

Synthesis and Properties of Hyperbranched Aromatic Polyamides from A₂ and B₃ Monomers

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ABSTRACT

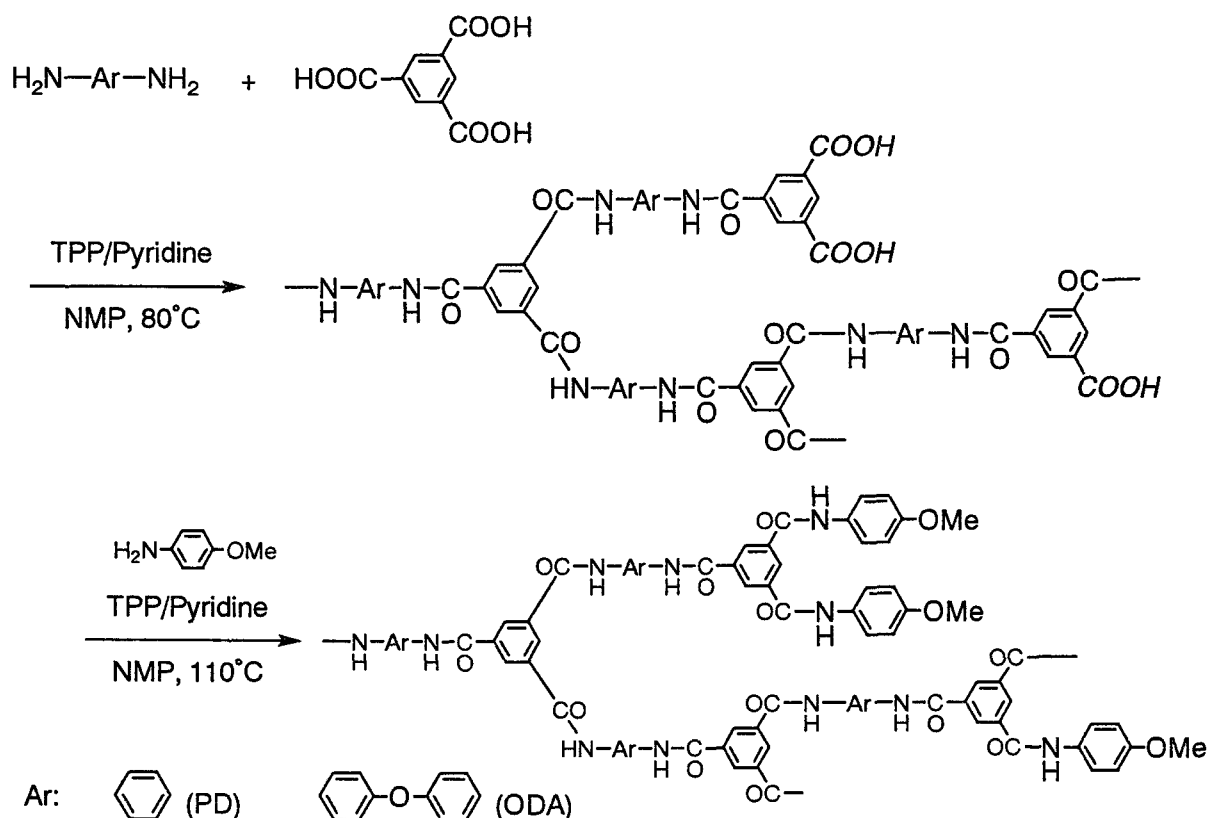
Hyperbranched aromatic polyamides were prepared by direct polycondensation of aromatic diamines (A₂) and trimesic acid (B₃) as starting materials. Gelation during the polymerization could be avoided after careful consideration of reaction conditions. Powdery polymers, soluble in aprotic polar solvents, were isolated in good yield. Spectroscopic measurements indicated the formation of the branched structure. The ratio of repeating units were determined and compared with the ratio calculated statistically. Yellow transparent films were prepared by casting the polymer solution onto glass plates and subsequent heating under vacuum. Young's moduli of ca. 2 Gpa were obtained by the tensile tests of the films, which suggests that the hyperbranched polyamides inherit good mechanical property of Aramids.

Introduction

Aromatic polyamides, Aramids, are one of the most important high performance polymers due to their excellent thermal and mechanical properties. All Aramids are unfortunately insoluble in organic solvents after the isolation from production process. It is well known that the introduction of flexible segments, bulky substituents and branched units improves the processability of the resulting polymers. Hyperbranched polymers composed of rigid aromatic segments might have both good thermal and mechanical properties and processability. In order to prepare hyperbranched polymers, it is necessary to design and prepare AB_x type monomers in advance. On the other hand, many difunctional compounds are commercially available as A₂ type monomers and some trifunctional compounds (B₃) used as branching or crosslinking agents are also available. In this paper, we report the direct polymerization of aromatic diamines (A₂) and trimesic acid (B₃) as a novel route to produce hyperbranched aromatic polyamides.

Experiments

A typical experiment is as follows. A three-necked flask was charged with 1.08 g (10 mmol) of PD, 2.10 g (10 mmol) of TMA, 7.5 mL of pyridine and 80 mL of *N*-methylpyrrolidinone (NMP). Triphenyl phosphite (7.82 mL, 30 mmol) was added to the solution after the monomers were dissolved completely. The mixture was heated at 80°C for 3 h and then, poured into 500 mL of methanol containing 10 mL of 12N HCl aq. The precipitated product was collected by filtration and purified by reprecipitation from NMP solution into methanol. The product was washed with hot methanol and



dried in vacuo at 100°C for 12 h.

End-capping reaction of unreacted carboxylic acid groups with *p*-methoxyaniline was carried out in the presence of triphenyl phosphite and pyridine at 110°C for 3 h.

Results and Discussion

Equimolar amounts of diamines, *p*-phenylene diamine (PD) or 4,4'-oxyphenylene diamine (ODA) and trimesic acid (TMA) were allowed to polymerize in the presence of triphenylphosphite and pyridine as condensation agents, as shown in Table 1. As predicted statistically, gelation was observed during the polymerization. When the polymerization was carried out in diluted solution at 80°C , powderly polymers were isolated after precipitation in methanol. The amount of triphenyl phosphite in the absence/presence of LiCl affected the polymerization. Polymers having the inher-

Table1. Direct Polycondensation of Diamines and Trimesic Acid in the Presence of Condensation Agents^a

Code	NMP (ml)	TPP (mmol)	Pyridine (ml)	LiCl (g)	Yield (%)	$\eta_{\text{inh}}^{\text{b}}$ (dL/g)
PD1	50	20	7.5	1.0	gel	
PD2	80	20	7.5	1.0	86	0.48
PD3	80	30	7.5	0	92	0.78
ODA1	80	20	7.5	1.0	gel	
ODA2	100	20	5.0	1.0	86	3.27
ODA3	100	20	5.0	0.6	87	1.14
ODA4	100	20	5.0	0.4	84	0.86

^a The polymerization was carried out with an equimolar amount of an diamines(10mmol) and TMA(10mmol) in the presence of triphenyl phosphite and pyridine at 80°C for 3h.

^b Measured at a concentration of 0.5g/dL in DMF containing LiBr(0.01mol/L) at 30°C .

ent viscosity around 0.8 dL/g were prepared in high yield after optimization of reaction conditions. The resulting polymers are soluble in organic solvents, similar to hyperbranched polymers prepared by AB₂ type monomers. It is interesting to note that the inherent viscosity of resulting polymers is relatively high, indicating partially crosslinked structure. Yellow transparent films could be prepared by casting the polymer solution onto glass plates and subsequent heating under vacuum. GPC measurements for the polymers end-capped with p-methoxyaniline suggested the molecular weight over 10⁵. It was difficult to determine accurate molecular weight due to aggregation in GPC eluent (DMF containing 0.01mol/L of LiBr).

The structure of resulting polymers was confirmed by spectroscopic measurements, such as IR, ¹H and ¹³C NMR. A broad absorption band from 3400 to 3200 cm⁻¹ and strong carbonyl absorption at 1659 and 1713 cm⁻¹ were observed in IR spectrum of the polymer prepared from PD and TMA. These data suggested the formation of amide bond and the presence of carboxylic acid groups in the polymer. The absorption at 1713 cm⁻¹ disappeared after the end-capping reaction. In ¹H NMR, a broad peak at 12-14 ppm attributed to carboxylic acid protons was observed for both PD-TMA and ODA-TMA polymers. Amide protons and aromatic protons derived from TMA were also observed at 10.6 and 8.6-8.8 ppm, respectively. Integration ratio of aromatic protons suggested that the diamine components are incorporated slightly more than TMA ones, although the equimolar amount of monomers were allowed to be polymerized. ¹³C NMR spectra of the resulting polymers are shown in Figure 1. Two peaks observed from 165 to 167 ppm and three peaks from 163 to 165 ppm were assigned to carbons derived from carboxylic acid groups and amide groups, respectively. The possible repeating units in resulting poly-

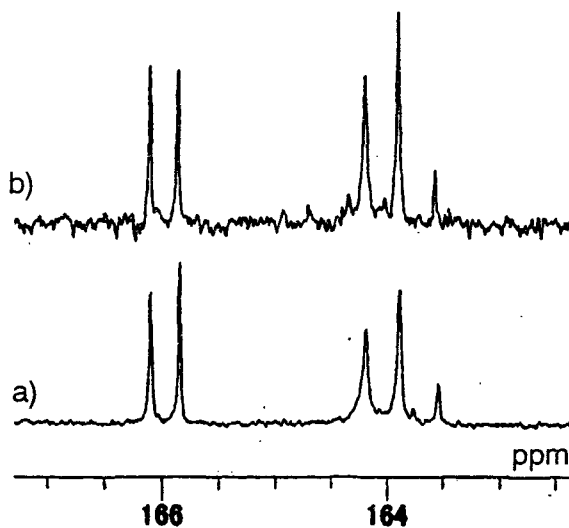


Figure 1 ¹³C NMR spectra of hyperbranched aromatic polyamides: a) PD-TMA; b) ODA-TMA.

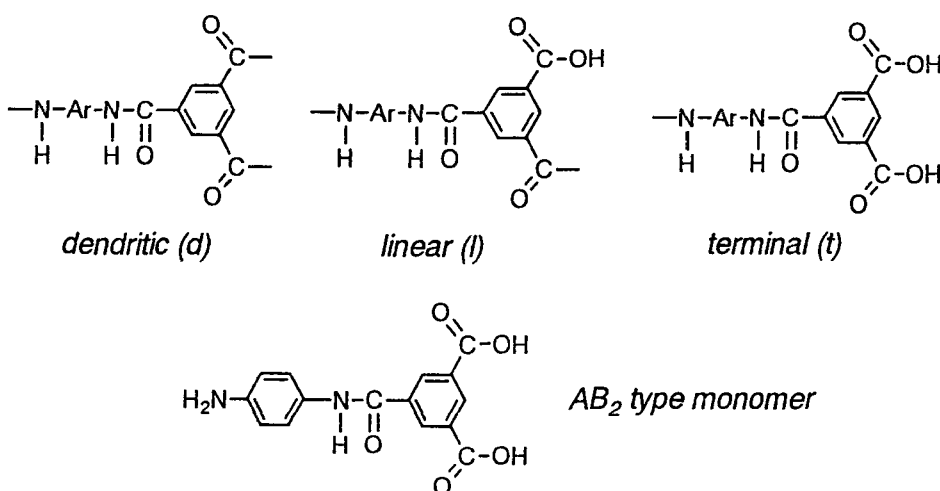


Figure 2 The structure of possible repeating units and AB₂ type monomer.

mers are described in Figure 2. According to the comparison of the spectrum for the AB₂ monomer, the peaks at 161.1 and 163.9 ppm are attributed to the linear units. The integration ratio of the peaks allows us to estimate the ratio of repeating units, as shown in Table 2. It is known that hyperbranched polymers prepared from AB₂ monomers are statistically composed of 50% of linear units, 25% of dendritic and terminal units. Both PD-TMA and ODA-TMA contained dendritic units more than 30%, which indicates that the resulting polymer contains a large number of trisubstituted trimesic acid units. The trisubstituted units might act as crosslinking points and increase the inherent viscosity of resulting polymers.

The resulting polymers were thermally stable up to 300°C and the temperature for 10% weight loss was 470°C for PD-TMA and 490°C for ODA-TMA. Initial decomposition temperatures for both PD-TMA and ODA-TMA were risen 30 °C by the end-capping reaction. Dynamic mechanical analysis (DMA) was carried out to determine glass transition temperature (T_g), as shown in Figure 3. The T_g s for PD-TMA and ODA-TMA determined by the initial decrease of storage modulus were 260°C and 240°C, respectively. It is interesting to note that the decrease of the storage modulus after the glass transition was fairly small, which might suggest the crosslinking reaction.

Tensile tests for the cast films prepared from resulting polymers were carried out in order to investigate the mechanical properties. Stress-strain curves for PD-TMA and ODA-TMA are described in Figure 4. The Young's modulus determined by initial slope of the curves were about 2 GPa. The high modulus suggests that the resulting polymers have good mechanical property originated by rigid aromatic amide structure. The stress at breaking point was about 95 MPa and independent on diamine structure. On the other hand, the elongation at break for ODA-TMA film was larger than that for PD-TMA film. It is obvious that the introduction of ether linkage made the resulting film more flexible.

Table 2 The ratio of repeating units in hyperbranched aromatic polyamides^{a)}

Monomer	d (%)	t (%)	l (%)
PD-TMA	31	19	50
ODA-TMA	31	18	51
Statistical ^{b)}	25	25	50

^{a)} The ratio was calculated by the integration of ¹³C NMR spectra. ^{b)} The ratio calculated statistically for the hyperbranched polymer prepared from AB₂ monomers.

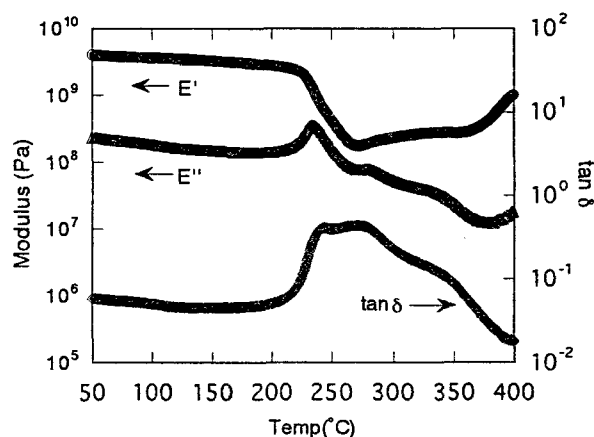


Figure 3 DMA curves of the ODA-TMA film with a heating rate of 3°C/min.

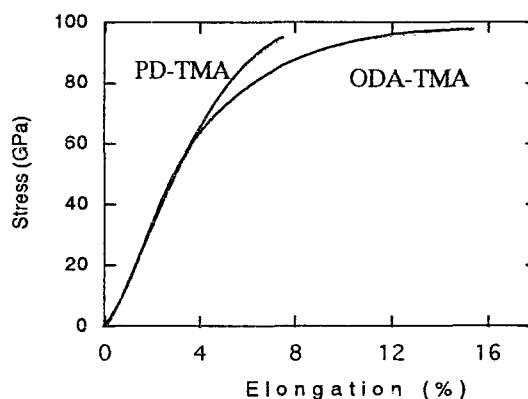


Figure 4 Stress-strain curves of PD-TMA and ODA-TMA films