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POLYMERIZATION OF β-LACTONES INITIATED BY ALKALI METAL NAPHTHALENIDES. A CONVENIENT ROUTE TO TELECHELIC POLYMERS†

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ABSTRACT

The polymerization of β-lactones initiated by potassium naphthalenide and its mechanism are discussed on the basis of ^{1}H NMR 300 MHz measurement, GC-MS experiments, and model reactions. It was demonstrated that the initiator was not incorporated into the polymer chains, but unsaturated groups were formed as the dead endgroups of the polymer chains due to proton abstraction from the monomer. The salts of unsaturated acids, formed at the initiation step, are responsible for the growth of polymer chains at the propagation step.

INTRODUCTION

The past decade has brought about an enormous advance of knowledge about fundamental aspects of polymerization processes. It is obvious from the excellent work of Vogl et al. [1] that a better understanding of polymerization mechanisms can be achieved due to oligomerization studies and precisely defining the respective structures of the first polymerization products. This approach also enables proper identification of active species, which can be different at consecutive polymerization steps [2].

†Dedicated to Prof. Otto Vogl on the occasion of his 65th birthday with deep feelings of admiration for his outstanding scientific achievements.

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On the other hand, studies of novel initiators and additives have demonstrated their utility for "living" polymerization, not only in anionic [3, 4] but also in cationic systems [5, 6]. Association, complexation, and solvation phenomena, and their influence on the kinetics of polymerization and the structures of the resulting polymers, have also been studied [7, 8]. These interesting results are mainly concerned with the polymerization of olefins, dienes, acrylates, 1,4-diisopropenyl benzene, and haloacetaldehydes [1-4, 9].

Recent developments in anionic ring-opening polymerization of lactones initiated with alkali metal naphthalenide are discussed in this paper.

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EXPERIMENTAL

Materials

β-Propiolactone (PL, from Aldrich) was dried as described previously [2]. The fraction boiling at 51°C (10 mmHg) was collected. β-Butyrolactone (BL, from Fluka) was purified in a similar manner. 18-Crown-6 (from Fluka) was purified as described previously [2]. Cryptand [222] (from Fluka) and naphthalene (POCh, Poland) were sublimated before use. THF was purified as described in Ref. 2 and was then distilled over a sodium-potassium alloy in a dry argon atmosphere.

Preparation of Initiator

A 0.1 mol/L THF solution of potassium naphthalenide was obtained at 20°C by contact of the THF solution of naphthalene with a potassium mirror.

Polymerization Initiated by Potassium Naphthalenide

The polymerization conditions are presented in Table 1. The required amount of 0.1 mol/L potassium naphthalenide solution in THF was introduced under an argon atmosphere into the THF solution of monomer containing the equimolar with respect to an initiator amount of 18-crown-6 or cryptand [222]. After completion of polymerization the polymers were precipitated in cold pentane and filtered off. The pentane filtrate was analyzed by the GC-MS technique. The polymers obtained were dissolved in dichloromethane, and the acid ion-exchange resin (Lewatit S 1080, from Merck) 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 from BL was determined by GPC (in THF) according to polystyrene standards with low polydispersity.

Model Reactions of PL and BL with Potassium Naphthalenide and Its Complex with 18-Crown-6

Model experiments involving the equimolar reactions of PL and BL with potassium naphthalenide were conducted under an argon atmosphere in a THF solution at 20°C and were quenched by protonation with Lewatit S 1080 ion-exchange resin. The unsaturated acids, i.e., acrylic acid in the reaction of PL and

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TABLE 1. Results of Anionic Polymerization of β-Lactones Initiated by Potassium Naphthalenide (at 20°C)

Monomer	Cation complexing agent	$[M]_0/[I]_0$	Time, h	Yield, %	M_n (VPO)[a]	M_w/M_n[b]
β-Propiolactone	None	50[c]	20	10	–	–
β-Propiolactone	18-Crown-6	40[c]	5	92	2,500	–
β-Propiolactone	Cryptand [222]	200[d]	10	90	13,600	–
β-Propiolactone	Cryptand [222]	2000[d]	24	89	120,500[e]	–
β-Butyrolactone	None	50[c]	200	8	–	–
β-Butyrolactone	18-Crown-6	40[c]	96	90	2,800	1.28
β-Butyrolactone	Cryptand [222]	40[c]	96	98	2,950	1.22
β-Butyrolactone	Cryptand [222]	75[d]	110	97	6,200	1.25
β-Butyrolactone	Cryptand [222]	150[d]	200	97	11,000	1.29

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

[b] Determined by GPC according to polystyrene standards with a low polydispersity.

[c] Conducted in THF, $M_0 = 2.0$ mol/L.

[d] Conducted in THF, $M_0 = 3.0$ mol/L.

[e] Estimated from viscometric measurement.

crotonic acid in the reaction of BL, were obtained in 80% yields. The structures of the acids obtained were established from ^{1}H-NMR, IR, and MS analyses.

Acrylic Acid. IR (capillary cell) $\nu_{max} = 1700, 1656$ cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.7–6.8$ (m, 3H), 10.2 (s 1H); MS *m/z* (relative intensity) 55 (60), 72 (70, M^+).

Analysis. Calculated for $C_3H_4O_2$: C, 50.01; H, 5.60%. Found: C, 50.03; H, 5.58%.

Crotonic Acid. IR (capillary cell) $\nu_{max} = 1700, 1600$ cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.9$ (d, 3H,); 5.9 (d, 1H,); 7.0–7.2 (m, 1H); 9.1 (s, 1H,) ppm. MS *m/z* (relative intensity) 69 (30), 86 (100, M^+).

Analysis. Calculated for $C_4H_6O_2$: C, 55.81; H, 7.02%. Found: C, 55.80; H, 7.09%.

The model experiments involving the equimolar reactions of PL and BL with the potassium naphthalenide/10-crown-6 complex were conducted similarly, but instead of the ion-exchange resin, the methyl iodide was added for quenching. The formation of methyl esters of the corresponding unsaturated acids (methyl acrylate from PL and methyl crotonate from BL), naphthalene, 1,2,- and 1,4-dihydronaphthalenes was revealed by GC-MS analysis. The esters obtained were separated by preparative GC and additionally characterized by ^{1}H-NMR and IR spectroscopy.

Methyl Acrylate. IR (capillary cell) $\nu_{max} = 1740, 1660$ cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.72$ (s, 3H), 5.75–6.43 (m, 3H); MS *m/z* (relative intensity) 42 (12), 55 (100), 56 (70), 85 (12), 86 (2, M^+).

Analysis. Calculated for $C_4H_6O_2$: C, 55.81; H, 7.02%. Found: C, 55.83: H, 7.08%.

Methyl Crotonate. IR (capillary cell) ν_{max} = 1745, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.89 (dd, 3H), 3.73 (s, 3H), 5.86 (dq, 1H), 6.9–7.1 (m, 1H); MS *m/z* (relative intensity) 15 (10), 28 (5), 29 (4), 38 (3), 39 (25), 41 (48), 43 (3), 53 (2), 55 (3), 59 (5), 68 (3), 69 (100), 70 (5), 85 (23), 100 (19, M^+), 101 (2).

Analysis. Calculated for $C_5H_8O_2$: C, 59.99; H, 8.05%. Found: C, 59.99; H, 8.06%.

Measurements

The ^1H-NMR spectra were recorded by 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 THF solution at 35°C using a Spectra-Physics 8800 gel permeation chromatograph. GC-MS analyses were run on 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 equipped with a semipreparative unit.

The carboxyl end groups were determined by the method described by Shiota et al. [10].

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RESULTS AND DISCUSSION

Alkali metal naphthalenides are known as efficient initiators of styrene polymerization [11, 12] as well as of the ring-opening polymerization of oxiranes, thiiranes [13, 14], and thietane [15]. However, potassium naphthalenide has been claimed not to polymerize β-lactones at room temperature [16].

It has been demonstrated that polymerization of β-lactones proceeds smoothly in the presence of potassium naphthalenide only after the addition of a cation complexing ligand such as 18-crown-6 or cryptand [222].

The ^1H-NMR spectra of polymers obtained by initiation with potassium naphthalenide in the presence of a cation complexing agent revealed signals of unsaturated end groups but no signals of naphthalene from the initiator (Fig. 1).

The presence of naphthalene and dihydronaphthalenes was revealed in the filtrate by GC-MS analysis after polymer precipitation (Fig. 2).

Carboxylate anions are the propagating species in the polymerization of β-butyrolactone and β-propiolactone, as demonstrated by chemical analysis using the Shiota method [10].

The polymers obtained from BL were found to be atactic, their ^{13}C-NMR spectra being similar to that reported previously for a typical poly(β-hydroxybutyrate) [17].

The observation that polymerization of β-butyrolactone and β-propiolactone initiated with potassium naphthalenide proceeds only in the presence of a complex-

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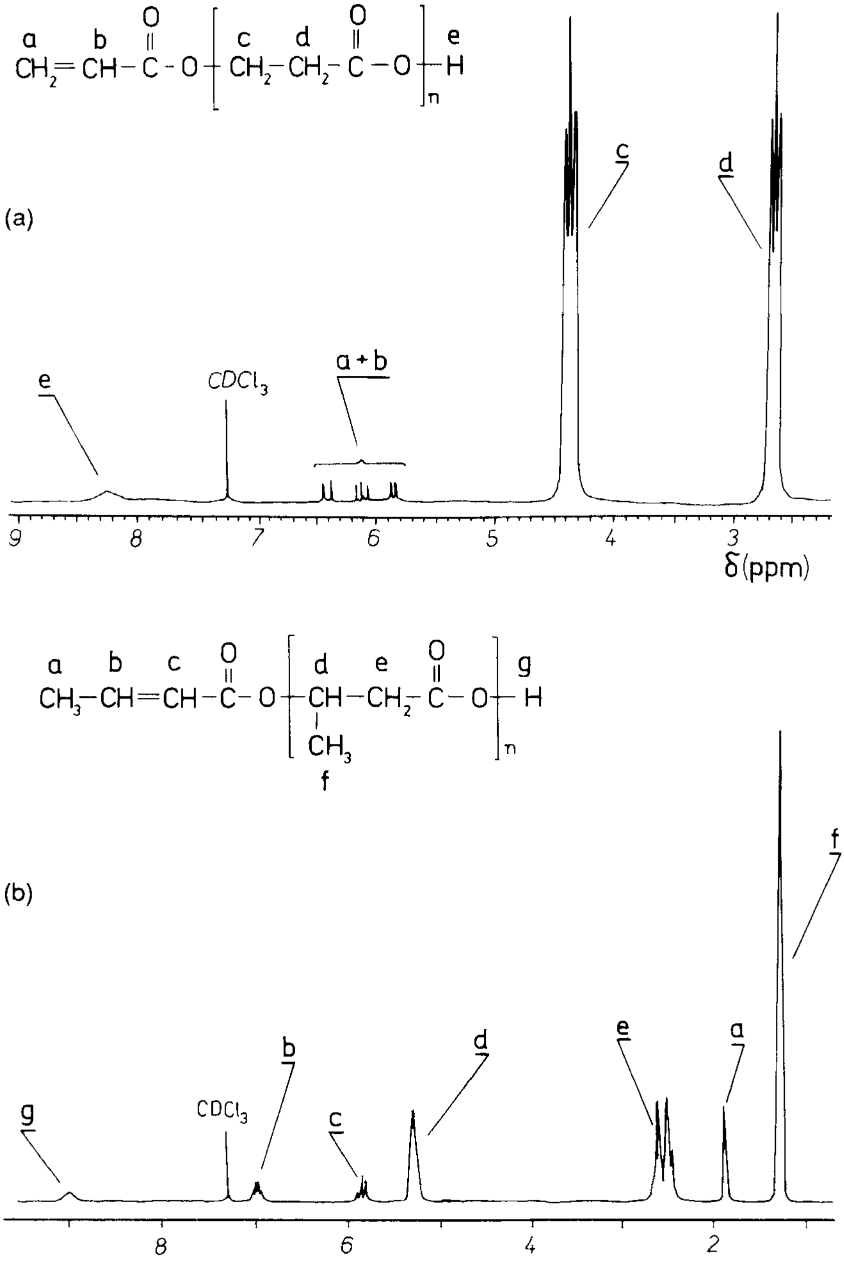

FIG. 1. ^{1}H-NMR (300 MHz) spectra of polyesters obtained in the presence of the potassium naphthalenide/18-crown-6 complex. (a) Poly-β-propiolactone. (b) Poly-β-butyrolactone.

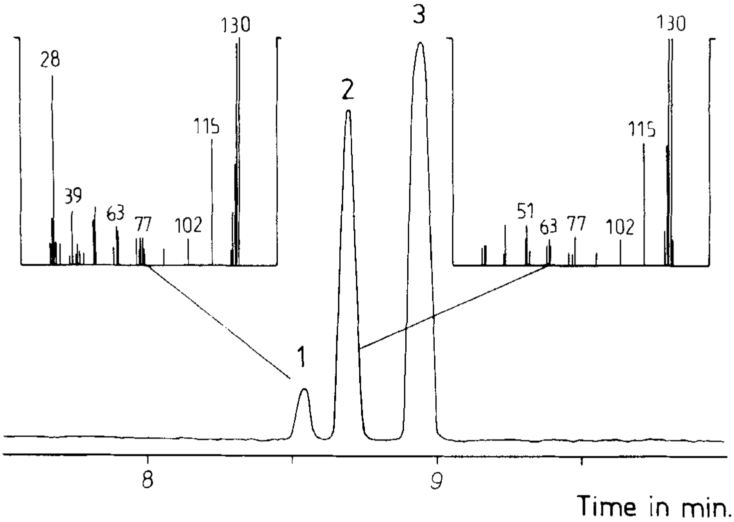

FIG. 2. GC-MS trace of pentane filtrate obtained after precipitation of poly-β-butyrolactone; (1) 1,2-dihydronaphthalene; (2) 1,4-dihydronaphthalene; (3) naphthalene.

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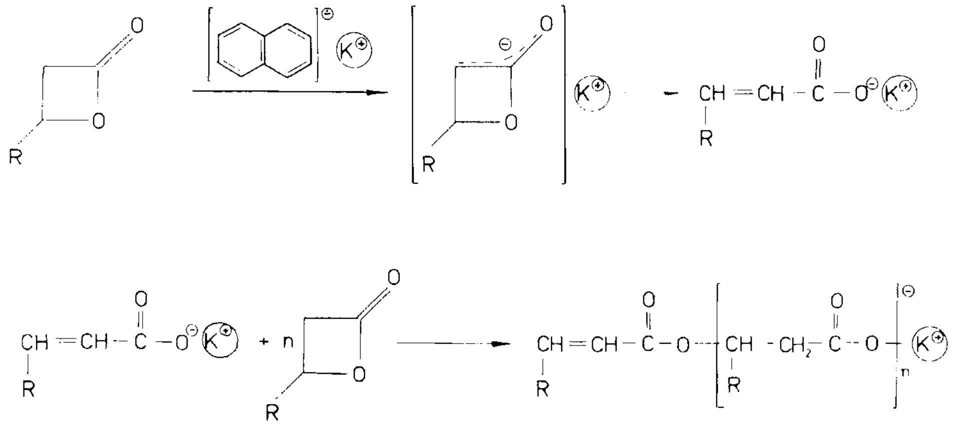
ing agent 18-crown-6 indicates that the propagation is operating due to loose ion pairs or free anions, producing polymers with narrow molecular weight distributions (1.22-1.29, Table 1).

The polymerization mechanism was elucidated on the basis of the results of model reactions of a monomer with potassium naphthalenide in an equimolar ratio (1:1), as described in the Experimental Section, and also by endgroup analyses.



R = H or CH_3

(K⊕) = (K^+/18-crown-6) complex

SCHEME 1.

First, the lactone enolate is formed due to α-proton abstraction with the formation of dihydronaphthalenes. The rearrangement of cyclic enolate, formed by proton abstraction of β-lactone, leads to the potassium salt of the corresponding unsaturated acid. In the presence of crown or cryptand, the latter is capable of acting as an initiator, inducing further polymerization with carboxylate anions as active centers (Scheme 1). The proposed mechanism explains the formation of telechelic polyesters due to alkyl-oxygen bond scission of the monomer in the polymerization of β-butyrolactone and β-propiolactone.

In the reaction with β-lactones the potassium naphthalenide acts first of all as a strong base, being able to abstract a proton. Therefore, the mechanism proposed differs from that operating in the polymerization of vinyl monomers where the electron transfer reactions prevail.

The results of the present work present an example of the versatility of alkali metal naphthalenides as initiators in anionic polymerization, for they are able to abstract a proton from a heterocyclic monomer or to cause electron transfer in the polymerization of vinyl monomers.

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CONCLUSIONS

Potassium naphthalenide was found to initiate β-lactones polymerization in the presence of a crown ether or a cryptand.

The initiation reaction via α-deprotonation of a β-lactone to lactone enolate leads to the potassium salts of the corresponding α,β-unsaturated carboxylic acid. The potassium naphthalenide acts as a proton acceptor. Naphthalene and its hydrogenated derivatives are by-products in this reaction.

The propagation proceeds via alkyl-oxygen bond scission in the monomer, similar to the case of β-lactones polymerization with salts of simple carboxylic acids as initiators.

The final products are telechelic polymers with unsaturated endgroups.

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