Facile Synthesis of Semiaromatic Poly(amic acid)s from *trans*-1,4-Cyclohexanediamine and Aromatic Tetracarboxylic Dianhydrides

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Received February 4, 2007

Revised Manuscript Received April 5, 2007

Introduction. Polyimides (PIs) are a class of polymers used extensively in a variety of industrial fields because of the excellent properties such as high thermoxidative stability, high mechanical strength, excellent electrical properties, and high chemical resistance. In the electronics applications they have been used as buffer coatings to protect bare chips from stresses induced by fillers or thermal mismatches between a passivation layer and molding materials.[1] PIs are generally prepared by thermal or chemical imidization of poly(amic acid)s (PAAs), which are synthesized from aromatic diamines and aromatic tetracarboxylic dianhydrides in solutions. Recently, much attention has been paid to semiaromatic PIs with high transparency and low dielectric constant in the application as optoelectronics and interlayer dielectric materials.[2] Formation of inter- or intramolecular charge-transfer complexes, which increases the dielectric constant and lowers the transparency, will be reduced by introducing alicyclic structures. Moreover, a bulky alicyclic unit effectively decreases a molecular density, giving a semiaromatic PI with a lower dielectric constant.[3] Semiaromatic PIs are easily prepared from aromatic diamines and alicyclic tetracarboxylic dianhydrides.[2] On the other hand, the synthesis of semiaromatic PIs from aromatic tetracarboxylic dianhydrides and aliphatic or alicyclic diamines is rather difficult.[4] The carboxylic acids of PAAs form salts or gels with aliphatic or alicyclic diamines because the basicity of aliphatic or alicyclic diamines (pK_a of the ammonium ion: 10.7) is much higher than that of aromatic diamines (pK_a of the ammonium ion: 4.6). This salt formation and gelation prevents the formation of high-molecular-weight PAAs. Several techniques involving a high-temperature polymerization[5] and a N-silylation method[6] have been reported to avoid the formation of salt in the synthesis of PAAs. However, the high-temperature polymerization is not versatile, and in the latter case the silyl residues are usually remained in the final compounds even after the thermal treatment, which limits this method for the electronics applications. Therefore, an alternative method to prepare high-molecular-weight PAAs from aromatic tetracarboxylic dianhydrides and aliphatic or alicyclic diamines is still challenging to expand the scope of PIs.

Generally speaking, a salt formed from a strong base and a weak acid acts as a weak base in a solution. Thus, we expected that the polymerization of aromatic tetracarboxylic dianhydrides with aliphatic or alicyclic diamines would proceed when the resulting salts are dissolved in solutions. The salts from aliphatic or alicyclic diamines and monocarboxylic acids such as acetic acid would have higher solubility in organic solvents than those from aliphatic or alicyclic diamines and PAAs.

In this paper, we report a successful synthetic method of high-molecular-weight semiaromatic PAAs from aromatic tetracarboxylic dianhydrides and *trans*-1,4-cyclohexyldiamine (CHDA) in the presence of acetic acid. It is well-known that the polymerization of aromatic tetracarboxylic acids with CHDA is completely inhibited by the salt formation between PAAs and CHDA.[4,5] Therefore, CHDA was selected as an alicyclic diamine. Our method usually gives PAAs with higher inherent viscosities compared with the conventional low-temperature solution polymerization of CHDA with aromatic tetracarboxylic dianhydrides.

Experimental Section. a. Materials. CHDA (mp 72−73 °C) purchased from Tokyo Chemical Industry Co., Ltd., was purified by recrystallization from hexane and dried in vacuo at room temperature for 24 h before use. 4,4′-Biphthalic anhydride (BPDA) (mp 299 °C by DTA), 4,4′-oxydiphthalic anhydride (ODPA) (mp 226−227 °C), 3,3′,4,4′-benzophenonetetracarboxylic anhydride (BTDA) (mp 223−224 °C), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (mp 247−248 °C) purchased from Tokyo Chemical Industry Co., Ltd., were purified by recrystallization from acetic anhydride and dried in vacuo at 160 °C for 24 h before use. *N*,*N*-Dimethylacetamide (DMAc) was purified by vacuum distillation. The structures of the monomers used are shown in Figure 1. The inherent viscosities (η_{inh}) of the PAAs were measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

b. Typical Polymerization Procedure. CHDA (0.114 g, 1.00 mmol) was charged in a 5 mL vial pot at 70 °C and dissolved in DMAc to adjust the concentration of 15 wt %. The solution was cooled down to room temperature, and then acetic acid (0.132 g, 2.20 mmol) was slowly added. After 10 min, a solid aromatic tetracarboxylic dianhydride (1.00 mmol) was added into the solution, and the solution was stirred at room temperature for the set time. The inherent viscosities (η_{inh}) of the PAAs were measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

Results and Discussion. a. Selection of Monocarboxylic Acids. As monocarboxylic acids, bromoacetic acid, benzoic acid, and acetic acid were selected. The polymerization of BPDA with CHDA was carried out in DMAc in the presence of these monocarboxylic acids at room temperature for 6 h (Figure 2). The acidity of monocarboxylic acids and the results of the polymerization are summarized in Table 1. No polymer was obtained without monocarboxylic acids, which indicates the salt from the PAA and CHDA is not soluble in DMAc at room temperature. The polymer with sufficiently high viscosity is obtained in the presence of benzoic acid and acetic acid. On the other hand, bromoacetic acid afforded the polymer with a moderate viscosity because the formation of the resulting salt has a weaker nucleophilicity compared to that of the salts from benzoic acid and acetic acid.

b. Change of Molecular Weight with Time. To investigate the solution stability of the resulting PAA, the polymerization of BPDA with CHDA was carried out in DMAc in the presence of acetic acid at room temperature, and the η_{inh} of PAA was monitored at the set time (Figure 3). The heterogeneous solution of the CHDA−acetic acid salt is turned into the viscous and homogeneous solution in 30 min after BPDA was added. Then the η_{inh} of PAA decreases as the time passes and becomes a

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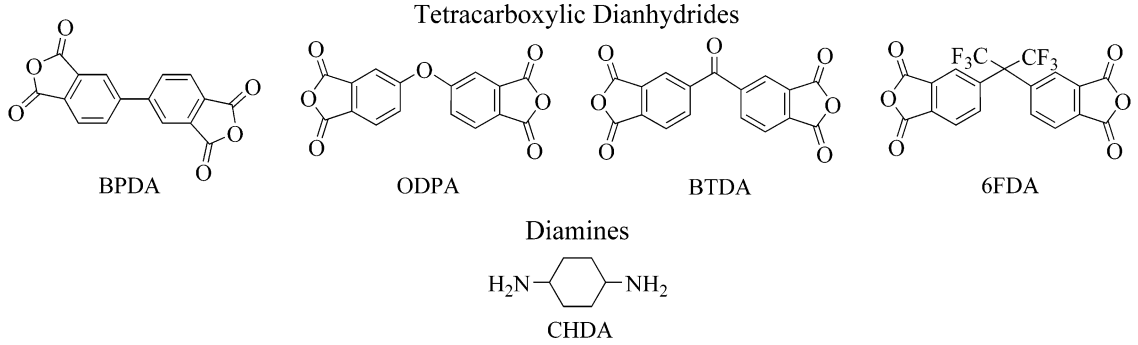

Figure 1. Structures and abbreviations of monomers.

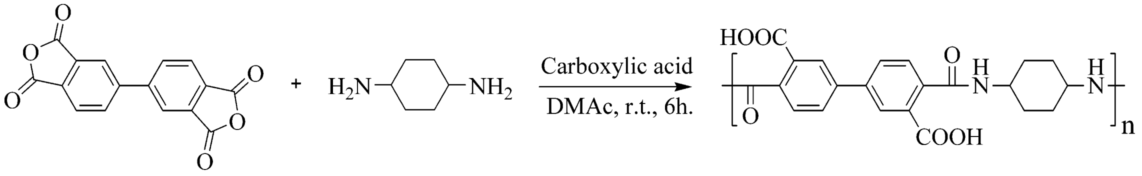

Figure 2. Synthesis of semiaromatic PAA consisting of BPDA and CHDA.

Table 1. Preparation of PAA from BPDA and CHDA in the Presence of Various of Monocarboxylic Acids[a]

acid	bromoacetic acid	benzoic acid	acetic acid	no additive
pK_a	2.90	4.20	4.76	–
inherent viscosity[b] [dL/g]	0.40	0.96	1.26	–

[a] Polymerization was carried out with 1.0 mmol of each monomer and 2.2 mmol of the acid in DMAc (15 wt %) at room temperature for 6 h. [b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

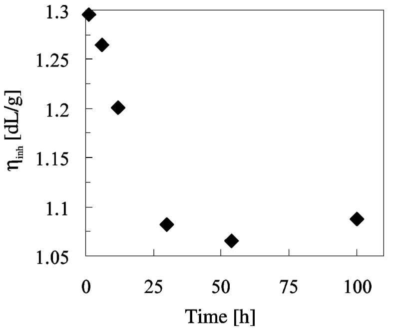

Figure 3. Viscosity change of PAA solution in DMAc.

Table 2. Effect of the Amount of Acetic Acid on the Polymerization of BPDA with CHDA[a]

acetic acid [equiv]	0.5	1.0	2.2	4.0	8.0
inherent viscosity[b] [dL/g]	–	1.20	1.26	0.88	0.63

[a] Polymerization was carried out with 1.0 mmol of each monomer in DMAc (15 wt %) at room temperature for 6 h. [b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

Table 3. Preparation of PAAs from Various Tetracarboxylic Dianhydrides and CHDA in the Presence of Acetic Acid[a]

aromatic tetracarboxylic dianhydride	additive [dL/g][b]	
	none	acetic acid
BPDA	–	1.26
BTDA	0.47	1.55
ODPA	0.63	0.98
6FDA	0.50	1.63

[a] Polymerization was carried out with 1.0 mmol of each monomer and 2.2 mmol of acetic acid in DMAc (15 wt %) at room temperature for 6 h. [b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

constant value in 30 h. This slow decrease of the viscosity is explained by the equilibrium reaction between PAA and the corresponding anhydride and amine in the solution and has been observed in all kinds of aromatic PAAs.[7]

c. Amounts of Acetic Acid. The polymerization of BPDA with CHDA was carried out in DMAc in the presence of various amount of acetic acid at room temperature for 6 h, and the each η_{inh} of PAAs is summarized in Table 2. The polymerization does not proceed in the presence of 0.5 equiv of acetic acid for CHDA because the salt formation of CHDA with PAA occurs. A high-molecular-weight PAA is obtained when more than 1 equiv of acetic acid is used. These results suggest that acetic acid more than 1 equiv to CHDA is required to suppress the salt formation from PAA and CHDA. However, the excess amount of the acid interferes with the polymerization, resulting in a rather low viscous polymer. Acetic acid is not good solvent for PAA; thus, a large amount of acetic acid prevents the homogeneous polymerization and gives the low-molecular-weight PAA.

d. Polymerization with Other Aromatic Tetracarboxylic Dianhydrides. To investigate the versatility of our new method, the polymerization of other dianhydrides such as ODPA, BTDA, and 6FDA with CHDA was carried out in the presence of acetic acid. Table 3 summarizes the results of the polymerization. In all of the cases, acetic acid acts as an inhibitor for the salt formation between the carboxylic acids of PAAs with CHDA in monomers or oligomers, resulting in higher-molecular-weight PAAs compared with the conventional solution polymerization.

Conclusion. A new synthetic method to produce semiaromatic PAAs with high molecular weights from CHDA and aromatic tetracarboxylic dianhydrides has been developed. The polymerization of the organic salt consisting of CHDA and acetic acid with various aromatic tetracarboxylic dianhydrides was carried out and gave PAAs with high inherent viscosities compared with the polymerization of CHDA with aromatic tetracarboxylic dianhydrides in the absence of acetic acid. This new method can be applied for the PAA synthesis from aliphatic or alicyclic diamines with aromatic tetracarboxylic dianhydrides on an industrial scale.

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MA070302M