.05	212	478	0.212	0.50	95	−
4e[d]	0.89	29 000	68 100	2.35	200	457	0.175	0.55	95	c
4f[d]	0.90	33 100	92 600	2.80	200	441	0.207	0.54	99	c
4g[d]	0.92	27 900	139 700	5.00	213	475	0.264	0.52	93	c, p
4h[d]	0.93	25 900	135 000	5.22	213	456	0.280	0.53	96	c, p
4i[d]	0.95	29 500	138 700	4.71	216	451	0.29	0.54	95	c, p
4j[d]	0.96	19 900	75 100	3.78	214	466	0.334	0.63	90	c, p, d
4k[d]	1.00	27 200	59 300	2.20	214	490	0.46	0.81	88	c, p, d

[a] Determined with TriSEC method in NMP (0.05 M LiBr) at 65 °C. [b] Yield determined assuming complete conversion of A groups. [c] Synthesized using single step solid addition of A′.[5] [d] Synthesized using single step solution addition of A′.[5] [e] Films cast from 10 wt % DMAc solution at 150 °C for 30 min (−) discontinuous film, (c) continuous film, (p) film intact when peeled from glass substrate, and (d) film can be creased in half without breaking.

wt % volatiles (solvent or water). ^{1}H NMR (d_6-DMF) showed that the termination step was 95+% complete as evidenced by the absence of residual resonances from TBDMS groups, and only aromatic proton resonances were observed which is consistent with the assigned structure.[1,5]

Results

The PEI AB/AB$_2$/A′ copolymers of constant elemental composition were synthesized in a one-pot double-addition method, producing materials that ranged in molecular architecture from hyperbranched ($x_{AB} = 0$) to linear ($x_{AB} = 1$). ^{1}H NMR and CHN analysis showed that the termination step of adding A′ monomer **3** resulted in quantitative conversion of the remaining B (TBS) groups which was necessary in order to maintain constant elemental composition.[5] Further examination of the NMR spectra showed a nearly identical proton spectra for each copolymer in the series, indicating constant elemental composition. As presented in Table 1, the molecular weight analysis shows no significant trends between the M_w and x_{AB}; however, the number-average molecular weight, M_n, generally decreases with x_{AB}. As a result, the polydispersity index increases, contrary to predictions put forth by Flory.[6] Thermal analysis indicates no observable trend in the decomposition temperature or in the glass transition temperature with x_{AB}. The glass transition temperature behavior is inconsistent with our previous results,[2] which showed an increase with x_{AB}.

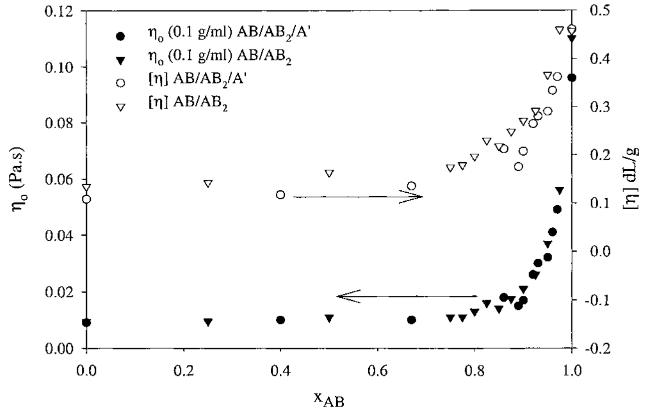

Figure 1. Plots of intrinsic viscosity ([η]) and zero shear solution viscosity (η_0) vs starting molar fraction of AB monomer (x_{AB}) for AB/AB$_2$ and AB/AB$_2$/A′ PEI copolymers.

Figure 1 shows the zero-shear rate viscosity, η_0, dependency on x_{AB} for dilute solutions of both the PEI AB/AB$_2$/A′ and PEI AB/AB$_2$ copolymer series. Within experimental error, the η_0 dependency on x_{AB} for both copolymer series is the same. Initially, negligible changes in η_0 are observed up to the critical composition at $x_{AB} \sim 0.80$, followed by a sharp increase in η_0 at higher fractions of AB monomer. Since rheological properties usually correlate with M_w, which for both PEI copolymer series show no trend with x_{AB}, the observed changes in η_0 are most likely due to changes in molecular architecture at $x_{AB} \sim 0.80$. The intrinsic viscosity [η] also shows the same dependence on x_{AB} as η_0, further indicating the change in molecular architecture at the critical composition of linear segments. From changes in the Mark Houwink coefficient, a, it can be inferred that the branching density decreases for $x_{AB} > 0.8$ (see Table 1), further indicating a change in molecular architecture.[2,7,8] Therefore, up to $x_{AB} \sim 0.80$ copolymer structures are highly branched and rigid, similar to HBP's ($x_{AB} = 0$), followed by increasingly more linear

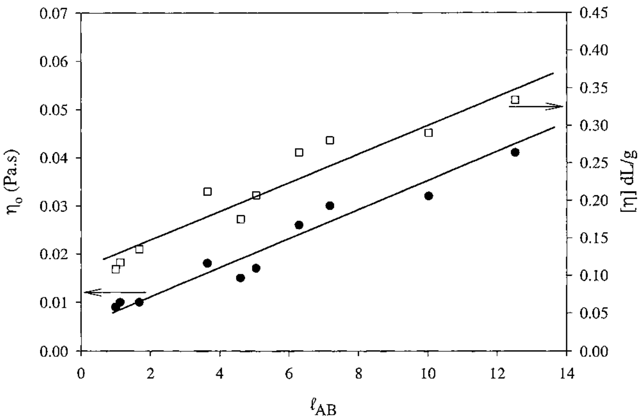

Figure 2. Plots of intrinsic viscosity ($[\eta]$) and solution viscosity (η_0) vs average linear distance between branches (ℓ_{AB}) for AB/AB$_2$/A′ PEI copolymers.

structures at higher fractions of linear segments. However, in the PEI AB/AB$_2$ series, both molecular architecture and elemental composition change with x_{AB}, making it difficult to decouple the two effects. Since the PEI AB/AB$_2$/A′ copolymers have a constant elemental composition with x_{AB}, it can be inferred that the observed rheological trends can be attributed to changes in molecular architecture alone.

In our previous publication we showed that for PEI AB/AB$_2$ copolymers both the intrinsic viscosity and the zero shear viscosity in dilute solutions exhibit a linear correlation with the distance between branches, ℓ_{AB},[2] as calculated by Frey and Hölter,[9] where r is defined as

$$\ell_{AB} = \frac{1}{2}\frac{r^2 + 2r + 2}{r + 1} \qquad (1)$$

$x_{AB}/(1 - x_{AB})$. The plots of $[\eta]$ and η_0 of PEI AB/AB$_2$/A′ copolymer vs ℓ_{AB}, presented in Figure 2, clearly indicate that the same linear dependence is observed. Therefore, the distance between branch points appears to be the dominant architectural parameter that affects the rheological properties of dilute solutions of branched polymers.

For the previous studies with PEI AB/AB$_2$ copolymers, qualitative and quantitative improvements in mechanical properties of films with x_{AB} were observed for copolymers with $x_{AB} \geq 0.90$.[2] This same trend was observed with the PEI AB/AB$_2$/A′ (see Table 1). This most likely reflects higher degrees of *inter*molecular entanglement as the molecular structure becomes more open and linear.

Conclusion

Herein we presented the synthesis and the physical properties study of poly(etherimide) AB/AB$_2$/A′ copolymer series. By varying the ratio of AB and AB$_2$ monomers, and terminating with the appropriate amount of A′ monomer, copolymers were synthesized with constant elemental composition and geometries ranging from hyperbranched ($x_{AB} = 0$) to linear ($x_{AB} = 1$). The differences in molecular architecture due to changes in monomer ratios were shown to affect the properties of the copolymers. The properties of PEI AB/AB$_2$/A′ copolymers exhibited the same dependence on x_{AB} as PEI AB/AB$_2$ copolymers, indicating that variations in elemental composition have a negligible effect on the observed rheological property trends with x_{AB}. In particular, the molecular architecture appears to go through a transition from a highly branched, dense structure to a rapidily increasing open structure once at or above the same critical composition of $x_{AB} \sim 0.80$. Since the chemical composition of PEI AB/AB$_2$/A′ copolymers is constant with x_{AB}, the observed property trends can be attributed to the changes in molecular structure alone. From the trends observed with the PEI AB/AB$_2$/A′ and PEI AB/AB$_2$ copolymer series, one concludes that the functionality and concentration of the end groups have no effect on structural changes and therefore the architecture-dependent property trends with x_{AB}. However, the elemental composition, size, and structure of end groups can have significant effects on properties such as solubility and glass transition temperature as well as the magnitude of the rheological and mechanical properties.[10]

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Supporting Information Available: Experimental Section, table of elemental composition of AB/AB$_2$/A′ PEI copolymer, and ^{1}H NMR spectra of AB/AB$_2$ and AB/AB$_2$/A′ copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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