Notes

Polymers Based on *p*-Aminophenol. 7. New Synthetic Approaches to the Simplest Wholly Aromatic Poly(imide ester) via the Corresponding Poly(amic acid) Precursor

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Introduction

Aromatic poly(imide ester)s are one of the most important classes of high-performance polymers[1,2] and attract attention for outstanding properties and potential liquid crystalline nature.[3] We have been interested in the preparation of a wholly aromatic poly(imide ester) with the simplest structure (1) and have examined the possibilities of various synthetic approaches based on *p*-aminophenol and trimellitic acid derivatives. 1 can be synthesized from monomers containing a preformed imide linkage (2)[2,3] or from monomers containing a preformed ester linkage (3).[4] The latter monomers were much superior since the polymerization proceeded through imide formation that is much easier and more quantitative than the ester formation of 2. The resulting poly(imide ester) showed quite high thermooxidative stability and ranked among the highest performance polymeric materials.[4] It is, however, insoluble in ordinary organic solvents and thus poor in tractability. In order to make easy fabrication possible, we have examined another synthetic approach involving the formation of the corresponding poly(amic acid) (4) precursor. We report the deprotection polymerization of the monomers 3 and 5 that are prepared by acylation of N-protected *p*-aminophenol with trimellitic anhydride chloride. On hydrolysis or hydrogenation, the free amino group was regenerated, resulting in a spontaneous polymerization to form the poly(amic acid), which was converted to the poly(imide ester) (Scheme I).

Experimental Section

General Data. *p*-Aminophenol was recrystallized from water under nitrogen. Benzyl chloroformate was of reagent grade (purity 90%) and used as received. Preparation of monomers 3 was reported elsewhere.[4] IR and NMR spectra were recorded on a JASCO IRA-1 or IR-700 spectrophotometer and a JEOL JNM-GX270 spectrometer, respectively. GPC analysis was carried out on a JASCO 880-PU liquid chromatograph with polystyrene standards (Columns: Shodex GPC AD-803/s and 805/s. Eluent: tetrahydrofuran (THF)).

***N*-Carbobenzoxy-*p*-aminophenol.** A dispersion of 26.16 g (0.24 mol) of pulverized *p*-aminophenol in 150 mL of THF was cooled in an ice bath, and to this was added a solution of 22.9 g (0.12 mmol based on 90% purity) of benzyl chloroformate in 40 mL of THF dropwise over a period of 20 min with stirring. The mixture was allowed to warm to room temperature and stirred for 2 h. The precipitated *p*-aminophenol hydrochloride was filtered off, and the filtrate was evaporated under reduced pressure. The residual solid was recrystallized from benzene/methanol to give 18.76 g (64%) of the product as colorless needles: mp 156-157 °C (lit.[5] mp 160 °C); IR (KBr) 3300 (O-H and N-H) and 1700 cm^{-1} (C=O).

Monomer 5. To a solution of 3.44 g (0.015 mol) of *N*-carbobenzoxy-*p*-aminophenol and 3.16 g (0.015 mmol) of trimellitic anhydride chloride in 75 mL of THF was added 1.52 g (0.015 mol) of triethylamine dropwise over a period of 5 min at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and then at room temperature for 2 h. The hydrochloride was removed by filtration, and the filtrate was evaporated under reduced pressure to give a pale yellow solid. It was recrystallized from THF/hexane to give 5.22 g (86%) of colorless needles: mp 220-222 °C; IR (KBr) 3360 (N-H), 1845, 1780, and 1725 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) 5.19 (s, 2, CH_2), 7.22-8.61 (m, 12, arom H), and 9.91 (s, 1, NH). Anal. Calcd for $C_{22}H_{13}NO_7$: C, 65.51; H, 3.25; N, 3.47. Found, C, 65.41; H, 3.55; N, 3.73.

Hydrolysis Polymerization of 3. To a solution of 0.224 g (0.5 mmol) of monomer **3d** (X = *p*-NO_2) in 2.5 mL of THF were added 1 mL of aqueous THF containing 0.5 mmol of water and 0.5 mL of a THF solution containing 0.07 mmol of triethylamine. The solution was stirred at 40 °C for 24 h and poured into 200 mL of benzene. The precipitate was collected by filtration, washed with benzene, and dried to give 0.075 g (53%) of the poly(amic acid) as a white solid. The molecular weight was 870 as determined by GPC.

The poly(amic acid) was heated at 200 °C for 2 h at 2 mmHg to give the poly(imide ester) as a pale tan powdery material in 60% yield. The inherent viscosity was 0.25 dL g^{-1} (in concentrated sulfuric acid, $C = 0.25$ g dL^{-1}, 25 °C).

Hydrogenation Polymerization of 5. In a flask equipped with a three-way stopcock, 0.417 g (1 mmol) of monomer **5** was dissolved in 8 mL of *N,N*-dimethylacetamide (DMAc), and a catalytic amount of 10% Pd/C was added. The atmosphere in the flask was replaced with hydrogen (1.4 kg cm^{-2}) three times, and the mixture was stirred at 50 °C for 15 h. After the polymerization, the mixture was filtered, and the filtrate was poured into 200 mL of benzene. The precipitate was filtered, washed with benzene, and dried to give 0.091 g (32%) of the poly(amic acid). The molecular weight was 2820 as determined by GPC.

On heating the poly(amic acid) at 200 °C for 2 h at 2 mmHg, the poly(imide ester) was obtained as a pale tan powdery material with an inherent viscosity of 0.19 dL g^{-1} (in concentrated sulfuric acid, $C = 0.25$ g dL^{-1}, 25 °C). The yield was 80%.

Results and Discussion

Deprotection Polymerization by Hydrolysis. Regeneration of the free amino groups was first examined by hydrolysis of the carbamate linkages of monomer **3** with the expectation of spontaneous polymerization through attack of the anhydride groups by the amino groups to give the corresponding poly(amic acid) **4**. Since the resulting poly(amic acid) would be susceptible to hydrolysis, it is necessary to hydrolyze the carbamate linkage selectively with a calculated amount of water. Monomers **3c** (X = *m*-Cl) and **3d** (X = *p*-NO_2) showed more facile dissociation of the carbamate linkages than **3a** (X = H) and **3b** (X = *p*-Cl) on heating, and were thus considered to be suitable for the selective hydrolysis polymerization (Scheme II).

Monomer **3c** was found to be rather stable in aqueous THF, and no evidence of hydrolysis was obtained at temperatures up to 60 °C maintained for 24 h. The reaction was carried out in the presence of a catalyst such as py-

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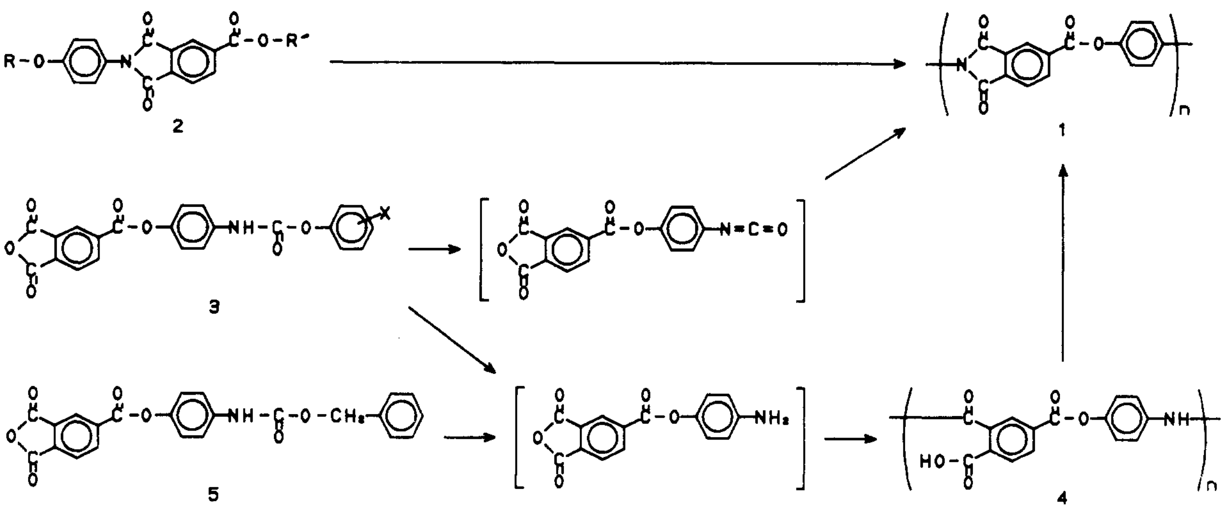
Scheme I



Scheme II

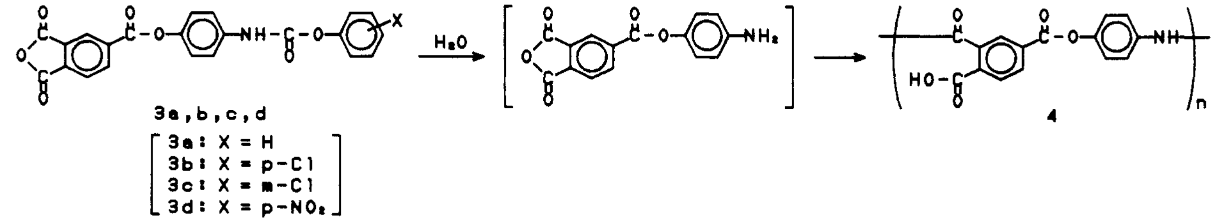


Table I
Polymerization of 3 by Hydrolysis Deprotection[a]

monomer	catalyst	temp, °C	time, h	precipitation solvent	yield, %	$\bar{M}_n$[b]
3c	triethylamine	50	24	hexane	86	520
3c	triethylamine	60	24	benzene	42	810
3c	pyridine	60	24	benzene	50	660
3c	pyridine	60	48	benzene	41	660
3d	triethylamine	30	24	benzene/hexane	73	750
3d	triethylamine	40	24	benzene	53	870
3d	pyridine	30	24	benzene/hexane	72	490
3d	pyridine	40	24	benzene	42	780
3d	pyridine	50	24	benzene/hexane	91	780

[a] Monomer 3 (0.5 mmol), solvent (THF, 4 mL), and water (0.5 mmol). [b] Determined by GPC with polystyrene standards.

ridine or triethylamine. The typical results of the polymerization are listed in Table I. The molecular weights were low regardless of the kinds of bases probably owing to the difficulty in selective hydrolysis. **3d** was then subjected to polymerization since it shows more facile thermal dissociation and is expected to be more suited for selective hydrolysis. As shown in Table I, polymers with somewhat higher molecular weights were obtained at lower temperatures.

In the IR spectra of the polymers, bands due to anhydride groups disappeared completely, but a weak band due to carbamate N–H was sometimes observed at 3350 cm^{-1}, indicating the reaction selectivity is not sufficient even with the monomers with electron-withdrawing groups such as chloro and nitro groups. There is some difficulty in the preparation of **3d** because of sensitivity toward water, and hence preparation of monomers having more electronegative groups would be quite difficult. These results imply that the hydrolysis polymerization has limitations in preparing the high molecular weight poly(amic acid).

The poly(amic acid) prepared here was converted to the poly(imide ester) on heating at 200 °C in vacuum. Although the molecular weight of the poly(amic acid) was low, the inherent viscosity of the resulting poly(imide ester) was around 0.25 dL g^{-1}, suggesting the occurrence of postpolymerization during the thermal conversion. The IR spectra of the poly(imide ester) was almost identical with that of the poly(imide ester) prepared by pyrolytic polymerization of 3[4] except that a weak isocyanate band was sometimes observed at 2250 cm^{-1}. This is reasonably interpreted in terms of thermal dissociation of the unreacted carbamate linkage leading to some postpolymerization.

Deprotection Polymerization by Hydrogenation. Because of some difficulties in the hydrolytic deprotection, we then examined deprotection in the absence of water. For this purpose, catalytic hydrogenation of (benzyloxy)carbonyl protection is considered to be promising.

The amino group of *p*-aminophenol was first protected by acylation with benzyl chloroformate. The reaction proceeded selectively when an additional equivalent mole of *p*-aminophenol was used as the acid acceptor.[6] Subsequent acylation with trimellitic anhydride chloride gave monomer **5** (Scheme III).

Deprotection behavior of **5** was examined in detail in a hydrogen atmosphere with Pd/C under various conditions, and some typical results are summarized in Table II. When the hydrogenation was carried out under mild conditions, e.g., with 5% Pd/C at room temperature or lower temperatures, to minimize degradation of the resulting poly(amic acid), the reaction was generally incomplete as suggested by low molecular weight and the weak bands in the IR spectra due to the remaining carbamate and anhydride groups.

The hydrogenation polymerization proceeded smoothly with 10% Pd/C compared to 5% Pd/C, and DMAc appeared to be superior to THF as a solvent, judging from the molecular weight and the IR spectra. Regarding the polymerization temperature, around 50 °C was appropriate, although the differences were not pronounced from 40 to 60 °C. The molecular weight of the poly(amic acid) increased with reaction time initially and tended to level off after 15–24 h. They were higher than those obtained

Scheme III

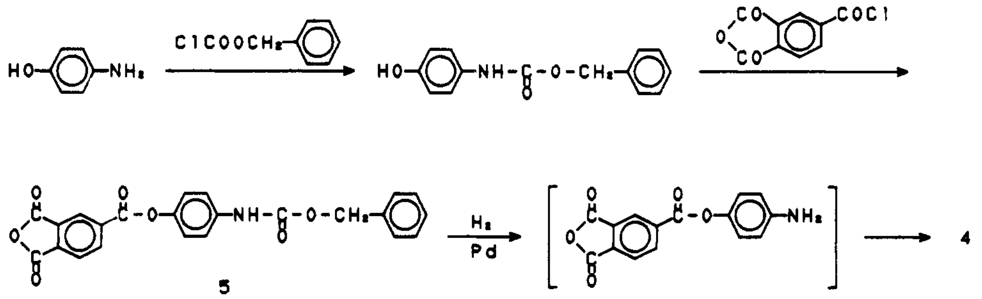


Table II
Polymerization of 5 by Hydrogenation Deprotection[a]

catalyst	solvent (mL)	temp, °C	time, h	yield, %	$\bar{M}_n$[b]
5% Pd/C	THF (8)	rt	6.5	43	1420
5% Pd/C	THF (8)	50	6.5	11	1690
10% Pd/C	THF (8)	40	6.5	22	1920
10% Pd/C	DMAc (8)	40	6.5	33	2110
10% Pd/C	DMAc (8)	50	6.5	33	2250
10% Pd/C	DMAc (8)	50	15	32	2820
10% Pd/C	DMAc (8)	50	24	27	2610
10% Pd/C	DMAc (8)	60	24	23	2670
10% Pd/C	DMAc (5)	50	24	41	2230
10% Pd/C	DMAc (5)	60	24	43	2320

[a] Monomer 5 (0.417 g, 1 mmol), H_2 (1.4 kg cm^{-2}), and precipitation solvent (benzene). [b] Determined by GPC with polystyrene standards.

by the hydrolysis method and in the level of 2500–2800. The polymers were obtained as white powdery materials readily soluble in polar organic solvents such as DMAc and DMSO to give clear viscous solutions, but the molecular weights appeared not high enough for casting self-supporting films.

Figure 1 illustrates the IR spectrum of the poly(amic acid). It shows typical features of the spectra of common poly(amic acid)s, having broad bands due to the amic acid groups at 3400–2400 cm^{-1} and amide bands at 1650 and 1540 cm^{-1}. Strong bands at 1730–1700 cm^{-1} are attributable to the carbonyl of carboxyl and ester groups.

When the poly(amic acid) was heated at 200 °C, it was converted to the poly(imide ester) 1. Quantitative cyclization to the poly(imide ester) was supported by the change in the IR spectra shown in Figure 1. Absorption bands of the poly(amic acid), especially those at 3400–2400 cm^{-1} disappeared completely, and characteristic bands due to imide and ester groups appeared at 1780 and 1720 cm^{-1}. The spectrum of the poly(imide ester) is identical with that of the poly(imide ester) prepared by pyrolytic polymerization of 3.[4] The inherent viscosity of the poly(imide ester) derived from the poly(amic acid) with a molecular weight of 2820 was 0.19 dL g^{-1}.

In summary, the present study shows the possibility of preparing the poly(amic acid) precursor for the simplest aromatic poly(imide ester). The viscosity of the poly(imide ester) obtained by this method is higher than that obtained by thermal polymerization of 2[2] but lower than that obtained by pyrolytic polymerization of 3.[4]

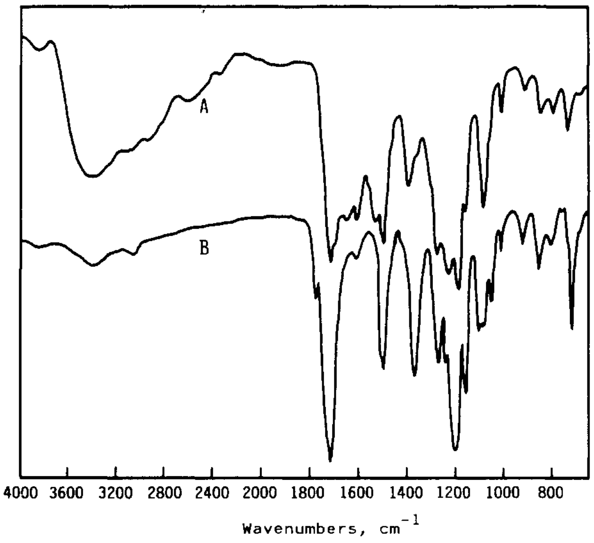


Figure 1. IR spectra of (A) poly(amic acid) and (B) poly(imide ester) (KBr method).

References and Notes

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Registry No. 1 (SRU), 31625-40-8; **3c** (homopolymer), 126425-05-6; **3d** (homopolymer), 136892-93-8; 4 (SRU), 137028-39-8; **5**, 136919-97-6; **5** (homopolymer), 136919-98-7; THF, 109-99-9; DMAc, 127-19-5; Pd, 7440-05-3; C_6H_6, 71-43-2; $H_3C(CH_2)_4CH_3$, 110-54-3; Et_3N, 121-44-8; $PhCH_2OC(O)NHC_6H_4$-*p*-OH, 7107-59-7; pyridine, 110-86-1; trimellitic anhydride chloride, 1204-28-0.