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Polymers Based on *p*-Aminophenol. 6. Facile Synthesis of the Simplest Wholly Aromatic Poly(imide–ester) by Pyrolytic Polymerization of Monomers Containing Preformed Ester Linkages

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ABSTRACT: An improved synthetic procedure for a wholly aromatic poly(imide–ester) with the simplest structure has been examined. The polymer was synthesized through imide formation polymerization by pyrolytic condensation of monomers containing preformed ester linkages and evaluated as a high performance polymer. The monomers were prepared by first N-protection of *p*-aminophenol with phenyl chloroformates followed by acylation of the remaining hydroxyl group with trimellitic anhydride acid chloride. Thermal analysis revealed that these monomers underwent pyrolysis to split off the corresponding phenols and carbon dioxide giving rise to the poly(imide–ester). Pyrolysis behavior was closely associated with the substituents on the phenol moiety; the monomers having electron-withdrawing groups showed improved thermal dissociation and hence resulted in the formation of poly(imide-esters) with higher viscosities. This procedure was much superior to the previous one involving the ester-forming polymerization. The resulting poly(imide–esters) had inherent viscosities up to 0.38 dL/g in concentrated sulfuric acid. Thermogravimetric analysis showed high thermal stability with a weight loss of only 2% at 500 °C with a heating rate of 5 °C/min in air.

Introduction

Although *p*-aminophenol has been used only in limited numbers in polymer syntheses, it is an interesting starting material because of the presence of two functional groups with different reactivities.[1-5] In the field of high performance polymers, it is considered a useful building block for preparing poly(imide–esters). We have already reported the synthesis of the simplest wholly aromatic poly(imide–ester) (**3**) starting from *p*-aminophenol and trimellitic anhydride, where a hydroxy acid monomer containing an imide linkage (**2**) and its derivatives were used as monomers. The polymerization proceeded through ester formation (Scheme I). The resulting polymer was shown to rank among the highest performance polymers in spite of low viscosities.[6]

This suggests that in order to prepare a poly(imide–ester) with high viscosity, polymerization should proceed through imide formation using the monomers containing preformed ester linkages. This alternative approach to poly(imide-ester) synthesis proved much more effective as expected, and some preliminary results were reported.[7] A further improvement in the polymerization has been achieved by introducing electron-withdrawing substituents on the phenol moiety of the monomer. This paper describes the detailed study on the effects of electron-withdrawing substituents on the polymerization behavior and the improved synthetic procedure for the poly(imide–ester) from the new monomers (Scheme II).

Experimental Section

General Data. *p*-Aminophenol was recrystallized from water under nitrogen. Phenyl chloroformate and trimellitic anhydride acid chloride were distilled under reduced pressure. Triethylamine and solvents were purified in usual manners. *m*-Terphenyl was dried under vacuum with phosphorus pentoxide. IR and NMR spectra were recorded on a JEOL IR-1 and a JEOL JNM-GX270 spectrometer, respectively. DTA and TG data were obtained by a Rigaku Thermoflex 8100 instrument. DSC spectra were run with a Perkin-Elmer DSC-2 spectrometer.

***m*-Chlorophenyl Chloroformate (5c).** A solution of 12.9 g (0.1 mol) of *m*-chlorophenol in 100 mL of dry tetrahydrofuran (THF) was cooled to 0 °C, and 7.5 mL (11.9 g, 0.06 mol) of trichloromethyl chloroformate[8] was added. To the solu-

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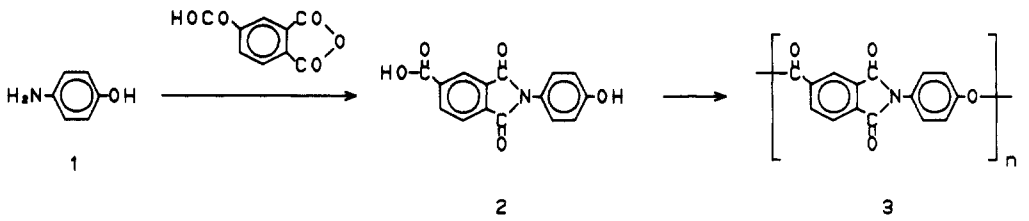
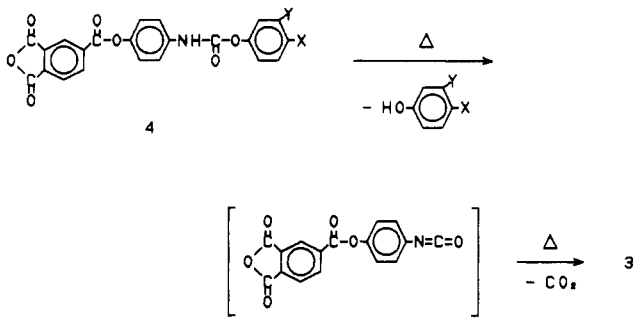
Scheme I



Scheme II



tion was added 12.7 mL (12.1 g, 0.1 mol) of *N,N*-dimethylaniline over a period of 5 min. The mixture was stirred at 0 °C for 10 min and then at room temperature. The reaction time was 6 h in total. The white precipitate was filtered, and the filtrate was concentrated under reduced pressure. The residual liquid was dissolved in 100 mL of benzene, and the solution was washed consecutively with 100 mL of 0.2 M hydrochloric acid, 100 mL of 0.2 M sodium hydroxide, and finally three 100-mL portions of water. It was dried over sodium sulfate and evaporated under reduced pressure to give a liquid. On distillation, 13.5 g (71%) of pure **5c** was obtained as a colorless liquid, bp 79–80 °C (3.5 mmHg) [lit.[9] mp 98–100 °C (13 mmHg)].

p-Chlorophenyl chloroformate (**5b**), bp 109 °C (14 mmHg) [lit.[10] bp 108 °C (19 mmHg)], and *p*-nitrophenyl chloroformate (**5d**), bp 115–117 °C (2 mmHg) (lit.[10] mp 159–162 °C (19 mmHg)], were prepared by the same method.

Phenyl *N*-(*p*-Hydroxyphenyl)carbamate (6a). To a dispersion of 8.72 g (80 mmol) of finely powdered *p*-aminophenol in 100 mL of dry THF was added a solution of 5.02 g (40 mmol) of phenyl chloroformate in 20 mL of THF over a period of 20 min at 0 °C with stirring. *p*-Aminophenol hydrochloride precipitated out soon. The mixture was allowed to warm to room temperature and stirred for 3 h. The hydrochloride was removed by filtration, and the filtrate was evaporated under reduced pressure. The residual pale brown solid was recrystallized from chloroform to give 8.77 g (96%) of **6a** as colorless needles, mp 152–154 °C (lit.[11] mp 153.5–155.5 °C).

p-Chlorophenyl *N*-(*p*-hydroxyphenyl)carbamate (**6b**) was prepared in a similar manner and recrystallized from THF/chloroform (colorless needles): yield 73%; mp 212–215 °C; IR (KBr) 3320 (O–H and N–H) and 1715 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{10}NO_3Cl$: C, 59.22; H, 3.82; N, 5.31. Found: C, 59.05; H, 3.66; N, 5.24.

m-Chlorophenyl *N*-(*p*-hydroxyphenyl)carbamate (**6c**) was prepared similarly and recrystallized from chloroform (colorless needles): yield 67%; mp 154–156 °C; IR (KBr) 3320 (O–H and N–H) and 1715 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{10}NO_3Cl$: C, 59.22; H, 3.82, N, 5.31. Found: C, 59.07; H, 3.52; N, 5.09.

p-Nitrophenyl *N*-(*p*-hydroxyphenyl)carbamate (**6d**) was prepared similarly and recrystallized from ethyl acetate/hexane (colorless needles): yield 68%; mp 187–189 °C; IR (KBr) 3310 (O–H and N–H) and 1700 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{10}N_2O_5$: C, 56.93; H, 3.68; N, 10.22. Found: C, 56.88; H, 3.82; N, 10.20.

Monomer 4a. To a solution of 6.87 g (30 mmol) of **6a** and 6.32 g (30 mmol) of trimellitic anhydride acid chloride in 150 mL of THF was added 4.20 mL (3.04 g, 30 mmol) of triethylamine at 0 °C. The mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature. After the mixture was stirred for 1 h, the precipitated salt was filtered and then THF was evaporated. The residual pale yellow solid was recrystallized from THF/hexane to give 11.13 g (92%) of **4a** as colorless needles: mp 220–222 °C; IR (KBr) 3340 (N–H), 1865, 1840, 1780, 1770, 1730, and 1715 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ 7.17–8.73 (m, 12, arom H) and 10.33 ppm (s, 1, NH). Anal. Calcd for $C_{22}H_{13}NO_7$: C, 65.51; N, 3.25; N, 3.47. Found: C, 65.41; H, 3.55; N, 3.73.

Monomer **4b** was prepared similarly and recrystallized from ethyl acetate (slightly yellow plates): yield 53%; mp 196–199 °C; IR (KBr) 3360 (N–H), 1870, 1850, 1780, 1750, and 1720 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ 7.17–8.45 (m, 11, arom H) and 10.47 ppm (s, 1, NH). Anal. Calcd for $C_{22}H_{12}NO_7Cl$: C, 60.36; H, 2.76; N, 3.20. Found: C, 60.36; H, 2.64; H, 3.18.

Monomer **4c** was prepared similarly and recrystallized from ethyl acetate (colorless needles): yield 82%; mp 191–193 °C; IR (KBr) 3360 (N–H), 1850, 1775, 1740, and 1720 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ 7.23–8.41 (m, 11, arom H) and 10.46 ppm (s, 1, NH). Anal. Calcd for $C_{22}H_{12}NO_7Cl$: C, 60.36; H, 2.76; N, 3.20. Found: C, 59.66; H, 2.54; N, 2.98.

Monomer 4d. All the synthetic procedures were carried out in a glovebox under nitrogen. After the reaction, the mixture was filtered, and hexane was added to the filtrate. The precipitated yellow solid was collected by filtration and purified by repeated reprecipitation using THF and hexane to give slightly yellow small needles: yield 67%; mp 175–178 °C; IR (KBr) 3360 (N-H), 1860, 1845, 1780, 1740, and 1720 (shoulder) cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ 7.30–8.65 (m, 11, arom H) and 10.60 ppm (s, 1, NH). Anal. Calcd for $C_{22}H_{12}N_2O_9 \cdot H_2O$: C, 56.66; H, 3.03; N, 6.01. Found: C, 56.80; H, 2.98; N, 5.97.

Pyrolytic Polymerization of 4a in Bulk. **4a** (0.403 g, 1 mmol) was heated at 240 °C for 1 h in a nitrogen stream. It melted, and the melt solidified soon. The solid was then heated at 240 °C at 20 mmHg for 3 h. The resulting pale brown solid was pulverized well and heated at 300 °C at 1 mmHg for 10 h to give poly(imide–ester) **3**: yield 0.19 g (72%); inherent viscosity 0.33 dL/g (in concentrated H_2SO_4, C = 0.25 g/dL, 25 °C). Weight loss at 500 °C (5 °C/min, in air) was 2%. Anal. Calcd for $(C_{15}H_7NO_4)_n$: C, 67.93; H, 2.66; N, 5.28. Found: C, 68.10; H, 2,29; N, 5.05.

Pyrolytic Polymerization of 4a in Solution. A mixture of 0.403 g (1 mmol) of **4a** and 3 g of *m*-terphenyl was gradually heated to 300 °C. *m*-Terphenyl melted at around 90 °C and dissolved the monomer. The solution was heated at 300 °C for 6 h. The polymer separated out as a fine precipitate during the heating. The reaction mixture was cooled to room temperature, and benzene was added to dissolve *m*-terphenyl. The insoluble material was collected by filtration and washed with benzene thoroughly to give **3**: yield 0.22 g (83%); inherent viscosity 0.34 dL/g (in concentrated H_2SO_4, C = 0.25 g/dL, 25 °C).

Results and Discussion

Synthesis of Monomers. In order to promote the polymerization through imide formation instead of ester formation, N-protected *p*-aminophenol derivatives containing a trimellitic anhydride group linked by ester linkages were expected to be promising. The synthetic procedure for these monomers involves selective N-phenoxycarbonylation of *p*-aminophenol followed by acylation of the remaining hydroxyl group with trimellitic anhydride acid chloride as shown in Scheme III. On heating these monomers, the carbamate linkages would dissociate into the corresponding isocyanate and phenols, and the isocyanate group in turn reacts with the anhydride group, resulting in the formation of the imide with lib-

Scheme III

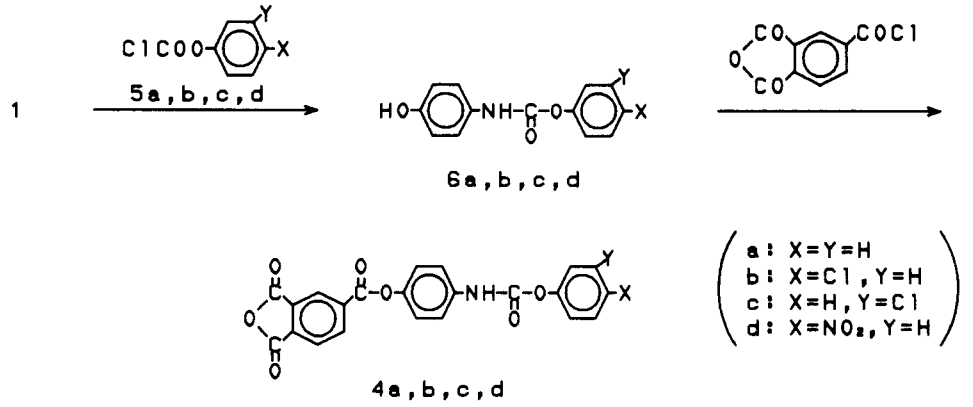


Table I
Thermal Analysis of Monomers 4a–d[a]

monomer	DTA endotherm: T (commencement), °C	DTA endotherm: T (peak), °C	TGA weight loss: temp range, °C	TGA weight loss: percentage obsd	TGA weight loss: percentage calcd
4a	217	231	217–320	35	34
4b	193	199	194–320	38	39
4c	191	196	192–300	39	39
4d	176	187	176–280	42	43

[a] At a heating rate of 5 °C/min in air.

eration of carbon dioxide (Scheme II). Electron-withdrawing groups on phenyl chloroformates are expected to promote the thermal dissociation and hence the polymerization, and besides the unsubstituted phenyl chloroformate (**5a**), *p*-chlorophenyl, *m*-chlorophenyl, and *p*-nitrophenyl chloroformates (**5b–d**) were also employed.

In the monomer preparation, *p*-aminophenol was first treated with phenyl chloroformates to protect the amino group. The reaction depended on the kind of acid acceptor, and pyridine or triethylamine resulted in only poor reaction selectivity giving rise to mixtures of O-substituted, N-substituted, and N,O-disubstituted derivatives. Weak bases increase the extent of N-substitution as in the tosylation of aminophenols,[12] and with *p*-aminophenol itself the reaction proceeded selectively and only at the amino group to give the expected products **6a–d** in high yields.

Acylation of the N-protected *p*-aminophenols (**6a–d**) with trimellitic anhydride acid chloride proceeded smoothly in THF to give four kinds of monomers, **4a–d**. Monomer **4d** was, however, too susceptible to hydrolysis because of the presence of the nitro group, and the preparation had to be carefully carried out in a dry nitrogen atmosphere. The structures of all the monomers were unambiguously confirmed by spectral and elemental analysis data. Monomer **4d** was isolated as a monohydrate.

Thermal Properties of the Monomers. The monomers were subjected to thermal analysis including differential thermal analysis (DTA) and thermogravimetry (TG) in air at a heating rate of 5 °C/min to elucidate the thermal dissociation behavior. Heat absorptions due to melting commenced at 217, 193, 191, and 176 °C in DTA for monomers **4a**, **4b**, **4c**, and **4d**, respectively, and weight loss takes place almost simultaneously in all the cases as evident by the data in Table I and by the typical DTA and TG curves in Figure 1. The weight loss of **4a** started at 217 °C, while those of the monomers containing chloro groups started at much lower temperatures, 194 and 192 °C for **4b** and **4c**, respectively. Introduction of a nitro group even lowered the decomposition temperature further, markedly to 176 °C, where dehydration took place simultaneously.

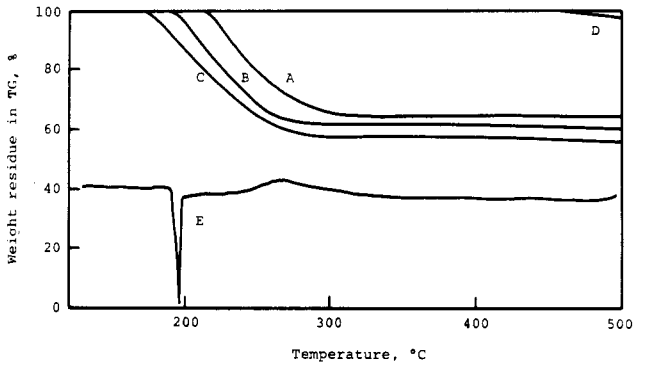


Figure 1. TG curves for (A) **4a**, (B) **4c**, (C) **4d**, and (D) **3** and a DTA curve for (E) **4c** at a heating rate of 5 °C/min in air.

The weight losses by pyrolysis were complete until about 320 °C, **4d** showing the lowest temperature, and corresponded to the thermal cleavage of the carbamate linkages and the subsequent reaction of the resulting isocyanate group with the acid anhydride group to give the imide linkages. These results confirm that the introduction of electron-withdrawing groups promoted thermal dissociation of the carbamate linkages effectively and hence the polymerization as expected, and the order of enhancement of dissociation coincides with the electron-withdrawing ability as expressed by Hammett's constants.

The weight losses accounted for 35, 38, 39, and 42% of the initial weights of **4a**, **4b**, **4c**, and **4d**, respectively, which are in good agreement with the theoretical values calculated for the elimination of phenols and carbon dioxide. After the first weight loss, the pyrolysis products were quite stable, and no further considerable weight losses were observed until 450 °C, indicating the formation of highly heat-resistant polymers. The results of thermal analysis are summarized in Table I.

Pyrolytic Polymerization of the Monomers. Pyrolytic self-condensation polymerization was conducted first without solvent using the monomers of high purity, **4a–4c**. The influence of the substituents on the polymerization was evaluated by heating them at 300 °C for 3 h and then at 350 °C for 10 h under reduced pressure, as suggested from the results of thermal analysis of the monomers. When heated, they melted at the melting points and then the melts solidified soon. The inherent viscosities of the resulting poly(imide–esters) were obviously dependent on the structure of the monomers and were 0.12, 0.27, and 0.30 dL/g for **4a**, **4b**, and **4c**, respectively, indicating the chloro substituent to effectively promote the polymerization as a result of improved thermal dissociation.

Table II
Pyrolytic Polymerization of Monomers 4a-c

monomer	method[a]	yield, %	η_{inh}, dL/g[b]
4a	bulk	72	0.33
4b	bulk	79	0.36
4c	bulk	75	0.37
4a	solution	83	0.34
4b	solution	89	0.37
4c	solution	91	0.38

[a] Bulk: heated at 240 °C for 4 h and then at 300 °C for 10 h. Solution: heated in *m*-terphenyl at 300 °C for 6 h. [b] Measured in concentrated sulfuric acid at C = 0.25 g/dL at 25 °C.

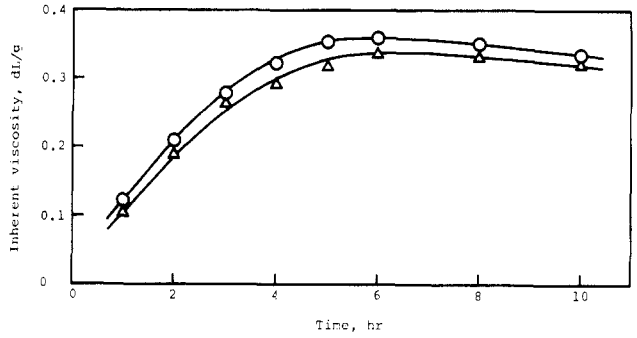


Figure 2. Progress of the pyrolytic polymerization of **4a** (△) and **4c** (○) to **3** in *m*-terphenyl at 300 °C.

The polymerization conditions in bulk were then examined in detail, and a little milder conditions, heating at 240 °C for 4 h and finally at 300 °C for 10 h, were found appropriate. The monomers were thus polymerized under these conditions. The resulting inherent viscosities were up to 0.37 dL/g as summarized in Table II. The bulk polymerization, however, resulted in poor reproducibility on account of the reaction in the solid state, and the viscosities were generally in the range of 0.25–0.37 dL/g. Moreover, the monomers undergo some sublimation on heating at high temperatures, leading to decreases in the polymer yields.

The polymerization was thus also examined in solution in more detail, since much more reproducible results of both the viscosity and the yield could be obtained in solution polymerization than in bulk polymerization. *m*-Terphenyl was chosen as the solvent because of its high thermal stability and inactive nature. The monomers dissolve in this solvent above 90 °C where the solvent liquefies, and the resulting polymers gradually precipitated out of the solution.

The time courses of the polymerization were examined at 300 °C, and the results are illustrated in Figure 2. The polymerization proceeded smoothly and much more quantitatively in solution than in bulk. Similar behavior was observed for each of the three kinds of monomers; the inherent viscosities increased with time but leveled off at about 6 h. The viscosities were 0.34, 0.37, and 0.38 dL/g for the polymers obtained after heating **4a**, **4b**, and **4c** at 300 °C for 6 h, respectively, and the solution polymerization results are included in Table II. The superiority of monomers **4b** and **4c** to **4a** is again observed and explained in terms of the enhanced thermal dissociation as a result of the introduction of a chloro group. Only negligible amounts of reduction were observed in some cases even after heating at 300 °C for 15 h.

Structure of the Poly(imide-ester). The poly(imide-esters) obtained here showed identical IR spectra with each other regardless of the kinds of starting monomers and methods of polymerization. The most characteristic absorption bands were observed at 1780, 1730, and 1710 cm^{-1}, corresponding to the presence of both the imide and ester linkages. The bands due to N–H observed in the spectra of the monomers disappeared completely on polymerization. Figure 3 illustrates the IR spectra of monomer **4c** and poly(imide-ester) **3**. If the heating was insufficient in the bulk polymerization, a weak absorption band of the isocyanate was sometimes found at 2270 cm^{-1}, indicating the imidization reaction by the acid anhydride and the isocyanate requires rather thorough heating to achieve high polymerization in the solid state. The structure of the poly(imide-ester) was also unambiguously confirmed by elemental analysis.

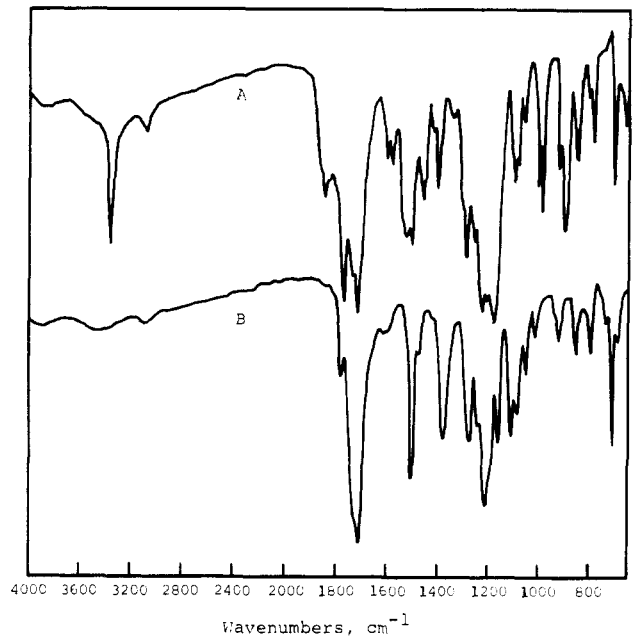


Figure 3. IR spectra of (A) **4c** and (B) **3** (KBr).

Properties of the Poly(imide-ester). The poly(imide-esters) were obtained as pale brown powdery materials. As revealed by the TG curve in Figure 1, the poly(imide-esters) exhibit excellent thermooxidative stability in air. No weight loss was observed until about 450 °C. At 500 °C, the weight loss was only 2–4% of the original weight, and moreover, the color of the polymer had changed little. This indicates that this type of poly(imide-ester) is rated in the highest class among aromatic heat-resistant polymers. DSC analysis showed no distinct inflection point corresponding to T_g.

The solubility of the poly(imide-ester) obtained here was poor as expected from the structure. It was soluble in concentrated sulfuric acid but insoluble in common organic solvents. The polymer was fairly stable in concentrated sulfuric acid but degraded slowly with time judging from the viscosity change; an inherent viscosity of 0.35 dL/g was reduced to around 0.20 dL/g after 24 h at 25 °C. Bulky articles of commercial aromatic polyimides are usually obtained by high-temperature and -pressure molding of polyimides rather than of the more processible polyamic acids to avoid hydrolysis by the water produced on imidization of polyamic acids. The poly(imide-ester) prepared here may be suitable for fabrication by such processing technology.[13]

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Ring-Opening Polymerization of 5,6-Dihydro-4*H*-1,3-oxazin-6-ones, Six-Membered "Azlactones", to Poly(*N*-acyl-β-peptide)s

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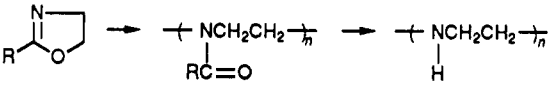
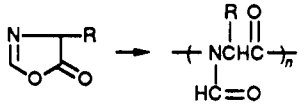
ABSTRACT: Five cyclic monomers, **1a–e**, having the ring structure of a six-membered azlactone, 5,6-dihydro-4*H*-1,3-oxazin-6-one (abbreviated as 6-oxazinone), have been prepared. 2-Ethyl- (**1b**), 2-isopropyl- (**1c**), and 4-phenyl-6-oxazinones (**1e**) were obtained in pure form. 2-Methyl-6-oxazinone (**1a**) and unsubstituted 6-oxazinone (**1d**) were not very stable and were obtained only as a nitrobenzene solution. Cationic polymerization of monomers **1a–c** gave polymers having clear-cut structures of poly(*N*-acyl-β-peptide)s **2a–c**, respectively. Polymers from **1d** and **1e**, however, have structures containing **2d** and **2e**, as well as other unit(s) due to side reaction(s). Thermal polymerization of **1a** and **1e** produced polymers consisting exclusively of structures **2a** and **2e**, respectively.

Introduction

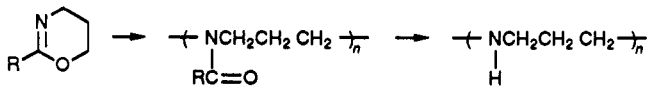
For more than a decade we have been studying extensively the ring-opening polymerizations of 2-oxazolines to produce poly(*N*-acylethylenimine)s or poly(*N*-formylethylenimine).[1] Hydrolysis of these polymers is a versatile method to prepare linear poly(ethylenimine).[2]



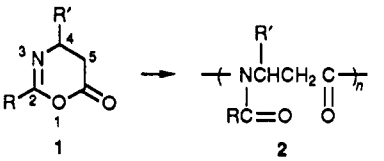
Very recently we have reported a new ring-opening polymerization of 2-unsubstituted 5-oxazolones (five-membered "azlactones"), an analogue of 2-oxazolines, giving rise to poly(*N*-formyl-α-peptide)s.[3]



A six-membered ring family of 2-oxazolines is 5,6-dihydro-4*H*-1,3-oxazines, whose ring-opening polymerizations have been accomplished[1,4] and product polymers gave linear poly(trimethylenimine) via hydrolysis.[2]



Studies on these reactions have been extended to examine the ring-opening polymerization of six-membered azlactones, 5,6-dihydro-4*H*-1,3-oxazin-6-ones (abbreviated as 6-oxazinones,[5] **1**), to give rise to poly(*N*-acyl-β-peptide)s and poly(*N*-formyl-β-peptide)s (**2**). We now report the polymerization results of **1**.

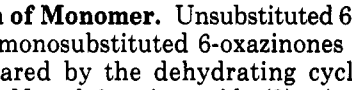


1 **2**

a: R = Me, R′ = H
b: R = Et, R′ = H
c: R = *i*-Pr, R′ = H
d: R = R′ = H
e: R = H, R′ = Ph

Results and Discussion

Preparation of Monomer. Unsubstituted 6-oxazinone (**1d**) and four monosubstituted 6-oxazinones (**1a–c** and **1e**) were prepared by the dehydrating cyclization of *N*-formyl- and *N*-acyl-β-amino acids (**3**). As the dehydration agent of **3**, *N*,*N*′-dicyclohexylcarbodiimide (DCC)[3] or ethyl chloroformate[5a] was employed. Monomers **1a** and **1d** were found to be less stable and obtained only as a nitrobenzene solution after vacuum codistillation using nitrobenzene as a carrier solvent. This codistillation technique was successfully applied previously for the isolation of 2-unsubstituted 5-oxazolones in solution.[3] 2-Ethyl- (**1b**), 2-isopropyl- (**1c**), and 4-phenyl-6-oxazinone (**1e**), on



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