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Novel Polymerization of β-Butyrolactone Initiated by Potassium Naphthalenide in the Presence of a Crown Ether or a Cryptand

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ABSTRACT: The potassium naphthalenide complex with 18-crown-6 or cryptand [222] is able to initiate the anionic polymerization of β-methyl-β-propiolactone (β-butyrolactone). The polyester macromonomers with unsaturated end groups and low polydispersity are formed in high yield as final products of the polymerization. The possible mechanism of this novel polymerization reaction has been elucidated.

Introduction

The anionic polymerization of β-lactones has been for many years a well-known method of producing polyesters. Recent studies have provided new information about a novel initiator system applied and novel mechanistic features of the β-lactone ring-opening polymerization.[1-3]

According to the previous state of art the ring cleavage in β-lactones was believed to proceed via alkyl–oxygen or acyl–oxygen bond scission.[4] However, with recently discovered alkali-metal anions associated by crowned or cryptanded metal cations as initiators,[5] the α carbon to β carbon bond scission at the initiation stage and formation of "living" polyesters from β-lactones were observed.[6,2,3]

On the other hand, alkali-metal naphthalenides, known as very effective initiators in anionic styrene polymerization,[7] were claimed not to polymerize β-propiolactone at room temperature.[8,9] Thus, anionic polymerization of oxiranes and thiranes initiated with alkali-metal naphthalenides was reported.[10,11]

In the present paper we report on β-methyl-β-propiolactone (4-methyl-2-oxetanone, β-butyrolactone) polymerization initiated by potassium naphthalenide complex with 18-crown-6 or cryptand [222].

In order to elucidate the possible mechanism of the initiation step, the model reaction using an equimolar ratio of monomer and initiator was performed.

Also the model experiments involving polymerization of β-methyl-β-propiolactone with potassium acetate and potassium crotonate in the presence and without crown ether were performed.

Experimental Section

Materials. β-Butyrolactone (from Fluka) was distilled twice over calcium hydride in an atmosphere of dry argon. The fraction boiling at 47 °C (5 mmHg) was collected. 18-Crown-6 (from Fluka) was purified as described previously.[5] Cryptand [222] (from Fluka) and naphthalene (POCh, Poland) were sublimated before use. THF was purified as described in ref 12 and was then distilled over a sodium–potassium alloy in an atmosphere of dry argon.

Preparation of the Initiator and Polymerization. The 0.1 mol/L THF solution of potassium naphthalenide was obtained at a temperature of 20 °C due to the contact of the THF solution of naphthalene with the potassium mirror. Then the required amount of potassium naphthalenide solution was introduced under the argon atmosphere into the THF solution of monomer containing the equimolar with respect to initiator amount of 18-crown-6 or cryptand [222]. After a specified period of time, the polymerization was terminated by addition of methanol solution of HCl.

The β-butyrolactone polymerizations initiated with potassium acetate, potassium crotonate, and their complexes with 18-crown-6 were conducted similarly.

Model Reactions of Potassium Naphthalenide with β-Butyrolactone. The model experiments involving the equimolar reaction of the monomer with potassium naphthalenide were conducted in conditions similar to those for polymerization. The first reaction (i) was carried out without cation complexing agent and the second one (ii) in the presence of crown ether.

(i) Into a 40-mL solution of 0.1 mol/L THF of potassium naphthalenide was added dropwise 0.344 g (0.004 mol) of β-butyrolactone in 3 mL of dry THF with intensive stirring using a glass-covered magnetic stirring bar. The reaction temperature was maintained at 20 °C. After 30 min, the THF was partly evaporated and precipitate formed was filtered and washed with THF. Then, the precipitate was dissolved in diethyl ether containing ion-exchange resin (Lewatit S 1080, from Merck) in acid form. The resin was filtered off, and after solvent evaporation the product obtained was characterized as crotonic acid (yield 83%): IR (CCl$_4$) ν_{max} 2980, 1710, 1700, 1660, 1440, 1310, 1280, 1220, 970 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.9 (d, 3 H, CH$_3$), 5.9 (d, 1 H, CH), 7.0–7.2 (m, 1 H, CH$_3$CH); 9.1 (s, 1 H, COOH).

(ii) Into a 40-mL solution of 0.1 mol/L THF of potassium naphthalenide was added dropwise the solution of 0.344 g (0.004 mol) of β-butyrolactone and 1.06 g (0.004 mol) of 18-crown-6 in 6 mL of THF, and reaction was carried out as described above. After its completion, 0.25 mL (0.004 mol) of methyl iodide in 2 mL of THF was subsequently added. The reaction mixture was filtered, and the filtrate was analyzed by GC–MS technique. The following compounds were identified. 2-Butenoic acid methyl ester (E)[13] (92% GC yield): MS (int) *m/e* 28 (4.8), 29 (3.9), 38 (3.0), 39 (25.2), 41 (47.9), 43 (3.0), 53 (1.9), 55 (2.9), 59 (4.9), 68 (2.0), 69 (100.0), 70 (4.9), 85 (23.2), 100 (19.1), 101 (2.0). 1,2-Dihydronaphthalene: MS (int) *m/e* 28 (13.2), 51 (5.4), 63 (3.7), 64 (4.1), 65 (4.2), 77 (8.1), 78 (3.9), 89 (2.8), 102 (7.8), 115 (44.0), 116 (4.1), 126 (4.3), 127 (21.6), 128 (43.6), 129 (73.0), 130 (100.0), 131 (11.0). 1,4-Dihydronaphthalene: MS (int) *m/e* 77 (4.5), 85 (4.1), 87 (4.6), 102 (11.1), 115 (50.6), 116 (5.5), 127 (13.2), 128 (31.0), 129 (93.7) 130 (100.0), 131 (8.2). Naphthalene: MS (int) *m/e* 50 (6.3), 51 (12.5), 62 (2.9), 63 (7.5), 64 (10.7), 74 (4.7), 75 (5.1), 76 (3.3), 77 (4.1), 78 (2.7), 101 (2.8), 102 (7.1), 126 (6.2), 127 (9.9), 128 (100.0), 129 (11.0).

Measurements. The NMR spectra were recorded by using a Varian VXR-300 multinuclear spectrometer. The ^{1}H NMR spectra were run in CDCl$_3$ by using TMS as the internal standard. The ^{39}K NMR spectra were taken in THF, chemical shifts being referenced to an aqueous solution of potassium fluoride.

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena spectrophotometer.

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Table I
Results of Anionic Polymerization of β-Butyrolactone (Carried Out at a Temperature of 20 °C)

initiator	cation-complexing agent	$[M]_0/[I]_0$	time, h	yield %	M_n (VPO)^a	M_w/M_n^{b}
NaphK	none	50^c	200	8		
NaphK	18-crown-6	40^c	96	90	2800	1.28
NaphK	cryptand [222]	40^c	96	98	2950	1.22
NaphK	cryptand [222]	75^d	110	97	6200	1.25
NaphK	cryptand [222]	150^d	200	95	11000	1.29
CH_3COOK	none	50^c	200	0		
CH_3COOK	18-crown-6	40^e	100	92	2800	1.29
$CH_3CHCHCOOK$	none	25^c	200	5		
$CH_3CHCHCOOK$	18-crown-6	25^c	80	96	1900	1.28

[a] Number-average molecular masses were determined by the VPO technique in $CHCl_3$ using Knauer vapor pressure osmometer. [b] Determined by GPC according to polystyrene standards with a low polydispersity. [c] Conducted in THF, M_0 = 2.0 mol/L. [d] Conducted in THF, M_0 = 3.0 mol/L. [e] Conducted in bulk.

ESR measurements were conducted by using a Bruker ESP-300 spectrometer at 9.62 GHz.

Number-average molecular weights were determined by the VPO technique in $CHCl_3$ using a Knauer vapor pressure osmometer.

GPC experiments were conducted in THF solution at 20 °C, by using the IChF-302 gel permeation chromatograph.

GC-MS analyses were run on a 30-m-long DB-1701 fused-silica capillary column, by using a Varian 3300 gas chromatograph equipped with Finnigan MAT 800AT ion trap detector.

Results and Discussion

We have previously reported that the anionic polymerization of β-lactones in the presence of alkali-metal anions associated by complexed metal cations results in the formation of "living" polymers of β-propiolactones and its α- and β-alkyl-substituted derivatives.[1,2,14] The successful syntheses of polyesters from β-lactones and particularly from β-alkyl-substituted β-lactones in the presence of "blue" alkali-metal solution abounded in alkali-metal anions induced us to reexamine the utility of alkali-metal naphthalenides in β-lactone polymerization. In our experiments we have used potassium naphthalenide with 18-crown-6 or cryptand [222] as initiator and racemic β-butyrolactone as monomer.

Properties of Polymers Obtained. The results presented in Table I indicate that potassium naphthalenide without crown ether or cryptand is not active in the β-butyrolactone polymerization. It turns however out that, after addition of 18-crown-6 or cryptand [222] in equimolar amount as related to potassium naphthalenide, the polymerization of β-methyl-β-propiolactone occurs. Similarly, the polymerization of β-butyrolactone initiated by potassium acetate or potassium crotonate only takes place in the presence of the cation-complexing agent, e.g., 18-crown-6 (Table I).

The polymers were found to be atactic since their ^{13}C NMR spectra were the same as compared with those of typical atactic poly(β-hydroxybutyrate) previously reported.[14,15]

The end-group analysis of the polyesters obtained, carried out according to Shiota,[16] revealed the presence of carboxylate end groups, nearly one carboxylic group per one polymer chain.

The ^1H NMR two-dimensional spectra of polymers obtained in the presence of potassium naphthalenide with cation-complexing agents indicated that besides the signals corresponding to the protons of the polyester chain the signals of the crotonyl end group were also present, and no signals of the naphthalene were observed (Figure 1). The intensities of the signals corresponding to the crotonyl end group were found to decrease with an increase of the polyester molecular weight and were found to be nearly equal to one double bond per polymer chain.

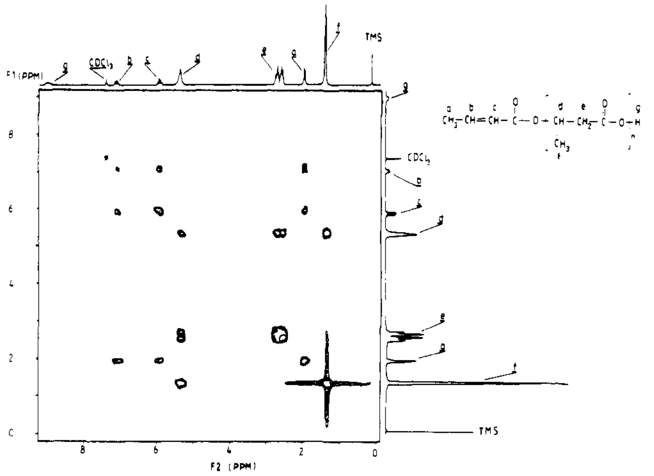


Figure 1. 2D ^1H NMR (300-MHz) spectrum of poly(β-butyrolactone) obtained in the presence of potassium naphthalenide/18-crown-6.

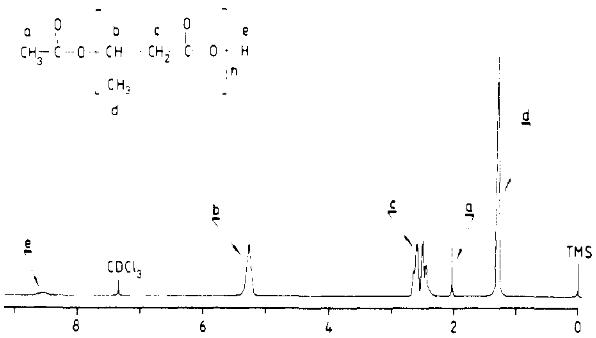


Figure 2. ^1H NMR (300-MHz) spectrum of poly(β-butyrolactone) obtained in the polymerization initiated by potassium acetate/18-crown-6 complex and conducted in bulk at a temperature of 20 °C.

Signals of the crotonyl end group at the same positions were observed also in ^1H NMR spectra of polyesters obtained when the polymerization of β-butyrolactone was initiated with potassium crotonate/18-crown-6 complex but not in the case of β-butyrolactone polymerization initiated with the complex of potassium acetate/18-crown-6 (Figure 2). Therefore, it may be assumed that the unsaturation was introduced to the polyesters in the presence of potassium naphthalenide at the initiation step and not as a result of the chain transfer.

The obtained results indicate that potassium naphthalenide with 18-crown-6 or cryptand [222] initiates the anionic polymerization of β-butyrolactone, resulting in the formation of atactic polyesters with unsaturated end groups and narrow molecular weight distributions.

The observation that the polymerization of β-butyrolactone initiated with potassium naphthalenide as well as

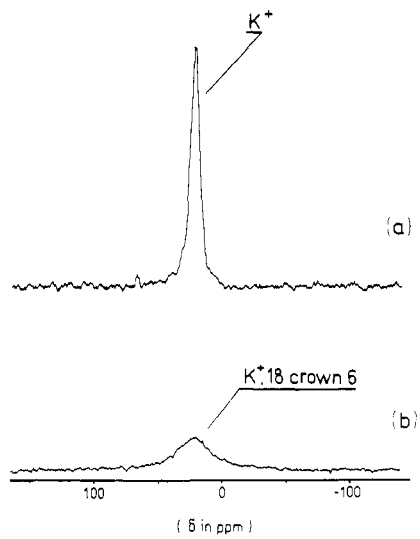


Figure 3. ^{39}K NMR spectra of THF solutions of (a) potassium naphthalenide and (b) potassium naphthalenide after addition of 18-crown-6.

with common initiators as potassium acetate (or crotonate) at room temperature proceeds only in the presence of complexing agent, e.g., a crown ether or a cryptand, indicates that the propagation is effective due to the activity of loose ion pairs (or free anions) and not due to tight ion pairs:

$$\underset{\text{tight}}{\mathrm{Naph}^{\bullet -}\mathrm{K}^+} \rightleftarrows \underset{\text{loose}}{\mathrm{Naph}^{\bullet -}/\mathrm{K}^+} \rightleftarrows \underset{\text{free ions}}{\mathrm{Naph}^{\bullet -}\ \mathrm{K}^+}$$

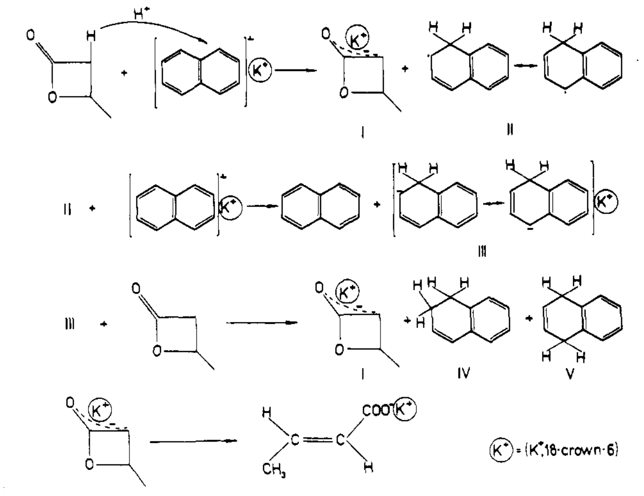
Mechanism of the Polymerization. Initiation. The outcome of a model reaction of β-butyrolactone with potassium naphthalenide in an equimolar ratio 1:1, conducted in THF at 20 °C, indicated that potassium crotonate was formed (see the Experimental Section). The dihydronaphthalenes, i.e., 1,4-dihydronaphthalene and 1,2-dihydronaphthalene (in mole ratio 4:1), were also formed. The quantitative GC analysis showed that ca. 40% of introduced naphthalene was reduced to the corresponding dihydronaphthalenes.

In the ^{39}K NMR spectrum of a solution 0.1 mol/L THF of potassium naphthalenide serving as initiator, the signal of potassium cation at δ 20 with line width (full-width at half-height) of ca. 100 Hz was observed (Figure 3a). After addition of a crown ether, the signal of a potassium cation was still visible at the same position; however, its line width was much larger due to the cation complexation by crown ether. No signal of potassium anion at δ −100[17] was found to be present (Figure 3b). Therefore, one can assume on that basis that the prepared potassium naphthalenide solution is free from metallic potassium, and only crowned K^+ is present.

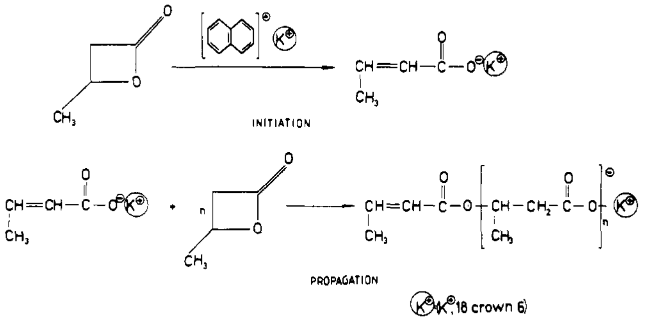
According to the results of the experiments, the mechanism in Scheme I of the initiation step of the investigated polymerization may be proposed. Due to the α-proton abstraction from β-butyrolactone by potassium naphthalenide, the cyclic enolate of β-butyrolactone (I) and radical II are formed at the first step. The formation of cyclic enolates as intermediates was confirmed independently by the outcome of an equimolar reaction of five-membered γ-butyrolactones (which do not homopolymerize due to thermodynamic reasons) with potassium naphthalenide and methyl iodide.[18]

Radical II reacts next with potassium naphthalenide with the formation of anion III and naphthalene. This step is evidenced by the change of deep green to transient red (being attributed to the formation of anion III)[10] and the disappearance of the ESR signal of potassium naphthalenide. The anion III next deprotonates the β-butyrolactone molecule, yielding enolate I and dihydronaphthalenes (IV and V).

Scheme I



Scheme II



Finally, the intramolecular rearrangement of intermediate cyclic enolate I formed at first the third stage leads to potassium crotonate (see Scheme I and the Experimental Section).

The initiation of the β-butyrolactone polymerization carried out in the presence of potassium naphthalenide is different from that proposed by us for β-lactone polymerizations initiated with potassium anions.[2,3,6,19] The observed differences in the reactivity of potassium anions as compared with that of potassium naphthalenide are probably due to the different ability to electron transfer and proton abstraction of those potassium species.

The ambivalence of alkali-metal naphthalenides being able either to electron transfer or to proton abstract was previously suggested.[20] It has been revealed in the present work that in the reaction with β-butyrolactone the potassium naphthalenide acts first of all as a strong base being able to proton abstract. The similar ability of alkali-metal naphthalenides was reported in reactions with proton donors, e.g., alcohols or water.[21,22]

Propagation. In the presence of cation-complexing agents, the potassium crotonate formed in the first step of the β-butyrolactone reaction with potassium naphthalenide is capable of acting as an initiator inducing further polymerization. The chain growth takes place on carboxylate centers due to the alkyl–oxygen bond scission of the monomer molecule, the potassium cations (complexed by a crown ether or a cryptand) being counterions (Scheme II).

The formation of crotonate end groups in the polymerization of β-butyrolactone using common anionic initiators (e.g., triethylamine, pyridine, potassium *tert*-butoxide, etc.) was recently reported by Kricheldorf and Scharnagl, and two deprotonation mechanisms were proposed.[23] However, in the reaction conditions described in their paper, the chain-transfer reaction[16] as well as possible chain scission at the ester groups due to the six-membered ring ester decomposition process[24] should also be taken into account. This is probably the reason that only low molecular weight polymers could be obtained in contrast to "living" macromonomers produced by a potassium naphthalenide complex initiator.

Conclusions

The anionic polymerization of β-butyrolactone initiated by potassium naphthalenide with 18-crown-6 or cryptand [222] takes place via potassium crotonate formed due to the α-deprotonation of β-lactone followed by β-elimination in intermediate cyclic potassium enolate. In the presence of cation-complexing agents, potassium crotonate initiates further polymer chain growth on a carboxylate active species due to the alkyl–oxygen bond scission of the monomer.

Thus synthesis of "living" poly(β-hydroxybutyrate) macromonomers with unsaturated end groups and narrow molecular weight distribution, by anionic polymerization, has been demonstrated. The described synthetic approach may be considered as a new method of macromonomer synthesis, along with those previously reported.[25]

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Registry No. β-Butyrolactone, 3068-88-0; β-butyrolactone (homopolymer), 36486-76-7; β-butyrolactone (SRU), 26744-04-7; potassium naphthalenide, 4216-48-2; 18-crown-6, 17455-13-9; cryptans (2,2,2), 23978-09-8; (*E*)-2-butenoic acid methyl ester, 18707-60-3; 1,2-dihydronaphthalene, 447-53-0; 1,4-dihydronaphthalene, 612-17-9; naphthalene, 91-20-3.