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Polylactones. 4.* Cationic Polymerization of Lactones by Means of Alkylsulfonates

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ABSTRACT

Cationic polymerizations of β-propriolactone (Prop), ϵ-caprolactone (Capr), and glycolide (Glyc) were initiated by various alkylsulfonates, such as methyl fluorosulfate, ethyl fluorosulfate, methyl trifluoromethanesulfonate (triflate), methyl methanesulfonate, methyl p-nitrobenzene sulfonate, γ-propane sultone, and δ-butane sultone. Systematic variation of reaction time and temperature revealed that only methyl fluorosulfate and methyl triflate can give high yields, yet the temperature must be kept in a narrow range (50 ± 10°C). Due to the living character of the cationic endgroups, high temperatures may cause rapid degradation of the initially formed polylactones. However, at appropriate temperatures, the living chain ends permit the synthesis of block copolyesters. The sequences of the two-block copolyesters built up of Prop and Glyc or Capr and Glyc units were characterized by means of ^{13}C-NMR spectra and compared to random copolylactones. The DSC curves

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of the two-block copolyesters display the expected two melting endotherms, whereas those of the random copolyesters do not.

INTRODUCTION

Recently, the cationic polymerization of lactones has attracted new interest, first because cationic initiators are better than many other initiators for the synthesis of random copolyesters of glycolide [1, 2], and second, because the mechanism of cationic polymerizations has become a matter of controversy [3-5]. Various classes of cationic initiators, such as protic acids (e.g., sulfonic acid), Lewis acids (e.g., ferric chloride or boron trifluoride), acylating reagents (e.g., acetylium perchlorate), and alkylating reagents (e.g., triethyloxomium salts or methyl fluorosulfate) can be used to polymerize lactones. Thus the question arises as to which initiators are best suited for preparative purposes or mechanistic studies. For preparative applications, properties such as stability on storage, low sensitivity to moisture, and good solubility in organic solvents are desirable in addition to a high efficiency with regard to yield and reaction rate. From this point of view, alkylsulfonates are more attractive than ionic alkylating reagents, which are more difficult to handle. For mechanistic studies the formation of stable, spectroscopically detectable endgroups (e.g., ester or ether groups) are desirable. In this respect, alkylating reagents are advantageous over protic acids or Lewis acids. Therefore, it was the purpose of the present work to study the preparative aspects of alkylsulfonate-initiated polymerization of lactones. The mechanistic aspects will be discussed in the succeeding part of this series.

EXPERIMENTAL

Materials

Glycolide, a gift of Boehringer & Sohn (Ingelheim, FRG), was recrystallized from dry ethanol and dried over phosphorus pentoxide in vacuo. ϵ-Caprolactone and β-propiolactone, purchased from Fluka AG (Buchs, Switzerland), were distilled under nitrogen over oligomeric methylene diphenyldiisocyanate. Nitrobenzene was refluxed and distilled in vacuo over phosphorus pentoxide. High molecular weight poly(ϵ-caprolactone) with a T_m of 60°C was purchased from Aldrich Co. (U.S.A.).

Polymerizations

(A) The homopolymerizations were conducted with solutions of 40 mmol lactone in 25 mL nitrobenzene. The initiator was added in the form of an 1-M solution in dry nitrobenzene. Erlenmeyer flasks (50 mL) with ground glass joints closed with glass stoppers and steel springs were used as reaction vessels. They were silanized with dimethyldichlorosilane and purged with nitrogen prior to use. The reaction vessels were completely immersed in the thermostated oil bath to prevent distillation of monomer to colder parts of the flask. After a given time the reaction mixture was diluted with ~20 mL methylene chloride and poured into ~600 mL cold methanol. The precipitated polyesters were isolated by filtration and dried at 60°C in vacuo.

(B) The copolymerizations were conducted with mixtures of 20 mmol glycolide and 20 mmol β-propiolactone as described above (A).

(C) The block copolymerizations were started with solutions of 25 mmol ϵ-caprolactone or β-propiolactone in 20 mL nitrobenzene. After a reaction time of 24 h, a freshly prepared solution of 25 mmol glycolide in 20 mL warm nitrobenzene was rapidly added. Afterward, the polymerization was continued and worked up as described above (A).

Degradation of Poly(ϵ-Caprolactone)

Poly(ϵ-caprolactone) (40 mmol) was dissolved in 25 mL warm nitrobenzene, and methyl triflate (M/I = 100:1) was added in the form of an 1-M solution in nitrobenzene. The reaction mixture was thermostated under nitrogen in a closed Erlenmeyer flask and finally poured into ~500 mL cold methanol. The precipitated polyester was isolated by filtration and dried at 60°C in vacuo. The yields given in Fig. 1(B) refer to a sample that was dissolved and precipitated without treatment with methyl triflate.

Measurements

The comonomer ratios were determined from the signal intensities of 360 MHz ^{1}H-NMR spectra. These spectra were measured on a Bruker AM-360 FT spectrometer with solutions of 50 mg copolyester in 1 mL of deuterated trifluoroacetic acid (TFA).

The ^{13}C-NMR sequence analyses were conducted with a Bruker WP 80 FT spectrometer. Solutions of 300 mg copolyester in 2 mL of a mixture of TFA and $CDCl_3$ (1:3 by volume) were measured in 10 mm o.d. sample tubes. A pulse width of ~45° was used along with a spectral width of 8K/5 000 Hz and a relaxation delay of 1 s. Zero filling was used before Fourier-transform, and ~10 000 transients were accumulated.

The DSC measurements were conducted with a Perkin-Elmer DSC-4 machine at a heating rate of 20°C/min. In Fig. 5, the first heating curves are shown because repeated heating may change the sequence due to transesterification.

The intrinsic viscosities in benzene used for the calculation of weight-average molecular weights (cf. Footnotes of Tables 1 and 2) were determined at 30°C by means of automated Ubbelohde viscometers.

RESULTS AND DISCUSSION

Optimization of the Reaction Conditions

In general, cationic polymerizations of both α-olefins and cyclic monomers are not considered to be the optimum method for preparative purposes, because in many cases unavoidable side reactions limit both yield and molecular weight of the resulting polymers. In two previous papers of this series, various acidic catalysts were tested as initiators of the copolymerization of glycolide and ε-caprolactone or δ-valerolactone. From these experiments it was learned that reaction conditions favoring high rates of polymerization also favor a fast degradation of the initially formed polyester.

Hence, in the case of cationic polymerization of lactones, a high reactivity of the system is not necessarily optimum for preparative purposes. In some preliminary experiments with the two most reactive initiators, methyl fluorosulfonate and methyl triflate, it was found that a reaction temperature of 0°C is too low for a satisfactory polymerization of glycolide, β-propiolactone, or ε-caprolactone. Thus, all further polymerizations (Tables 1-3 and Figs. 1 and 2) were conducted at 25°C or above.

The relative reactivities of the various alkylsulfonates and the influence of both reaction time and temperature were studied in a series of homopolymerizations of ε-caprolactone (Table 1). A monomer/initiator ratio of 100:1 was used for all polymerizations of this series, and nitrobenzene was the preferred reaction medium. From the yields of poly(ε-caprolactone) obtained at 50 or 100°C, the following order of reactivity may be deduced for the initiators: Me triflate > Me fluorosulfate >> Et fluorosulfate > Me p-nitrobenzenesulfonate > γ-propane sultone > δ-butane sultone ≈ Me methanesulfonate.

The results listed in Table 1 clearly demonstrate that the four less reactive alkylsulfonates are not suitable as initiators for preparative purposes because the yields never exceeded 35% even at temperatures up to 150°C (Nos. 19-28, Table 1). Yet, even when the two most reactive initiators were used, reaction time on the order of 1-2 days is required at 50°C to obtain yields around 90%. Of course, higher temperatures accelerate the polymerization and shorten the reaction time. Yet, when ε-Capr was polymerized at 100°C, a "boomerang effect" on the yields was observed. The rapid polymerization gave yields above 70% within 2 h. However, at longer reaction times the yields of poly(ε-caprolactone) insoluble in methanol decreased to 0% within 3 days (Fig. 1A). Even in the initial period of the polymerization, yields

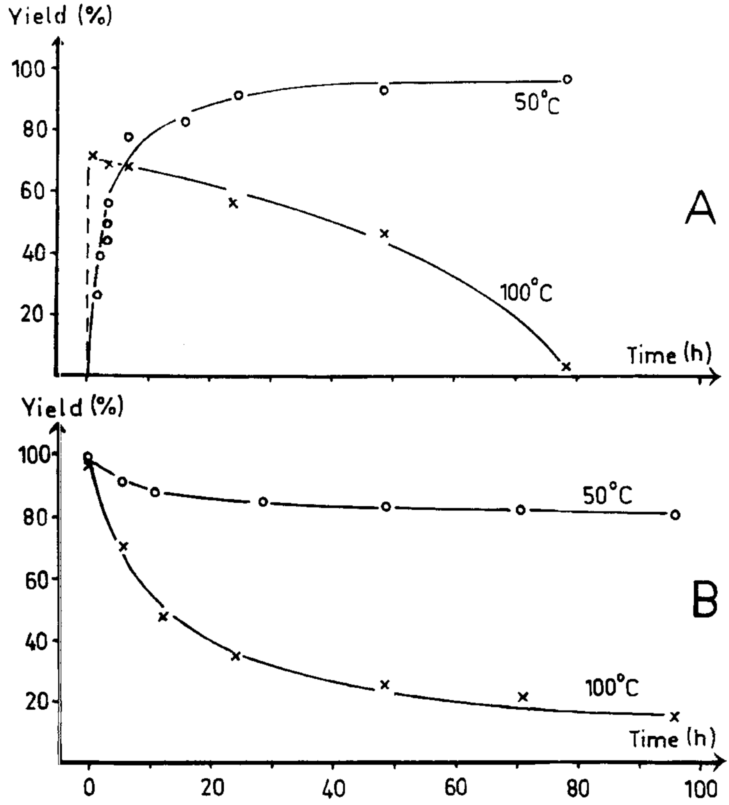

FIG. 1. (A) Time/yield curves of methyl triflate-initiated polymerizations of ϵ-caprolactone in nitrobenzene. (B) Methyl triflate-catalyzed degradation of poly(ϵ-caprolactone) in nitrobenzene.

above 80% were never obtained because the faster degradation partially counterbalances the chain growth.

In order to check whether this interpretation of the time/conversion curves is correct, poly(ϵ-caprolactone) isolated after various reaction times from methanol demonstrates that this polyester is highly sensitive to cationic degradation (Fig. 1B). As expected from the time-conversion curves of Fig. 1A, the degradation of poly(ϵ-caprolactone) is fast at 100°C and slow, but clearly detectable, at 50°C. The slopes of the degradation curves (Fig. 2B) do not exactly agree with those of the time-conversion curves for two reasons. First, for the polymerizations, chain growth and degradation compete with each other. Second, the cationic attack of methyl triflate in the degradation experiments of Fig. 1(B) is necessarily an intermolecular reaction, whereas the de-

TABLE 1. Polymerization of ϵ-Caprolactone by Means of Various Alkylsulfonates

No.	Initiator	M/I	Reaction medium	Temperature, °C	Time, h	Yield, %	η_{inh},[a] dL/g
1	FSO_3CH_3	100	Nitrobenzene	50	12	27	-
2	FSO_3CH_3	100	Nitrobenzene	50	24	47	0.405[b]
3	FSO_3CH_3	100	Nitrobenzene	50	48	74	0.331
4	FSO_3CH_3	100	Nitrobenzene	50	72	86	0.312
5	FSO_3CH_3	100	Nitrobenzene	50	96	89	0.317
6	$FSO_3CH_2CH_3$	100	Nitrobenzene	50	12	6	-
7	$FSO_3CH_2CH_3$	100	Nitrobenzene	50	24	11	-
8	$FSO_3CH_2CH_3$	100	Bulk	50	12	3	-
9	$FSO_3CH_2CH_3$	100	Bulk	50	24	25	-
10	$FSO_3CH_2CH_3$	100	Bulk	50	48	31	-
11	$FSO_3CH_2CH_3$	100	Bulk	100	48	35	-
12	$FSO_3CH_2CH_3$	100	Bulk	100	96	54	0.242
13	$CF_3SO_3CH_3$	100	Nitrobenzene	50	4	55/50	0.230
14	$CF_3SO_3CH_3$	100	Nitrobenzene	50	8	77/-	0.330[c]

15	$CF_3SO_3CH_3$	100	Nitrobenzene	50	16	84/82	0.355
16	$CF_3SO_3CH_3$	100	Nitrobenzene	50	24	91/88	0.338
17	$CF_3SO_3CH_3$	100	Nitrobenzene	50	48	93/89	0.315
18	$CF_3SO_3CH_3$	100	Nitrobenzene	50	96	97/-	-
19	$CH_3SO_3CH_3$	100	Nitrobenzene	50	48	0	-
20	$CH_3SO_3CH_3$	100	Nitrobenzene	100	48	0	-
21	$pNO_2C_6H_4SO_3CH_3$	100	Nitrobenzene	50	48	17	-
22	$pNO_2C_6H_4SO_3CH_3$	100	Nitrobenzene	100	48	10	-
23	$pNO_2C_6H_4SO_3CH_3$	100	Nitrobenzene	100	72	24	-
24	γ-Propanesultone	100	Nitrobenzene	50	48	7	-
25	γ-Propanesultone	100	Nitrobenzene	100	48	17	-
26	γ-Propanesultone	100	Nitrobenzene	150	48	35	-
27	δ-Butanesultone	100	Bulk	100	72	0	-
28	δ-Butanesultone	100	Nitrobenzene	150	72	9	-

[a] Measured with c = 2 g/L in $CHCl_3$ at 20°C.

[b] $\overline{M}_w = 17\ 000$ calculated from $[\eta] = 9.94 \times 10^{-5}\ \overline{M}^{0.82}$ [6].

[c] $\overline{M}_w = 15\ 000$ calculated from $[\eta] = 9.94 \times 10^{-5}\ \overline{M}^{0.82}$ [6].

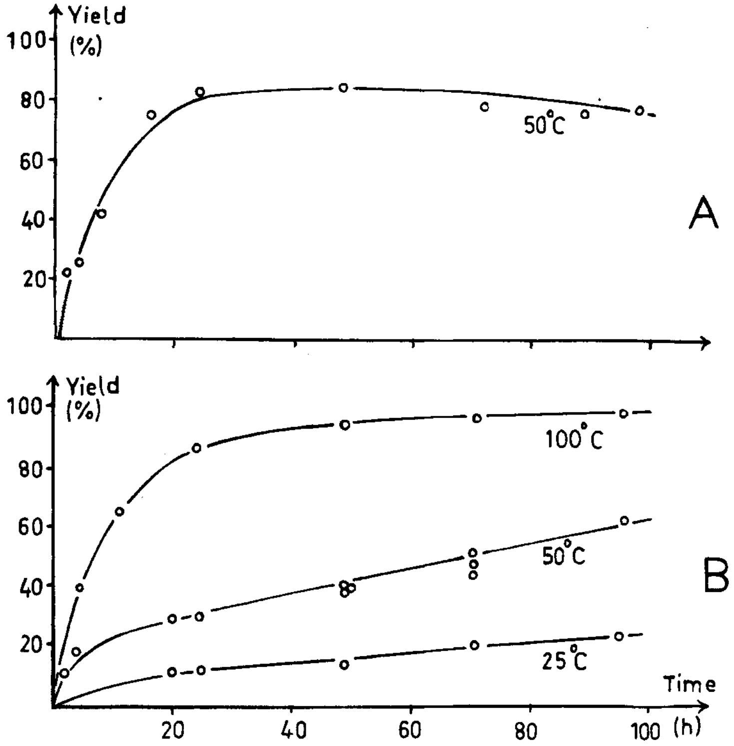

FIG. 2. Time/yield curves of cationic polymerizations of lactones in nitrobenzene initiated by means of methyl triflate (M/I = 100:1): (A) β-propiolactone, (B) glycolide.

gradation following the polymerization might be an intramolecular zip mechanism involving the active chain end.

It is characteristic for so-called living polymerizations that the average degree of polymerization ($\overline{DP}$) is proportional to the initial monomer-initiator ratio and to the conversion. It is obvious that the cationic polymerization of ω-lactones cannot obey this rule exactly when degradation competes with polymerization. Only for short reaction times (< 24 h) is a rough agreement expected between calculated and measured $\overline{DP}$'s (the results of NMR spectroscopic endgroup analyses will be reported and discussed in the succeeding paper). However, the competition between polymerization and degradation not only affects the relationship between the $\overline{DP}$ and the M/I ratio (or other parameters), but it also affects the maximum yield obtainable at various M/I ratios, because low M/I ratios not only accelerate the polymerization but also the degradation. Two series of polymeriza-

TABLE 2. Polymerization of ε-Caprolactone Initiated by $CF_3SO_3CH_3$ in Nitrobenzene at Various M/I Ratios

No.	M/I	Temperature, °C	Time, h	Yield, %	η_{inh},[a] dL/g
1	10/1	50	48	59	0.082
2	25/1	50	48	83	0.117
3	50/1	50	48	88	0.125
4	100/1	50	48	93	0.259
5	200/1	50	48	98	0.278[b]
6	10/1	50	120	3	-
7	25/1	50	120	18	0.143
8	50/1	50	120	65	0.165
9	100/1	50	120	89	0.232
10	200/1	50	120	94	0.291[c]
11	400/1	50	120	97	0.161

[a] Measured at c = 2 g/L in $CHCl_3$ at 20°C.

[b] $\overline{M}_w = 12\ 000$ from $[\eta] = 9.94 \times 10^{-5}\ \overline{M}_w^{\ 0.82}$ [6].

[c] $\overline{M}_w = 13\ 000$ from $[\eta] = 9.94 \times 10^{-5}\ \overline{M}_w^{\ 0.82}$ [6].

tions with variation of the M/I ratio were conducted at 50°C. The results, listed in Table 2, demonstrate that the yields indeed decrease with the M/I ratio and with the reaction time, indicating that low M/I ratios involve substantial degradation even at 50°C.

When all results of Table 1 and Fig. 1 are considered, methyl triflate is clearly the most effective initiator. Yet for a successful preparative application, the reaction temperature must be kept in a narrow range (50 ± 10°C), while reaction times of 1-3 days and M/I ratios of 50 or above are required for optimum yields. The slightly lower yields obtained with methyl fluorosulfate do not necessarily indicate a lower reactivity. From the acidity of fluorosulfonic acid and from various alkylation reactions in organic chemistry, it is known that this so-called "magic methyl' is an extremely powerful alkylating reagent. However, the fluorine of FSO_3^- is highly reactive and thus prone to various side reactions in contrast to the trifluoromethyl group. For this reason and because of the high toxicity, methyl fluorosulfate is a less attractive initiator than methyl triflate.

When lactones other than ϵ-caprolactone are considered, the close resemblance of δ-valerolactone and ϵ-caprolactone is noteworthy. The cationic copolymerizations of glycolide with ϵ-caprolactone and δ-valerolactone described previously [1, 2] prove experimentally that both lactones react very similarly in cationic polymerizations. Because reactivity and reaction mechanisms of β-lactones may differ largely from those of higher membered homologs, β-propiolactone was studied in more detail. However, the results summarized in Table 2 and Fig. 2(A) indicate that even β-propiolactone resembles ϵ-caprolactone with regard to cationic polymerization. Methyl triflate as initiator and reaction temperatures near 50°C again seem to be the optimum conditions.

However, it is noteworthy that, with "magic methyl," degradation of poly(propiolactone) sets in even at 50°C, and at reaction times of 2 days or more degradation seems to occur even with methyl triflate (Fig. 2A). Because yields above 90% were never obtained and the success of cationic polymerizations strongly depend on the temperature, it is obvious that anionic initiators are advantageous for the homopolymerization of β-lactones. Yet, due to the high reactivity of β-lactones with anions, it is rather difficult to achieve copolymerization of β-lactones and other lactones, even when glycolide is the comonomer [2]. In this respect, cationic initiators are by far superior.

Glycolide, which differs from other lactones in this reactivity [1, 2], was polymerized by means of methyl triflate at three different temperatures (Fig. 2B). In contrast to the ω-lactones, the highest temperature gave the best results. The lower reactivity of glycolide in these homopolymerizations agrees well with the lower rates of incorporation found for all cationic copolymerizations [1, 2]. The lower reactivity of the monomer and the lower sensitivity of poly(glycolide) to cationic degradation have seemingly the same origin, namely a lower basicity of the ester groups compared to ω-lactones. This conclusion is supported by the fact that glycolic acid is more acidic than higher ω-hydroxy acids, due to the I-effect of the oxygen in the α-position. On the other hand, it is obvious that the rapid crystallization of poly(glycolide) from the reaction medium also protects this polyester against rapid degradation.

Finally, the viscosity data and molecular weights listed in Tables 1-2 need discussion. In living systems devoid of equilibration and degradation equilibria, optimization of yields automatically includes optimization of molecular weights. This cannot be expected for cationic (or anionic) polymerizations of lactones under conditions that involve transesterification and, in particular, backbiting. Thus, it is not surprising that, in Nos. 2-5 of Table 1, Nos. 13-17 of Table 1, and Nos. 4-10 of Table 3, the maximum viscosity is not found together with the maximum yield, but at shorter reaction times. This result is obviously a consequence of back biting degradation. The weight-average molecular weights ($\overline{M}_w$) calculated from intrinsic

TABLE 3. Polymerization of β-Propiolactone in Nitrobenzene by Means of Various Alkylsulfonates

No.	Initiator	M/I	Temperature, °C	Time, h	Yield, %	η_{inh}[a] dL/g
1	FSO_3CH_3	100	50	24	57	-
2	FSO_3CH_3	100	50	72	46	-
3	FSO_3CH_3	100	50	96	43	-
4	$CF_3SO_3CH_3$	100	50	2	21	0.078
5	$CF_3SO_3CH_3$	100	50	4	27	0.082
6	$CF_3SO_3CH_3$	100	50	8	42	0.098
7	$CF_3SO_3CH_3$	100	50	16	66	0.094
8	$CF_3SO_3CH_3$	100	50	24	81	0.091
9	$CF_3SO_3CH_3$	100	50	48	85	0.083
10	$CF_3SO_3CH_3$	100	50	72	79	0.075
11	$CH_3SO_3CH_3$	100	100	92	0	-
12	$p\text{-}NO_2C_6H_4SO_3CH_3$	100	100	92	0	-
13	γ-Propanesultane	100	50	92	6	-
14	δ-Butanesultane	100	50	92	0	-

[a] Measured at c = 2 g/L in $CHCl_3$ at 20°C.

viscosities [6] are all below 20 000 (Tables 1 and 2). Since transesterification causes broadening of the molecular weight distribution, the $\overline{M}_w/\overline{M}_n$ ratios should not be lower than 2. Hence, the number-average molecular weights ($\overline{M}_n$) of the poly(caprolactone) samples listed in Tables 1 and 2 certainly do not exceed 8 000. The low inherent viscosities of the poly(β-propiolactone) samples in Table 3 indicate even lower $\overline{M}_n$. Thus, all results together suggest that true cationic polymerizations of lactones are not suited for the preparation of high molecular weight polylactones.

Copolymerizations of Glycolide with ω-Lactones

As demonstrated in previous papers [1, 2], anionic initiators, such as quaternary ammonium or phosphonium salts, are not useful for the copolymerization of glycolide or β-propiolactone and other lactones. In most experiments, mainly homopolymerization of the most reactive monomer took place. On the other hand, acidic initiators, such as fluorosulfonic acid, boron trifluoride, and ferric chloride, were found to yield copolyesters with nearly random sequences due to their transesterification activity. Random copolyester should be noncrystalline, and such amorphous, nonimmunogenic, and nontoxic copolyesters are highly interesting as drug-delivery systems because the lack of crystallinity eases their biodegradation. For the preparation of such amorphous copolyesters, the above-mentioned acidic catalysts have the shortcoming that they do not allow systematic variation of the molecular weight. In this regard, alkylsulfonates might be advantageous if they permit the preparation of copolyesters in good yield. Furthermore, the living chain ends should make possible the preparation of two-block copolyesters by batchwise copolymerization of two lactones. Such two-block copolyesters might be interesting as compatibilizing additives for blends of polyesters and other polymers.

In order to test the usefulness of methyl triflate as an initiator for copolymerizations, two series of experiments were conducted, namely the batchwise copolymerization of glycolide with ε-caprolactone or β-propiolactone (Table 4) and the preparation of random copolyesters (Table 5). The block copolymerizations with ε-caprolactone (Nos. 1-6, Table 4) were conducted such that ε-caprolactone was polymerized first at 50°C for 2 days, so that, according to Fig. 1(A), a nearly complete homopolymerization was obtained. Then glycolide was added, and because of its lower reactivity, the temperature was raised to 100°C. However, obviously the degradation outstripped the polymerization, and regardless of the Glyc/Capr ratio, no copolyester was ever isolated (Nos. 1-3, Table 4). When the polymerization temperature of glycolide was lowered to 50°C, acceptable yields of block copolyesters were obtained (Nos. 4-6, Table 4), indicating that the copolymerization of glycolide also requires reaction temperatures near 50°C.

360 MHz ^{1}H-NMR spectra revealed that even the block copolyesters prepared at 50°C contain ~5% by-products insoluble in methanol, which possibly stem from the cationic degradation of the polyester blocks.

The block character of the sequences prepared at 50°C was confirmed by means of ^{13}C-NMR spectroscopy (Fig. 3). The ^{13}C-NMR sequence analysis of copolyesters prepared from glycolide and ω-lactones was discussed in great detail in previous papers [1, 2, 7]. A comparison of the spectra in Figs. 3(A) and 3(B) clearly demonstrates that, in the spectra of the block copolyesters, the dyad and triad peaks representing the crossover steps (y', x', x") are absent. On the other hand, these ^{13}C-NMR spectra do not allow differentiation between two-block copolymers and a blend of homopolyesters. This

TABLE 4. Reaction Conditions and Results of Block Copolymerizations of Glycolide with ϵ-Caprolactone or β-Propiolactone Initiated by Methyl Triflate in Nitrobenzene

No.	Comonomer	Glycolyl[a]/Comonomer	Comonomer/Initiator	Temperature, °C	Time, h	Yield, %	Glycolyl[b]/Comonomer	Character of sequence[c]
1	ϵ-Caprolactone	1/10	100/1	50/100	48/72	0	-	-
2	ϵ-Caprolactone	1/5	100/1	50/100	48/72	0	-	-
3	ϵ-Caprolactone	1/1	100/1	50/100	48/72	0	-	-
4	ϵ-Caprolactone	1/10	100/1	50/50	48/72	79	1/10.0	Two blocks
5	ϵ-Caprolactone	1/5	100/1	50/50	48/72	91	1/3.8	Two blocks
6	ϵ-Caprolactone	1/1	100/1	50/50	48/72	43	1/1.7	Two blocks
7	β-Propiolactone	1/10	100/1	50/50	24/72	71	-	-
8	β-Propiolactone	1/5	100/1	50/50	24/72	65	1/4.0	Block
9	β-Propiolactone	1/1	100/1	50/50	24/72	54	1/3.7	Block

[a] Molar ratio of glycolyl and ω-lactone units in the initial monomer mixture.

[b] Molar ratio of glycolyl and ω-lactone units in the isolated copolyester.

[c] Determined from ^{13}C-NMR carbonyl signals.

TABLE 5. Reaction Conditions and Results of Various Copolymerizations of Glycolide with ϵ-Caprolactone or β-Propiolactone Initiated by Methyl Triflate in Nitrobenzene

No.	Comonomer	Glycolyl[a]/Comonomer	Comonomer[b]/Initiator	Temperature, °C	Time, h	Yield, %	Glycolyl[c]/Comonomer	Average block lengths[d] $\overline{L}_G$	Average block lengths[d] $\overline{L}_L$
1	ϵ-Caprolactone	1:1	67/1	20	24	12	-	-	-
2	ϵ-Caprolactone	1:1	67/1	60	24	63	-	3.2	2.6
3	ϵ-Caprolactone	1:1	67/1	100	24	41	-	-	-
4	β-Propiolactone	1:1	67/1	20	24	43	20.0:1	> 15.0	> 5.0
5	β-Propiolactone	1:1	67/1	60	24	70	1.1:1	12.0	14.0
6	β-Propiolactone	1:1	67/1	100	24	66	1.0:1	3.9	1.9

[a] Molar ratio of glycolyl and ω-lactone units in the initial monomer mixture corresponding to a glycolide/ω-lactone ratio of 1:2 according to the equation $\overline{L}_G = \frac{I_x + I_{x'}}{I_{x''}} + 1$ (see Ref. 1).

[b] Molar ratio of ω-lactone and methyl triflate, corresponding to a total monomer/initiator ratio of 100:1.

[c] Molar ratio of glycolyl and ω-lactone units in the isolated copolyester (from ^{1}H-NMR spectra).

[d] Determined from the ^{13}C-NMR carbonyl signals according to the equation $\overline{L}_L = \frac{I_y}{I_{y'}} + 1$ (see Ref. 1).

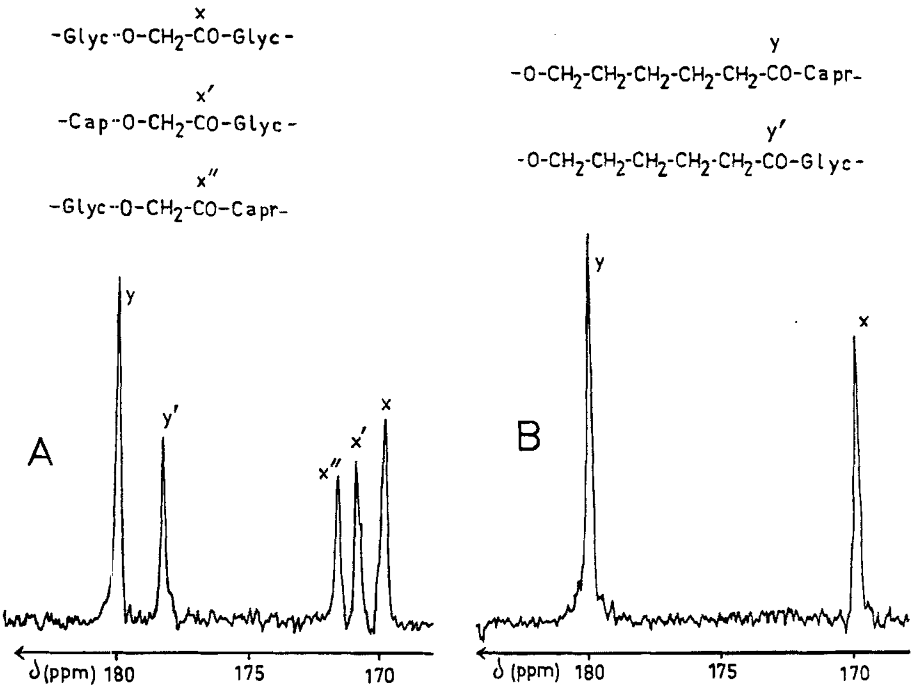

FIG. 3. 20.3 MHz ^{13}C-NMR spectra of copolyesters prepared from ε-caprolactone and glycolide by means of methyl triflate: (A) copolymerization of 60°C (No. 2, Table 5); (B) batch block copolymerization at 50°C (No. 5, Table 4).

problem was solved by solubility tests. Poly(ε-caprolactone) is soluble in chloroform and many other solvents. Oligo- or poly(glycolide) is insoluble in all organic solvents. All block copolyesters listed in Table 4 were soluble in a mixture of chloroform and trifluoroacetic acid (3:1 by volume). Only in the case of No. 6 did ~5% remained suspended. Furthermore, Sample No. 5, Table 4, was fractionated by means of pure chloroform. The soluble fraction showed a Capr/Glyc ratio of 6.5, and the insoluble fraction a ratio of 0.8 (Fig. 5). Both findings (the solubility of glycolide blocks in chloroform and the insolubility of caprolactone blocks) clearly indicate that caprolactone and glycolide blocks are covalently bound to each other. The fractionation also demonstrates that both blocks possess a broad block length distribution. Due to the existence of polymerization/depolymerization equilibria during the synthesis of both blocks, a narrow block length distribution may not be expected. However, the existence of a broad block length distribution does not necessarily mean that intermolecular transesterifica-

TABLE 1. Polymerization of III with Bromine

Experiment no.	(V) (mmol)	Br_2 (mmol)	Solvent	Conversion (%)	Additional conditions
1	6.0	10	CCl_4	10	a
2	5.0	5.1	CCl_4	7.3	a
3	5.0	0.10	CCl_4	0	a
4	5.0	1.0	CCl_4	0	a
5	5.0	5.1	CH_2Cl_2	15	0.10 mmol hydroquinone present
6	6.0	5.1	CH_2Cl_2	10	In vacuo (10^{-6} torr)
7	5.0	5.1	Et_2O	22	-78°C
8	5.0	5.1	CH_3COCH_3	0	5.0 mmol LiBr present
9	5.0	5.1	CH_2Cl_2	0	5.0 mmol pyridine present

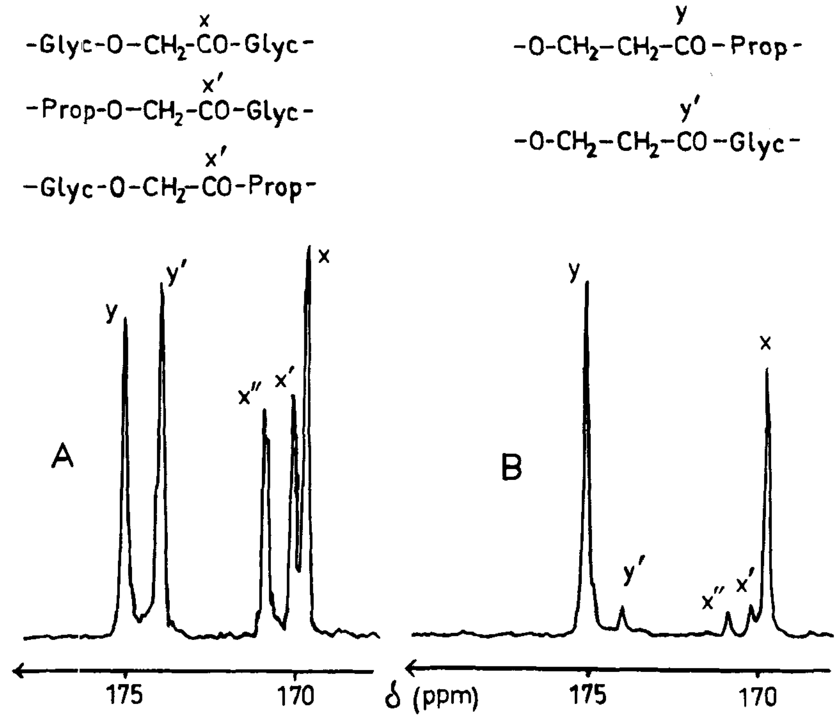

FIG. 5. 20.3 MHz ^{13}C-NMR spectra of copolyesters prepared from β-propiolactone and glycolide by means of methyl triflate (A) copolymerization at 100°C (No. 6, Table 5); (B) copolymerization at 60°C (No. 5, Table 5).

complete conversion of β-propiolactone in the first stage of the copolymerization is responsible for the latter result.

In the second series of copolymerizations (Table 5), mixtures of glycolide and ε-caprolactone or β-propiolactone were polymerized by means of methyl triflate in nitrobenzene. Both the comonomer ratio (1:2) and the M/I ratio (100:1) were kept constant, whereas the temperature was varied. It turned out that the copolymerizations of ε-caprolactone and β-propiolactone again gave quite different results. With ε-caprolactone only a low yield of oligo(ε-caprolactone) was obtained at 20°C due to the lower reactivity of glycolide. At 60°C (No. 2, Table 5) a waxy copolyester was obtained in moderate yield and the comonomer ratio was close to unity. The ^{13}C-NMR spectrum revealed (Fig. 3B) that the sequence was nearly random in nature. Even in this case the carbonyl signal of the Capr-Glyc-Capr triad was not detectable, indicating that intermolecular transesterification was absent. At 100°C a deeply colored syrupy copolyester was obtained with a comonomer ratio of 1:1 and with an entirely random sequence. These results agree well with the previously reported cationic copolymerization which also yield more or less random Glyc/Capr copolyesters at temperatures above 50°C.

When β-propiolactone was used as comonomer, again a nearly perfect homopolymerization was observed at 20°C (No. 4, Table 5). However, in contrast to ε-caprolactone (No. 1, Table 5), the yield of the poly(propiolactone) was as high as ~80% with respect to β-propiolactone, and in agreement with a higher $\overline{DP}$, a white solid material was isolated. At 60°C (No. 5, Table 5) a copolyester with a monomer ratio near unity was obtained yet in contrast to the corresponding copolymerization of ε-caprolactone, this copolyester possessed blocky sequences (Fig. 5B). These results suggest that the reactivities of glycolide and

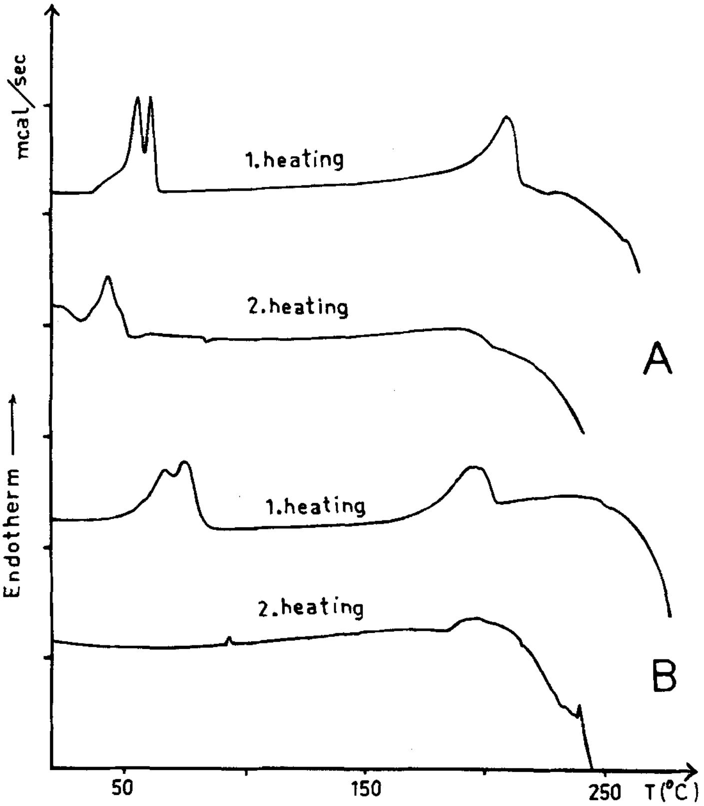

FIG. 6. DSC curves of two copolyesters measured at a heating rate of 20°C/min: (A) block copolyester of ε-caprolactone and glycolide (No. 5, Table 4); (B) copolyester of β-propiolactone and glycolide (No. 5, Table 5).

β-propiolactone differ more than those of glycolide and ϵ-caprolactone. This hypothesis is confirmed by the time/conversion curves of Figs. 1(A) and 2(A), which show a faster polymerization of β-propiolactone.

The copolyester obtained at 100°C (No. 6, Table 5) had a syrupy consistency, and in agreement with this character, the ^{13}C-NMR spectrum indicates a random sequence (Fig. 5A). The slightly lower yield compared to the blocky copolyester No. 5, Table 5, does not necessarily indicate a higher degree of degradation. Since random copolymers are more easily soluble in all solvents than block copolymers, the better solubility in methanol may be responsible for the lower yield. The most interesting aspect of copolymerizations listed in Table 5 is the observation that a moderate change of the reaction temperature has a huge influence on both molar composition and sequence of the copolyesters.

Finally, it is noteworthy that the DSC measurements fully agree with the ^{13}C-NMR spectroscopic sequence analyses. The DSC curves of the block copolyesters of Table 4 display melting endotherms at temperatures slightly below those of the corresponding homopolyesters. In contrast, the DSC curves of the random copolyesters Nos. 2, 3, and 6 (Table 5) did not exhibit any melting endotherms. Two details are noteworthy concerning the DSC traces of the block copolyesters. First, the blocks of the ω-lactones show two closely neighboring endotherms, which probably reflect the existence of two different sizes of crystallites. On the other hand, the broad endotherm of the glycolide blocks indicates a broad distribution of crystallite sizes. Second, when the samples were rapidly cooled down and heated again, the melting endotherms almost completely disappeared (Fig. 6) due to rapid transesterification in the molten state. Since, after precipitation from methanol, cationic chain ends must be absent, only traces of trifluoromethanesulfonic acid may be responsible for the rapid transesterification. However, a similar "DSC pattern" was also found for copolyester prepared by anionic initiators [2]. Thus, the present and previous DSC measurements demonstrate that only the first heating of copolyesters may give reliable information on relationships between crystallinity and sequence.

REFERENCES

[1] H. R. Kricheldorf, T. Mang, and J. M. Jonté, Macromolecules, 17, 2173 (1984).

[2] H. R. Kricheldorf, T. Mang, and J. M. Jonté, Makromol. Chem., In Press.

[3] H. Cherdron, H. Ohse, and F. Korte, Makromol. Chem., 56, 179 (1962).

[4] A. K. Khomyakov, E. B. Ludvig, A. T. Gorelikov, and N. N. Shapet'ko, Vysokomol. Soedin., Ser. A, 19 867 (1977).

[5] A. Hofmann, R. Szymanski, S. Stomkowski, and S. Penczek, Makromol. Chem., 185, 655 (1984).

[6] I. B. Rashhov, I. Gitsov, I. M. Panayotov, and J.-P. Pascault, J. Polym. Sci., Polym. Chem. Ed., 21, 923 (1983).
[7] H. R. Kricheldorf, J. M. Jonté, and M. Berl, Makromol. Chem., In Press.

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