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Hans R. Kricheldorf[a]; Nico Scharnagl[a]
[a] Institut für Technische und Makromolekulare Chemie der Universität, Hamburg 13, Federal Republic of Germany

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POLYACTONES. 17. ANIONIC POLYMERIZATION OF ß-D,L-BUTYROLACTONE

HANS R. KRICHELDORF* and NICO SCHARNAGL

Institut für Technische und Makromolekulare Chemie
der Universität Hamburg
Bundesstrasse 45, D-2000 Hamburg 13, Federal Republic of Germany

ABSTRACT

β-D,L-Butyrolactone was polymerized at 50°C in deuterated solvents of different polarity, and both the conversion and the formation of crotonate groups were directly determined from the reaction mixture by means of ^{1}H-NMR spectroscopy. Two classes of initiators, namely nonionic ones, such as tertiary amines or triphenylphosphine, and ionic ones, such as potassium salts of alcohols, phenols, and carboxylic acids, were used. In almost all polymerizations, formation of crotonate end groups was detected. Two deprotonation mechanisms are discussed. This side reaction is the main reason why high molecular weight poly(*β-C,L*-butyrolactone) could not be obtained even when the monomer/initiator ratio was varied by a factor of 40. In contrast, the nonionic initiator tributyltin methoxide yielded poly(*β-D,L*-butyrolactone) free of crotonate groups. When potassium salts of *N*-protected *L*-amino acids were used as initiators, again crotonate end groups were formed even at +5°C, and the resulting poly(*β-D,L*-butyrolactone) was almost atactic.

INTRODUCTION

Numerous papers have appeared dealing with the anionic polymerization of β-lactones [1-5]. However, only few papers deal with the anionic polymerization of *β-D,L*-butyrolactone [6-10], partially because this monomer was

believed to be insensitive to anionic initiation due to the electronic and steric effect of the methyl group in the β-position. The polymerization of *β-D,L*-butyrolactone is of particular interest because poly(*β-D*-butyrolactone) is a biopolymer and thus a nontoxic, biodegradable material.

Recently, Jedlinski and coworkers [8-10] reported on the anionic polymerization of *β-D,L*-butyrolactone initiated by solutions of elementary potassium in crown ether/tetrahydrofuran. This initiator system is difficult to handle due to the high reactivity of the dissolved potassium, and thus it was one purpose of the present work to study the role of easily accessible stable initiators. Another purpose of this study was the elucidation of side reactions, such as deprotonation. The formation of acrylate ions from β-propiolactone has been reported by two research groups [10, 11], yet a detailed study of this phenomenon is lacking. Finally, the influence of optically active initiators on the stereoselectivity of the anionic polymerization should be studied.

EXPERIMENTAL

Materials

β-D,L-Butyrolactone was purchased from Aldrich Co. (St. Louis, Missouri) and distilled over oligomeric 4,4′-diisocyanatodiphenylmethane under nitrogen. Triphenylphosphine and potassium *t*-butylate were also purchased from Aldrich Co. and used without further purification. The tertiary amines were gifts of BASF AG (D-6700 Ludwigshafen, FRG); they were distilled over freshly powdered calcium hydride. The potassium salts of benzoic acid, 4-*t*-butylphenol, and 4-chlorothiophenol were prepared by means of potassium *t*-butylate in a solution of dry isopropanol. Potassium benzylxanthogenate was prepared from distilled benzyl alcohol, potassium *t*-butylate, and carbon disulfide in dry isopropanol under nitrogen. All potassium salts were dried over phosphorus pentoxide *in vacuo*.

Polymerizations

A. Tables 1 and 2

β-D,L-Butyrolactone (86 mg, 1 mmol) was weighed into a 5-mm o.d. NMR tube containing a 0.1 mol/L solution of an initiator in dry $CDCl_3$, CD_5NO_2 (dried by storage over P_4O_{10}), or DMSO-d_6. The NMR tube was sealed and thermostated at 50 ± 1°C. After 48 h, ^{1}H-NMR spectra were recorded and

TABLE 1. Detection of Crotonate Groups in the Anionic Polymerization of *β-D,L*-Butyrolactone with Nonionic Initiators[a]

No.	Initiator	Solvent	Conversion, %	Crotonate	
				Monomer units[b]	Initiator[c]
1	Pyridine	$CDCl_3$	66	1:3.0	1:0.4
2	Pyridine	$C_6D_5NO_2$	75	1:2.5	1:0.3
3	2,6-Dimethylpyridine	$CDCl_3$	25	1:5.5	1:2.5
4	2,6-Dimethylpyridine	$C_6D_5NO_2$	–	–	–
5	*N*-Methylmorpholine	$CDCl_3$	10	1:40	1:5.0
6	*N*-Methylmorpholine	$C_6D_5NO_2$	10	1:3.0	1:3.0
7	Triethylamine	$CDCl_3$	40	1:30.0	1:10.0
8	Triethylamine	$C_6D_5NO_2$	50	1:40.0	1:5.0
9	Triphenylphosphine	$CDCl_3$	42	1:27.0	1:7.0
10	Triphenylphosphine	$C_6D_5NO_2$	15	1:2.5	1:2.0

[a]Initial molar monomer/initiator ratio 10:1; 50°C; 48 h.

[b]Molar ratio of crotonate to monomer units of the polymeric fraction, as determined by ^{1}H-NMR spectroscopy, in the reaction mixture.

[c]Molar ratio of crotonate groups to initiator in the reaction mixture.

TABLE 2. Detection of Crotonate Groups in the Anionic Polymerization of β-*C,L*-Butyrolactone with Ionic Initiators[a]

No.	Initiator	Solvent	Conversion, %	Crotonate	
				Monomer units[b]	Initiator[c]
1	K benzoate	$CDCl_3$	98	d	d
2	K benzoate	$C_6D_5NO_2$	98	d	d
3	K benzoate	DMSO-d_6	99	1:12	1:1.2
4	K benzoate	DMSO-d_6	99	1:9	1:0.8
5	K benzoate + dibenzo-18-crown-6	$CDCl_3$	0	–	–
6	K 4-(*t*-butyl)phenoxide	$C_6D_5NO_2$	67	1:27	1:3.2
7	K 4-(*t*-butyl)phenoxide	DMSO-d_6	99	1:5	1:0.5
8	K *t*-butoxide	$CDCl_3$	65	1:37	1:4.9

9	K *t*-butoxide	$C_6D_5NO_2$	99	1:2.6	1:2.6
10	K *t*-butoxide	DMSO-d_6	99	1:5	1:0.5
11	K *t*-butoxide + dibenzo-18-crown-6	DMSO-d_6	99	1:5	1:0.5
12	K 4-chlorophenylsulfide	$C_6D_5NO_2$	99	d	d
13	K 4-chlorophenylsulfide	DMSO-d_6	99	1:1.7	1:1.7
14	K *O*-benzylxanthogenate	$C_6D_5NO_2$	27	0	0
15	K *O*-benzylxanthogenate	DMSO-d_6	98	1:2.1	1:2.0

[a]Initial molar monomer/initiator ratio 10:1, 50°C; 48 h.

[b]Molar ratio of crotonate to monomer units in the polymeric fraction as determined by ^{1}H-NMR spectroscopy in the reaction mixture.

[c]Molar ratio of crotonate groups to initiator in the reaction mixture.

[d]Not measurable because of high viscosity.

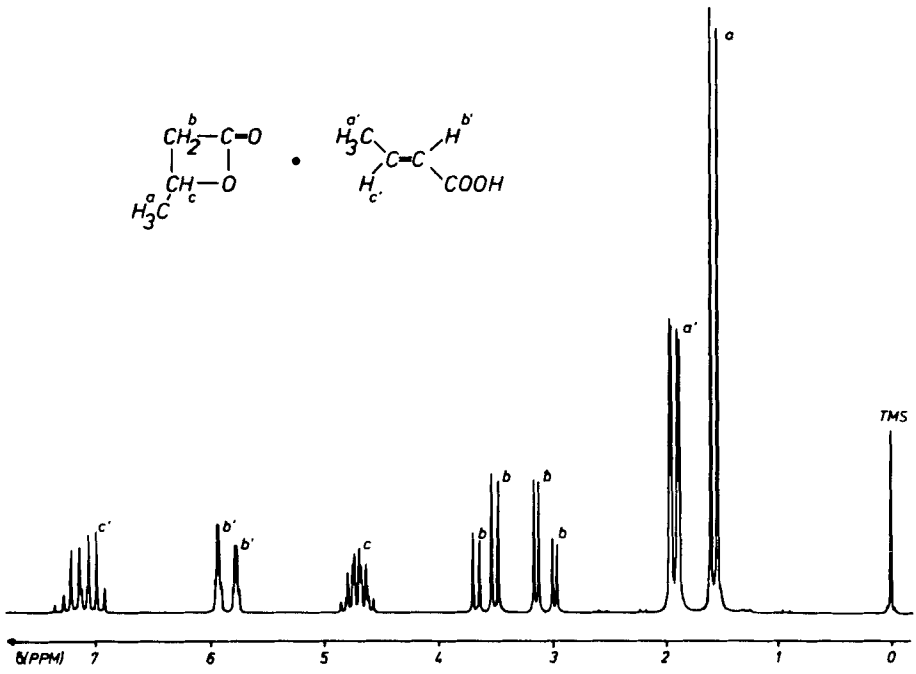


FIG. 1. 100 MHz ^{1}H-NMR spectrum of a mixture of β-*D,L*-butyrolactone and crotonic acid in $CDCl_3$.

compared with the spectra of pure lactone, polylactone, and crotonic acid (Figs. 1-3).

B. Table 3

β-*D,L*-Butyrolactone (52 g, 60 mmol) was weighed under nitrogen into a 25-mL Erlenmeyer flask with a ground-glass joint and silanized glass walls (pretreated with dimethyldichlorosilane). The initiator was added by means of a syringe, and the reaction vessel was closed with a glass-stopper and steel spring and thermostated at 50°C. After 48 h, the reaction product was dissolved in 50 mL dichloromethane and precipitated into 1:1 v/v diethyl ether and ligroin. After storage at ~5°C for several hours, the solvent mixture was decanted, the syrupy polylactone washed with a small amount of a diethyl ether/ligroin mixture, and dried *in vacuo*.

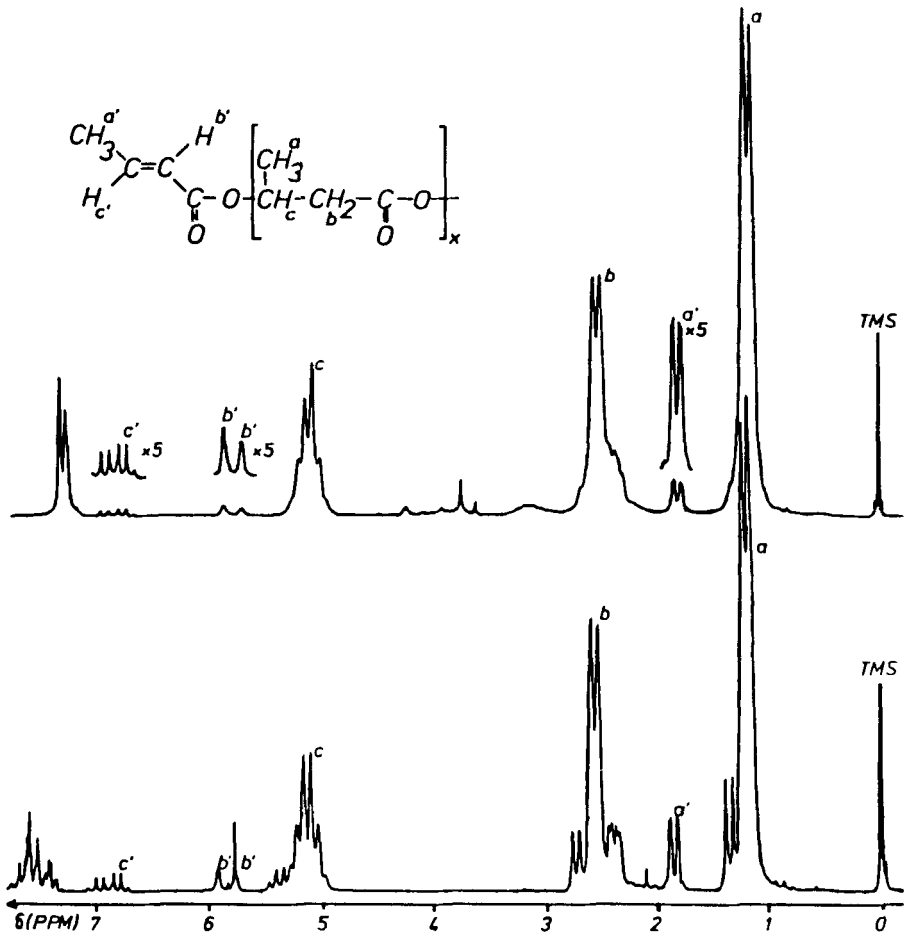


FIG. 2. 100 MHz ^{1}H-NMR spectra of reaction mixtures measured after 48 h at 50°C. Top: Initiator potassium benzylxanthogenate (No. 15, Table 2). Bottom: Initiator potassium benzoate (No. 3, Table 2).

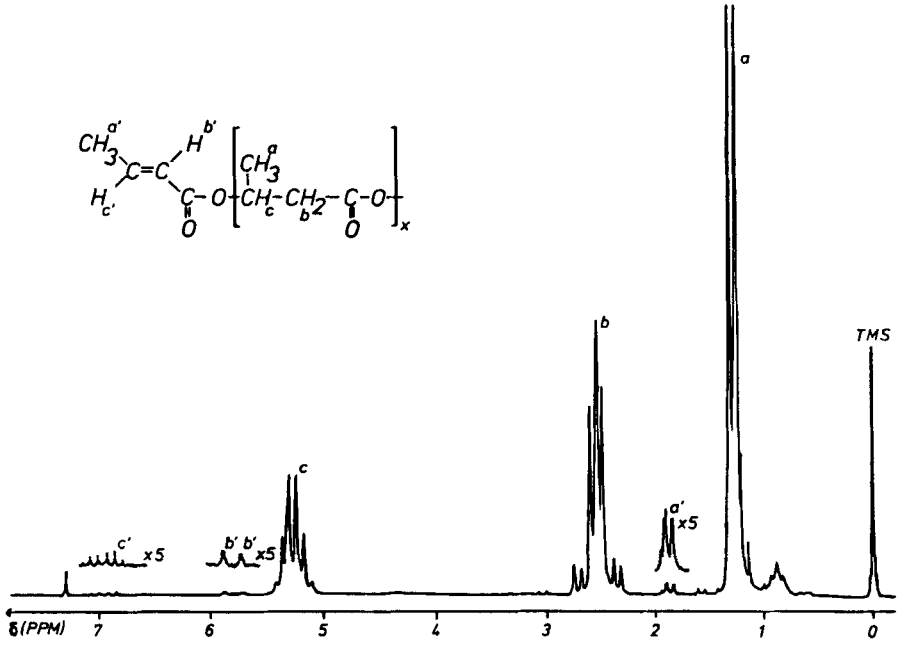


FIG. 3. 100 MHz ^{1}H-NMR spectrum of isolated poly(β-*D*,*L*-butyrolactone) prepared by triethylamine-initiated polymerization of β-*D*-*L*-butyrolactone at 50°C (No. 23, Table 3).

C. Table 4

These polymerizations were conducted as described for B but the reaction mixtures of Experiments Nos. 1, 2, 5, and 6 were stored in a refrigerator at 5 ± 1°C.

Measurements

The ^{1}H-NMR spectra were recorded with a Bruker AC-100 FT-NMR spectrometer in 5 mm o.d. sample tubes.

The inherent viscosities were measured in dichloromethane at a concentration of 2 g/L with an Ubbelohde viscometer thermostated at 25°C.

The GPC measurements were conducted at 25°C in a BPC/HPCL chromatograph equipped with a differential refractometer (Waters 410) as detector. A

TABLE 3. Results of Anionic Bulk Polymerizations of β-*D,L*-Butyrolactone at 50°C

No.	Initiator	M/I[a]	Yield, %	Crotonate[b] Monomer units	η_{inh},[c] dL/g	Elution time,[d] min
1	K benzoate	20:1	97	1:40	0.07	30.4
2	K benzoate	50:1	94	1:35	0.10	28.2
3	K benzoate	100:1	89	1:35	0.10	27.1
4	K benzoate	200:1	79	1:50	0.18	–
5	K benzoate	400:1	52	1:55	0.10	–
6	K benzoate + dibenzocrown-6	100:1	98	1:145	0.11	28.0
7	K *t*-butoxide	20:1	95	1:30	0.14	30.8
8	K *t*-butoxide	50.1	95	1:40	0.13	28.7
9	K *t*-butoxide	100:1	93	1:50	0.11	28.8
10	K *t*-butoxide	200:1	80	1:50	0.26	–
11	K *t*-butoxide	400:1	42	1:55	0.08	–
12	K *t*-butoxide + dibenzocrown-6	100:1	98	1:65	0.10	27.8
13	K *O*-benzylxanthogenate	20:1	89	1:25	0.04	32.1

(continued)

TABLE 3 (continued)

No.	Initiator	M/I[a]	Yield, %	Crotonate[b] Monomer units	η_{inh},[c] dL/g	Elution time,[d] min
14	K *O*-benzylxanthogenate	50:1	94	1:80	0.06	29.5
15	K *O*-benzylxanthogenate	100:1	88	1:135	0.46	28.4
16	K *O*-benzylxanthogenate	200:1	86	1:75	0.06	–
17	K *O*-benzylxanthogenate	500:1	64	1:85	0.10	–
18	K 4-chlorophenylsulfide	20:1	93	1:35	–	33.0
19	K 4-chlorophenylsulfide	50:1	84	1:50	–	30.8
20	K 4-chlorophenylsulfide	100:1	70	1:50	–	30.5
21	Triethylamine	20:1	60	1:17	–	29.3
22	Triethylamine	50:1	78	1:35	–	28.3
23	Triethylamine	100:1	79	1:40	–	27.8

[a]Initial molar monomer/initiator ratio.
[b]Molar ratio of crotonate end groups to monomer units.
[c]Measured at 2 g/L concentration in dichloromethane at 25°C.
[d]Elution time of GPC in dichloromethane at 25°C.

TABLE 4. Anionic Polymerizations of *β-D,L*-Butyrolactone with Potassium Salts of *N*-Protected *L*-Amino Acids

No.	Initiator[a]	Temperature, °C	Time, d	Yield, %	Crotonate[b] end groups	η_{inh},[c] dL/g
1	Z-L-Ala-K	5	28	0	–	–
2	Z-L-Ala-K + Crown 6	5	28	0	–	–
3	Boc-L-Ala-K	50	14	83	Not detectable	0.08
4	Boc-L-Ala-K + Crown 6	50	14	99	Not detectable	0.08
5	Boc-L-Pro-K	5	28	5	–	–
6	Boc-L-Pro-K + Crown 6	5	28	97	1:200	0.12
7	Boc-L Pro-K	50	14	94	1:65	0.10
8	Boc-L-Pro-K + Crown 6	50	14	99	1:65	0.11

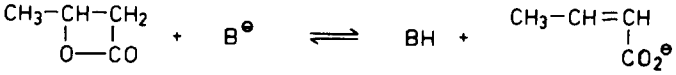
[a]A monomer/initiator molar ratio of 100/1 was used.
[b]Molar crotonate/monomer unit ratio as determined from ^{1}H-NMR spectra of isolated polymers.
[c]Measured at 2 g/L concentration in dichloromethane at 25°C.

combination of four Ultrastyrogel columns was used with effective molecular weight ranges of 50-1500, 10^2-10^4, 2×10^2-3×10^4, and 5×10^3-6×10^5. Dichloromethane was used as solvent, with a flow rate of 1 mL/min. For data recording and calculation, the microprocessor Anacomb 220 and plotter 800 of Kontron were used.

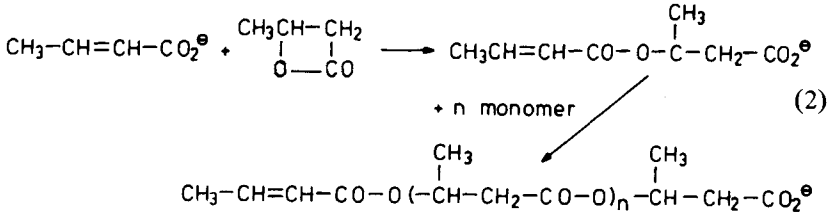
RESULTS AND DISCUSSION

Detection of Deprotonation

The deprotonation of *β-D,L*-butyrolactone results in the formation of crotonate anions (Eq. 1), which possibly can act as anionic initiator by nucleophilic attack on the β-lactone (Eqs. 2 and 3). The NMR spectroscopic identification of crotonate groups was thus considered to permit a reliable and routine detection of the deprotonation process.



(1)



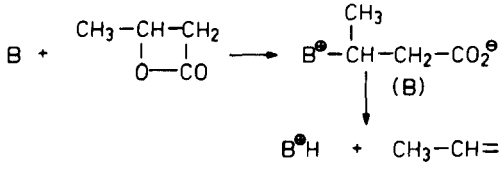
(2)

(3)

In order to obtain direct evidence for the formation of crotonate groups, two series of polymerizations (Tables 1 and 2) were conducted in NMR tubes and directly examined by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of monomer, isolated poly(*β-D,L*-butyrolactone) and commercial methyl crotonate allowed a straightforward analysis of the reaction mixtures (Figs. 1-3). Deuterated chloroform was used as a relatively nonpolar solvent and nitrobenzene as a polar solvent. Two classes of initiators were investigated, namely neutral bases, such as tertiary amines or triphenylphosphine (first

series, Table 1), and potassium salts of alcohols, phenols, and acids (second series, Table 2). Owing to the low solubility of these potassium salts in the aforementioned solvents, dimethylsulfoxide was used as an additional reaction medium for the second series.

The basicity of the initiators was varied over a wide range; for instance, between $pK_a \approx 5$ (pyridine) and $pK_a \approx 11$ (triethylamine) in the first series or between $pK_a \approx 5$ (benzoic acid) and $pK_a \approx 18$ (*t*-butanol) in the second series. Another important quality of all initiators is their nucleophilicity, which is responsible for the efficiency of the nucleophilic attack at C-3 of the lactone:



(4)

(5)

The following qualitative order of the nucleophilicity/basicity (n/b) ratio is important for the discussion of the results in Table 1: triphenylphosphine > pyridine > *N*-methylmorpholine > triethylamine. An expected result in the data of Table 1 is the higher yield of crotonate groups in nitrobenzene solvent. The formation of ionic reaction products from neutral starting materials is favored by a higher dipole moment of the reaction medium. More interesting is the finding that pyridine gave the highest yield of crotonate groups, and the strongest base, i.e., triethylamine, gave the lowest yield. Even the initiator with the highest n/b (triphenylphosphine) produced a sizable amount of crotonate groups. It is obvious that this result does not fit in with the deprotonation mechanism of Eq. (1).

An alternative mechanism results from the nucleophilic attack at C-3 (Eq. 4) followed by elimination of the protonated base (Eq. 5). The formation of a positive charge close to the β-carbon increases the acidity of the α-protons, and thus favors deprotonation by a weak base (including solvent molecules). In other words, it is most likely that this deprotonation is a base-supported bimolecular elimination (E_{2CB}) and not a monomolecular reaction. A similar deprotonation mechanism was postulated by Yamashita et al. [11] to explain the high yields of acrylate groups in pyridine-initiated polymerization of β-propiolactone. On the other hand, it is unlikely that a sterically hindered base, such as triethylamine, reacts according to Eqs. (4) and (5). This assumption is supported by the fact that betains were only obtained from reactions of lactones with pyridine but never from trimethylamine. Hence, it

is obvious that two deprotonation mechanisms exist (Eqs. 1 and 4 + 5), and the n/b of the initiator determines which one prevails.

The results of the second series (Table 2) prove again that deprotonation is favored in highly polar solvents. Furthermore, the high yields of crotonate groups resulting from polymerizations initiated by *t*-butoxide or 4-chlorothiophenolate prove that direct deprotonation of the monomer (and possibly of the polyester) does occur. In these cases the nucleophilic attack at C-3 yields ethers or thioethers (e.g., Eq. 6), which are less sensitive to deprotonation than the monomer itself. The only experiment which did not yield crotonate groups was the reaction of benzylxanthogenate in nitrobenzene (No. 14, Table 2). However, it is not clear whether side reactions between the sulfur anion and nitro group of the solvent are responsible for this result or the high n/b.

Of particular interest is the formation of crotonate groups on addition of potassium benzoate (Nos. 3 and 4, Table 2). Since n/b of the benzoate

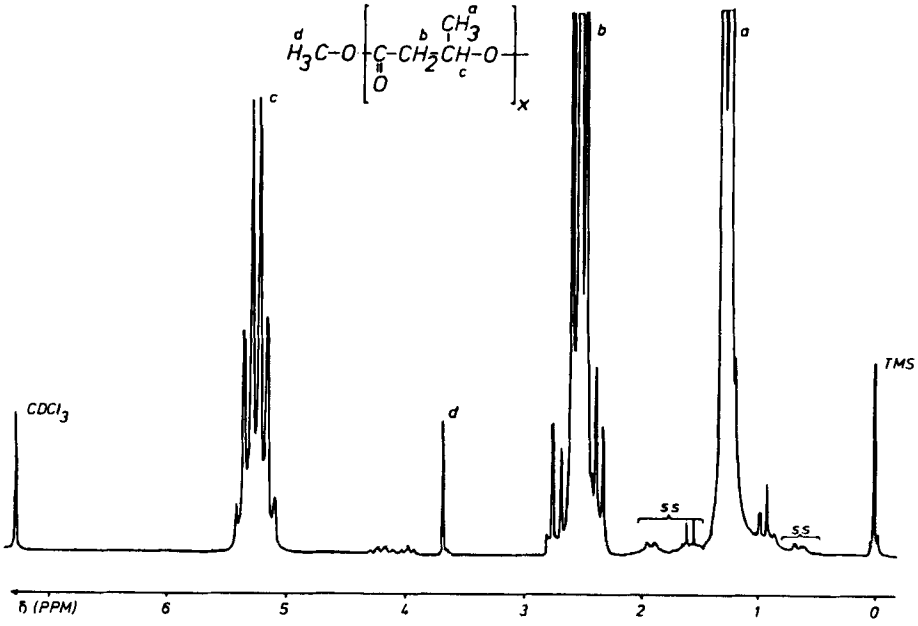
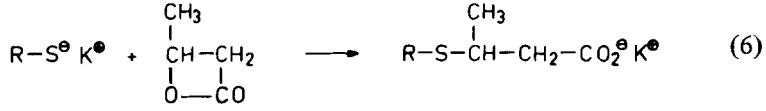


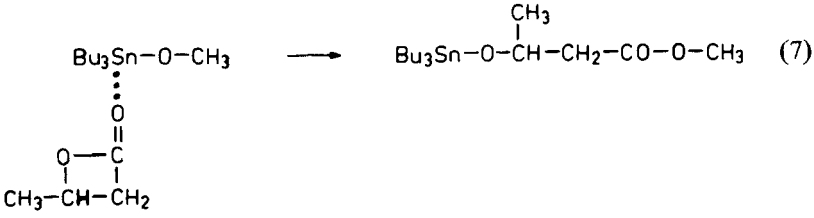
FIG. 4. 100 MHz ^{1}H-NMR spectrum of isolated poly(β-*D,L*-butyrolactone) prepared by tributyltin-methoxide-initiated polymerization of β-*D,L*-butyrolactone at 50°C (monomer/initiator ratio 50/1).

ion is similar to that of the growing chain, the active chain end should be capable of undergoing transfer reactions with the monomer (Eqs. 1 and 2). Such transfer reactions are known from anionic polymerizations of β-propiolactone and prevent the formation of high molecular weight poly(β-propiolactone) [12], unless crown ethers and low reaction temperatures are used [13, 14].



(6)

In addition to the anionic polymerizations in Tables 1-3, two bulk polymerizations were conducted at 50°C with tributyltin methoxide as initiator (*M/I* ratio 50/1). The poly(β-butyrolactone) was isolated after 2 and 8 days and was examined by ^{1}H-NMR spectroscopy. As demonstrated in Fig. 4, these samples possess methyl ester end groups but no crotonate end groups. This result agrees perfectly with the nonionic insertion mechanism of Eq. (7) which was formulated and discussed in a previous paper [15]. Thus, the absence of crotonate end groups may serve as additional proof for the existence of such a nonionic mechanism, which is characteristic for all metal alkoxides or phenoxides with free p or d orbitals.



(7)

Preparative Aspects

The results in Tables 1 and 2 clearly demonstrate that simple anionic initiators, such as potassium benzoate, phenolate, or *t*-butylate, can initiate an almost complete polymerization of β-*D,L*-butyrolactone. This observation raises the question whether high molecular weight poly(β-*D,L*-butyrolactone) is obtainable when anionic polymerizations are conducted with high monomer/initiator (*M/I*) ratios. In order to answer this question, 23 polymerizations were conducted with five quite different basic initiators (Table 3). In two cases a crown ether was added and the *M/I* ratio was varied between 20

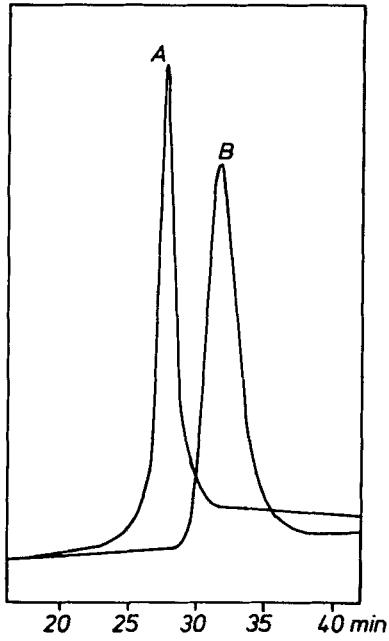


FIG. 5. GPC traces of reaction mixtures obtained after 48 h at 50°C: (A) with potassium *t*-butylate (No. 8, Table 3); (B) with potassium 4-chlorothiophenolate (No. 19, Table 3).

and 400. All polymerizations were conducted in bulk to accelerate them and to avoid side reactions of the solvent.

Two interesting results may be noted in Table 3. First, crotonate groups were identified in all samples of directly isolated poly(β-*D,L*-butyrolactone). The crotonate groups were found again after individual samples had been reprecipitated. Thus, these crotonate groups are end groups covalently bound to the polyester chain. This finding proves that the initially formed crotonate ions react as initiators (Eqs. 1 and 2), in perfect analogy to the acrylate ions in the anionic polymerization of β-propiolactone. Second, although absolute molecular weights were not determined, both inherent viscosities and GPC measurements agree in that the molecular weights of the products were not high. Since the GPC measurements did not indicate formation of cyclic oligomers (resulting from backbiting, cf. Fig. 5), it is concluded that transfer reactions to monomer and polymer are mainly responsible for the low molecular weights.

Finally, potassium salts of *N*-protected optically active amino acids, namely *N*-*t*-butoxycarbonyl-*L*-alanine (Boc-L-Ala-K), *N*-benzyloxycarbonyl-*L*-alanine (Z-L-Ala-K), and *N*-*t*-butoxycarbonyl-*L*-proline (Boc-L-Pro-K), were used as initiators (Table 4). In agreement with the potassium benzoate results (Nos. 1-5, Table 3), these potassium salts initiated almost complete bulk polymerizations of *β-D,L*-butyrolactone at 50°C (Nos. 3, 4 and 7, 8, Table 4). The addition of a crown ether only slightly increased yields and inherent viscosities. Interestingly, no crotonate end groups were detectable when Boc-L-Ala-K was used as initiator, whereas a low concentration of unsaturated end groups was found with Boc-L-Pro-K. Possibly the urethane group of Boc-L-Ala-K solvates the carboxylate ion via a H-bond, and thus reduces their basicity.

When the polymerizations were repeated at +5°C, no conversion took place with Z-L-Ala-K (Nos. 1 and 2, Table 4). With Boc-L-Pro-K, a high yield was obtained when a crown ether was added (6, Table 4). Such a conspicuous increase of the reactivity of anionic initiators after addition of crown ethers has also been reported by various other authors [13, 14]. The failure in the case of Z-L-Ala-K/crown ether (No. 2, Table 4) may again be explained by the formation of H-bonds between anion and carboxylate ion. As expected, the lower reaction temperature lowered the concentration of crotonate end groups, yet the viscosity was not significantly improved.

Another disappointing result was obtained with regard to the stereochemical course of these polymerizations. All samples isolated from the experiments listed in Table 4 were transparent syrups, and both DSC and ^{13}C-NMR measurements confirmed the atactic sequence and the amorphous character of these products. Thus, it may be concluded that true anionic polymerizations of *β-D,L*-butyrolactone are not well suited for the preparation of isotactic blocks. However, it will be demonstrated in future parts of this series that complexing catalysis which initiate so-called pseudoanionic polymerizations, or, in other words, insertion mechanisms [15], favor the stereoselective polymerization of *β-D,L*-butyrolactone.

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