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Registry No. MBPE-5 (copolymer), 115529-45-8; MBPE-7 (copolymer), 115529-46-9; MBPE-9 (copolymer), 115529-47-0; MBPE-11 (copolymer), 115529-48-1; MBPE-5/9 (copolymer), 117068-59-4; MBPE-5/7 (copolymer), 115529-49-2; MBPE-5/11 (copolymer), 117068-60-7; MBPE-7/9 (copolymer), 117068-61-8; MBPE-7/11 (copolymer), 117068-62-9; MBPE-9/11 (copolymer), 117068-63-0.

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Nature of the Active Centers and the Propagation Mechanism of the Polymerization of β-Propiolactones Initiated by Potassium Anions

Zbigniew Jedliński* and Marek Kowalczuk

Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland.

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ABSTRACT: The chemical structure of the active centers formed during the polymerization of β-propiolactones initiated by potassium anions has been elucidated on the basis of the results of spectroscopic (^{1}H NMR, IR), chemical, and elemental analyses. In the initial step of propagation, two types of active species, carboxylate and alkoxide anions, are formed. The alkoxide anions disappear during the polymerization, and carboxylate anions are eventually the main propagation species.

Introduction

In our previous studies concerning the polymerization of β-propiolactones initiated by potassium anions, the formation of living polymers and also block polyesters was reported.[1,2] The proposed mechanism of ring opening involves in the initiation step the cleavage of the α carbon to β carbon bond in the monomer.[3,4] However, the propagation step of this polymerization has not been studied in detail.

New results concerning the nature of the active species in the polymerization of the β-propiolactones initiated by potassium anions are described in this paper.

Experimental Section

Materials. β-Propiolactone (**1**, from Fluka) was dried as described in ref 5 and distilled twice in an atmosphere of dry argon. The fraction boiling at 51 °C (10 mmHg) was collected. β-Butyrolactone (**2**, from Fluka) was dried in a similar manner. The fraction boiling at 47 °C (5 mmHg) was collected (99.8% GC). THF was purified as previously described[6] and was then distilled over a sodium–potassium alloy in an atmosphere of dry argon.

Preparation of the Initiator. A potassium solution rich in potassium anions was obtained by adding a THF solution of 18-crown-6 to a potassium mirror at 25 °C.[7] The concentration of potassium anions was taken as one-half of the total potassium concentration, as determined by the titration of the hydrolyzed sample with 0.03 N HCl.

Dimerization Reaction of β-Propiolactone (1) Initiated by Potassium Anions. The reaction was conducted in the apparatus described in ref 3. Into a potassium solution containing 0.004 mol of potassium anions, 0.576 g (0.008 mol) of β-propiolactone in 5 mL of dry THF was introduced under an argon atmosphere at a temperature of 25 °C. After 10 min, 2 g of acidic ion-exchange resin (Lewatit S 1080) were 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, the solvent was evaporated, and the product mixture was dried under high vaccum; yield 0.54 g (92%); IR (neat) $\nu_{\max}$ = 3500, 3300, 2900, 1740, 1460, 1400, 1180, 1100 cm^{-1}. Elemental analysis for $C_6H_{10}O_4$: calcd C 49.31%, H 6.90%; found C 49.26%, H 7.02%. Molecular weight was 146 as determined by vapor pressure osmometry (VPO). The number of carboxyl end groups was equal to 0.60 and that of the hydroxyl end groups was equal to 0.42 per molecule of the product.

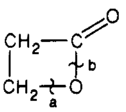
Polymerization of β-Lactones 1 and 2 Initiated by Potassium Anions. The polymerization experiments were conducted at a temperature of 25 °C as described previously.[3] The monomer concentration was equal to 0.4 mol/L in each experiment, and the concentration of potassium anions varied from 0.013 to 0.054 mol/L.

Measurements. The ^{1}H NMR spectra of the purified oligomers and polymers were run in $CDCl_3$ by using TMS as internal standard on either a Varian XL-100 or a Varian VXR-300 spectrometer.

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena spectrophotometer.

Number-average molecular weights were determined by the VPO technique in $CHCl_3$ using a Knauer vapor pressure osmometer.

Scheme I



The carboxyl end groups of oligomers were determined by the method described by Shiota et al.[5]

The hydroxyl groups were determined by IR spectroscopy as described in ref 8. The spectra were obtained on neutralized samples so that the carboxyl and hydroxyl O–H stretches did not overlap.

Results and Discussion

According to the literature, in the anionic polymerization of 2-oxetanone, two modes (a or b) of ring cleavage of β-lactone were generally proposed[9] (Scheme I).

Yamashita proposed acyl–oxygen bond scission (b, Scheme I) and formation of alcoholate active species when strong nucleophiles such as alcoholates or carbanions were used as initiators.[10,11] However, we have recently found that in the polymerization of β-propiolactone 1 initiated by potassium anions, carboxylate active species are formed due to alkyl–oxygen bond scission (a, Scheme I), on the basis of the end group analysis of polyesters with molecular weights (M_n) higher than 3000.[1]

To clear up the above discrepancies and elucidate the nature of the active centers formed at various stages of the polymerization of β-propiolactone initiated by potassium anions, several model experiments were conducted, and oligomers with the molecular weights ranging from 146 (dimer) to 2600 were investigated.

As active growing centers, both alkoxy and carboxylic groups were found. It was particularly pronounced in the dimerization reaction, where the initial molar ratio of β-propiolactone 1 to potassium anions was equal to 2. The ^{1}H NMR spectrum of the product of the dimerization reaction indicates the formation of two dimers (Figure 1). The structure of these compounds was additionaly confirmed by IR spectroscopy and elemental and end group analysis (see the Experimental Section). Therefore, the formation of both alkoxy and carboxylate anions at the initial stage of propagation of β-propiolactone polymerization initiated by potassium anions was assumed (Scheme II).

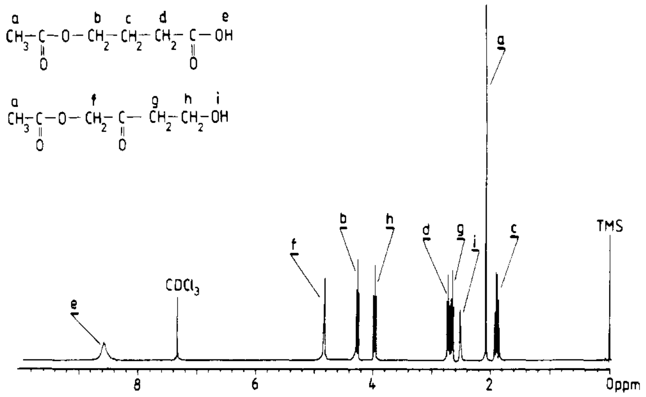


Figure 1. ^{1}H NMR (300 MHz) spectrum of the dimers obtained in the reaction of potassium anions with β-propiolactone.

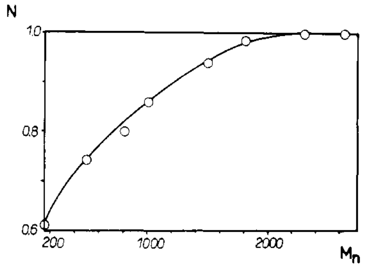
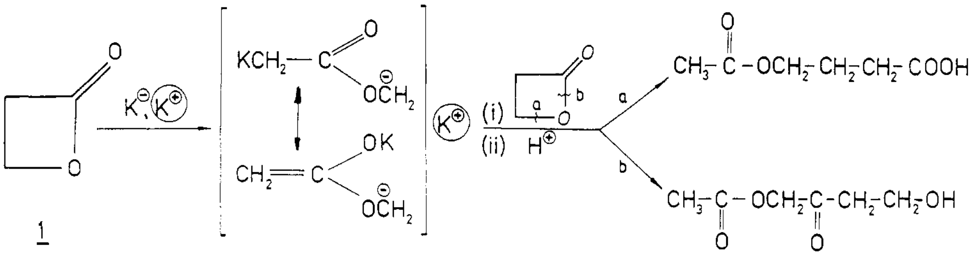


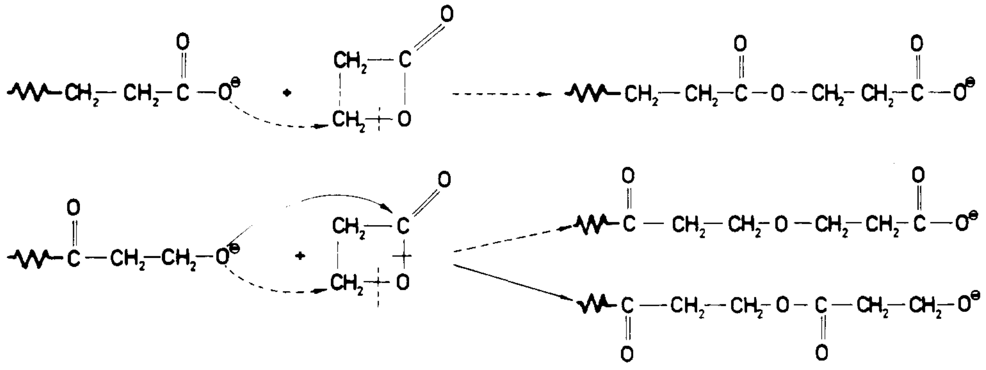
Figure 2. Relationship between the number of carboxyl end groups per oligomer chain (N) and molecular weight (M_n) of oligoesters obtained from the reactions of β-propiolactone with potassium anions, carried out in THF at 25 °C.

It was also found that the number of the carboxylate end groups per polymer chain increased during the course of polymerization, and for degrees of polymerization greater than 25, the carboxylate anions represented the only propagation centers in this system (Figure 2). Because carboxylate anions are much weaker nucleophiles than alkoxides, they are unable to give rise to acyl–oxygen bond scision (b, Scheme I). Therefore, if the propagation center is a carboxylate anion, it stays as such (Scheme III).

Scheme II



Scheme III



These observations clearly showed that although two types of active species are formed initially, the carboxylate anions are eventually responsible for most of the growth of macromolecules in the anionic polymerization of β-propiolactone.

Similar results were obtained in the polymerization of β-butyrolactone **2** initiated by potassium anions. This unexpected behavior of β-butyrolactone, which was believed not to polymerize by anionic initiators but rather by coordinative ones,[12,13] is possibly due to the very fast initiation by potassium anions and the complexation of counterions by crown ether.

The formation of an enolate in the initiation step of this polymerization (Scheme II) might suggest that both carbanion and enolate sites of this intermediate are able to react with the next lactone molecule. However, the ^1H NMR spectrum (Figure 1) indicates clearly that the polymer exhibits acetate and not β-diketo end groups. Moreover, the polymerization of β-propiolactone by the enolate of potassium acetate showed that the polymerization reaction is much faster than possible Claisen ester condensation.[14] Thus, the enolate of potassium acetate as well as the intermediate enolate carbanion formed in the initiation step of the β-lactone polymerization by potassium anions react regioselectively with β-propiolactones.

The results of this work confirm previous observations that in the anionic[15] as well as cationic[16] polymerization of heterocycles, two different mechanisms may operate simultaneously and thus indicate the existence of a more complex process of ionic ring-opening polymerization than was suggested previously.

Conclusions

These results indicate that in the polymerization of β-lactones by potassium anions, the C–C cleavage at the α to β position in a β-lactone molecule takes place in the initiation step. Then, both alkyl–oxygen and acyl–oxygen bond cleavage occur to form carboxylate and alkoxide anions. Finally, the alkoxide active species disappear, and carboxylate anions are responsible for most of the polymer chain growth.

Registry No. K^-, 19128-96-2; $H_3CCO_2(CH_2)_3CO_2H$, 26976-72-7; $H_3CCO_2CH_2CO(CH_2)_2OH$, 119908-63-3; β-propiolactone, 57-57-8.

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(14) The enolate of potassium acetate was prepared in THF solution from potassium acetate and potassium naphthalenide according to Angelo et al.[17] The polymerization of β-propiolactone in the presence of the above initiator was conducted under the conditions used for the polymerization with potassium anions. After the polymerization was terminated, the polymer was precipitated in methanol, filtered, and dried under high vacuum. The polyester was subsequently analyzed by ^1H NMR and VPO techniques. The ^1H NMR spectrum of the polyester (M_n = 1200) revealed that besides the signals of the protons of the polyester chain (δ = 2.7 and δ = 4.3 ppm) only the singlet of the acetate end group (δ = 2.1 ppm) was observed, which indicates that the polymerization reaction proceeds much faster than Claisen ester condensation.
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Morphological Study of Supported Chromium Polymerization Catalysts. 2. Initial Stages of Polymerization

Edward L. Weist, Ahmed H. Ali, Bharat G. Naik, and Wm. Curtis Conner*

Department of Chemical Engineering, University of Massachusetts,
Amherst, Massachusetts 01003.
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ABSTRACT: The changes in morphology due to the formation of polyethylene in the pores of three silica-supported, chromium oxide catalysts were followed by using mercury porosimetry and electron microscopy. Ethylene polymerization from 0.1 to 20 g of polymer/g of catalyst was carried out from the gas phase in a fluid bed reactor at 1-atm total pressure with a nitrogen diluent. A catalyst with 1.7 cm^3/g pore volume fragmented due to the formation of polymer in the pores and thereby maintained an open structure. Catalysts containing 1.1 and 2.3 cm^3/g pore volume did not fragment extensively, and the product polymer congested the pores and impeded the continued polymerization. Total pore volume and pore size are not the only controlling factors in the fracturing process. Mercury porosimetry showed that fracture of the 1.7 cm^3/g catalyst started after a polymer yield of just 0.4 g_{PE}/g_{cat}, maintaining monomer access to the active sites. The 0.1–1-μm catalyst fragments contained a pore microstructure much like that of the starting material, thus demonstrating how the pore structure of the original catalyst particles may influence the polymerization process after fragmentation is complete.

Introduction

The morphology of supported, ethylene polymerization catalysts has a great influence on the polymerization process. Several studies have shown that chromium and titanium deposited on supports with greater initial pore volume and larger average pore sizes exhibit greater po-

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