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What Is the Real Mechanism of Anionic Polymerization of β-Lactones by Potassium Alkoxides? A Critical Approach

In spite of a great deal of research done on β-lactone polymerization, there still exist different opinions about the mechanism of initiation of β-lactone polymerization by alkali-metal alkoxides. Yamashita postulated the acyl-oxygen bond scission and formation of alcoholate active species at the initiation step of β-propiolactone polymerization by sodium ethoxide.[1] He observed also carbon-carbon double bonds in the polymers obtained. The formation of both alkoxylate and carboxylate active species (formed in nearly equal proportions) at the initiation stage of the β-propiolactone polymerization in the presence of potassium methoxide/dibenzo-18-crown-6 complex in DMF was later suggested by Hofman, Słomkowski, and Penczek. According to the proposed mechanism, the initiator was incorporated into the growing polymer chains forming methoxy and methyl ester (dead) end groups, but double bonds had not been observed.[2]

The above-mentioned statements are, however, inconsistent with the results published later in more recent publications.[3,4] Dale[3] did not find any *tert*-butyl end groups from initiator; instead unsaturated groups were observed in polymers obtained via β-propiolactone polymerization initiated by potassium *tert*-butoxide. Similar observation was reported by Kricheldorf and Scharnagl[4] in the case of β-butyrolactone polymerization carried out in the presence of potassium *tert*-butoxide with or without crown ether. The authors proposed the α-deprotonation of monomer molecule in the course of the initiation step of the polymerization.

Discrepancies in the previously reported results[1-4] stimulated us to examine again the process of β-lactone polymerization by simple alkoxides. Two monomers were selected for this investigation: β-propiolactone (2-oxetanone) (**1a**) and β-methyl-β-propiolactone or so-called β-butyrolactone (4-methyl-2-oxetanone) (**1b**), and potassium methoxide/18-crown-6 complex was used as initiator.[5] The process of initiation was followed by ^{1}H NMR (300-MHz Varian VXR-300 NMR instrument) and also by model reactions.

The end-group analysis of the polyester obtained from β-propiolactone (**1a**) as well as that from β-butyrolactone (**1b**) carried out according to Shiota et al.[6] revealed the presence of a carboxylate end group. It means that carboxylate anions were the eventually propagating species in this polymerization. Moreover, in the ^{1}H NMR spectra of investigated polymers, there were no signals of $CH_3OC(O)$ and CH_3O groups (3.67 and 3.30 ppm, respectively) as proposed previously by Penczek et al.[2] for the β-propiolactone polymerization initiated by potassium methoxide. It means that the initiator was not incorporated in the growing polymer chain. However, distinct signals of C=C bonds and hydroxyl end groups were found in the obtained polymers (Figure 1). Our experimental results are in accordance to some extent with data provided by Dale[3] and Kricheldorf,[4] who have found no traces of *tert*-butoxide initiator in their polymers or oligomers produced from β-propiolactone as well as from β-butyrolactone.

The model experiments involving reactions of monomers with potassium methoxide and with potassium methoxide/18-crown-6 complex (initiator/monomer ratios equal 1:1) were conducted in THF at a temperature of 20 °C. The reaction products were isolated by chemical methods (distillation) and preparative GC and identified by ^{1}H NMR and GC-MS techniques.[7] According to the experimental evidence, unsaturated esters **2** (methyl acrylate or methyl crotonate depending on the lactone used) and potassium hydroxide are formed as first products of equimolar reaction of β-lactone with potassium methoxide with very high yields (ca. 80%) as shown in Scheme I.

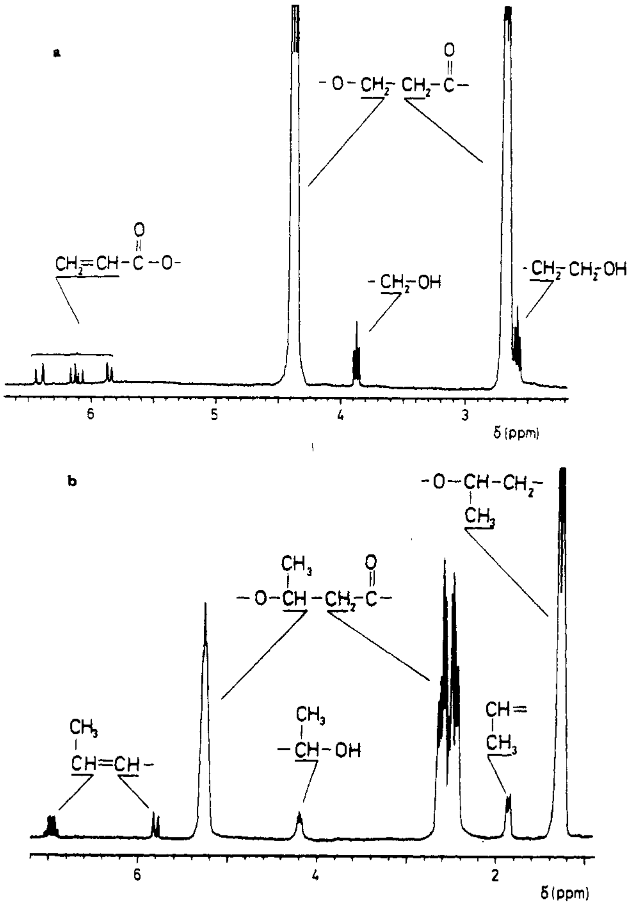
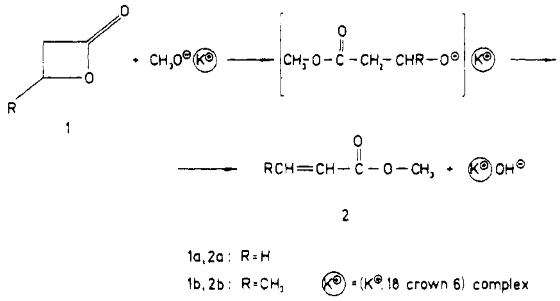


Figure 1. ^{1}H NMR spectra of poly(β-propiolactone) and poly(β-butyrolactone).

Scheme I



The esters **2** are unreactive in the further polymerization (indeed their presence in the filtrate after polymer precipitation was detected by GC-MS analysis in the molar amount corresponding to nearly that of the initiator used), and potassium hydroxide acts as a real initiator. The latter can react with the next molecules of the monomer to produce polymer chains with carboxylate anions as propagating species and both hydroxyl and unsaturated end groups on the other ends (Scheme II). The proposed novel mechanism of β-lactone polymerization (Scheme II) induced by alkali-metal alkoxides is in good agreement with the almost forgotten results of β-propiolactone alkaline methanolysis published by Bartlett and Rylander,[8] who suggested acyl-oxygen bond scission followed by water

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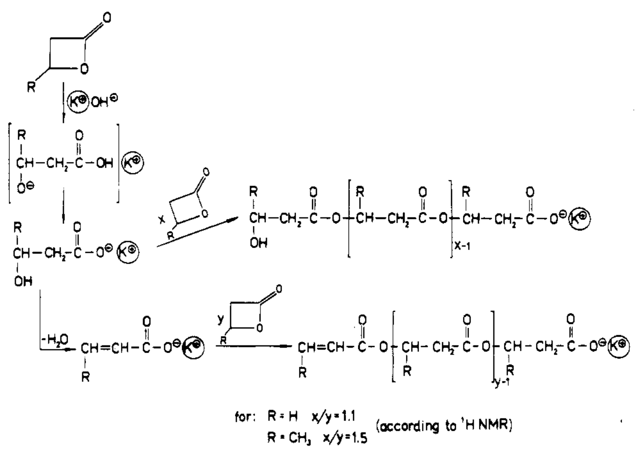
Scheme II



elimination and formation of methyl acrylate in the methanolysis reaction of the β-propiolactone conducted in the presence of sodium methoxide.

In conclusion it should be emphasized that anionic polymerization of β-lactones is more complex than suggested in some previous papers.[1,2] Therefore, reinvestigations are necessary sometimes to avoid possible mistakes and misinterpretation.

References and Notes

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(5) The polymerization experiments were conducted at a temperature of 20 °C in THF solution. The monomer concentration was equal to 1.3 mol/L in each experiment, and the concentration of CH_3OK/18-crown-6 complex, varied from 0.150 to 0.026 mol/L. The polymers were precipitated in cold pentane and filtered off. The pentane filtrate was analyzed by GC–MS techniques. The polymers obtained were dissolved in dichloromethane, and the acidic 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 vacuo.

(6) Shiota, T.; Goto, Y.; Hayashi, H. *J. Appl. Polym. Sci.* **1967**, *11*, 753.

(7) The model experiments involving the equimolar reaction of monomers with potassium methoxide as well as with potassium methoxide/18-crown-7 complex were conducted under the argon atmosphere in THF solution at a temperature of 20 °C. Into the reactor containing 6.68 g (0.02 mol) of CH_3OK/18-crown-6 in 80 mL of THF was added the solution of an equimolar amount of β-propiolactone **1a** (1.44 g in 5 mL of THF) dropwise with intensive stirring using a glass-covered magnetic stirring bar. After 15 min, 1.5 g of acidic ion-exchange resin (Lewatit S 1080) was introduced into the reaction mixture (the resin was used as an acidification agent and also as 18-crown-6 adsorber). The solution was then filtered off, and the filtrate was analyzed by GC–MS techniques. The following compounds were identified. 2-Propenoic acid methyl ester (methyl acrylate) (**2a**) (91% yield GC), MS: m/z (intensity) 31 (62), 42 (11.6), 43 (3.6), 53 (2.8), 55 (100), 56 (4.1), 58 (8.4), 59 (5.2), 85 (12.2), 86 (2.1); hydroxypropionic acid methyl ester (9% yield GC), m/z (intensity) 31 (62.4), 43 (100), 44 (17.9), 45 (29.2), 55 (17.0), 58 (5.4), 59 (10.8), 71 (10.5), 73 (46.7), 74 (53.6), 84 (5.2), 85 (7.3). In the case of β-butyrolactone (**1b**) reaction was provided in a similar manner and the following compounds were identified by GC–MS analysis. 2-Butenoic acid methyl ester (methyl crotonate) (**2b**) (87% GC yield of both *Z* and *E* isomers formed in mole ratio 1:15). MS: isomer *Z*, m/z (intensity) 38 (8.1), 39 (5.0), 40 (4.9), 41 (75.7), 42 (7.3), 55 (3.2), 59 (15.2), 68 (18.9), 69 (100), 70 (4.7), 85 (3.5), 100 (55.6), 101 (32.0); isomer *E* (separated by preparative GC), m/z (intensity) 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). ^1H NMR ($CDCl_3$): δ 1.89 (d, 3 H, CH_3CH), 3.69 (s, 3 H, $CH_3OC(O)$), 5.9 (d, 1 H, CH), 6.9–7.1 (m, 1 H, $CHCH_3$). 3-Hydroxybutanoic acid methyl ester (13% GC yield, separated by preparative GC). MS: m/z (intensity) 31 (71.4), 39 (10.1), 41 (11.1), 42 (28.0), 43 (100), 44 (11.8), 45 (58.1), 59 (18.2), 61 (12.8), 71 (27.9), 74 (51.1), 87 (16.1), 103 (17.9), 117 (10.1). ^1H NMR ($CDCl_3$): δ 1.23 (d, 3 H, CH_3CH), 2.37–2.54 (m, 3 H, CH_2 and OH), 3.69 (s, 3 H, $CH_3OC(O)$), 4.14–4.23 (m, 1 H, $CHOH$). The same results were obtained when potassium methoxide without crown ether was used.

(8) Bartlett, P. D.; Rylander, P. N. *J. Am. Chem. Soc.* **1951**, *73*, 4273.

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Registry No. **1a**, 57-57-8; **1b**, 3068-88-0; $CH_3O^-K^+$, 865-33-8; 18-crown-6, 17455-13-9.