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bulk but with a different (exaggerated) concentration profile, and we have provided quantitative data from both techniques to support the model.

Conclusions

In summary the following points can be made:

(1) Block copolymers of BPAC/DMS show a distinct surface preference for the lower surface energy DMS segments over a wide range of compositions. This segregation, while seen in previous work, is given quantitative significance.

(2) The ISS technique provides a strong complement to ESCA for the study of polymer surfaces. In this case, ISS analysis detailed a very shallow surface change not seen by ESCA.

(3) The morphology of the surface region of BPAC/DMS block copolymers can be explained as consisting of microdomains of each component oriented perpendicularly to the surface, with a depth greater than the sampling depth of ESCA. Therefore, while the composition of the surface is very different from that of the bulk, the morphology of both is similar.

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Registry No. PBAC (copolymer), 25037-45-0; BPAC (SRU), 24936-68-3.

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Polymerization of β-Lactones Initiated by Potassium Solutions

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ABSTRACT: Polymerization of β-lactones **1** by alkali metal solutions proceeds fast with a yield higher than 90%. Polyesters with a molecular mass ($\bar{M}_n$) higher than 100 000 can be obtained when the concentration of that initiator is sufficiently low. The initiation step of polymerization involves an unusual, till now unreported, scission of the C–C bond in the β-lactone ring.

Introduction

Polymerization of β-propiolactone and its derivatives constitutes the subject of intensive studies of many authors.[1-3]

However, the polymerization of β-lactones by alkali metals has not been investigated in great detail. One of the supposed reasons may be the very low yields obtained in the polymerization of these monomers by suspensions of alkali metals.[4,5] A quite different picture provides the polymerization of β-propiolactone **1a**, initiated by potassium and sodium solutions, i.e., in a homogenous system.[6] The same initiators, i.e., alkali metal solutions, were found previously to be very active in the polymerization of vinyl monomers.[7]

The aim of this work was to study the ring-opening polymerization of β-lactones **1** initiated by potassium solutions. The β-propiolactone (**1a**), α-methyl,α-ethyl-β-propiolactone (**1b**), and β-butyrolactone (**1c**) were selected as model monomers.

Experimental Section

Measurements. The ^{1}H NMR spectra were run in $CDCl_3$ with Me_4Si as internal standard, using a Varian Xl-100 spectrometer. The GPC experiments were conducted in CH_2Cl_2 solution at 20 °C with a Waters GPC-200 gel permation chromatograph connected to a flow-through cell equipped with a Wilks IR detector (1735 cm^{-1}). Gas chromatographic analyses were run on a 2-m-long glass column packed with OV-17, 15% Chromosorb W AW DMSC 60–80 mesh, using a Varian 2700 gas chromatograph. Number-

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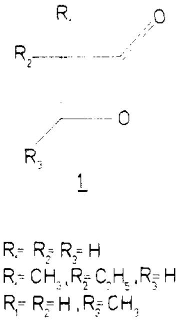
Table I
Polymerization of β-Lactones 1 Carried Out in the Presence of Selected Anionic Initiators at 25 °C

monomer	initiator	solvent	$I_0 \times 10^2$, mol·L^{-1}	C_0, mol·L^{-1}	reactn time, h	% yield	$\bar{M}_n$
1a	triethylamine	CH_2Cl_2	5.0	2.0	300	85	1 400[a]
1a	KOH	Me_2SO	5.0	1.0	18	80	500[a]
1a	KOH/18-crown-6	THF	1.6	3.0	12	89	10 100[a]
1a	potassium solution	THF	1.6	3.1	3	98	12 000[a]
1a	potassium solution	THF	0.16	3.3	10	90	110 000[b]
1b	potassium solution	THF	1.52	2.5	3	92	15 000[a]
1b	potassium solution	THF	0.16	3.0	16	90	180 000[b]
1c	potassium solution	THF	5.5	3.9	150	85	5 600[a]
1c	CH_3ONa[c]	THF	5.8	5.8	360	0	

[a] Determined by VPO technique in CH_2Cl_2. [b] Estimated from viscosimetric measurements. [c] Data by Araki et al.[11]

Chart I



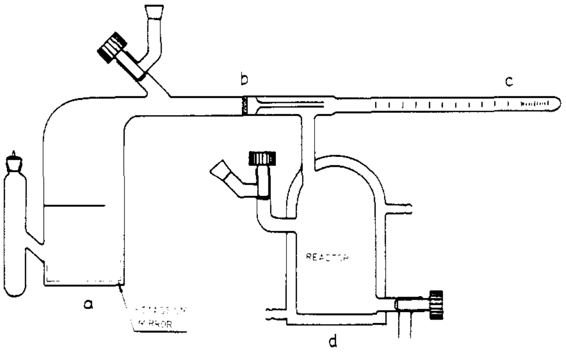


Figure 1. Apparatus used for the preparation of potassium solution initiator and polymerization.

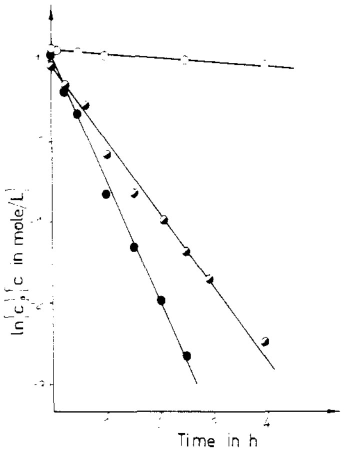


Figure 2. Kinetic plot for the polymerization of β-lactones **1** (conversion determined by GC analyses) initiated by potassium solution in THF at 25 °C: (●) $[\mathbf{1a}]_0 = 3.0$ mol/L, $I_0 = 5 \times 10^{-3}$ mol/L; (◐) $[\mathbf{1b}]_0 = 2.54$ mol/L, $I_0 = 5 \times 10^{-3}$ mol/L; (○) $[\mathbf{1c}]_0 = 3.49$ mol/L, $I_0 = 5 \times 10^{-2}$ mol/L.

average molecular masses were determined by VPO in CH_2Cl_2 with a Knauer vapor pressure osmometer. UV spectra were recorded on a Specord UV–vis spectrophotometer (Carl Zeiss, Jena).

Monomers. β-Propiolactone (**1a**) (Fluka) was purified according to a described method[8] or was distilled twice over CaH_2 in an atmosphere of dry argon. The fraction boiling at 51 °C (10 mmHg) was collected (99.7% GC). α-Methyl-α-ethyl-β-propiolactone (**1b**) was obtained as described in ref 1 and distilled twice over CaH_2. The fraction boiling at 66 °C (16 mmHg) was collected (99.6% GC). β-Butyrolactone (**1c**) (Fluka) was dried in a similar manner. The fraction boiling at 47 °C (5 mmHg) was collected (99.8% GC).

Solvent. THF was purified according to a described method[9] and was then distilled over a sodium–potassium alloy in an atmosphere of dry argon.

Preparation of Initiator and Polymerization. Preparation of the potassium solution and polymerization were conducted in an apparatus depicted in Figure 1. That apparatus was dried before use for several hours under high vacuum at 60 °C. A potassium mirror was obtained by high-vacuum distillation of metallic potassium (Figure 1, part a). The potassium solution was formed by the contact of the potassium mirror with a solution of 18-crown-6 in THF (0.1 mol/L). After strictly 15 min the required amount of resulting blue solution was filtered through a coarse frit (b) to the calibrated tube (part c, Figure 1). The polymerization of the β-lactones was initiated in the reactor (d) by the introduction of the potassium solution from the tube (c) into the THF solution of the corresponding monomer at room temperature. The concentration of potassium anions was taken as half of the total potassium concentration, determined by titration of the hydrolyzed sample of the potassium solution with 0.03 HCl. The course of polymerization was monitored by GPC or gravimetrically. Polymerizations were terminated by addition of methanol, ethanol, or water.

Results and Discussion

Properties of Polymers Obtained. It was demonstrated that polymerization of β-propiolactone (**1a**) initiated by alkali metal solutions proceeded rapidly, and under proper conditions the yield may exceed 90%. This specific, new initiation system makes it possible to obtain high molecular mass polyesters starting from lactone **1a** ($\bar{M}_n >$ 100 000). A comparison of the polymerization results of β-lactones **1a**–**c** carried out in the presence of potassium solutions with those obtained with common anionic initiators is presented in Table I. It was found that not only β-propiolactone (**1a**) but also its α- and β-alkyl-substituted derivatives could be polymerized by potassium solutions, giving the corresponding polyesters with a considerably high yield. It is worth emphasizing that even β-butyrolactone (**1c**), whose polymerization by common anionic initiators was unknown,[10,11] polymerized in the presence of this particular initiation system.

The rates of polymerizations monitored gravimetrically or by GC analysis are illustrated in Figure 2. The studied β-lactones may be arranged in the following order of decreasing reactivity in polymerization initiated by potassium solution: **1a** > **1b** > **1c**.

Polymers formed from β-lactones possess unimodal molecular mass distribution, as shown in the Figure 3.

The conversion–molecular mass dependence for the polyesters obtained seems to indicate the living nature of

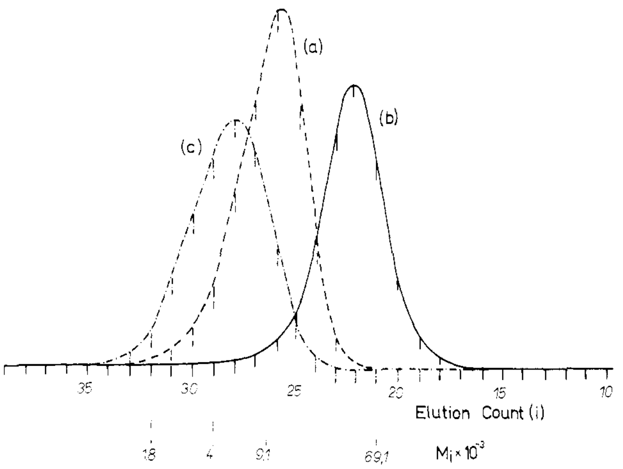


Figure 3. GPC chromatograms of polymers obtained in the polymerization of lactones 1 initiated with potassium solutions: (a) poly-**1a**, M_n = 11 000; (b) poly-**1b**, M_n = 67 000; (c) poly-**1c**, M_n = 6500.

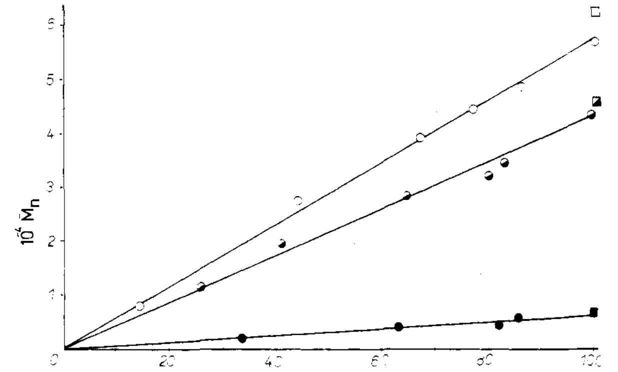


Figure 4. Dependence of M_n/conversion for poly(β-lactones) obtained in the presence of potassium solutions: (◑) **1a**, C_0/I_0 = 640, I_0 = 0.005 mol/L M_n(cal) = 46 000 and indicated by ◪; (○) **1b**, C_0/I_0 = 552, I_0 = 0.005 mol/L M_n(cal) = 62 900 and indicated by □; (●) **1c**, C_0/I_0 = 78, I_0 = 0.05 mol/L M_n(cal) = 6 700 and indicated by ■. $M_n(\text{cal}) = (C_0/I_0)M_1$.

the polymerization taking place in this system (Figure 4). The polymerization was found to proceed further after the addition of a new portion of monomer into the reaction mixture. Block copolymers of the lactone **1a** with **1b** or **1c** can be obtained in this way. There are no double bonds in the polyester chain formed, which indicates that no transfer reaction to the monomer occurs. Such a transfer reaction generally takes place in the polymerization of lactone **1a** initiated by potassium acetate.[12]

Mechanism of the Polymerization of β-Lactones. The end-group analysis of polyester derived from β-propiolactone (**1a**) with a molecular mass of several thousand, obtained by potassium solution, showed the existence of carboxyl groups whose number was nearly equal to one COOH group per polymer molecule. This result might suggest that similarly, as in the case of some anionic initiators, e.g., the complex of potassium acetate with 18-crown-6,[8] the ring opening of lactone **1a** proceeds with a cleavage of the alkyl–oxygen bond. However, the ^{1}H NMR spectra of low molecular mass poly(β-propiolactone) ($\bar{M}_n$ = 1900) obtained in the polymerization initiated by potassium solutions and after several minutes terminated in methanol, ethanol, or water showed that besides the signals corresponding to the CH_2 group of the polyester chain an additional singlet at δ = 2.06, which may be ascribed to CH_3 protons of the acetoxy group, was also present (Figure 5). A similar signal was also observed in the ^{1}H NMR spectra of poly(β-propiolactone) obtained with the complex of potassium acetate and 18-crown-6 as initiator. In the latter case, however, the presence of the acetoxy group in the polymer chain is due to the incorporated initiator molecule.

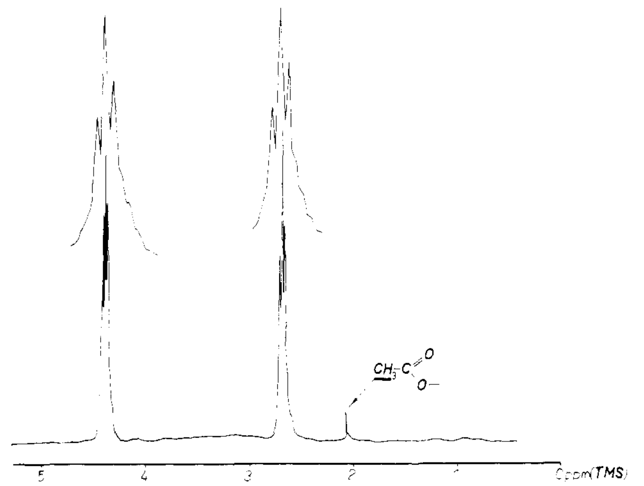


Figure 5. ^{1}H NMR (360 MHz) spectrum of poly(β-lactone) **1a** obtained with potassium solution as initiator ($\bar{M}_n$ = 1 900).

As reported earlier[13] the solubility of alkali metals in THF is exceedingly low. A minute but constant concentration of un-ionized atoms (M^0) is maintained when a solvent is kept in contact with solid alkali metal

$$\text{M (metal in contact with solvent)} \rightleftarrows M^0 \text{ (in solution)} \qquad (1)$$

Dissolved metal atoms are in equilibrium with the products of their ionization

$$M^0 \rightleftarrows M^+ + e^-, \quad \text{solvated electron} \qquad (2)$$

Further equilibrium is established between M^0 and e^-

$$M^0 + e^- \rightleftarrows M^- \qquad (3)$$

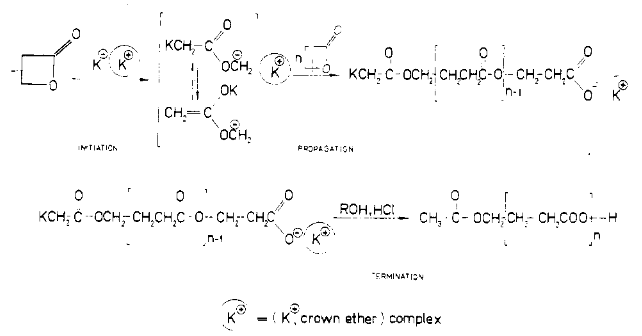
yielding negative alkali ions.[14] In the presence of cation-solvating agents such as crown ethers or kryptates, the amount of dissolved alkali metals substantially increases due to the complexation of the cation with the comlexing agent

$$M^+ + \text{crown ether (or kryptate)} \rightleftarrows (M^+\text{, crown ether (or kryptate) complex)} \qquad (4)$$

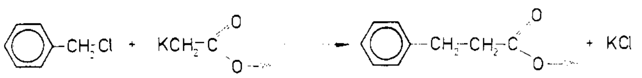
raising the concentration of the anions and the complexed cations to that of the added crown. The new equilibrium is established, and as has been found by one of us recently,[15] solvated electrons and crown-complexed K^+ ions are the primary products of potassium dissolution in THF solutions of crown ethers. However, after 15 min (at 25 °C) the potassium anions (due to reaction 3) and crown-complexed cations (K^+) are the predominant species in such solutions.[15]

On the basis of the above-mentioned experimental results, the polymerization mechanism shown in Scheme I may be proposed. According to this mechanism, the potassium anion attacks the β-lactone ring to cleave the σ CH_2–CH_2 bond and forms a carbanion that is stabilized by a tautomeric equilibrium with its enolate form.[16] This anion can react with the next β-lactone molecule by the opening of the alkyl–oxygen bond, forming carboxylic active centers. The propagation reaction, therefore, proceeds by reaction of the carboxylate anion active centers. By addition of the polymerization mixture into methanol, ethanol, or water, the presence of the acetoxy end group can be observed in the ^{1}H NMR spectrum of the low

Scheme I



Scheme II

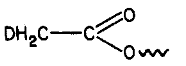


molecular mass polyesters formed (Figure 5). The proposed mechanism was confirmed by the following additional experiments:

(i) In the ^{1}H NMR spectrum of a polyester obtained in the polymerization of lactone **1a** initiated by potassium solution and quenched by benzyl chloride, signals corresponding to the phenyl end group formed due to the reaction of the enolate end group with benzyl chloride were observed (Scheme II). The presence of the phenyl group incorporated into the polymer chain was also confirmed by UV spectroscopy (Figure 6, line a).[17]

(ii) The well-known reaction of enolates with acyl halides leading to the formation of β-keto esters[16] was applied for the quenching of the β-propiolactone polymerization initiated with potassium solution. Poly(β-propiolactone), precipitated in KOH–water solution after polymerization initiated by potassium solution and quenching with benzoyl chloride, contained a phenyl group incorporated into the polyester chain as detected by UV spectroscopy (Figure 6, line b). The presence of anhydride bonds formed due to the possible reaction of carboxylic end groups with benzoyl chloride was excluded since in the IR spectrum of that polymer no signals corresponding to the stretching vibrations of the anhydride carbonyl groups at the 1820 cm^{-1} were observed.

(iii) The polymerization of β-lactone **1a** initiated by potassium solutions was quenched in deuterated water. In the ^{1}H NMR spectrum of the polymer obtained, a poorly resolved triplet was observed instead of the singlet at δ 2.06, which is most probably due to the formation of the following end group:



$DH_2C-C(=O)O\sim$

(iv) In the ^{1}H NMR spectra of polyesters obtained in the polymerization of lactone **1b** by potassium solution and terminated in methanol, the singlet at δ 2.06 was not observed. That singlet, however, was present in the ^{1}H NMR spectra of the polyesters obtained from lactone **1c** under the same conditions, and its intensity decreased with increasing polymer molecular mass (Figure 7), as already observed in the case of the potassium solution initiated polymerization of unsubstituted lactone **1a**.[6]

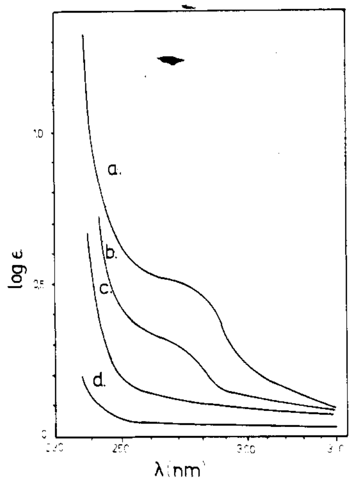


Figure 6. UV spectra (cell with 1-cm path length) in CHCl$_3$: (a) Poly(β-propiolactone) **1a** ($\bar{M}_n$ = 1 600) obtained in the polymerization initiated by potassium solution and quenched with benzyl chloride; (b) Poly(β-propiolactone) **1a** ($\bar{M}_n$ = 2 000) obtained in the polymerization initiated by potassium solution and quenched with benzoyl chloride; (c) Poly(β-propiolactone) ($\bar{M}_n$ = 1 800) obtained in the polymerization initiated by potassium solution and terminated in methanol; (d) Poly(β-propiolactone) ($\bar{M}_n$ = 1 600) obtained in the polymerization initiated by the complex of potassium acetate and 18-crown-6, mol ratio 1:1, and quenched with benzyl chloride.

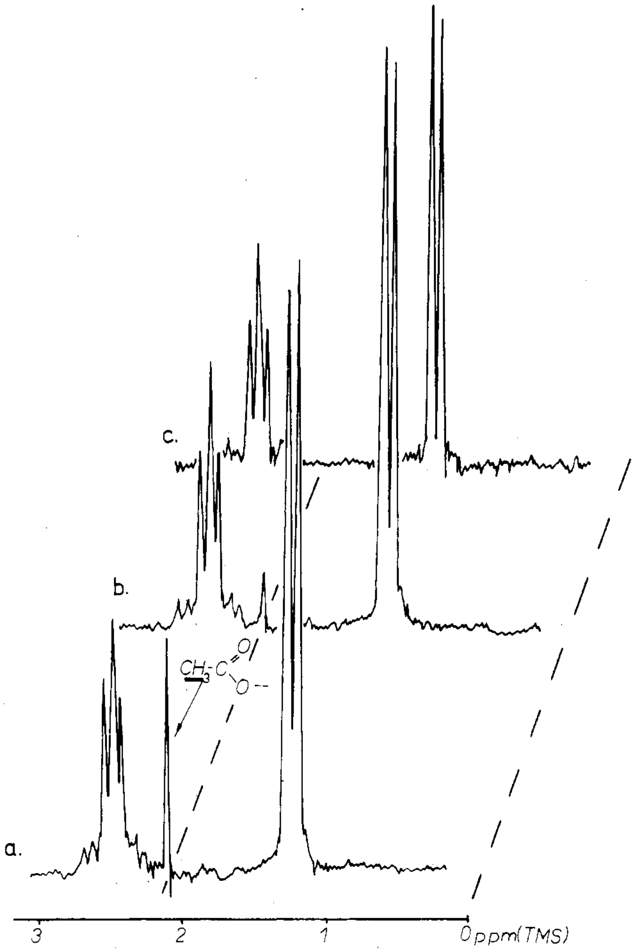


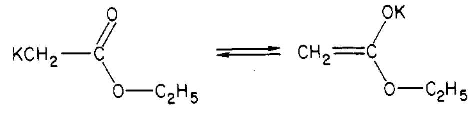
Figure 7. ^{1}H NMR spectra of poly(β-propiolactones) **1c** obtained with potassium solutions as initiators: (a) $\bar{M}_n$ = 1800; (b) $\bar{M}_n$ = 3000; (c) $\bar{M}_n$ = 8000.

The cleavage of the C–C bond of the lactone ring occurring at the initial step of the polymerization initiated by potassium solution and resulting in the formation of carbanions as active centers is to the best of our knowledge the first example of such a reaction observed for the polymerization of oxacyclic compounds. However, cleavage of the carbon–carbon bond of substituted hydrocarbons with bulky substituents, e.g., phenyl or naphthyl, was discussed in the early work of Schlenk[18] on the reaction of "dissociable ethanes" cleaved to the corresponding sodium derivatives in the presence of sodium amalgam.

These results, confirmed by several authors, imply a direct cleavage of the carbon–carbon bond by alkali metals.[19-22]

It has been demonstrated in the recently published study[23] of the reactions of selected aliphatic hydrocarbons with a THF dispersion of Cs–K–Na alloys that the cleavage of the σ bond between primary, secondary, or tertiary carbons takes place with good yields when substituents such as phenyl or vinyl groups are present in the molecules of these aliphatic compounds.

Possible growth of the polymer chain due to the β-propiolactone polymerization by an enolate end group formed in the initial step of β-lactone polymerization by potassium solution (Scheme I) is negligible. A proof for that was provided in an experiment in which the potassium enolate of ethyl acetate **2** was used as initiator.[24]



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It has been found that after 24 h of the β-propiolactone polymerization initiated with enolate **2** at 25 °C in THF (initial monomer concentration $c_0 = 3$ mol/L, initial enolate concentration $I_0 = 1.6 \times 10^{-2}$ mol/L) the yield of the polyester formed was less than 1% (gravimetrically). Under similar conditions the yield of poly(β-propiolactone) obtained in the polymerization initiated with potassium solution was greater than 98% after 3 h (Table I).

The obtained results indicate that the initiation reaction of the β-propiolactone polymerization by potassium enolates is very slow.

Conclusion

The alkali metal solutions were found to be active initiators of the polymerization of β-propiolactone (**1a**) and its alkyl derivatives **1b** and **1c**. The cleavage of the β-lactone ring in the polymerization initiated by alkali metal solutions abounded in K^- anions was found to take place differently than previously reported.

Both C–C bond and C–O bond scissions take place, resulting in the formation of carbonium anions (at the initial step) and carboxylic active centers (at further propagation). In spite of the fact that cleavage of the C–C bond in substituted aliphatic hydrocarbons by Cs–K–Na alloys in solution was recently reported[23] it is to our knowledge the first observation concerned with the C–C bond cleavage in the ring-opening polymerization of heterocycles. These results provide also yet another example of anionic ring-opening polymerization occurring with formation of different active centers under the same reaction conditions.[26,27] Further investigations of the lactone polymerization by alkali metal solution are under way.

Acknowledgment. We express our thanks to Professor M. Szwarc for fruitful discussions and to Professor R. W. Lenz for kindly supplying the sample of α-methyl-α-ethyl-β-propiolactone. We are also indebted to Dr. R. Tymczyński for performing GPC experiments and K. Zbikowska for VPO measurements.

Registry No. 1a, 57-57-8; **1a** (homopolymer), 25037-58-5; **1a** (SRU), 24938-43-0; **1b**, 1955-42-6; **1b** (homopolymer), 25188-78-7; **1b** (SRU), 25265-43-4; **1c**, 3068-88-0; **1c** (homopolymer), 36486-76-7; **1c** (SRU), 26744-04-7; potassium 18-crown-6, 31270-13-0.

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