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Anionic Polymerization of β-Lactones Initiated with Alkali-Metal Alkoxides: Reinvestigation of the Polymerization Mechanism

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ABSTRACT: The mechanism of anionic polymerization of β-propiolactone (PL) and β-butyrolactone (BL) initiated by potassium alkoxides (methoxide and *tert*-butoxide) with 18-crown-6 was reinvestigated on the basis of polymer end-group analysis and model reactions. It has been found that corresponding unsaturated esters (unreactive in further polymerization) and potassium hydroxide are the initial products of the initiation step. The latter acts as the real initiator in this system. Polyesters with hydroxy or unsaturated dead end groups are produced, with carboxylate anions formed due to the alkyl–oxygen bond cleavage of the monomer molecule being the exclusive propagation species. The proposed novel mechanism seems to be a general one as far as the polymerization of unsubstituted and β-substituted β-lactones by alkali-metal alkoxides is concerned.

Introduction

A great deal of research has been done on the anionic polymerization of four-membered lactones. Early papers[1–3] reported that β-lactone polymerization initiated with weak bases proceeds unquestionably via alkyl–oxygen bond scission of the monomer and carboxylate anions are the propagating species, also in the presence of organic ligands.[4]

It turned out, however, that the anionic polymerization of β-lactones with strong bases, e.g., alkali-metal alkoxides, is more complex and still discrepancies exist in the literature as far as the mechanism of this reaction is concerned. It has been reported that in the anionic polymerization of β-propiolactone (PL) with a strong base, e.g., potassium ethoxide, as the initiator acyl–oxygen bonds of the monomer are cleaved to produce alcoholate ions as propagating centers.[5]

In more recent papers it was claimed that propagation proceeds due to both alcoholate and carboxylate anions formed via acyl–oxygen and alkyl–oxygen bond scission, the latter being eventually prevailing at higher conversions. It was also suggested that the initiator is incorporated to the polymer and both ether and ester end groups are formed in the polymerization of β-propiolactone initiated by potassium methoxide.[6,7] The latter results were, however, inconsistent with the data published recently by Dale[8] and Kricheldorf[9] concerned with β-propiolactone and β-butyrolactone (BL) polymerization initiated with potassium *tert*-butoxide. Both authors found unsaturated double bonds as the end groups and no traces of the initiator in the resulting polymers.

Some attempts made to explain the above-mentioned discrepancies were not convincing[10] and prompt us to reinvestigate anionic polymerization of β-lactone polymerization with alkoxides as the initiators. PL and BL (β-methyl-β-propiolactone) were employed as monomers, with potassium methoxide and potassium *tert*-butoxide complexes with 18-crown-6 being used as the initiators.

Experimental Section

Materials. PL (from Aldrich) was dried as described previously.[11] The fraction boiling at 51 °C (10 mmHg) was collected. BL [from Fluka; bp 47 °C (5 mmHg)] was purified in a similar manner. 18-Crown-6 (from Fluka) was purified as described previously.[12] The potassium methoxide/18-crown-6 complex (mole ratio 1:1) was obtained by reacting dry methanol with a potassium mirror, and after completion of the reaction 18-crown-6 was added, in an equimolar amount with respect to that of the alkali metal, with the excess of methanol being removed by evaporation. The obtained product was heated at 60 °C in an ampule attached to the high-vacuum line (during 60 h). The potassium *tert*-butoxide/18-crown-6 complex (mole ratio 1:1) was obtained by dissolution of equimolar amounts of potassium *tert*-butoxide (from Aldrich) and crown ether in dry THF. Potassium hydroxide (from POCh) was dried as described in ref 13. THF was purified as described in ref 14 and was then distilled over a sodium–potassium alloy in an argon atmosphere. The ion-exchange resin Lewatit S 1080 (from Merck) in acid form was used as the protonation agent. Methyl iodide and ethyl iodide (both from Aldrich) were used as alkylation agents.

Measurements. ^{1}H NMR spectra were recorded using a Varian VXR-300 spectrometer in $CDCl_3$ with TMS as the internal standard. Number-average molecular weights were determined by the VPO technique in $CHCl_3$ using a Knauer vapor-pressure osmometer. GPC experiments were conducted in a THF solution at 35 °C, using a Spectra-Physics 8800 gel permeation chromatograph. GC–MS analyses were run on a 30-m-long fused-silica capillary column, DB-1701, using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800AT ion trap detector. Preparative GC separations were conducted on a glass column packed with OV-17, 15% on Chromosorb W, 45–60 mesh, using a Varian 2800 gas chromatograph with a semipreparative unit.

The carboxyl end groups were determined by the method described by Shiota et al.[15]

Polymerization of β-Propiolactone and β-Butyrolactone Initiated by Potassium Methoxide/18-Crown-6 and *tert*-Butoxide/18-Crown-6 Complexes. Polymerization experiments were conducted at a temperature of 20 °C in a THF solution. The monomer concentration was equal to 1.3 mol/L in each experiment, and the concentration of the initiator varied from 0.065 to 0.026 mol/L. The polymers were precipitated in cold pentane and filtered off. The pentane filtrate was analyzed by a GC–MS technique. The polymers obtained were dissolved in dichloromethane, and the acid ion-exchange resin was introduced into the polymer solution. Then the ion-exchange resin was filtered off, and the polymer was reprecipitated in cold pentane and dried in vacuum. The molecular weight distribution of the polymers obtained was determined by GPC according to polystyrene standards with a low polydispersity.

Polymerizations initiated with the potassium hydroxide/18-crown-6 complex (used as the reference initiator) were conducted in a similar manner.

Potassium alkoxides without cation complexing agents applied as the initiators induce polymerization of PL in a manner similar

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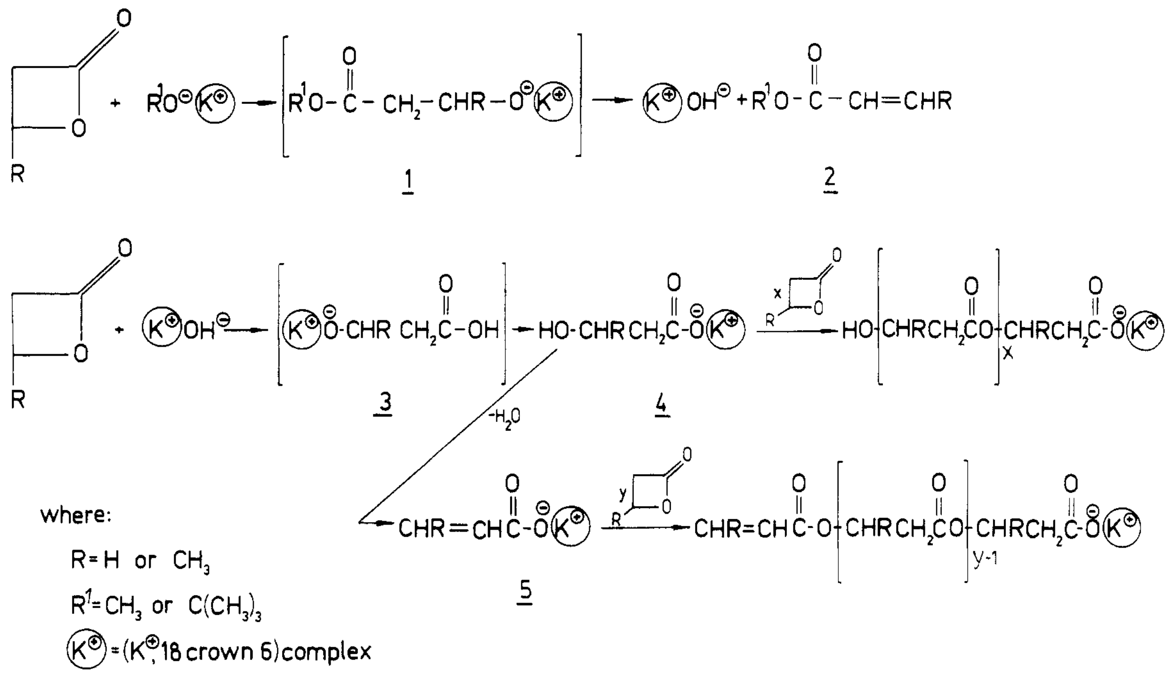
Scheme I



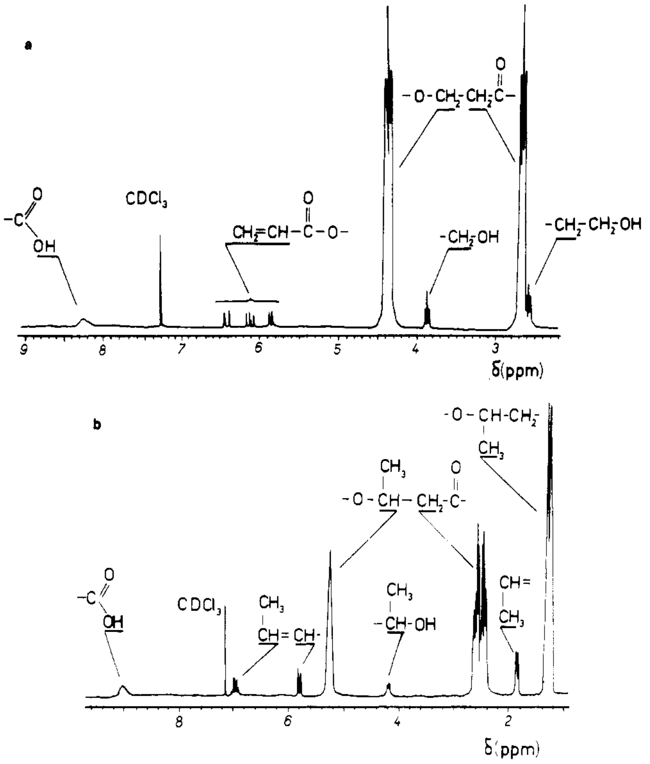


Figure 1. ^{1}H NMR spectra of polyesters obtained in the presence of the *tert*-butoxide/18-crown-6 complex: (a) poly(β-propiolactone), (b) poly(β-butyrolactone).

to that in the presence of a crown ether; however, in the polymerization of BL only low molecular weight oligomers were obtained in minor yield.

Model Reactions of β-Propiolactone and β-Butyrolactone with Potassium Alkoxide/18-Crown-6 Complexes. (i) The model experiments involving the equimolar reactions of PL and BL with the potassium methoxide/18-crown-6 complex were conducted under an argon atmosphere in a THF solution in a temperature of 20 °C and were quenched by protonation with Lewatit S 1080 ion-exchange resin.

The model experiments involving the equimolar reactions of PL and BL with the potassium *tert*-butoxide/18-crown-6 complex were conducted as described above.

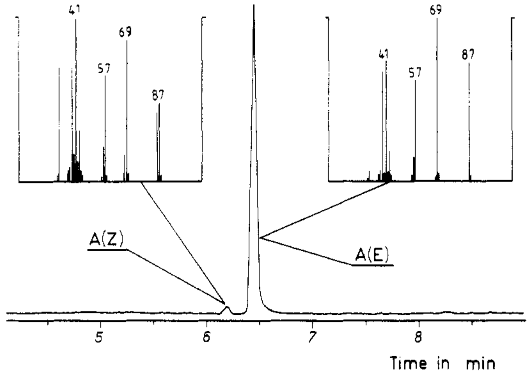
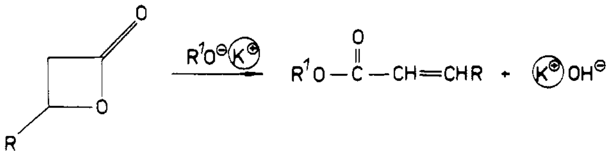


Figure 2. GC–MS trace of the filtrate obtained after precipitation of poly(β-butyrolactone) obtained in the presence of the potassium *tert*-butoxide/18-crown-6 complex. A(Z): 2-Butenoic acid *tert*-butyl ester (*Z*). A(E): 2-Butenoic acid *tert*-butyl ester (E).

Scheme II



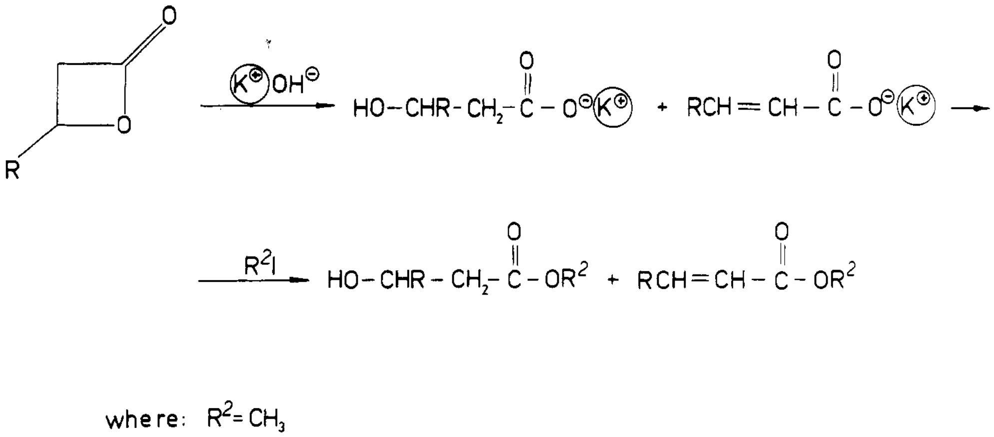
(ii) The model reactions in which the mole ratio of PL or BL to the potassium methoxide/18-crown-6 complex was equal to 2:1 were conducted in a manner similar to that described in paragraph (i), but instead of the ion-exchange resin the ethyl iodide was added for quenching. The reaction mixture was filtered off, and the filtrate was analyzed by a GC–MS technique.[16]

The model reactions in which the mole ratio of PL or BL to potassium *tert*-butoxide/18-crown-6 complex was equal to 2:1 were conducted in a manner similar to that described above but the methyl iodide was added for quenching.

Model Reactions of PL and BL with the Potassium Hydroxide/18-Crown-6 Complex. The equimolar model reactions of PL and BL with the potassium hydroxide/18-crown-6 complex were conducted in a manner similar to that described above and were terminated by alkylation with methyl iodide.

In the reaction of PL the following compounds were identified by GC–MS analysis: 2-propenoic acid methyl ester (methyl acrylate; 49% yield GC) and 3-hydroxypropanoic acid methyl ester (51% yield GC).

Scheme III



In the model reaction of BL the following compounds were identified: 2-butenoic acid methyl ester (methyl crotonate; 54 % yield GC of isomers *E* and *Z*) and 3-hydroxybutanoic acid methyl ester (46% yield GC).

Results and Discussion

Polymerization. The end-group analysis revealed that in the polymerization or oligomerization of β-lactones (PL and BL) initiated with the potassium methoxide/18-crown-6 complex, alkyl–oxygen bonds of monomers are cleaved and consequently carboxylate anions constitute the propagating species.[17] The same course of propagation has been observed now with the potassium *tert*-butoxide/18-crown-6 system as the initiator.

The polymers were found to possess a unimodal molecular weight distribution (e.g., for poly(β-butyrolactone) of M_n = 4000, M_w/M_n was equal to 1.2).

^{1}H NMR (300 MHz) shows no signals corresponding to *tert*-butyl ester or *tert*-butyl ether end groups (Figure 1), derived from the initiator, in oligomers or polymers obtained. Instead, the signals of unsaturated and hydroxyl end groups were detected as previously reported in the case of polyesters synthesized with the potassium methoxide/18-crown-6 complex as the initiator.[17] The presence of unsaturated and hydroxyl end groups was also observed in ^{1}H NMR spectra of low molecular weight polyesters derived from PL and BL monomers when the potassium hydroxide/18-crown-6 complex was applied as the reference initiator. It was proof that all strong bases such as potassium methoxide, potassium *tert*-butoxide, or KOH used as initiators produce polymers with carboxylate propagating species and unsaturated or hydroxyl dead end groups.

Moreover, the presence of the respective unsaturated esters (i.e., methyl acrylate from PL polymerization and methyl crotonate from BL polymerization initiated with the potassium methoxide/18-crown-6 complex and *tert*-butyl acrylate from PL polymerization and *tert*-butyl crotonate from BL polymerization initiated with the potassium *tert*-butoxide/18-crown-6 complex) was detected by GC–MS analysis (see the Experimental Section) in the filtrates after precipitation of the polymers obtained (Figure 2). The amounts of these esters were nearly corresponding to that of the alkoxide used as the initiator.

Mechanism of the Polymerization. The above-presented results indicate that carboxylate anions constitute the only growing species in PL and BL polymerization with potassium alkoxides as the initiators, and the mechanism in Scheme I of the polymerization can be proposed.

The alkoxide anion of the initiator attacks the carbonyl carbon atom of the β-lactone to induce the monomer acyl–oxygen bond cleavage. The initial product, potassium β-alkoxide ester **1**, yields the corresponding unsaturated ester **2** (unreactive in further polymerization) and potassium hydroxide (Scheme I). The latter reacts with the next molecule of β-lactone, inducing acyl–oxygen bond scission and yielding unstable intermediate **3**, and the next corresponding potassium salts of β-hydroxy and unsaturated acids **4** and **5** responsible for further polymer chain growth are produced (Scheme I). As a result polyesters with hydroxyl and unsaturated dead end groups are formed due to propagation on carboxylate active centers.

The evidence of the mechanism proposed was provided also by the following model reactions:

(i) Equimolar model reactions of PL and BL with potassium methoxide/18-crown-6 or potassium *tert*-butoxide/18-crown-6 complexes yield KOH and corresponding unsaturated esters (Scheme II) which were isolated and identified (see the Experimental Section).

(ii) The results of equimolar model reactions of PL and BL conducted with the potassium hydroxide/18-crown-6 complex as a reference initiator and terminated with methyl iodide revealed that a mixture of the corresponding unsaturated esters and β-hydroxy esters is formed (Scheme III).

(iii) Model experiments performed using a mole ratio of the β-lactone monomer to the alkoxide initiator equal to 2:1 additionally confirm the proposed mechanism (Scheme I). The products of these reactions were analyzed by the GC–MS technique as described in the Experimental Section. A typical example of the GC–MS traces recorded for the reaction of BL with the potassium *tert*-butoxide/18-crown-6 complex (mole ratio 2:1) terminated with methyl iodide is presented in Figure 3. The above-described model reactions indicate that potassium hydroxide initially formed (Scheme II) reacts further with the next β-lactone molecule to produce the corresponding β-hydroxy and unsaturated acid salts which after alkylation (in the presence of 18-crown-6[18]) form the respective esters (Scheme IV).

Conclusions

Experimental results revealed that primary and tertiary alkoxides react with β-lactones according to the mechanism presented in Scheme I. Potassium hydroxide, formed at the initiation stage of β-lactone polymerization initiated with potassium alkoxides, reacts with the next monomer molecules and yields hydroxy and unsaturated carboxylates responsible for polymer chain growth. Therefore,

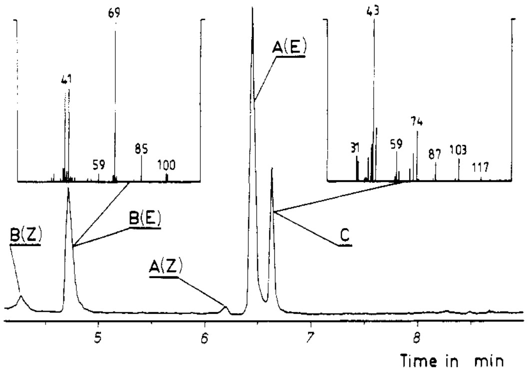
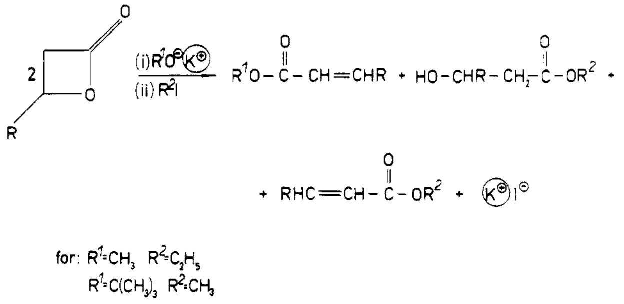


Figure 3. GC–MS trace of products of the model reaction of β-butyrolactone with the *tert*-butoxide/18-crown-6 complex (mole ratio 2:1) terminated with methyl iodide. A(Z): 2-Butenoic acid *tert*-butyl ester (*Z*). A(E): 2-Butenoic acid *tert*-butyl ester (*E*). B(Z): 2-Butenoic acid methyl ester (*Z*). B(E) 2-Butenoic acid methyl ester (*E*). C: 3-Hydroxybutanoic acid methyl ester.

Scheme IV



the polymerization proceeds exclusively on carboxylate anions as active centers. It is interesting to notice that in the case of β-propiolactones polymerization initiated by another strong base like potassium supramolecular complex propagation proceeds also on carboxylate active centers as reported by us previously.[19]

The end-group analysis performed by us using ^{1}H NMR (300 MHz) and model reactions is consistent to some extent with results of Dale[8] and Kricheldorf,[9] who found unsaturated end groups in their polymers. However, the possible α-deprotonation of a monomer molecule at the initiation step of polymerization of PL and BL by potassium *tert*-butoxide might be considered as a rather negligible minor reaction in this system since hydroxy dead end groups were detected in the polymers obtained by us. Furthermore, the formation of corresponding unsaturated *tert*-butoxy esters was demonstrated in the filtrate after polymer separation.

The results of the present study provide clear evidence that the initiator is not incorporated into the polymer chain and simultaneous alkyl–oxygen and acyl–oxygen bond cleavage in β-lactone monomers does not occur in the anionic polymerization initiated by potassium methoxide in spite of suggestions made previously by Penczek and Slomkowski.[6,7]

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Registry No. PL, 57-57-8; PL (homopolymer), 25037-58-5; BL, 3068-88-0; BL (homopolymer), 36486-76-7; K^+OMe^-, 865-33-8; $K^+OBu\text{-}t^-$, 865-47-4; $t\text{-}BuOCOCH{=}CHCH_3$, 3246-27-3; $t\text{-}BuOCOCH{=}CH_2$, 1663-39-4; $MeOCOCH{=}CHCH_3$, 18707-60-3; $MeOCOCH{=}CH_2$, 96-33-3; $HOCH(Me)CH_2CO_2Et$, 5405-41-4; $HO(CH_2)_2CO_2Et$, 623-72-3; $HOCH(Me)CH_2CO_2Me$, 1487-49-6; $HO(CH_2)_2CO_2Me$, 6149-41-3; $MeCH{=}CHCO_2Et$, 10544-63-5; $H_2C{=}CHCO_2Et$, 140-88-5.