Polymerization of Oxepan-2,7-dione in Solution and Synthesis of Block Copolymers of Oxepan-2,7-dione and 2-Oxepanone

Stefan Lundmark[a]; Maria Sjöling[a]; Ann-Christine Albertsson[a]

[a] Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden

PLEASE SCROLL DOWN FOR ARTICLE

POLYMERIZATION OF OXEPAN-2,7-DIONE IN SOLUTION AND SYNTHESIS OF BLOCK COPOLYMERS OF OXEPAN-2,7-DIONE AND 2-OXEPANONE

STEFAN LUNDMARK, MARIA SJÖLING,
and ANN-CHRISTINE ALBERTSSON*

Department of Polymer Technology
The Royal Institute of Technology
S-100 44 Stockholm, Sweden

ABSTRACT

The ring-opening polymerization of oxepan-2,7-dione was initiated with 1) cationic initiators such as $AlCl_3$ and $BF_3 \cdot (C_2H_5)_2O$, 2) anionic initiators such as $CH_3COO^-K^+$ and NaH, and 3) coordination-type initiators such as stannous 2-ethylhexanoate and dibutyltin oxide. The reactions were studied at 0, 20, and 40°C in methylene chloride. Oxepan-2,7-dione was also reacted with ε-caprolactone (2-oxepanone) in the presence of aluminum isopropoxide as a catalyst to generate A-B block copolymers.

INTRODUCTION

We recently reported the bulk polymerization of adipic anhydride (oxepan-2,7-dione) using stannous 2-ethylhexanoate as catalyst [1]. It was found that it is possible to ring-open the seven-membered cyclic anhydride at a faster rate and polymerize to higher molecular weights by using stannous 2-ethylhexanoate than it was without catalyst. It was further found that at elevated temperatures the tin catalyst functioned as a depolymerization catalyst. To our knowledge, no publication in the

15

literature deals with the ionic homopolymerization of the seven-membered cyclic anhydride, oxepan-2,7-dione. As an extension of the previous study, we here report the ionic and coordination polymerization of oxepan-2,7-dione in solution.

The study includes different types of cationic, anionic, and coordination-type catalysts taken from well-known reactions in lactone chemistry. The cyclic anhydride polymerization allows control of polymer end groups by selection of different initiating species. The type of end group probably plays an important role in both the thermal stability and hydrolytic stability of the resulting polyanhydride, in the same manner as it does for polyesters [2].

The idea of making block copolymers by ring-opening polymerization is relatively well known [3]. As a part of our effort to prepare aliphatic backbone-degradable materials based on polyanhydrides for hard crystalline materials in thermoplastic elastomers, we have copolymerized ϵ-caprolactone and oxepan-2,7-dione by using aluminum isopropoxide which has been used in the copolymerization of ϵ-caprolactone and L-lactide [4]. Other aliphatic hydrolyzable polymeric materials have been synthesized and characterized at this department [5]. The use of different heterocyclic monomers for ring-opening polymerization is an expanding field of polymer chemistry, and we have been carrying out syntheses and polymerizations of the 1,5-dioxepan-2-one (DXO) [6]. Hydrolyzable rubbers may be useful in slow release formulations [7, 8], and fiber-forming samples might find applications as sutures.

An effort is made to polymerize oxepan-2,7-dione and 1,2,7,8-diepoxyoctane by a ring-opening reaction in a melt at 80°C with aluminum isopropoxide as catalyst. The aim of this work was therefore to study the polymerization of oxepan-2,7-dione in solution, the block copolymerization between oxepan-2,7-dione and 2-oxepanone, and the crosslinking of the anhydride ring with a difunctional epoxide.

EXPERIMENTAL

Materials

Adipic acid (p.a.) was recrystallized from ethanol. Acetic anhydride (p.a.), chloroform (p.a.), petroleum ether (p.a.) and stannous 2-ethylhexanoate were used as received. $AlCl_3$, $BF_3 \cdot (C_2H_5)_2O$, $CH_3COO^-K^+$, 18-crown-6 ether, NaH, stannous 2-ethylhexanoate, and dibutyltin oxide

were used as received. All chemicals were purchased from Aldrich Chemical Co. except stannous 2-ethylhexanoate which was purchased from Sigma Chemical Corp. The ε-caprolactone (a commercial reagent) was dried over CaH_2 and purified by distillation under reduced pressure (82°C/1.5 mbar). The aluminum isopropoxide catalyst (Aldrich) was distilled under vacuum (120°C/0.9 mbar).

Monomer Synthesis

Oxepan-2,7-dione was prepared as described previously [1].

Polymerization

The solution polymerization of oxepan-2,7-dione (1) was carried out in the following manner. To a 20-mL serum bottle, containing a magnetic stirrer, 16.0 mmol of monomer (1), 10 mL of dichloromethane, and 0.06 mmol of the catalyst were added ([M]/[I] = 250) under nitrogen. The mixture was heated in the sealed tube at 40°C for 24 h. The polymer formed was then precipitated in dry petroleum ether, filtered, and dried to constant weight in a desiccator for 24 h.

Copolymerization

Copolymerization was carried out in a previously dried 20-mL serum bottle. Aluminum isopropoxide, CH_2Cl_2, and ε-caprolactone were added successively through a syringe under N_2 atmosphere.

Once the ε-caprolactone was completely polymerized, the oxepan-2,7-dione was also added in a N_2 atmosphere, and the copolymerization reactions were stopped by adding an excess of 2 N HCl. The organic phase was then successively washed with 0.5 N HCl and water. The crude copolymer product was precipitated in petroleum ether and dried at 40°C under vacuum.

Crosslinking

The crosslinking reaction was carried out in a 20-mL serum bottle to which 2 g of oxepan-2,7-dione, and 4 mol% of a difunctional aliphatic epoxide (1,2,7,8-diepoxyoctane) together with aluminum isopropoxide were added. The bottle was flushed with N_2 and the temperature was raised to 80°C.

Measurement

The polymers obtained were characterized by GPC, DSC, IR, and ¹H-NMR. A Waters 6000 A pump with five Shodex columns connected to a differential refractometer was used for GPC with chloroform as solvent. The flow rate was 1 mL/min. The apparatus was run at 34°C with a solvent pressure of 4.5 MPa (650 psi). PS standards were used for calibration. The apparatus used for DSC was a Perkin-Elmer DSC-7 with a heating rate of 10°C/min and a cooling rate of 20°C/min, giving the samples the same thermal history. The FTIR used was a Perkin-Elmer 1710. Spectra were taken on polymer films cast from chloroform solution on NaCl windows. The NMR used was a JEOL JNM-PMX 60 SI.

Samples were dissolved in dueterochloroform. The initiation step of the polymerization reactions was studied by IR spectroscopy. A mixture of oxepan-2,7-dione and initiator ([M]/[I] = 250) was held at room temperature for 5 min, and the characteristic IR frequencies were followed.

RESULTS AND DISCUSSION

Results of Synthesis

Following a depolymerization procedure described by Megna and Koroscil for the preparation of ε-caprolactone [9], an improved method of preparation of oxepan-2,7-dione was developed [1] by using poly-(adipic anhydride) to give the 7-membered anhydride ring analog.

Results of Polymerization

The polymerization of oxepan-2,7-dione was studied at 0, 20, and 40°C in three types of stepwise initiated polymerizations: a) cationic, b) anionic, and c) coordination initiation. The results are summarized in Tables 1–3. As can be seen in these tables, each initiator resulted in high yields of polymer, roughly 80–90% conversion in most cases, with very few exceptions.

At low temperatures, lower yields were obtained with cationic initiation by using $BF_3 \cdot (C_2H_5)_2O$ and coordination-type initiators such as dibutyltin oxide. The molecular weight attained at temperatures above 0°C was about 3000 (M_w). Deviations from this value were found with anionic initiation at higher temperatures which resulted in higher molec-

TABLE 1. Polymerization of Oxepan-2,7-dione in CH_2Cl_2 at 0°C, 24 h

Experiment	Initiator	$[M]/[I]^b$	Yield, %	Molecular weight, M_w
1	$BF_3 \cdot (C_2H_5)_2O$	250	83	1700
2	$AlCl_3$	250	99	1500
3	NaH	250	89	3200
4	$CH_3COO^-K^{+a}$	250	89	3400
5	$(C_4H_9)_2SnO$	250	73	3100
6	Sn-oct	250	93	3200

[a]In the presence of 18-crown-6 ether.
[b]Molar ratio.

TABLE 2. Polymerization of Oxepan-2,7-dione in CH_2Cl_2 at 20°C, 24 h

Experiment	Initiator	$[M]/[I]^b$	Yield, %	Molecular weight, M_w
1	$BF_3 \cdot (C_2H_5)_2O$	250	70	2300
2	$AlCl_3$	250	91	2700
3	NaH	250	91	4800
4	$CH_3COO^-K^{+a}$	250	88	4300
5	$(C_4H_9)_2SnO$	250	76	3700
6	Sn-oct	250	82	4700

[a]In the presence of 18-crown-6 ether.
[b]Molar ratio.

TABLE 3. Polymerization of Oxepan-2,7-dione in CH_2Cl_2 at 40°C, 24 h

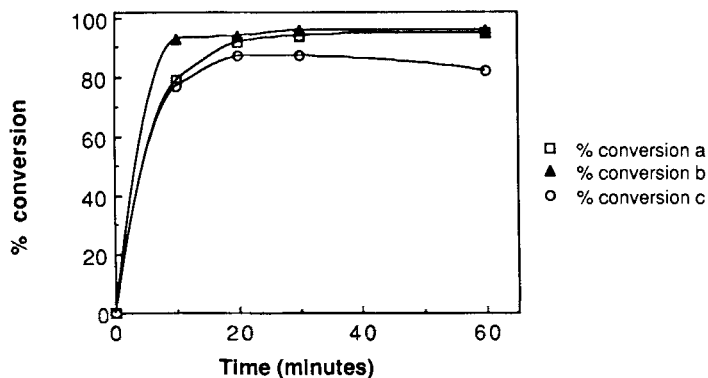| Experiment	Initiator	$[M]/[I]^b$	Yield, %	Molecular weight, M_w
1	$BF_3 \cdot (C_2H_5)_2O$	250	94	2400
2	$AlCl_3$	250	92	2200
3	NaH	250	91	4900
4	$CH_3COO^-K^{+a}$	250	92	4500
5	$(C_4H_9)_2SnO$	250	87	3200
6	Sn-oct	250	91	3800

[a]In the presence of 18-crown-6 ether.
[b]Molar ratio.

FIG. 1. Conversion as a function of time for the ring-opening polymerization of oxepan-2,7-dione in solution at 0°C with a) $AlCl_3$, b) $CH_3COO^-K^+$, and c) stannous 2-ethylhexanoate.

ular weights, 4000–5000 g/mol (M_w). The solvent chosen for these studies was CH_2Cl_2 even though it is not the ideal solvent for anionic polymerization. The ratio of monomer to initiator was 250, which was previously found to be suitable for the melt polymerization of oxepan-2,7-dione [1]. The initial polymerization path was studied using ^{1}H-NMR. The consumption of the monomer oxepan-2,7-dione was calculated from the ratio of the integrals of the $-CH_2-CO-O-CO-CH_2-$ protons in the ring and open form. Samples were taken at reaction times of 10, 20, 30, and 60 min at 0, 20, and 40°C.

Curves showing the conversion from monomer ring to open form as a function of time are presented in Figs. 1–3. At each temperature studied it was found that anionic initiation with $CH_3COO^-K^+$ was indeed very fast. The reaction was complete after 15 min. At 0°C the rate of reaction of every initiating type was slower than at 20 and 40°C.

At 40°C it was observed that stannous 2-ethylhexanoate might work as a depolymerization catalyst. This is in agreement with earlier observations found for the melt polymerization of oxepan-2,7-dione with stannous 2-ethylhexanoate [1].

Proposed polymerization mechanisms are presented in Figs. 4–6. The cationic ring-opening of oxepan-2,7-dione gives rise to an acid end group, the anionic reaction gives a ketone or, in the case of NaH, an aldehyde end group. The coordination type of initiation results in an anhydride end group.
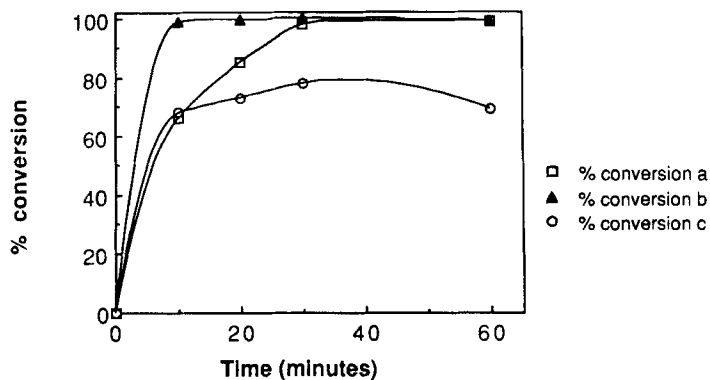
FIG. 2. Conversion as a function of time for the ring-opening polymerization of oxepan-2,7-dione in solution at 20°C with a) $AlCl_3$, b) $CH_3COO^-K^+$, and c) stannous 2-ethylhexanoate.
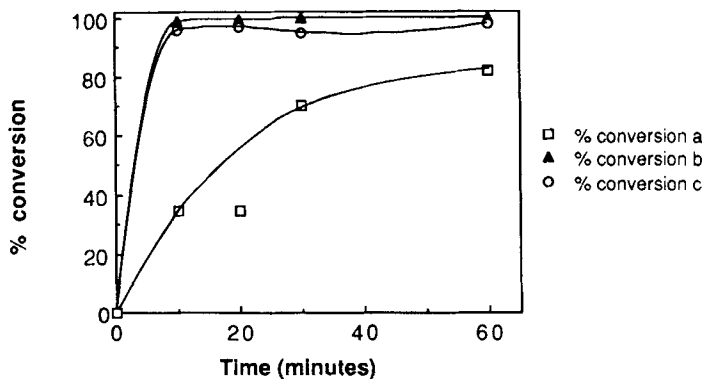

FIG. 3. Conversion as a function of time for the ring-opening polymerization of oxepan-2,7-dione in solution at 40°C with a) $AlCl_3$, b) $CH_3COO^-K^+$, and c) stannous 2-ethylhexanoate.
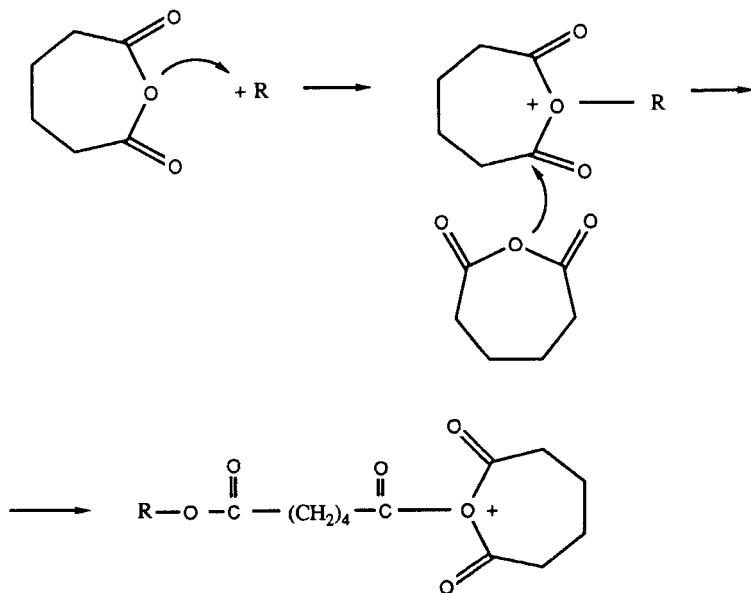
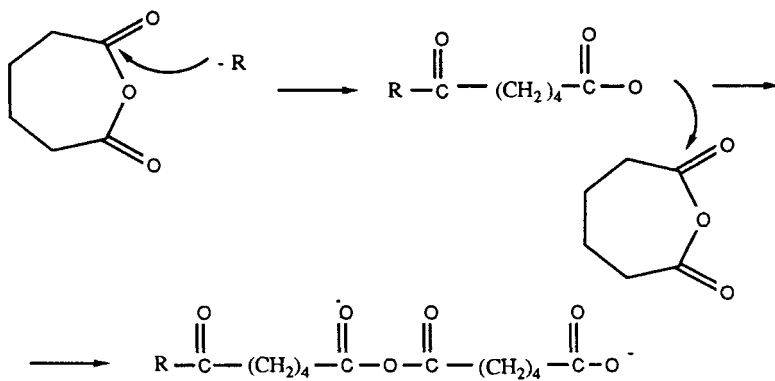FIG. 4. Reaction mechanism for the cationic initiation of oxepan-2,7-dione.

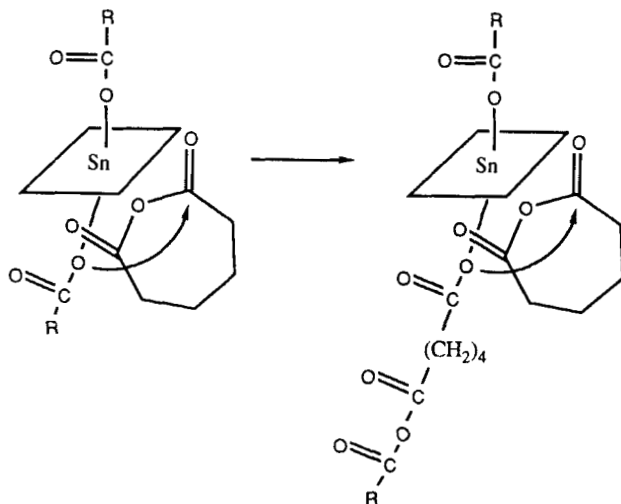FIG. 5. Reaction mechanism for the anionic initiation of oxepan-2,7-dione.

FIG. 6. Reaction mechanism for the coordination initiation of oxepan-2,7-dione.

The latter was confirmed by preparing equimolar amounts of initiator and monomer in CH_2Cl_2 at room temperature and measuring the shifts in IR frequencies of the resulting compounds. Characteristic IR frequencies of oxepan-2,7-dione after reactions with $AlCl_3$, NaH, and stannous 2-ethylhexanoate in CH_2Cl_2 at room temperature, $[M]/[I] = 1$, are presented in Table 4.

In small ring acid anhydrides in the carbonyl region, it is found that the intensity of the lower frequency band (asymmetric) is always much greater than the band at higher frequency (symmetric) [10]. The opposite is the case for open-chain compounds. Hence, the anhydride doublet intensities can be used to distinguish ring compounds from open-chain compounds.

The ketone aldehyde ester and acid groups can also be readily distinguished from one another in these polymers. All the results from the coordination experiments are summarized in Table 4.

Results of Copolymerization and Crosslinking

The A-B diblock copolymer of ε-caprolactone and oxepan-2,7-dione has been synthesized due to the nonterminated cationic end of the poly(ε-caprolactone) by using aluminum isopropoxide as a coordination
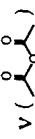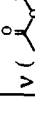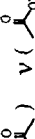
Exp.no.	Monomer/Initiator mixture	Time (minutes)	Original IR-frequencies (cm⁻¹)		Shifted or new IR-frequencies (cm⁻¹)		
			$\nu(\ )$	$\nu(\ )$	$\nu(\ )$	$\nu(\ )$	$\nu(\ )$
1	Oxepan -2,7-dione	5	1801,1757	-	1801,1757	-	-
2	AlCl$_3$ + Oxepan -2,7-dione	5	1801,1757	-	-	1650	1790
3	NaH + Oxepan -2,7-dione	5	1801,1757	-	-	1567	1734
4	Stann. 2-et. + Oxepan -2,7-dione	5	1801,1757	1708	1814,1759	1708	-

TABLE 4. Characteristic IR frequencies of Oxepan-2,7-dione after Reactions with AlCl$_3$, NaH, and Stannous 2-ethylhexanoate in CH$_2$Cl$_2$ at Room Temperature [M]/[I] = 1.
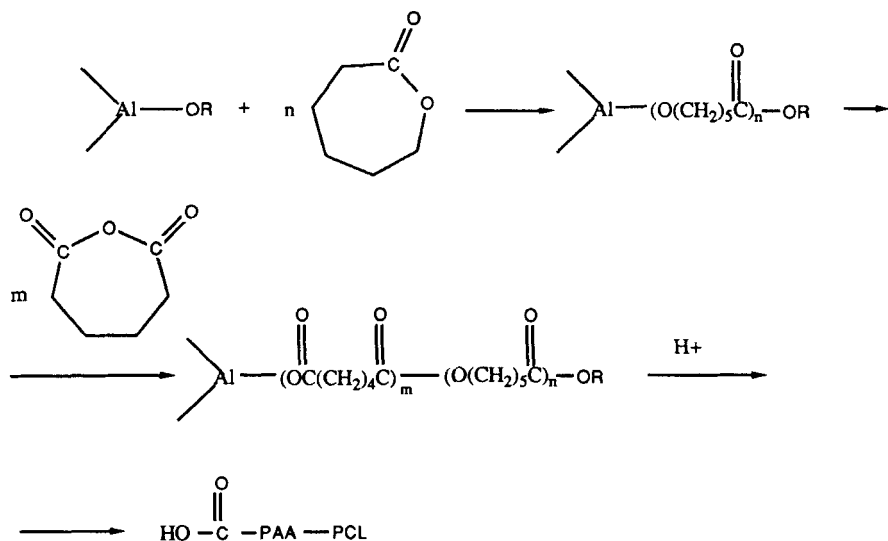
FIG. 7. Reaction of ε-caprolactone and oxepan-2,7-dione.

catalyst (Fig.7). The reaction was carried out at 90°C. When a portion of the polymer was melted on a glass plate, a rod could be immersed into the melt, and when the rod was removed, a fiber of the polymer occurred which exhibited some elasticity.

The chemical structure of the reaction product was studied by ^{1}H-NMR with the result shown in Fig. 8. Pure poly(adipic anhydride) gives signals at 1.75 and 2.5 ppm due to the $-CH_2CH_2-$ and $-CH_2-CO-O-CO-CH_2-$ protons, respectively [11]. The integrals have a 1:1 ratio. Chemical shifts occur at 1.5, 2.1, and 4.0 ppm for pure poly(ε-caprolactone) from the $-CH_2CH_2CH_2-$, $-O-CO-CH_2-$, and $-CH_2-O-CO-$ protons. The ratio between the integrals is 3:1:1. As can be seen in the NMR spectra in Fig. 8, the peaks at 2.1–2.5 and 1.5–1.75 include the poly(adipic anhydride). In pure poly(ε-caprolactone) the ratio A:C is 1:1 and the spectra show A < C.

The IR spectrum of the block copolymer is shown in Fig. 9. The spectrum shows half of the anhydride doublet around 1800 cm^{-1} and ester frequencies at 1728 cm^{-1} which overlap the antisymmetric vibration from the anhydride. The spectrum also shows the presence of terminal
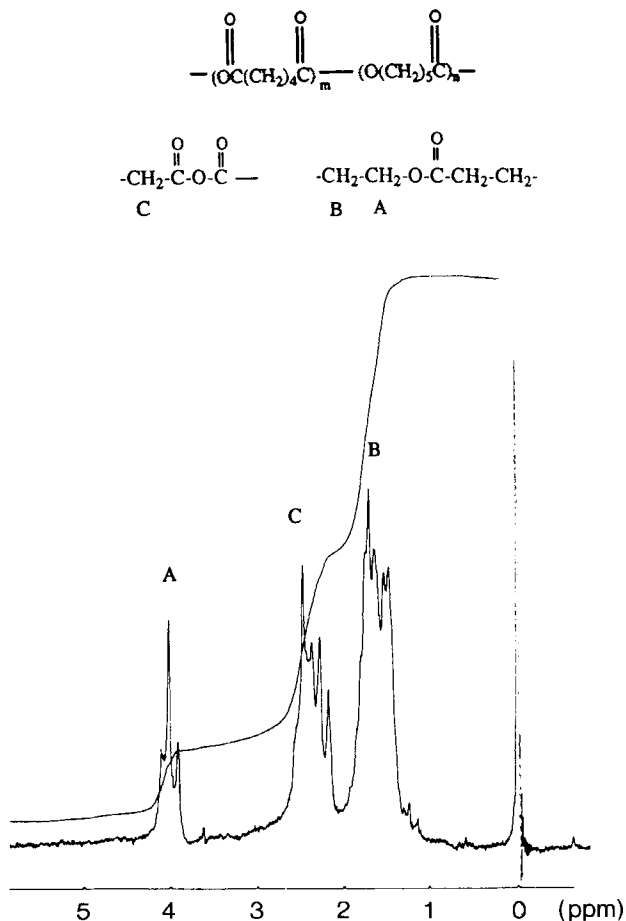
$$-(OC(CH_2)_4C)_m - (O(CH_2)_5C)_n -$$

$$-CH_2\text{-}C\text{-}O\text{-}C - \qquad -CH_2\text{-}CH_2\text{-}O\text{-}C\text{-}CH_2\text{-}CH_2\text{-}$$
$$\text{C} \qquad\qquad\qquad \text{B} \quad \text{A}$$

FIG. 8. ^{1}H-NMR spectrum of the ϵ-caprolactone and oxepan-2,7-dione co-polymer.

carboxylic groups (—OH vibration at 3400 cm^{-1} and —CO—OH stretching at 1567 cm^{-1}). The oxepan-2,7-dione was indeed block copolymerized onto the prepolymer as proved by the increase in molecular weight. The number-average molecular weight increased from 18,000 to 28,000, and the weight-average molecular weight increased from 47,000 to 58,000 after addition of oxepan-2,7-dione.

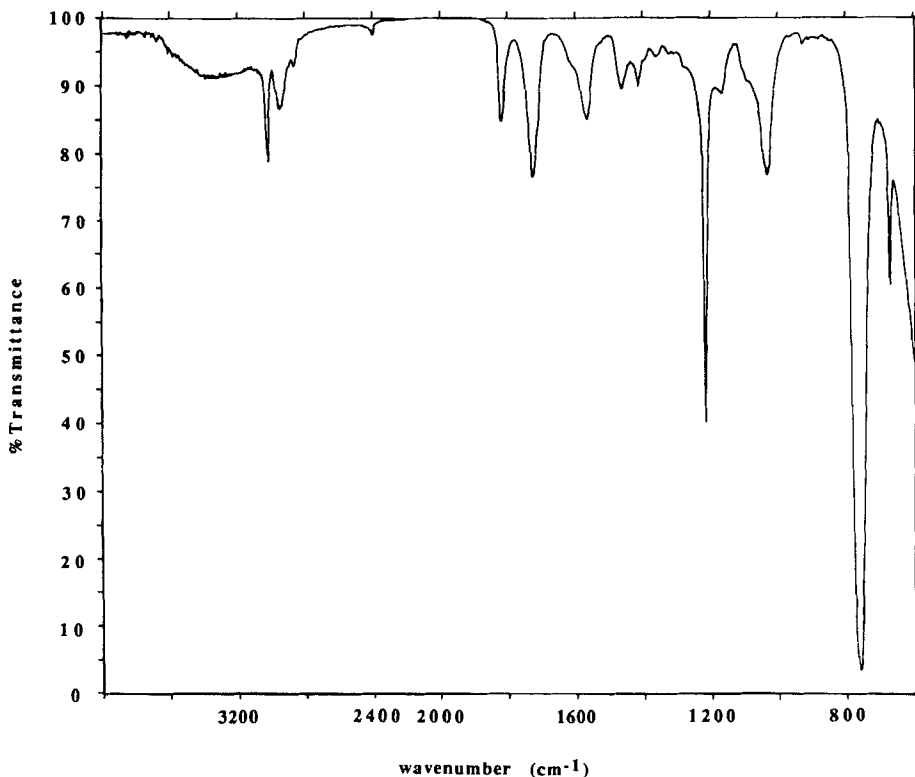Gel permeation chromatography curves of the block copolymers are

FIG. 9. IR spectrum of the ε-caprolactone and oxepan-2,7-dione copolymer.

very similar to those of poly(ε-caprolactone) homopolymer, and the molecular weight distribution of the block copolymers is about two to three, probably because initiation is not faster than propagation and because the initiator caused transesterification and anhydride-exchange reactions.

As an initial test, oxepan-2,7-dione was reacted with a difunctional aliphatic epoxide, 1,2,7,8-diepoxyoctane, with the purpose of achieving an elastic material. The resulting polymer showed rubberlike characteristics completely different from earlier polymers. This elastic effect is thought to be the result of crosslinking of the poly(adipic anhydride) with the difunctional epoxide.

CONCLUSIONS

This work shows that oxepan-2,7-dione can be polymerized by ring opening the seven-membered anhydride ring in solution by using cationic, anionic, and coordination-type catalysts. The ring opening occurs by acyl–oxygen cleavage in all cases. It is also possible to make A-B block copolymers between oxepan-2,7-dione and 2-oxepanone in the presence of aluminum isopropoxide as catalyst. In the presence of aluminum isopropoxide, a crosslinked hydrolyzable material can be obtained by reaction between oxepan-2,7-dione and an aliphatic difunctional epoxide, 1,2,7,8-diepoxyoctane.

ACKNOWLEDGMENTS

REFERENCES

[1] A.-C. Albertsson and S. Lundmark, *J. Macromol. Sci. – Chem.*, *27*, 397 (1990).
[2] G. L. Brode and J. V. Koleske, *Ibid.*, *A6*, 1109 (1972).
[3] R. D. Lundberg and E. F. Cox, Ring Opening Polymerization, Vol. 2 (K. C. Frisch and S. L. Reegan, eds.), Dekker, New York, 1969, p. 247.
[4] J. M. Vion, R. Jerome, P. Teyssié, M. Aubin, and R. E. Prud'homme, *Macromolecules, 19*, 1828 (1986).
[5] A.-C. Albertsson and O. Ljungquist, *Acta Polym.*, *39*, 95 (1988).
[6] T. Mathisen, K. Masus, and A.-C. Albertsson, *Macromolecules, 10*, 3842 (1989).
[7] A.-C. Albertsson and O. Ljungquist, *J. Macromol. Sci. – Chem.*, *A23*, 411 (1986).
[8] C. G. Pitt, Z-W. Gu, P. Ingram, and R. W. Hendren, *J. Polym. Sci., Polym. Chem. Ed.*, *25*, 955 (1968).
[9] I. S. Megna and A. Koroscil, *J. Polym. Sci., Part B, 6*, 653 (1968).

[10] B. George and P. McIntyre, *Infrared Spectroscopy*, Wiley, Chiches-
ter, 1987.
[11] A.-C. Albertsson and S. Lundmark, *J. Macromol. Sci. — Chem.,*
A25, 247 (1988).