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Communications to the Editor

Response to "On the Ambident Reactivity of β-Lactones in Their Reactions with Alcoholates Initiating Polymerization"

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The initiation of anionic polymerization proceeds *via* nucleophilic substitution or by electron transfer to a monomer, but sometimes proton abstraction from monomer may also occur. It is also well-known that the outcome of anionic polymerization depends on the nature of the monomer and initiator used and also on the reaction conditions.

The kinetics and mechanism of homogeneous anionic polymerization is controlled by ion–ion pair equilibria.[1] From this point of view the addition of an ion complexing agent as a crown ether or a cryptand to an alkali-metal alkoxide initiator may be useful in some reactions, increasing the reactivity of the system because of complex formation, e.g., of K^+ and 18-crown-6.[2] A similar effect was recently discovered in the case of addition of diorganomagnesium compounds,[3] as well as diorganozinc compounds,[4] to alkali-metal alkoxides.

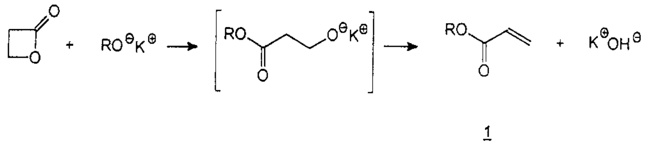
Some years ago Penczek *et al.* proposed the mechanism of β-propiolactone polymerization initiated with potassium methoxide in DMF, thus claiming incorporation of the methoxide groups ($-OCH_3$) from initiator into the growing polymer chains.[5] This proposal was based to a great extent on ^1H NMR measurements of polymers obtained; however, the characteristic region for double bonds (δ 5.8–6.5 ppm) was completely neglected[5] (see ^1H NMR spectrum in Figure 2, p 94 in ref 5).

Dale[6] and Kricheldorf[7] found somewhat later that not alkoxide but double bonds were the end groups in oligomers and polymers formed in this kind of anionic polymerization of β-propiolactone and β-butyrolactone initiated with potassium *tert*-butoxide or methoxide in CH_2Cl_2, THF, $CDCl_3$, $C_6C_5NO_2$, and DMSO-d_6.

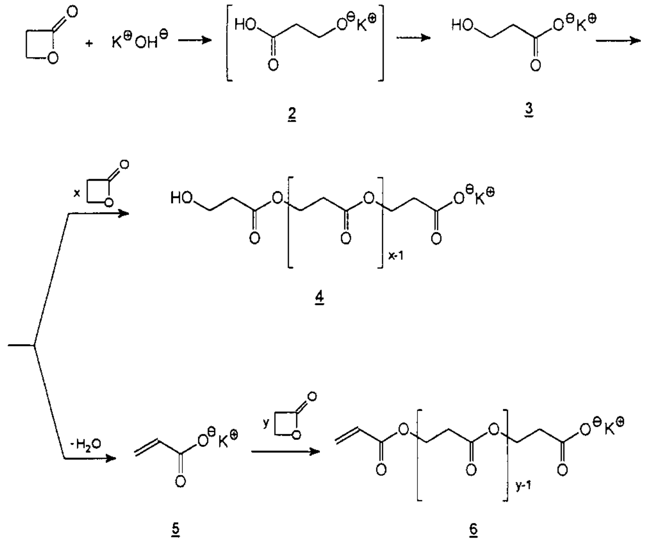
These discrepancies in literature prompted us to reinvestigate the mechanism of this polymerization process. It turned out that really double bonds, as claimed by Dale[6] and Kricheldorf,[7] and also hydroxyl end groups were present; however, incorporated initiator moieties were not found in polymers produced *via* polymerization of β-propiolactone or β-methyl-β-propiolactone (β-butyrolactone) initiated with potassium methoxide or potassium *tert*-butoxide in an aprotic solvent (THF).[8,9]

Further polymerization experiments confirmed that the polymerization of β-propiolactone in DMF even without crown ether proceeds according to the same mechanism as that found previously for the process carried out in THF as a solvent. The experimental details are described in ref 10. The ^1H NMR spectrum of pure polymer isolated from the reaction mixture is shown in Figure 1. The ^1H NMR spectrum (recorded using a Varian VXR-300 spectrometer) revealed distinct signals of double bonds and hydroxyl groups, but only a very weak signal corresponding to end groups derived from incorporated initiator (CH_3O-) at δ 3.7 ppm was observed (Figure 1).

Scheme 1



Scheme 2



These results were consistent with model experiments involving the equimolar reaction of β-propiolactone with potassium alkoholates carried out under an argon atmosphere in THF or in DMF at a temperature of 20 °C.[11]

According to the experimental evidence, the following general mechanism of the reaction of β-propiolactone with potassium alkoxides in aprotic solvents is proposed (Schemes 1 and 2). Eventually the KOH formed due to elimination reaction acts as the real initiator opening acyl–oxygen bonds and the polymerization proceeds as shown in Scheme 2.

The formation of corresponding unsaturated ester 1 (yield ca. 90%) at the initiation step due to acyl–oxygen bond cleavage of the lactone molecule followed afterward by KOH elimination (Scheme 1) was confirmed by GC–MS analysis (Figure 2). Due to rearrangement of the intermediate alkoxide of β-hydroxy acid **2**, the carboxylate anions are the only propagating species and polymers **4** and **6** bearing hydroxyl and/or double bonds as the dead end groups are formed.

In the note published recently (On the Ambident Reactivity of β-Lactones in Their Reactions with Alcoholates Initiating Polymerization. *Macromolecules* **1993**, *26*, 5526) concerned with the initiation of β-lactone polymerization with CH_3OK in methylene chloride, Penczek *et al.* have found that only about 10% of polymer chains contain incorporated initiator.[12] This means that incorporation of the initiator into growing polymer chains is a minor side reaction. Thus, using CH_2Cl_2 as a solvent

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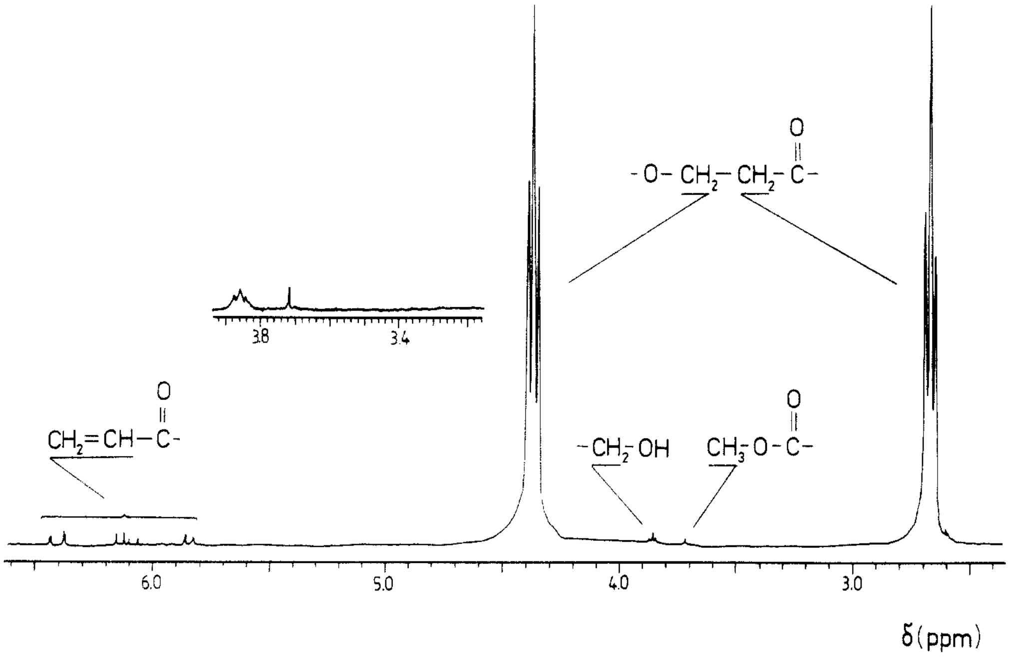

Figure 1. ^1H NMR spectrum (in $CDCl_3$) of isolated pure poly(β-propiolactone) obtained by polymerization with potassium methoxide in DMF.

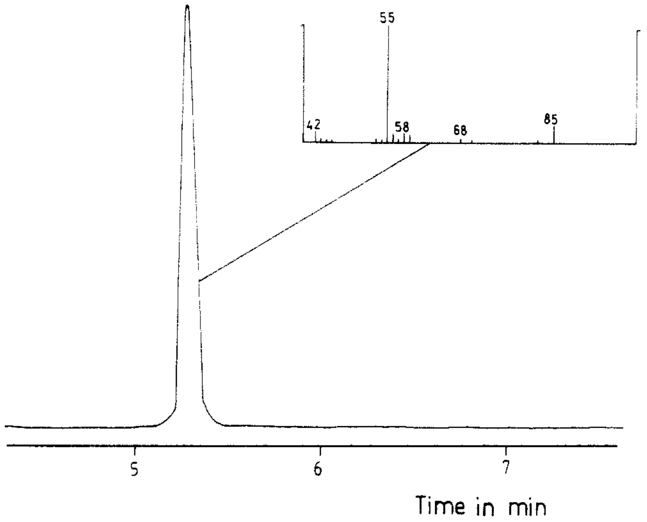

Figure 2. GC-MS trace of 2-propenoic acid methyl ester detected in the filtrate after separation of poly(β-propiolactone) from the DMF reaction mixture.

instead of DMF, the authors of this note[12] found the polymerization to proceed according to the mechanism claimed previously by us,[8,9] yielding polymers bearing hydroxyl and unsaturated end groups as observed also by Dale[6] and Kricheldorf.[7] Penczek *et al.* explain the discrepancies between their previous results (polymerization in DMF)[5] and the present ones (polymerization in CH_2Cl_2)[12] by the solvent effect. The solvent effect in the reactions of β-propiolactone and β-butyrolactone with alkali-metal alkoxides has been previously discussed and published by us.[11] The suggestion made in the note[12] that different mechanisms operate depending on the solventused (DMF or CH_2Cl_2) may be due to increased dissociation of alkoxide ion pairs, and formation of free alkoxide ions could not be confirmed by our present experiments, as well as by previously performed model reactions.[11] The dissociation of ion pairs should be controlled rather by the presence of a crown ether than by the polarity of the solvent used.[1]

Bartlett and Rylander have shown that the reaction of β-propiolactone with sodium methoxide in methanol leads to the products containing alkoxy end groups due to methanol addition to double bonds of an intermediate product—unsaturated ester formed at the first step.[13] Thus, observation made by Penczek *et al.* that polymers obtained in DMF solvent have methoxy end groups[5] might be due to the traces of methanol in methoxide initiator used.

On the other hand, from the description of experiments in their paper,[5] it is not clear whether the NMR spectra have been taken for isolated polymer or for the reaction-mixture containing according to our results[8,9] also low molecular side products inactive at the propagation step, however, bearing incorporated initiator (Scheme 1). Therefore, the interpretation of ^1H NMR spectra is ambiguous; moreover, the region characteristic for double bonds has not been considered in this paper.[5]

Experimental results presented in our paper indicate that polymerization of β-propiolactone performed in aprotic solvents and initiated with alkali-metal alcoholates proceeds in accordance with Schemes 1 and 2, irrespective of the nature of aprotic solvent used. These schemes are consistent with analyses of polymer end groups performed by three independent research groups (Dale,[6] Kricheldorf,[7] and ours[8,9,11]) and also with GC-MS analysis of side products. Thus, the suggestion of the ambident reactivity of β-lactones in their reactions with alkali-metal alkoxides due to the solvent effect (DMF, CH_2Cl_2) made in the note[12] could not be confirmed. Consequently, polymerization schemes presented by Penczek *et al.* in the papers,[5,12] indicating the presence of the initiator moieties in all polymer molecules obtained, are erroneous.

References and Notes

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(10) Polymerization of β-propiolactone initiated with potassium methoxide without or with dibenzo-18-crown-6 in DMF, at a temperature of 20 °C, was carried out under conditions similar to those described by Penczek *et al.*[5] The monomer concentration was equal to 1.1 mol/L, and the initiator concentration was equal to 2.8×10^{-2} mol/L. The polymer was precipitated from the reaction mixture in methanol and dried in vacuum at 20 °C. The isolated polymer was characterized by ^{1}H NMR spectroscopy (solvent: $CDCl_3$), and filtrate obtained after polymer separation was analyzed by a GC–MS technique using a Varian 3300 gas chromatograph (on a 30-m-long fused silica capillary column DB-1701) equipped with a Finnigan MAT 800 AT ion trap detector. In filtrate the presence of 2-propenoic acid methyl ester was demonstrated based on a comparison of the retention time and mass spectrum recorded with those of an original sample of 2-propenoic acid methyl ester.

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