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Synthesis and properties of poly(amide-imide)s with different microstructures based on trimellitimide and 4,4'-diphenyl ether

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Summary

Poly(amide-imide)s(PAIs) with different microstructures were prepared based on trimellitimide and 4,4'-diphenylether with varying the reaction conditions. The microstructures of PAIs were examined by 50OMHz ^{1}H-NMR spectroscopy. The head-to tail (HT-) PAI showed a sharp peak in WAXD curve, a large shift at around 1670 cm^{-1} for –C=O stretching in FT-IR spectra, and poor solubility in organic solvents, high density, Tg, tensile strength and modulus compared to head-to-head (HH-) PAI and copolymers of HT and HH. These results might be due to the higher packing tendency of the HT PAI than HH PAI or copolymers.

Introduction

One of the high performance polymers is PAIs which have amide and imide groups in the polymer backbone (1). Generally, PAI is prepared by low-temperature-solution polycondensation of trimellitic anhydride chloride (TMAc) with aromatic diamines (2). TMAc is an asymmetric monomer containing two functional groups in which the reactivity to the symmetric monomer is different. The polycondensation of a symmetric monomer with an asymmetric monomer gives rise to PAIs with different microstructures which can be expressed in terms of imide-amide sequence (hereafter referred to head-to-tail, HT), and imide-imide (head-to-head) or amide-amide (tail-to-tail) sequence which is noted as HH. Although several cases have been studied for the polycondensation of a symmetric monomer with an asymmetric monomer to obtain different microstructures, there are a few reports about how to prepare the PAIs with controlled microstructures and the correlation between the microstructure and the properties such as solubility, thermal and mechanical properties, etc (3-4). In this work, different reaction conditions have been used to obtain some PAIs with the same chemical composition but various microstructures, and we have studied to elucidate the microstructures by ^{1}H-NMR and the properties of PAIs with different regularities.

Experimental

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Materials ; 4,4'-Diaminodiphenyl ether (ODA,Aldrich), and trimellitic acid anhydride (TMA,Aldrich) were purified by recrystallization from THF and pseudocummene, respectively. TMAc (TCI) was vacuum distilled prior to use. N-methyl-2-pyrrolidone (NMP,Merck) and N,N'-dimethylacetamide(DMAc, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieve.

Synthesis of monomer

N-[4-(4'-nitrophenoxy)phenyl]trimellitimide (NPTI) : A mixture of trimellitic anhydride (38.42g, 0.2mol) and 4-amino-4'-nitro-diphenylether (46g, 0.2mol) were dissolved in IL of dry DMF at room temperature and stirred for 1h. About 300mL of toluene was then added, and the mixture was heated with reflux for 3h until about 3.6mL of water was azeotropically distilled off under a Dean-Stark trap. After cooling, the yellow precipitate of nitro acid was separated by filtration and purified by recrystallization from ethanol. Yield 85%, mp: 248~249°C, ^{1}H-NMR (DMSO-d_6) δ (ppm) 8.4(d,1H), 8.3(m,2H),8.1(d,1H),7.6(d,1H), 7.3(d,1),7.2(d,1H).

N-[4-(4'-aminophenoxy)phenyl]trimellitimide (APTI) : APTI was prepared by catalytic hydrogenation of NPTI(10g, 0.247mol) in a Parr hydrogenator using 1g of 10 % Pd/C as a catalyst in 200mL of DMF. Yield: 85%. mp: : 253.9°C (by DSQ. ^{1}H-NMR (DMSO-d_6), δ (ppm) 8.4(d, 1H), 8.3(s,1H), 7.3(d,1H), 6.9(d,1H), 6.8(d,1H), 6.6(d.1H) Anal. Calcd for $C_{21}H_{14}N_2O_5$ (374.34): C, 67.38%; H, 3.77%; N, 7.48%. Found: C, 66.94%; H, 3.78%; N, 7.45%.

Oxy-bis[N-(4-phenylene)-trimellitimide] (OBTI) : OBTI was prepared by condensing 2 mol of TMA and 1 mol of ODA in NMP according to literature method (5). Yield: 74 %, mp; 385.7°C (by DSQ)

Synthesis of polymer

HT-PAI : A mixture of APTI (11.23g 0.03mol), triphenylphosphite (TPP, 9.30g, 0.03mol), NMP(200ml), pyridine (Py, 50ml) and LiCl(10g) was stirred at 110°C for 3h under N_2. After cooling, the resulting homogeneous solution was poured into methanol (300mL) in a Waring blender. The precipitated polymer was washed with water and boiling methanol, collected by filtration and dried at 150°C under reduced pressure for 24h.

HH-PAI : The polymerization was proceeded similar to the synthesis of HT-PAI using the OBTI(8.17g, 0.015mol) and ODA(6.00g, 0.015mol).

Copoly-1: To a solution of ODA(10.01g, 0.05mole) in dry NMP(200 ml), TMA (9.61g, 0.05mole) was added all at once under N_2. Then the solution was stirred for 1h at room temperature. After xylene (100ml) was added, the mixture was heated to 210°C until water was azeotropically distilled off and about 150ml of mixed xylene and NMP was removed. After cooling the reaction mixture below 50°C, pyridine (50ml), TPP (31.29g, 0.1mol), and LiCl (10g) were added, and the solution was heated with stirring at 110°C for 3h. The resulting solution was poured into methanol (500mL) in a Waring blender. The precipitated polymer was washed with water and boiling methanol, separated by filtration and dried at 150°C under reduced pressure.

Copoly-2: To a solution of ODA(8.01g, 0.04mole) in dry NMP(143 ml), TMAc (8.42g, 0.04mole) was added all at once under N_2, then the reaction mixture was kept at temperatures in the range of 50~60°C for 3h. Propylene oxide (2.32g, 0.04mole) as the acid acceptor was added and the mixture was kept at room temperature for 10h. To the resulting polyamic acid solution, acetic anhydride (24ml), and pyridine (24ml) were added and the solution was kept at room temperature at 24h.

Copoly-2': The synthesis of this polymer was proceeded in the same manner as copoly-2 but in this case the order of addition was changed and the ODA was added slowly to the solution of TMAc.

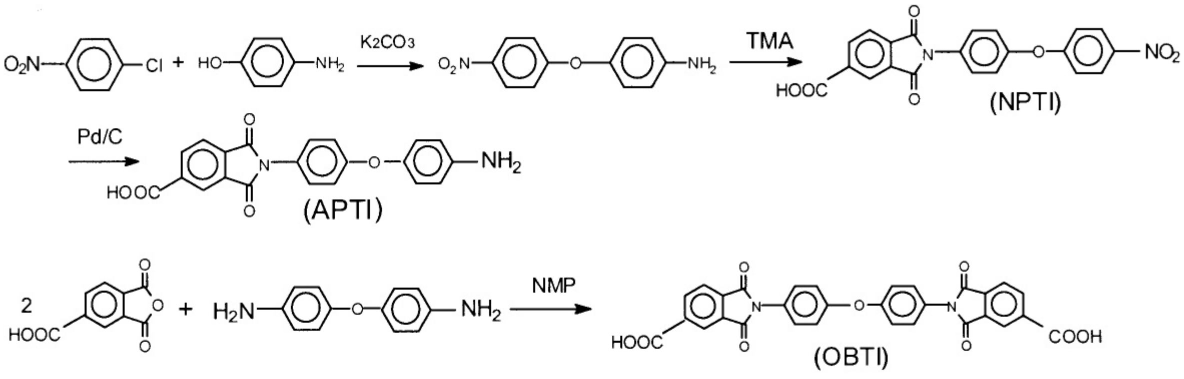
Film preparation : The 5~10 wt % solutions of the prepared PAIs in NMP were filtered using a Teflon membrane filter (0.45 μ m) and cast on a clean glass plate. The solvent was evaporated in a vacuum oven at 60°C for 4h, 120°C for 4h, and then 150°C for 2h. The films were removed from the glass plate by soaking it in cold water. Then they were dried in a vacuum oven at 250°C for 24h. The thickness of the PAI films were about 10~50 μ m.

Measurements : ^{1}H-NMR spectra were recorded on a Bruker AMX 500 using DMF-d_7 containing 1% LiCl as the solvent. Infrared spectra were obtained with a Bio-Rad Digilab Division FTS-165 FT-IR spectrometer. Tensile properties of PAI were measured according to ASTM 638 using an Instron universal tester (model 1125). Dynamic mechanical measurement was performed on the rectangular films in tension / compression mode at a heating rate of 3°C min^{-1} by a Rheometrics Scientific DMTA IV spectometer. The WAXD measurements were performed on a Rigaku X-ray diffractometer with Cu K_α radiation, wavelength =1.54Å. Inherent viscosities were measured with a Cannon-Fenske viscometer (No.75) at a concentration of 0.5 g dL^{-1} in DMAc at 30°C.

Results and Discussion

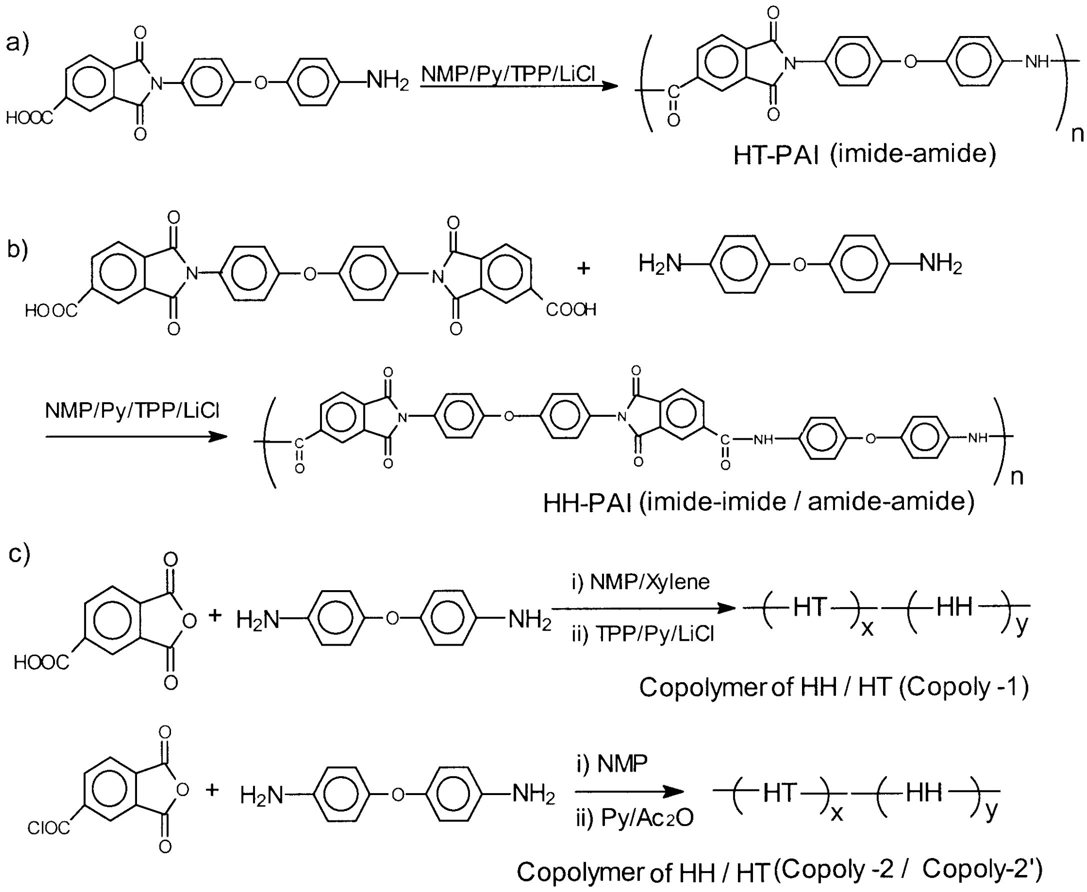
Synthesis

A simple monomer containing amino acid groups (APTI) and diimide-diacid (OBTI) was prepared according to the known procedure as shown in scheme 1. 1-Chloro-4-nitrobenzene reacted with an equimolar amount of 4-aminophenol at 150°C in the presence of potassium carbonate to yield 4-amino-4'-nitro-diphenylether. NPTI was synthesized from the condensation reaction of 4-amino-4-nitro-diphenylether with TMA. The complete cyclization of the intermediate amic acid was achieved by toluene-water azeotropic distillation. APTI was prepared by catalytic hydrogenation of the nitro compound. The structures of the intermediates and APTI were confirmed by means of elementary analysis, IR, and ^{1}H-NMR spectroscopy.



Scheme 1. Synthetic route to monomers

PAIs containing different microstructures were prepared by two different methods, that is, i) direct polycondensation reaction using TPP as a condensing agent in the presence of pyridine (Py) and lithium chloride (6) and ii) low-temperature solution polycondensation. Reactions according to scheme 2, a) gave polymers with only HT unit and b) yielded polymers with only HH or TT unit, and c) yielded copolymers of HT and HH units.



Scheme 2. Polymerization reaction

The prepared PAIs were characterized by 50OMHz ^{1}H-NMR. As shown Figure 1, peak areas for the benzene ring protons in diphenyl ether moiety were taken to calculate the mol % of HH versus HT unit by the following equation.

$$HH(mol\%) = \frac{(A_{7.32} + A_{7.06})/2}{(A_{7.32} + A_{7.06})/2 + A_{7.18}} \quad (A_{7.32} \text{ : integration area around 7.32 ppm peak})$$

The copolymerization reaction was proceeded readily around 10 wt% solution. While HH-PAI and HT-PAI could only be prepared at a lower monomer concentration, 3.5 wt% and 4.5 wt%, respectively due to the gelation during polycondensation (7). All of the PAIs were yellow with almost quantitative yield; the results of PAI preparation are summarized in Table 1.

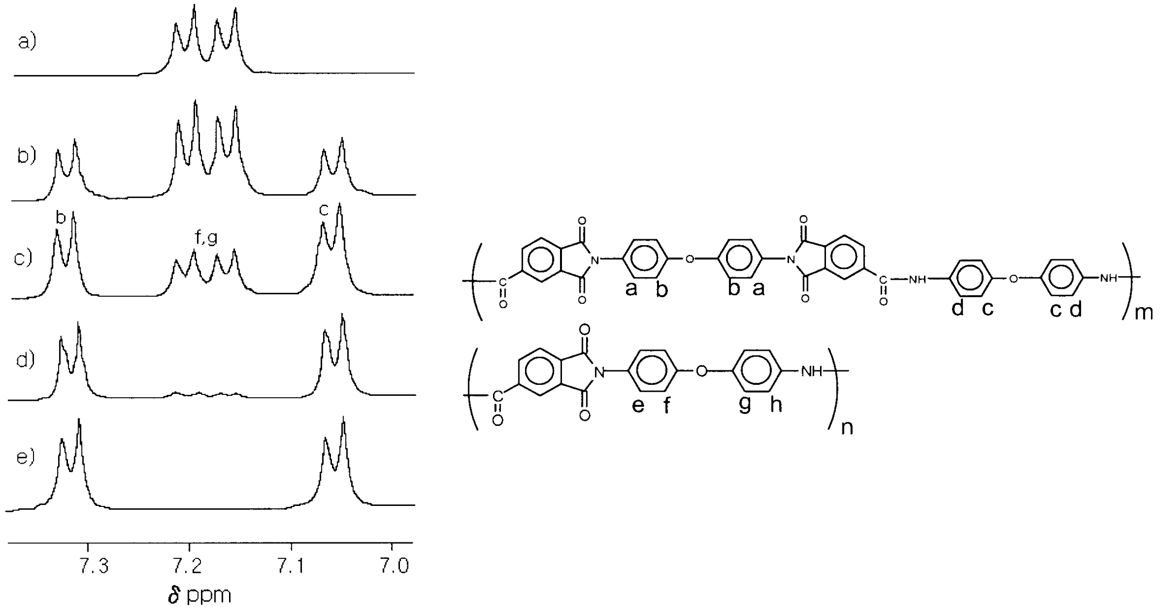


Figure 1. ^{1}H-NMR spectra for the benzene ring protons in 4,4′-diphenyl ether of the PAIs (DMF/d_7 containing 1wt% LiCl) a) HT-PAI, b) Copoly-1, c) Copoly-2, d) Coply-2′, e) HH-PAI.

Table 1. Preparation of PAIs with different microstructures.

Polymer	Monomer	Microstructure HH : HT (mol %)	η_{inh} (dL/g)[a]	$Mn(\times 10^4)$[b] (g/mole)	$Mw(\times 10^4)$ (g/mole)	Mw/Mn
HT-PAI	APTI	0 : 100	0.98	-	-	-
Copoly-1	TMA/ODA	31 : 69	0.60	3.70	6.68	1.81
Copoly-2	TMAc/ODA	49 : 51	0.92	4.04	7.69	1.90
Copoly-2′	TMAc/ODA	86 : 14	0.53	3.16	5.18	1.64
HH-PAI	OBTI/ODA	100 : 0	1.07	4.77	9.89	2.07

[a] Measured at a concentration of 0.5 g/dL at 30°C in DMAc or NMP (for HT-PAI).

[b] Measured by GPC at 80°C, correlating to standard polystyrene, in DMF containing 0.5 wt% LiBr. (flow 1.0 mL min^{-1})

The HT-PAI and HH-PAI were obtained by polycondensation from the corresponding monomers, APTI and OBTI, respectively, and could be confirmed readily with NMR spectra. It should be noted that the copolymers with a different content of HH and HT could be prepared by varying the monomer adding mode and the reaction conditions at an equimolar ratio of monomers (8-9). The Copoly-1 was prepared by two step reaction from TMA and ODA. In the first step, TMA was pre-reacted with an equimolar amount of ODA to form the mixture of ATPI, OBTI, and unreacted ODA in NMP. Then the mixture was polymerized by direct polycondensation without isolation of reaction products. The mole ratio of HH and HT in Copoly-1, 31/69 was obtained depending on the mole ratio of APTI and OBTI formed in the first step. APTI first formed from the reaction of ODA with TMA, and then could react with TMA to yield OBTI until TMA was consumed following the competing reaction with ODA and APTI, resulting in the higher mole ratio of HT to HH in the Copoly-1. While Copoly-2 and Copoly-2' were prepared from the same monomers, TMAc and ODA, with the different adding methods. Copoly-2 of 49 mol% HH was prepared by adding TMAc to the ODA solution while Copoly-2' of 86 mol% HH were prepared by reversing the adding mode, that is, yielding higher HH tendency for initial TMAc excess reaction. In case of copoly-2', ODA is added slowly to TMAc solution, diamide-containing dianhydride forms first, then this anhydride reacts with residual ODA, finally giving the HH-rich PAI. This illustrates that the ratio of HT and HH is greatly influenced by the reactivity difference of the functional groups and adding mode. In this work the PAIs with various microstructures were prepared successfully with varying the monomer structures and polymerization conditions.

Properties

The physical and thermal properties of the polymers are reported to be affected by the constitutional regularity of the backbone chains (10-11). Density, solubility, thermal and mechanical properties of PAIs with different microstructures were investigated. Wide angle X-ray diffraction diagrams were obtained on the PAI films. As shown in Figure 2, HT-PAI revealed a recognizable peak at around $2\theta = 20$ degree, while HH-PAI and copolymer have broad halo, meaning that HT-PAI has more ordered structure due to a better packing of polymer backbones than HH-PAI and copolymers. In FT-IR spectra of the PAI polymers (Figure 3), the hydrogen bonding between –C=O and –NH group also ensure the above results. The –C=O stretching band of HT-PAI shifted from 1674cm^{-1} to 1663cm^{-1} due to a stronger hydrogen bonding than that of HH-PAI and Copoly-2 (12). HT-PAI has the highest value among the polymers. The solubility and density of the PAIs are listed in Table 2. Most of the PAIs were readily soluble in amide type solvents such as DMF, DMAc except for HT-PAI. The copolymers revealed better solubility than HT-PAI or HH-PAI. HT PAI has the highest density value, which might result from the most ordered structure as seen in WAXD curves in Figure 2. Figures 4 and 5 show the dynamic mechanical and tensile properties of the PAI films. The dynamic mechanical properties were measured at a heating rate of 3°C /min and at 1 Hz.

Table 2. Solubilty and density of PAIs with different microstrutures.

Polymer	Density[a] (g/cm^3)	Solvents[b] NMP	DMF	DMAc	m-Cresol	Pyridine
HT-PAI	1.3802	+	– –	– –	– –	– –
Copoly-1	1.3556	+ +	+ +	+ +	+	– –
Copoly-2	1.3555	+ +	+ +	+ +	+	– –
Copoly-2′	1.3555	+ +	+ +	+ +	+ –	– –
HH-PAI	1.3566	+ +	+ –	+ +	– –	– –

[a] The density of PAIs film was measured with a density gradient column in n-hexane and chloroform mixture at 23°C.

[b] + + : soluble at RT, + : soluble by heating , + – : partially soluble by heating, – – : insoluble

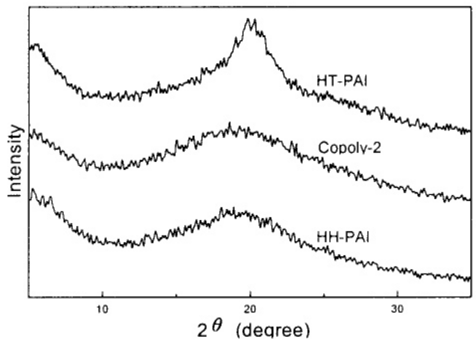


Figure 2. X-ray diffractograms of PAIs

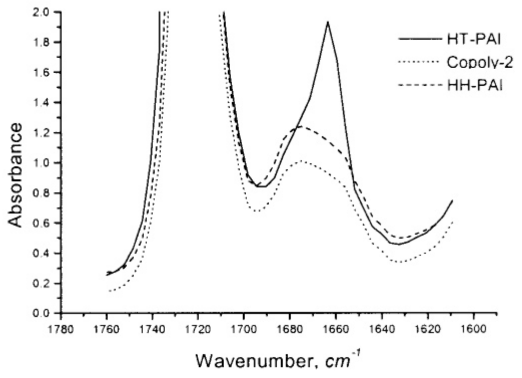


Figure 3. FT-IR spectra of PAIs

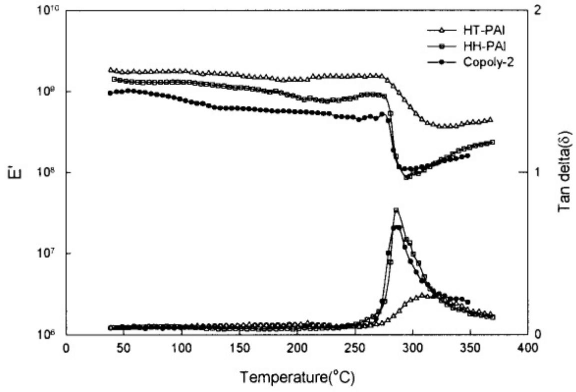


Figure 4. Dynamic mechanical spectra of PAIs

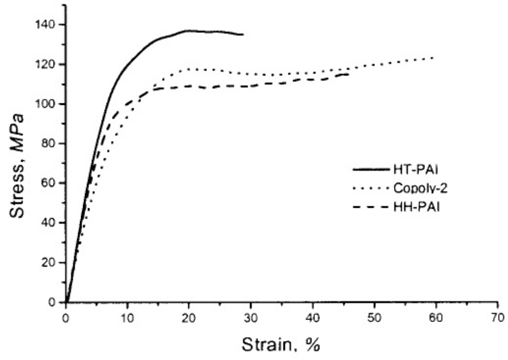


Figure 5. Tensile properties of PAIs

The glass transition temperatures (Tgs) were decided from tanδ peak temperature on DMTA curves. Tgs, tensile strength and modulus, and elongation of the prepared PAI polymers were obtained from the figures and listed in Table 3. HT-PAI has the highest Tg, 308°C, 20°C higher than HH-PAI or copolymers. The storage moduli of PAIs are in the order of HT-PAI, HH-PAI, and copolymer between room temperature and 250°C, i.e., the HT has the highest rigidity, resulting from the restricted chain mobility due to the most ordered structures for HT-PAI.

Table 3. Properties of PAIs with different microstructures.

Polymer	Tg[a] (°C)	Tensile strength[b] (MPa)	Elongation at[b] break (%)	Tensile modulus[b] (GPa)
HT-PAI	308	136.7	31.3	1.79
Copoly-1	280	128.9	61.2	1.25
Copoly-2	285	123.0	51.1	1.31
Copoly-2′	276	118.2	34.2	1.37
HH-PAI	288	114.7	45.8	1.67

[a] Tg was measured by DMTA.

[b] Tensile properties were measured according to ASTM 638.

These results correspond well with the previous explanation regarding to the molecular packing. Transitions of the storage modulus and tanδ at around 280°C are attributed to the onset of the segmental motion in the amorphous regions. As indicated in Figure 2, the HT-PAI revealed a sharp peak, implying it has crystalline regions which would reduce the fraction and the chain mobility of the amorphous regions, explaining the reduction in the peak height and the increase in the peak temperature, i.e., Tg in the tanδ curves.

Typical stress-strain curves of the PAIs films, which were cast from the NMP solutions with the same thermal history are shown in Figure 5. The tensile properties are summarized in Table 3. HT-PAI showed higher tensile modulus and tensile strength than HH-PAI and copolymers with lower elongation at break due to the ordered structure as explained before.

Conclusions

Homo-PAIs of HT and HH were prepared by tailoring the chemical structures of monomers from TMA and ODA. Direct polycondensation of APTI alone and OBTI with ODA yielded HT PAIs and HH PAIs, respectively. Copolymers of different HH contents were also synthesized with TMAc, TMA, and ODA by varying the reaction conditions. Copolymer of high HH content was obtained by adding ODA to TMAc solution, while the copolymer containing low HH content by one pot direct polycondensation of TMA with ODA. The microstructures of PAIs were confirmed by 500 MHz proton NMR spectoscopy.

HT-PAI showed a sharp peak in WAXD curve, a large shift at around 1670 cm^{-1} for –C=O stretching in FT-IR spectra, and poor solubility in organic solvents, high density, Tg, tensile strength and modulus compared to HH PAI and copolymers. These results might be due to the higher packing tendency of the HT PAI than HH PAI or copolymers.

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