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Notes

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

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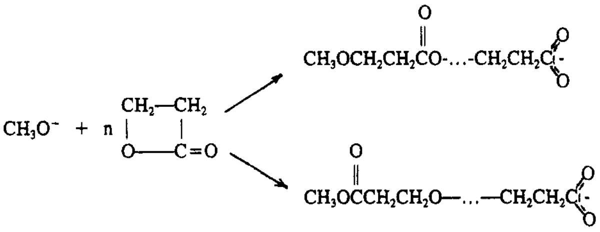
Several authors in the past proposed without proving either carboxylate or alcoholate active species for the polymerization of β-lactones.[1-3] We have shown by studying the reaction products of the active species with 2,4,6-trinitroanisole that these species are finally carboxylate anions.[4] These results were confirmed by end capping with diphenyl chlorophosphate and by using ^{31}P NMR for determination of the structure of thus obtained phosphates (alcoholate and carboxylate anions provide different reaction products).[5] We have also shown that in agreement with these findings simple carboxylate salts can be used to initiate the living polymerization of β-propiolactone (crowned Na^+ and K^+ were used).[6-8] This was the first observation of the living polymerization in the anionic polymerization of β-propiolactone and the first application of the crown ethers in these systems. Simultaneously, and independently of us, Boileau et al. have shown that application of cryptands also leads to the living process.[9] Thus, the carboxylate salts are initiators of choice, at least for β-propiolactone.[6-8,10]

Some time ago we presented experimental evidence that in DMF solvent potassium methoxide initiates polymerization of β-propiolactone in a way also providing eventually carboxylate growing species. Methyl groups from the initiator were found in the polymer chain.[4] We found that initiation proceeds ambidently, namely with acyl–oxygen and alkyl–oxygen bond scission, but at the later stages of the initiation process the alcoholate active centers are replaced with the carboxylate ones.


(1)

The conclusions that alkoxides can add β-propiolactone molecules with acyl–oxygen and alkyl–oxygen bond scission were confirmed later for the polymerization initiated with potassium solution in THF: it has been shown that the carboxylate and alcoholate anions are formed and the latter add monomer in a way leading eventually to carboxylates being the only active species responsible for propagation.[11]

On the other hand it was shown that when significant steric hindrance is involved, the reaction of alkoxides with β-lactones (e.g. *tert*-butoxide with β-propiolactone and/or methoxide with β-butyrolactone) proceeds differently, i.e. with proton transfer and formation of acrylate and/or crotonate anions, respectively.[12,13] More recently it has been indicated that in THF solvent at 20 °C crowned (in situ) potassium methoxide and potassium *tert*-butoxide react with β-propiolactone also this way, leading exclusively to macromolecules with hydroxyl and acrylate (crotonate in the case of β-butyrolactone) end groups.[14,15]

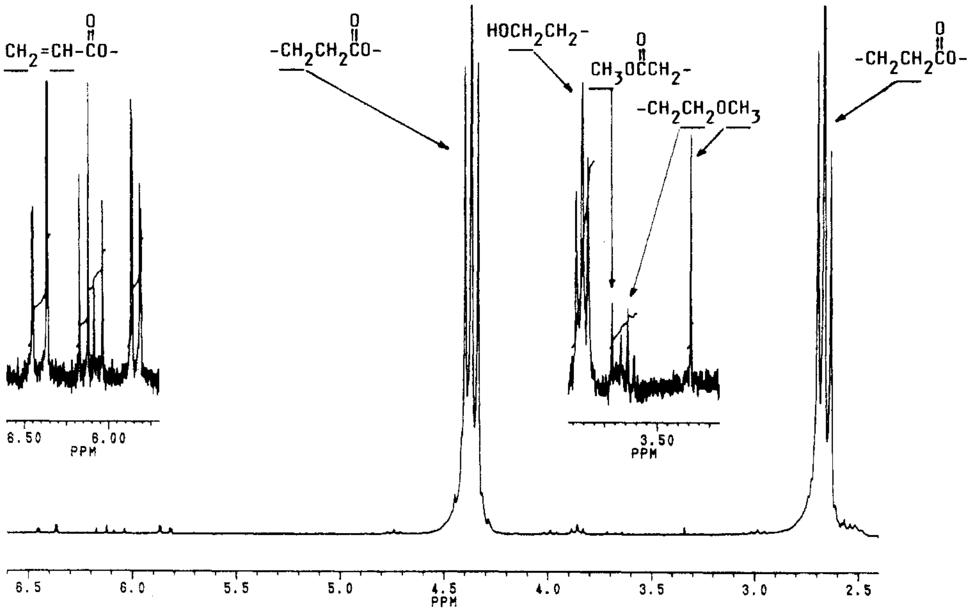


Figure 1. ^{1}H NMR spectrum of poly-β-propiolactone (solvent $CDCl_3$). Polymerization initiated with CH_3OK in CH_2Cl_2, $[β\text{-propiolactone}]_0 = 1.09$ mol/L, $[CH_3OK]_0 = 2.79 \times 10^{-2}$ mol/L.

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This difference between our earlier results in DMF solvent and these in THF solvent prompted us to check whether ambident reactivity of β-propiolactone, i.e. the proportion of the two initiation paths, is solvent dependent.

Thus, we initiated the polymerization of β-propiolactone with CH_3OK in CH_2Cl_2. Polymerization was initiated at −72 °C and then, after 1 h, the temperature was increased gradually to room temperature and polymerization was carried out for 16 h. The initial monomer and initiator concentrations were $[\beta\text{-propiolactone}]_0 = 1.09$ mol/L and $[CH_3OK]_0 = 2.79 \times 10^{-2}$ mol/L. All reagents were handled in high vacuum. The synthesized polymer was isolated by precipitation into ethyl alcohol, then twice reprecipitated into diethyl ether, and finally dried on the vacuum line. The ^1H NMR spectrum of the thus obtained polymer is given in Figure 1. In this spectrum there are signals for the following end groups: $\mathit{CH_2}{=}\mathit{CH}COO$– (m, from 5.80 to 6.45), $HO\mathit{CH_2}CH_2$– (t, 3.85), $\mathit{CH_3}OC(O)$– (s, 3.71), $CH_3O\mathit{CH_2}CH_2$– (t, 3.66), and $\mathit{CH_3}OCH_2CH_2$– (s, 3.33). The traces of solvents and nonsolvents used for the synthesis and for the polymer workup, if left, would give the following signals: (diethyl ether) $\mathit{CH_3}CH_2OCH_2\mathit{CH_3}$ (t, 1.16), $CH_3\mathit{CH_2}O\mathit{CH_2}CH_3$ (q, 3.36); (ethanol) $\mathit{CH_3}CH_2OH$ (t, 1.22), $CH_3\mathit{CH_2}OH$ (q, 3.70); CH_2Cl_2 (s, 5.3). Although integration can be misleading due to the NOE effect, for polymerization in the CH_2Cl_2 solvent approximately 10% of the macromolecules contains end groups formed by incorporation of initiator. Thus, the proportion of the two reaction paths looks to be solvent dependent. Thus, we can conclude that it is necessary to be extremely cautious when data resulting from experiments carried out at different conditions are compared. Moreover, the presence of adventitious water, when systems are not handled in high vacuum, can also give erroneous results.

It is possible that in the polar media the dissociation of alkoxide ion pairs into alkoxide anions is increased. The latter, being more nucleophilic, prefer to add monomer molecules than to participate in the side reactions (proton transfer to or elimination of hydroxyl anion from alkoxide). Similarly, even in much less polar CH_2Cl_2, the decreasing temperature facilities dissociation of alkoxide ion pairs and leads to the noticeable contribution of initiation with a monomer incorporation into the propagating chains. On the other hand, in THF and at room temperature, the whole initiation process becomes more complex, leading to macromolecules with the hydroxyl and double bond end groups.

In spite, however, of all these differences discussed above and complications, observed in some systems, polymerization eventually proceeds, as we have shown[4,5] and others confirmed,[11,13–15] on the carboxylate anions (paired and/or not paired). Alcoholates as initiators of β-lactones are now of rather historical importance, after crowned (cryptated) salts of carboxylic acids were used, giving quantitative initiation and leading to the living process, at least for β-propiolactone.

Thus, this work has shown that β-propiolactone reacts with potassium methoxide in the ambident way, forming different products. It is highly probably that alcoholates behave similarly in other systems and that the previously expressed views that this reaction proceeds in a unique way should be taken with more reservation.

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