Synthesis and Characterization of Biodegradable Poly(ester anhydride) Based on ε-Caprolactone and Adipic Anhydride Initiated by Potassium Poly(ethylene glycol)ate

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ABSTRACT: Novel biodegradable poly(ester anhydride) block copolymers based on ε-caprolactone (ε-CL) and adipic anhydride (AA) were prepared by sequential polymerization. ε-CL was first initiated by potassium poly(ethylene glycol)ate and polymerized into active chains (PCL-O^-K^+), which were then used to initiate the ring-opening polymerization of AA. The effects of the AA feed ratio, solvent polarity, monomer concentration, and temperature on sequential polymerization were investigated. The copolymers, obtained under different conditions, were characterized by Fourier transform infrared, ^{1}H NMR, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The GPC results showed that the weight-average molecular weights of the block copolymers were approximately 6.0×10^4. The DSC results indicated the immiscibility of the two components. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 1511–1520, 2003

Keywords: poly(ester anhydride); ring-opening polymerization; biodegradable; block copolymers

INTRODUCTION

In the family of aliphatic polyesters, poly(ε-caprolactone) (PCL) is well known for its biodegradability, biocompatibility, nontoxicity, and permeability. PCL is most commonly prepared by the ring-opening polymerization of ε-caprolactone (ε-CL) either in solution or in bulk. However, the relatively high crystallinity of PCL reduces its compatibility with soft tissues, lowers its biodegradability, and limits its applications. Poly(adipic anhydride) (PAA) is another biodegradable polymer characterized by nontoxicity and biocompatibility, and it has been used as a carrier in ocular drug delivery.[1] It can be prepared by different methods, such as (1) classical melt polycondensation from adipic acid and acetic anhydride, (2) melt polycondensation of adipic acid with ketene, and (3) ring-opening polymerization of adipic anhydride (AA).[2] However, polymers so obtained have low molecular weights and broad molecular weight distributions (MWDs) because of the intermolecular and intramolecular transacylation side reactions that perturb the chain propagation. In addition, the degradation rate of PAA is fast, and the degradation can be completed in 2 weeks.[1] Furthermore, PAA has a very low solubility in the usual organic solvents, such as acetone, toluene, and tetrahydrofuran (THF).

To overcome the aforementioned shortcomings of the corresponding homopolymers, researchers have made several efforts to synthesize block co-

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polymers based on ε-CL and AA. Albertsson and Lundmark[3] synthesized AB diblock copolymers of ε-CL and AA with aluminum isopropoxide as a coordination catalyst. However, the obtained copolymers had low molecular weights. Teyssie et al.[4,5] prepared high molecular weight homopolymers and block copolymers of AA with ε-CL, which had a narrow MWD, in the presence of functional aluminum alkoxide. However, for medical and pharmaceutical applications, PCL/PAA copolymers free of aluminum ions are desirable, and so the residue of aluminum alkoxide was removed by repeated extractions with an aqueous ethylenediamine tetraacetic acid (EDTA) solution.[5]

Poly(ethylene glycol) (PEG) has excellent biocompatibility, flexibility, and strong hydrophilicity and has been used widely in biomedical and pharmaceutical fields. In addition, the corresponding alcoholate has been shown to be an alternative to $SnOct_2$ in the ring-opening polymerization of lactones and lactides because of its low toxicity. In our recent studies, the macroinitiator potassium poly(ethylene glycol)ate (PEGOK) has successfully been used in the ring-opening polymerization of D,L-lactide (D,L-LA), ε-CL, and AA.[6–10] As an extension of that work, this article mainly deals with the synthesis of block copolymers based on ε-CL and AA.

EXPERIMENTAL

Materials

Adipic acid (analytical reagent, 99.0%), acetic anhydride (analytical reagent, 98.5%), petroleum ether (analytical reagent, boiling point: 60–90 °C), and ether (analytical reagent) were used as received. ε-CL (Aldrich) was dried over calcium hydride for 48 h at room temperature and then distilled under reduced pressure before use. Poly(ethylene glycol) 2000 (PEG-2000) was purified by precipitation from a chloroform solution into ether and dried to a constant weight under vacuum at 30 °C. Toluene and THF were dried over sodium and distilled under a nitrogen atmosphere before use.

Preparation of AA

AA was prepared as described elsewhere.[2,3,10,11] In a typical reaction, a solution of 30 g of adipic acid in 300 mL of acetic anhydride in a dry reaction vessel equipped with a reflux condenser and a magnetic stirrer was heated for 4 h while nitrogen was continuously bubbled through the solution. The formed acetic acid and the excess acetic anhydride were distilled off under reduced pressure (10 mmHg). The residue was transferred into a Claisen flask and distilled in the presence of zinc acetate under vacuum (0.1 mmHg). The obtained monomer was characterized by Fourier transform infrared (FTIR) and ^{1}H NMR. FTIR results show a doublet at 1800 and 1756 cm^{-1}, which is characteristic of AA, and a second doublet characteristic of the monomer at 961 and 986 cm^{-1}. ^{1}H NMR results show two signals at 2.74 and 1.98 ppm in a 1:1 ratio corresponding to the methylene groups in the α and β positions of carbonyl functions, respectively. These results are in agreement with the expected structure.[3,11]

Preparation of PEGOK[6–10]

One gram of PEG-2000 and fresh potassium particles (over stoichiometry) were placed in a previously flamed and nitrogen-purged glass reactor equipped with a magnetic stirring bar and a reflux condenser. THF (25 mL) was added through a rubber septum with a syringe. The reaction mixture was refluxed for 24 h and filtered. The concentration of the initiator was measured by titration with a 0.04 M aqueous solution of HCl. The result indicates that the two terminal hydroxyl groups of PEG were converted into alcoholate.

Polymerization Procedures

Random Copolymerization

A typical random copolymerization of AA and ε-CL was carried out as follows. ε-CL (1.076 g, 1.00 mL) and 0.610 g of AA were placed in a previously flamed and nitrogen-purged glass reactor equipped with a magnetic stirrer. THF (3 mL) was added through a rubber septum with a syringe. Then, 0.96 mL of PEGOK [*C*, concentration = 0.0914 g/mL; M/I, monomer, initiator = 1000/3 (molar ratio)] was added. The polymerization took place immediately and continued for 12 h at 24.6 °C. It was stopped by the addition of an excess of petroleum ether, and the precipitated polymer was recovered by filtration. The purification process was carried out in the following manner. The product obtained was dissolved in a small volume of chloroform, and several drops of acetic acid were added to acidify it. This solution

was washed with distilled water up to neutral pH and was then precipitated by petroleum ether. The precipitated product was dried and then characterized by FTIR and ^{1}H NMR.

Sequential Polymerization

The sequential polymerization of AA and ε-CL was conducted in two ways.

Method A. To a previously flamed and nitrogen-purged glass reactor equipped with a magnetic stirring bar, 0.610 g of AA was added, followed by 2 mL of THF and 0.33 mL of PEGOK [C = 0.0914 g/mL; M/I = 1000/3 (molar ratio)]. The reaction mixture was maintained at 24.6 °C for 30 min, and then 1.076 g of ε-CL (in 1 mL of THF) was added to the system through a syringe under strictly anhydrous conditions. The polymerization was continued for another 12 h and was stopped by the addition of an excess of petroleum ether. The purification procedure was similar to that mentioned previously.

Method B. ε-CL (1.076 g, 1.00 mL) was added to a nitrogen-purged glass reactor equipped with a magnetic stirring bar. Then, 2 mL of THF and 0.64 mL of PEGOK [C = 0.0914 g/mL; M/I = 1000/3 (molar ratio)] were added subsequently. The reaction mixture was maintained at 24.6 °C for 30 min, and then 0.610 g of AA (in 1 mL of THF) was added to the system through a syringe under strictly anhydrous conditions. The polymerization was continued for another 12 h and was terminated by the addition of a large volume of chloroform/acetic acid (50:1 v/v). The solution was washed with distilled water up to a neutral pH, and a large volume of THF was added. The solution was filtered, concentrated under reduced pressure, and then precipitated by petroleum ether. The precipitated polymer was dried at room temperature until no weight loss was observed.

Characterization

^{1}H NMR spectra of the copolymers were recorded on a Unity Inova 400 spectrometer at room temperature with $CDCl_3$ as the solvent and with tetramethylsilane (TMS) as the internal standard. FTIR spectra were recorded on a Nicolet MX-1 IR spectrometer. The molecular weight and its distribution were determined by gel permeation chromatography (GPC) with a Water Associates model ALC/GPC 2410 apparatus operating with THF and calibrated with polystyrene standards. The apparatus used for differential scanning calorimetry (DSC) was a PerkinElmer DSC 7 thermal analysis apparatus with a heating rate of 10 °C/min.

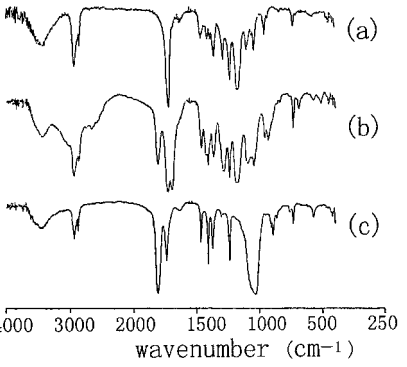


Figure 1. FTIR spectra of (a) PCL–PEG–PCL, (b) PAA–PCL–PEG–PCL–PAA, and (c) PAA–PEG–PAA.

RESULTS AND DISCUSSION

Synthesis of the Block Copolymers

ε-CL, D,L-LA, and AA can be polymerized quickly in the presence of PEGOK.[6–10] Furthermore, biodegradable block copolymers based on D,L-LA and ε-CL have been prepared with PEGOK as an initiator.[9] Similarly, the copolymerization of ε-CL and AA initiated by PEGOK has been investigated. The random copolymerization of ε-CL and AA was considered as a strategy to increase the molecular weight of PAA and to lower the crystallinity of PCL. However, the precipitation of the synthesized polymer from THF was observed; this was similar to the ring-opening polymerization of AA initiated by PEGOK.[10] The white powder obtained was characterized by FTIR [Fig. 1(c)] and ^{1}H NMR [Fig. 2(a)]. The spectral data are similar to those obtained from PAA–PEG–PAA.[10] These facts confirm the formation of PAA–PEG–PAA rather than a random copolymer of PCL and PAA.

When the sequential polymerization was conducted by method A, precipitation phenomena similar to those of random copolymerization were observed. The same spectra of FTIR and ^{1}H NMR indicate that no PCL–PAA–PEG–PAA–PCL, but only PAA–PEG–PAA, formed. These results indicate that PEGOK reacted preferentially with AA

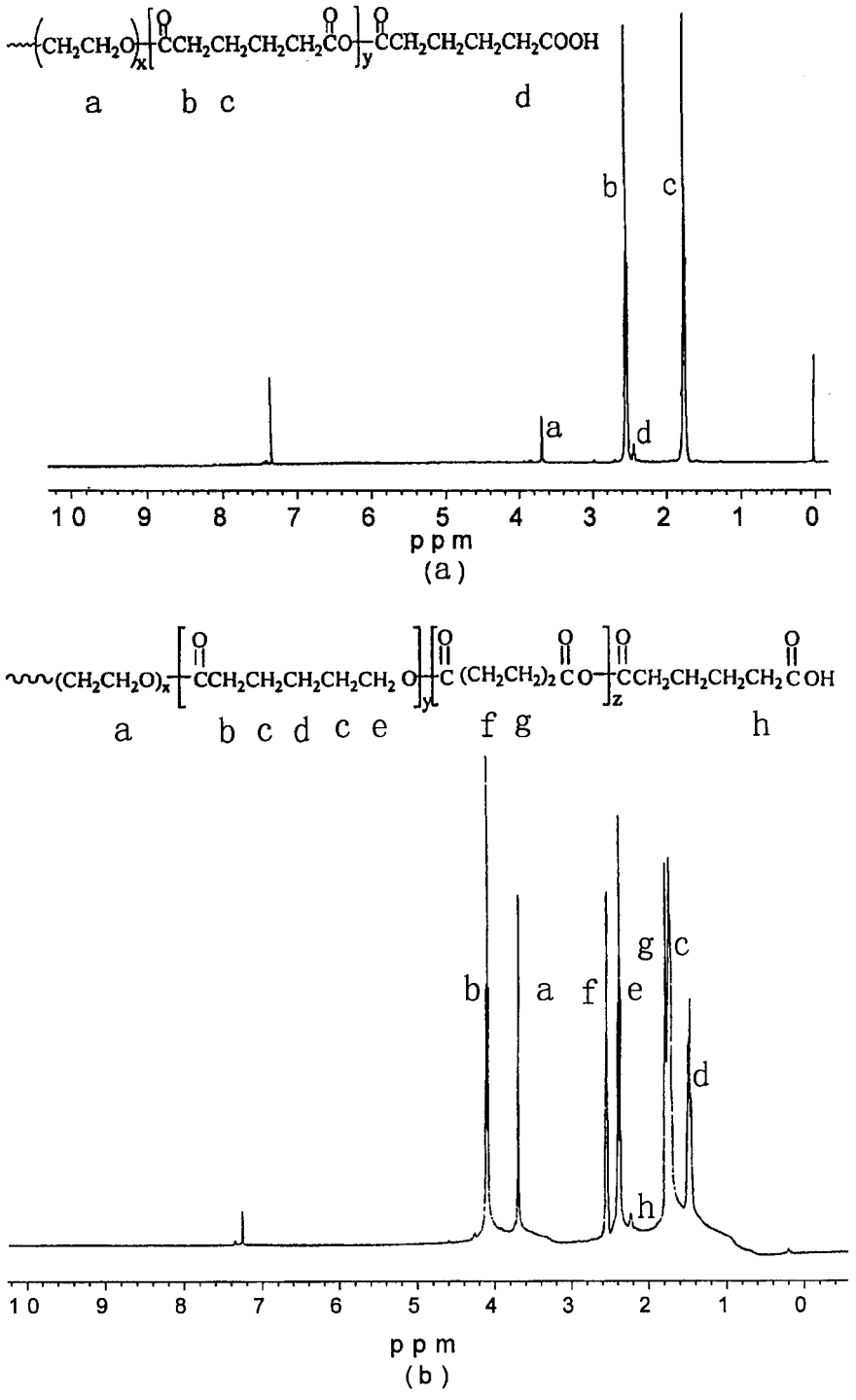
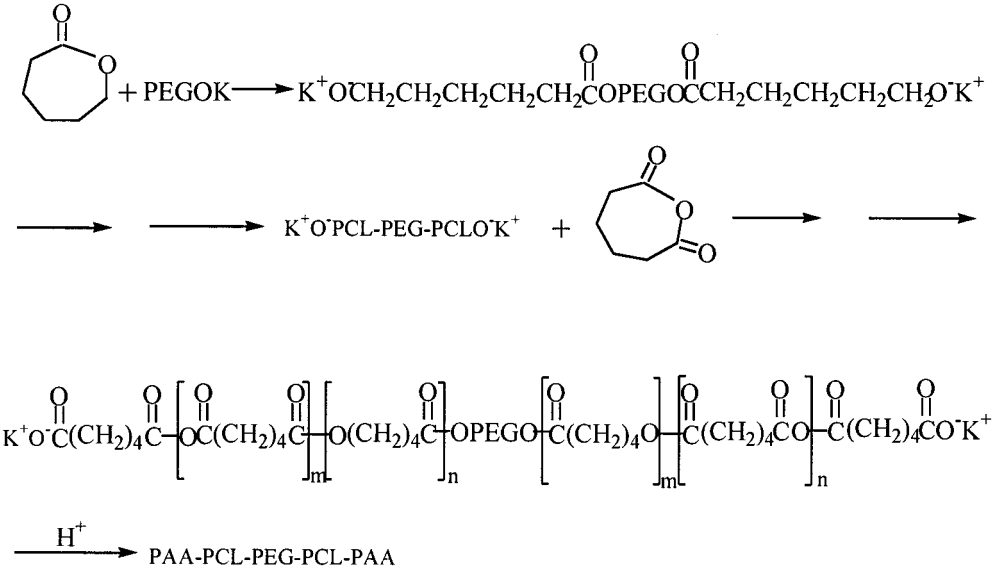


Figure 2. ^{1}H NMR spectra of (a) PAA–PEG–PAA and (b) PAA–PCL–PEG–PCL–PAA in $CDCl_3$.

to form PAA active chains that could not initiate the ring-opening polymerization of ε-CL.

Therefore, a contrary feed sequence was adopted (method B, Scheme 1).ε-CL was first polymerized into PCL active chains (PCL-O^-K^+) that were used to initiate the ring-opening polymerization of AA. The effective polymerization turned the transparent solution into a semi-opaque gel because of the increased viscosity. The polymer obtained was purified and analyzed by



Scheme 1. Reaction scheme for the synthesis of PAA–PCL–PEG–PCL–PAA block copolymers.

FTIR [Fig. 1(b)]. The spectrum of the copolymer obtained is different from the spectra of PCL–PEG–PCL and PAA–PEG–PAA [Fig. 1(a,c)]. The absorption bands at 1811, 1730, and 1697 cm^{-1} are attributed to anhydride and ester carbonyl. Furthermore, the signal intensity of the 1730-cm^{-1} band is greater than the highest frequency band (1811 cm^{-1}) because of the overlapping of the vibrations of anhydride and ester carbonyl. This contrasts with PAA–PEG–PAA [Fig. 1(c)].[10] The bands in the region of 1366–1466 cm^{-1} are assigned to the methylene groups in the copolymer. The bands in the region of 1181–1286 $cm^{-1}$are characteristic of —COO— bond vibrations in PAA segments. The bands at 1046 and 1095 cm^{-1} are ascribed to —C—O—C— bonds in the copolymer. To confirm the formation of the block copolymer further, we recorded the ^1H NMR spectrum, which is shown in Figure 2(b). The sharp singlet at 3.67 ppm is attributed to the methylene protons of homosequences of the PEG oxyethylene units. Peaks at 1.41, 1.67, 2.34, and 4.09 ppm are assigned to methylene protons of —C—CH_2—C—, —CH_2—C—CH_2—, —OCCH_2—, and —CH_2OOC—, respectively, in PCL units. Peaks at 2.50 and 1.75 ppm are assigned to α, β methylene protons in PAA units. The weak peak at 2.20 ppm is attributed to α-carboxyl methylene end groups (—CH_2COOH). These results are consistent with those obtained from PCL–PAA diblock copolymers prepared by the ring-opening polymerization of ε-CL and AA initiated by aluminum triisopropoxide.[4]

Further analyses were made by GPC, and the results are listed in Tables 1–3. The weight-average molecular weights (M_w's) of the block copolymers were approximately 6.0×10^4, higher than those of their corresponding homopolymers. A typical GPC graph is shown in Figure 3. The purified copolymer (curve b) had a narrow MWD, and the crude product (curve a) had a broad MWD caused by the formation of macrocyclic oligomers or homopolymers due to the chain-transfer reactions. It is well known that chain-transfer reactions occur extensively in the anionic ring-opening polymerizations of lactides, lactones, and AA.[2,3,6–10] The degree of chain-transfer reactions can be estimated from the percentage of low molecular weight oligomers or homopolymers. The broad peak at 8.0 min in Figure 3(a) ($M_w = 2.9 \times 10^4$) may be attributed to macrocyclic oligomers caused by chain-transfer reactions, and the peak at 10 min ($M_w = 289$) may be ascribed to the dimer of AA. A possible mechanism of the chain-transfer reactions is shown in Scheme 2 but needs to be further confirmed.

The properties of the comonomer have significant effects on the copolymerization. Table 1 shows the effects of the AA feed ratio on copolymerization in two typical solvents. The molecular weights of the copolymers decreased with an increase in the AA feed ratio for all the cases investigated. Further-

Table 1. Sequential Polymerization of ε-CL and AA in THF and Toluene at 24.6 °C for 12 h Initiated by PEGOK[a]

			Yield (%)		M_w ($\times 10^{-4}$)[a]		MWD[c]		PCL/PAA (Molar Ratio)[e]	
Samples	ε-CL (g)[b]	AA (g)	Toluene	THF	Toluene	THF	Toluene	THF	Toluene	THF
1[d]	2.154	—	97	93	3.610	3.315	—	—	—	—
2	1.076	0.610	87	62	6.489	6.700	1.65	1.60	78:22	80:20
3	1.076	1.220	78	66	6.287	6.008	1.70	1.78	66:34	71:29
4	1.076	1.800	79	61	5.988	5.858	1.79	1.83	49:51	63:37
5	1.076	2.440	86	74	5.712	5.701	1.87	1.88	31:69	28:72

[a] $[\varepsilon\text{-CL}]_0$ = 50% (volume ratio); $[AA]_0$ = 20% (volume ratio); $[PEGOK]/[\varepsilon\text{-CL}]_0$ = 3‰ (molar ratio).
[b] Prepolymerized with an initiator for 30 min and followed by AA.
[c] Measured by GPC.
[d] Calculated from $[\eta] = 1.09 \times 10^{-3} M_\eta^{0.6}$ (25 °C in THF).
[e] Estimated from ^{1}H NMR.

more, MWD tended to be broad for high feed ratios. In addition, the molar ratio of AA in the copolymers was lower than the feed ratio. These facts indicate that the chain-transfer reactions occurred to a significant extent at high feed ratios. However, the yields and molecular weights obtained in toluene were higher than those obtained in THF. It has been shown that the ring-opening polymerization ε-CL, D,L-LA, and AA initiated by PEGOK is a typical anion polymerization, which is influenced by solvent polarity.[6–10] Toluene cannot effectively dissociate compact ion pairs of active species into loose ion pairs and free ions, in contrast to THF. For toluene, this lowers the probability of chain-transfer reactions taking place, and so high yields and narrow MWDs are expected.

The formation of a semiopaque gel at a high monomer concentration (50%, volume ratio) was observed. Therefore, copolymerizations at different monomer concentrations were performed, and the results are summarized in Table 2. The molecular weights of the copolymers increased with an increase in the monomer concentration, and MWD tended to be narrow at high monomer concentrations. The PCL/PAA molar ratios changed slightly, even though the monomer feed ratios were the same. These results suggest that a low monomer concentration is beneficial for the chain-transfer reactions.

The effects of the temperature on the sequential copolymerization of ε-CL and AA were also investigated, and the results are listed in Table 3. The molecular weights of the copolymers decreased with increasing temperature (ranging from 24 to 70 °C), and MWD tended to be broad at high temperatures because of the chain-transfer reactions. Furthermore, the ratios of PCL in the copolymers increased with increasing temperature within the same temperature range. However, prepolymerized PCL precipitated from THF

Table 2. Effects of the Monomer Concentration on the Sequential Copolymerization of ε-CL and AA at 24 °C in THF Initiated by PEGOK[a]

Samples	ε-CL (g)[b]	AA (g)	THF (mL)	Yield (%)	M_w ($\times 10^{-4}$)[c]	MWD[c]	PCL/PAA (Molar Ratio)[d]
1	1.076	0.610	0.00	64	6.316	1.51	83:17
2	1.076	0.610	3.00	80	6.222	1.72	77:23
3	1.076	0.610	5.00	74	6.081	1.79	70:30
4	1.076	0.610	10.00	61	4.017	2.10	80:20

[a] $[PEGOK]/[\varepsilon\text{-CL}]_0$ = 3‰ (molar ratio).
[b] Prepolymerized with an initiator for 30 min and followed by AA.
[c] Measured by GPC.
[d] Estimated from ^{1}H NMR.

Table 3. Effects of the Temperature on the Sequential Copolymerization of ε-CL and AA in THF Initiated by PEGOK[a]

Samples	ε-CL (g)[b]	AA (g)	Temperature (°C)	Yield (%)	M_w ($\times 10^{-4}$)[c]	MWD[c]	PCL/PAA (Molar Ratio)[d]
1	1.076	0.610	0	70	6.049	1.44	90:10
2	1.076	0.610	24	75	6.065	1.76	80:20
3	1.076	0.610	40	77	5.920	1.81	81:19
4	1.076	0.610	70	92	5.956	1.80	89:11

[a] $[\varepsilon\text{-CL}]_0$ = 50% (volume ratio); $[AA]_0$ = 20% (volume ratio); $[PEGOK]/[\varepsilon\text{-CL}]_0$ = 3‰ (molar ratio).
[b] Prepolymerized with an initiator for 30 min and followed by AA.
[c] Measured by GPC.
[d] Estimated from ^{1}H NMR.

at 0 °C, and the reaction system changed from a homogeneous phase to a heterogeneous phase. This change might have rendered the polymerization of AA more difficult, thereby lowering the yield and PAA molar ratio in the copolymer obtained at 0 °C.

Thermal Properties of the Block Copolymers

Both PCL and PAA are crystalline polymers, and their melting temperatures are approximately 58–63[12] and 70–76 °C,[2,3,10,11] respectively. Copolymers with different composition were characterized by DSC analyses, as shown in Figure 4, and the data obtained are given in Table 4. The complete miscibility of the two components at low PAA contents (<30%, molar ratio) was observed. However, the miscibility of the two components decreased with increasing contents of PAA, and this was confirmed by the appearance of double melting peaks representing the fusion of the PCL block and PAA block. In addition, the melting temperatures were shifted slightly to the low values in comparison with their corresponding homopolymers. The heat of fusion decreased with increasing PAA contents and was lower than the values obtained for PCL–PEG–PCL and PAA–PEG–PAA. This may be explained by the reduced crystallinity of the two components due to the interactions of polymer chains. The melting temperature for the PEG segment cannot be observed on the heating curve. This is ascribed to the hindrance effects of the two components on the crystallization of a PEG segment.[10]

Solubility of the Block Copolymers

PAA has very low solubility in most common organic solvents, except chlorinated solvents, such

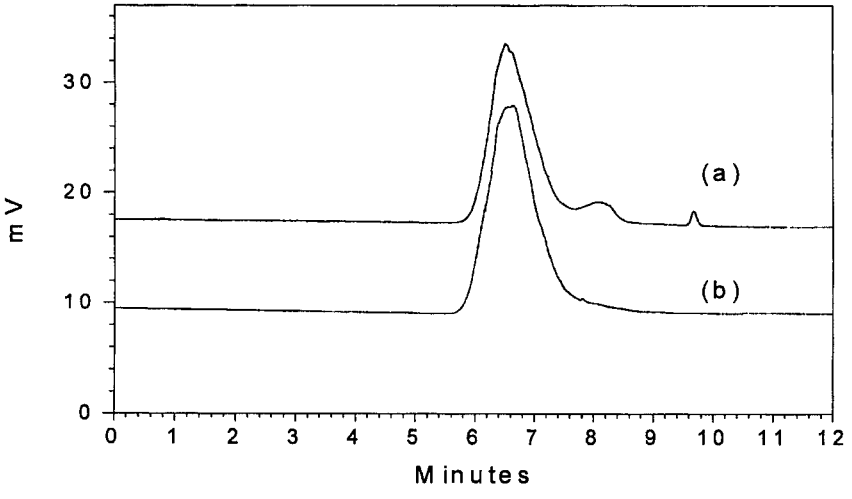
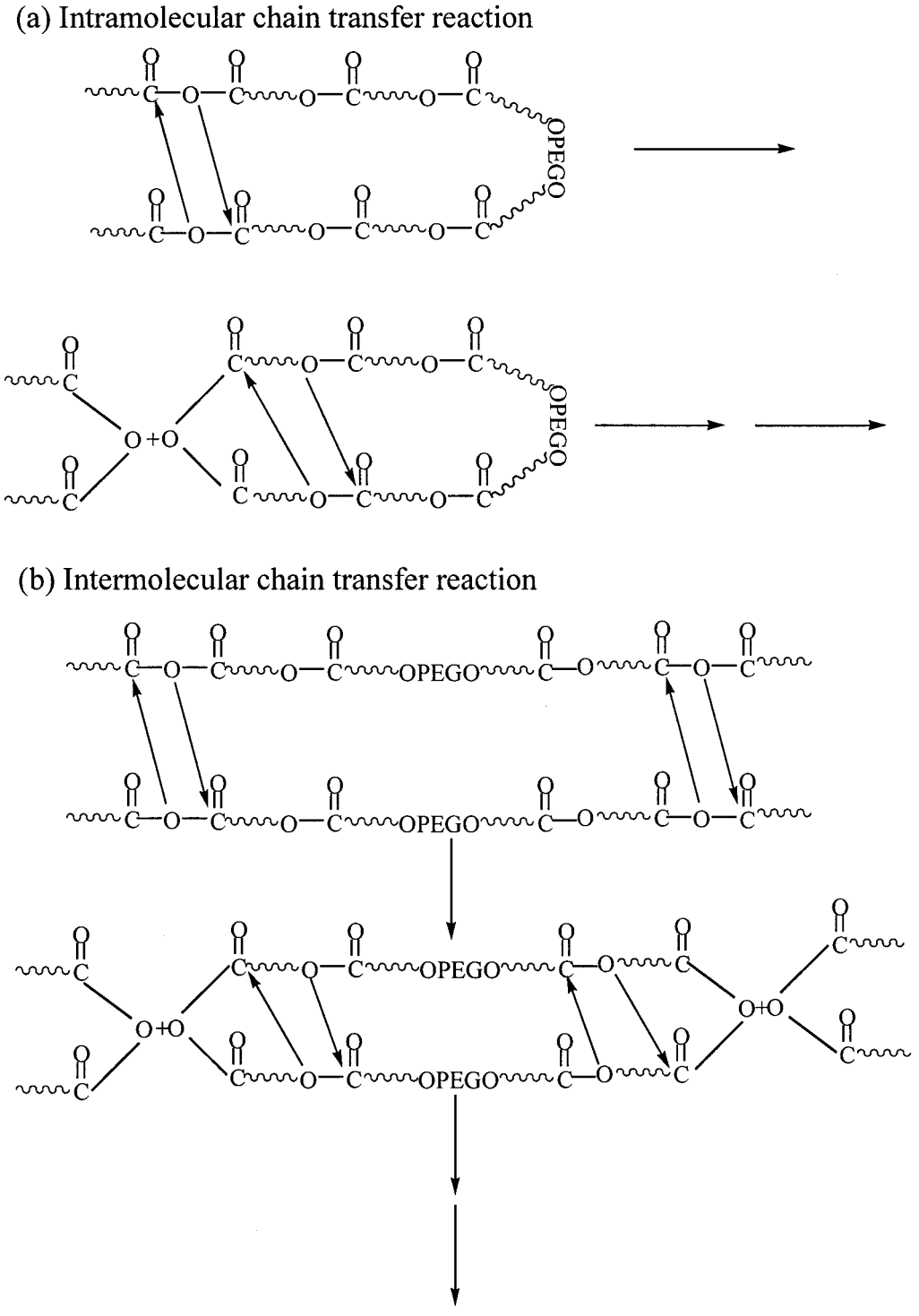


Figure 3. GPC traces of the PAA–PCL–PEG–PCL–PAA block copolymer (entry 2, Table 1): (a) before extraction and (b) after extraction.



Scheme 2. Possible mechanism of chain-transfer reactions.

as $CHCl_3$ and CH_2Cl_2.[4,5,10] However, the block copolymer can be dissolved in THF, toluene, acetone, and so forth. The solubilities of blends of PCL with PAA based on the same ratio used for the block copolymers were studied. The experimental results indicate that the solubility and flexibility of PAA cannot be improved by the blending of PAA with PCL. This fact indirectly confirms the formation of block copolymers and demonstrates that the solubility and film-forming

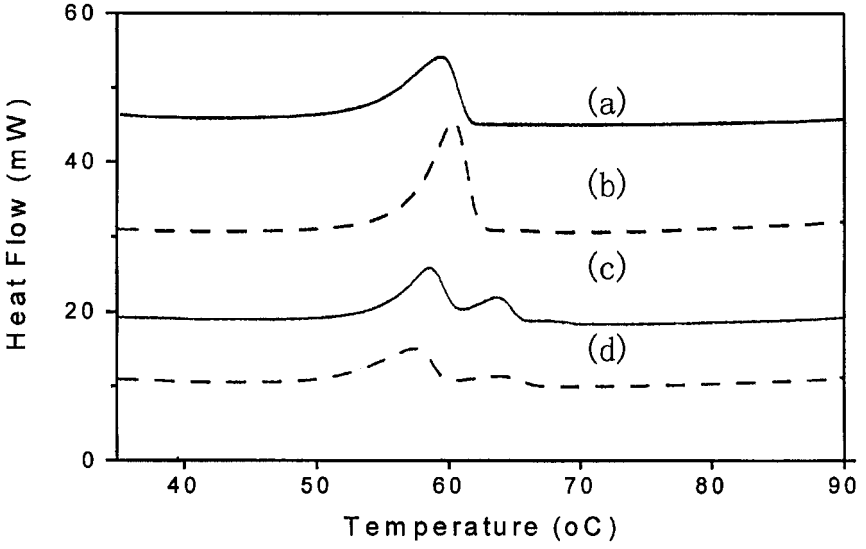


Figure 4. DSC curves of PAA–PCL–PEG–PCL–PAA block copolymers containing different PAA contents: (a) 0, (b) 34, (c) 51, and (d) 69%.

properties of PAA can be improved by the introduction of PEG and PCL into the polymer chains.

CONCLUSIONS

The ring-opening polymerization of ε-CL with AA initiated by nonpoisonous PEGOK has been investigated. FTIR and ^{1}H NMR results demonstrate that attempts to prepare random copolymers and block copolymers with the corresponding structure of PCL–PAA–PEG–PAA–PCL cannot be successful because the active chains (PAA-O$^-$K$^+$) cannot initiate the ring-opening polymerization of ε-CL. However, block copolymers can be obtained when ε-CL is first polymerized into active chains (PCL-O$^-$K$^+$), which are then used to initiate the ring-opening polymerization of AA. GPC results show that M_w's of the block copolymers are approximately 6.0×10^4, higher than those of the corresponding homopolymers. DSC results indicate the immiscibility of the two components. However, the crystallinity of the PCL segment is reduced in comparison with that of the homopolymer, and this is expected to improve its biocompatibility with soft tissues. The results of the solubility experiments show that the copolymers have high solubility in most of the usual organic solvents, and the film-forming property of PAA is improved by the introduction of

Table 4. DSC Data for PAA–PCL–PEG–PCL–PAA Block Copolymers Containing Different PAA Contents

Samples[a]	PCL/PAA (Molar Ratio)[b]	T_m (°C)[c]		ΔH_f (J/g)[c]	
		PCL	PAA	PCL	PAA
PCL–PEG–PCL	—	59.30	—	82.32	—
PAA–PCL–PEG–PCL–PAA	66:34	60.26	—	64.71	—
PAA–PCL–PEG–PCL–PAA	49:51	58.30	63.50	32.55	8.81
PAA–PCL–PEG–PCL–PAA	31:69	57.15	63.70	32.09	5.08
PAA–PEG–PAA	—	—	69.20	—	45.80

[a] All samples were obtained under the same conditions.
[b] Estimated from ^{1}H NMR.
[c] Obtained from DSC (samples weight = 3.08–3.53 mg; scanning rate = 10 °C/min).
T_m: melting temperature.
ΔH_f: heat of fusion.

PCL and PEG segments into the polymer chains. These novel properties of the block copolymers overcome the shortcomings of their corresponding homopolymers; as such, they make the copolymers desirable candidates for biomedical materials and, therefore, are expected to broaden their applications. Furthermore, this approach provides a convenient route for the synthesis of block copolymers based on lactones, lactides, and AA.

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