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Polylactones 33. The role of deprotonation in the anionic polymerization of β-propiolactone

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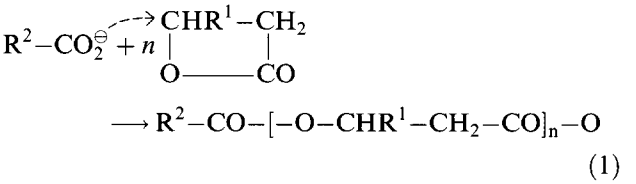
β-Propiolactone was reacted with triethylamine, pyridine, triphenylphosphine, potassium *tert*-butoxide, potassium (4-*t*-butylphenoxide) or potassium benzoate in $CDCl_3$ or dimethylsulfoxide in an n.m.r. tube. The ^1H n.m.r. analyses revealed in all cases formation of large amounts of acrylate groups. β-Propiolactone was polymerized at 20°C with triethylamine, pyridine or triphenylphosphine at a monomer/initiator ratio (M/I) of 50:1, and the endgroups of the isolated poly(β-propiolactone)s were characterized by ^1H- and ^{13}C-n.m.r. spectroscopy. Acrylate groups were found in all cases, even when the initiation with triphenylphosphine was conducted at −70°C. Sodium methoxide and potassium *t*-butoxide even attack polypropiolactone, yielding acrylate endgroups by deprotonation and elimination. In the presence of methanol, transesterification with formation of methyl ester endgroups also takes place. Only small amounts of acrylate groups were found when tributyltin methoxide served as initiator at 60–100°C. With aluminium isopropoxide acrylate endgroups were almost absent. Thus, the degree of deprotonation allows a differentiation between a true anionic polymerization and a nonionic insertion mechanism. Copyright © 1996 Elsevier Science Ltd.

(Keywords: β-propriolactone; anionic polymerization; deprotonation; acrylate endgroups; insertion mechanism)

INTRODUCTION

Numerous papers have appeared dealing with the anionic polymerization of β-propiolactone and β-butyrolactone[1–23]. These papers describe preparative, mechanistic or kinetic studies, and a propagation mechanism involving carboxylate anions and a preferential ring cleavage at the alkyl-oxygen bond, equation (1)[9]. Although it is difficult to obtain high molecular weight poly(β-propiolactone) or poly(β-*R,S*-butyrolactone) by anionic polymerizations, the papers published before 1986 contain little information about side reactions, such as deprotonation/elimination reactions yielding acrylate groups (β-propiolactone) or crotonate groups (β-butyrolactone). Only a paper by Yamashita *et al.*[5], dealing with pyridine-initiated polymerizations of β-propiolactone, mentioned an elimination reaction of the intermediately formed zwitterion [equations (2) and (3)], whereas previously a clean zwitterionic polymerization was postulated[3].

More recently, several publications have appeared showing that potassium alkoxides as initiators cause the formation of considerable amounts of acrylate and crotonate groups[15–23]. These side reactions are not surprising because alkoxides are strong bases (p*K*s 16–18) and relatively poor nucleophiles. It is well known from the organic chemistry of esters that ethoxide ions (p*K*s 17) catalyze an aldol type condensation of ethyl acetate, although the C–H acidity of the acetate group (p*K*s ~24) is lower than that of ethanol. Therefore it is obvious that alkoxide ions can deprotonate almost any kind of β-hydroxypropionic or β-hydroxybutyric acid derivative, including the lactones [equation (4)] and oligomers or polymers [equation (5)]. In other words, it was questionable if alkoxide anions were the optimum initiators for the polymerization of β-lactones with a proton in α-position. In this connection the question arises, whether more nucleophilic but less basic initiators give clean anionic polymerizations. Surprisingly, a first study in this direction based on β-*R,S*-butyrolactone[17] has demonstrated that even initiators with higher nucleophilicity/basicity ratios cause formation of crotonate groups. The ongoing studies and discussions in this field[18–23] prompted us to study the reactions of β-propiolactone with various nucleophiles in more detail.



(1)

$R^1 = H, CH_3$ $R^2 =$ alkyl, aryl

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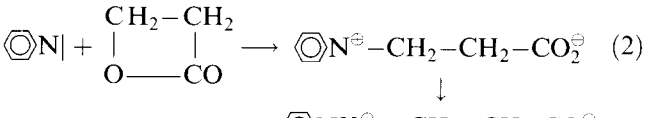

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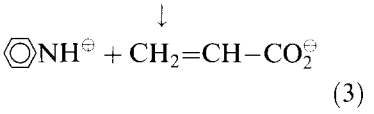

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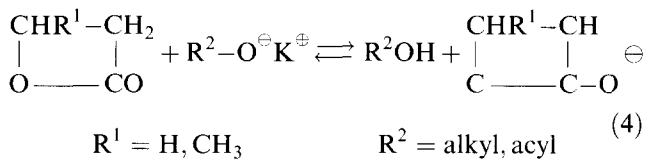

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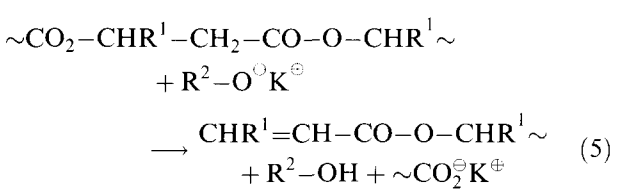

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EXPERIMENTAL

Materials

β-Propiolactone was a gift of E.I. DuPont Co. (Wilmington, DE); it was distilled under nitrogen over oligomeric 4,4′-diisocyanatodiphenylmethane. Poly(β-propiolactone) was a gift of BASF AG (Ludwigshafen). Triphenylphosphine, $CDCl_3$ and DMSO-d_6 were purchased from Aldrich Co. (Milwaukee, WI) and used without purification. Ethyl-β-*R,S*-hydroxybutyrate was purchased from Aldrich Co. and esterified with equimolar amounts of acetylchloride and pyridine in cold diethyl ether. The acetylated ethyl-β-*R,S*-hydroxybutyrate was distilled *in vacuo* and its structure was checked by ^{1}H n.m.r. spectroscopy. 1,4-Dioxane was distilled over sodium, $CDCl_3$ and dimethylformamide (DMF) were distilled over P_4O_{10}.

Polymerizations

All reaction mixtures were prepared in a glove box under nitrogen dried over P_4O_{10}.

(A) Polymerizations in n.m.r. tubes: β-propiolactone (5 mmol) was weighed into a 5 mm o.d. sample tube containing 0.7 ml of dry $CDCl_3$. A 2 m solution or suspension of the initiator in $CDCl_3$ was added, so that a monomer/initiator ratio of approx. 10:1 was obtained. Finally the sample tube was sealed and the reaction mixture measured after due time. Several experiments were repeated in such a way that the reagents were cooled to 0°C and weighed into the n.m.r. tube in under cooling with ice.

(B) Bulk polymerizations: β-propiolactone (50 mmol) was weighed into a 25 ml Erlenmeyer flask, the glass walls of which were silanized with dimethylchlorosilane. The initiator (1 mmol) was added in the form of a 2 M solution in dry nitrobenzene. The Erlenmyer flasks were then closed with glass stopper and steel spring. Finally the product was dissolved in 50 ml dichloromethane, precipitated into cold methanol, filtered off and dried at 40°C *in vacuo*.

(C) Polymerizations in solution: β-propiolactone (40 mmol) was dissolved in 40 ml of dry tetrahydrofuran in a 50 ml Erlenmeyer flask with silanized glass walls. After the reaction temperature was reached (+20 or *ca* −70°C) 0.8 ml of a 1 M solution of triphenylphosphine in dry tetrahydrofuran was injected with a syringe. The cold solution was kept at *ca* −70°C for 1 h and then slowly warmed to room temperature. Finally the reaction mixtures were precipitated into 500 ml of cold methanol.

(D) Polymerizations with Bu_3SnOMe as initiator: β-propiolactone (50 mmol) was weighed into a 25 ml Erlenmeyer flask with silanized glass walls, and Bu_3Sn OMe (1 mmol) was added in the form of a 1 M solution in toluene. After thermostatization the reaction product was dissolved in CH_2Cl_2, precipitated into cold methanol (+5°C) and dried at 40°C *in vacuo*. Two analogous polymerizations were conducted with $Al(OiPr)_3$ at a monomer/initiator ratio of 150/1. The results are summarized in *Table 2*.

Model reactions with ethyl-β-R,S-hydroxybutyrate

(A) With K_2CO_3: ethyl β-D,L-hydroxybutyrate (0.5 mmol) and dimethyl sulfoxide-d_6 (0.5 ml) were injected into a 5 mm o.d. n.m.r. sample tube. Dry K_2CO_3 (0.25 mmol) was added, and ^{1}H n.m.r. spectra were recorded immediately afterwards and after 24 h with continuous shaking at 25°C. The reaction mixture was then heated to 60°C and measured again after 24 h.

(B) With K.*tert*-butoxide: potassium *tert*-butoxide (0.5 mmol) was added to a mixture of ethyl-β-*R,S*-hydroxybutyrate (0.5 mmol) and DMSO-d_6 (0.5 ml) in a 5 mm o.d. sample tube. The reaction mixture was gently shaken at 25°C for 24 h, whereby it turned brown. ^{1}H n.m.r. spectra were recorded after 1 h and after 24 h. All reaction mixtures were prepared under dry nitrogen.

Model reactions with ethyl-β-R,S-acetoxybutyrate

All model reactions were conducted as described above using 0.5 mmol quantities of acetylated ethyl-β-*R,S*-hydroxybutyrate.

Degradation of poly(β-lactones) with $NaOCH_3$ *in methanol*

Poly-β-propiolactone (50 mmol) was dissolved in 50 ml of dry dioxane and/or DMF, and $NaOCH_3$ (5 mmol) (dissolved in 0.5 ml methanol) was added. After the desired reaction time, the reaction mixture was poured into *ca* 600 ml of cold methanol and the precipitated polyester was isolated by filtration. After drying at 40°C *in vacuo* the polyester was dissolved in dry dichloromethane, 50 ml, and poured into *ca* 600 ml of cold ethanol. The precipitated polyester was isolated by filtration and dried at 40°C *in vacuo*. An analogous degradation study was conducted with poly(β-*R*,L-hydroxybutyrate).

Degradation of poly(β-lactones) with dry $NaOCH_3$ *or* KOtBu

Dry $NaOCH_3$ (1 mmol) or dry KOtBu (1 mmol) were added to a solution of poly(β-propiolactone) (50 mmol) in dry DMF. After stirring for 24 h at 25°C the reaction mixture was precipitated into cold methanol and the isolated polyesters were dried at 40°C *in vacuo*.

Measurements

The 100 MHz ^{1}H n.m.r. spectra were obtained on a Bruker AC 100 FT spectrometer. The measurements were conducted in $CDCl_3$ or DMSO-d_6 as solvents,

containing TMS as internal standard. Solutions of 50 mg polyester in 1 ml solvent were measured in 5 mm o.d. sample tubes.

The 25.17 MHz ^{13}C n.m.r. spectra were obtained on a Bruker AC 100 FT spectrometer in 10 mm o.d. sample tubes containing 300 mg polyester dissolved in 2.5 ml $CDCl_3$. Aquisition was conducted with the following parameters: pulse width 45°, relaxation delay 2 s, 32 k data points/7000 Hz spectral width, 17 000 transients.

RESULTS AND DISCUSSION

^1H-n.m.r. analyses of reaction mixtures

In a first series of experiments β-propiolactone was reacted with six different basic initiators in $CDCl_3$ solution in 5 mm diameter samples tubes. The resulting reaction mixtures were directly analyzed by means of ^1H-n.m.r. spectroscopy without any further pretreatment. A low monomer/initiator (M/I) ratio of 10:1 was chosen to allow a quantification of the acrylate groups formed by deprotonation and to prevent precipitation. For a parallel series of measurements, deuterated DMSO was chosen as solvent to study the influence of the solvent polarity (or dielectric constant). Two series of experiments were conducted. The results listed in *Table 1* were obtained in such a way that the reaction mixture in the n.m.r. tube was prepared under dry nitrogen in a glove box, yet without cooling. Under these conditions the reaction mixture warmed up to temperature above 30°C due to the exothermic polymerization of β-propiolactone. Several experiments were repeated in such a way that the n.m.r. tubes were filled in air, yet under cooling with ice. The results were nearly identical. The concentration of acrylate groups obtained under cooling was slightly lower.

The initiators used for these experiments were triethylamine, pyridine and triphenylphosphine as representatives of neutral initiators. Their nucleophilicity/basicity ratio strongly increases in the given order, which may result in a change of the reaction mechanism. Furthermore, the following three anionic initiators were selected: potassium *t*-butoxide, potassium (4-*t*-butyl)-phenoxide and potassium benzoate. Again the nucleophilicity/basicity ratio increases in the given order because the acidity of *t*-butanol (p*K*s ~18) is 13 orders of magnitude lower than that of benzoic acid (p*K*s ~5).

The most important result of these experiments is the observation that even the least basic initiators, triphenylphosphine and potassium benzoate, produce nearly equimolar amounts of acrylate groups (*Table 1*). Since the active chain end (i.e. the β-oxypropionate ion) has a basicity similar to that of benzoate and acrylate ions, it may be possible that part of the acrylate groups results from the interaction between active chain ends and the polymer backbone (see below) and not only from the direct interaction between initiator and lactone. Anyway, it is remarkable that all initiators gave similar yields of acrylate groups. In the case of β-D,L-butyrolactone a significantly higher selectivity was found[15]. The more nucleophilic amines gave higher yields of crotonate groups than triethylamine.

Also the role of the solvent polarity played a greater role in the case of β-D,L-butyrolactone than in the case of β-propiolactone. A significant difference between chloroform and dimethylsulfoxide solutions was only found when potassium *t*-butoxide was used as initiator (*Table 1*). However the relatively low yields of acrylate groups found in chloroform may be due to a side reaction, because the *t*-butoxide ion is basic enough to deprotonate chloroform. Therefore, the main conclusion which may be drawn from these and previous experiments is that deprotonation/elimination reactions occur in both polar and nonpolar solvents.

The direct proton abstraction from the α-position of the β-lactone or of noncyclic β-hydroxyprionic acid derivatives is certainly the most obvious mechanism in the case of anionic initiators or anionic chain ends [equations (4), (5)]. Yet, in the case of highly nucleophilic

Table 1 Results of base-initiated polymerizations of β-propiolactone conducted with a M/I ratio of 10:1 in 5 mm o.d. n.m.r. tubes at 20–30°C

Initiator	Solvent	Conversion (%)	Acrylate[a] Monomer units	Acrylate[b] Initiator
Triphenylphosphine	$CDCl_3$	99	1:12	1:1.2
	DMSO-d_6	99	1:21	1:2.1
Pyridine	$CDCl_3$	99	1:6	1:0.6
	DMSO-d_6	99	1:8	1:0.8
Triethylamine	$CDCl_3$	99	1:6	1:0.6
	DMSO-d_6	99	1:5	1:0.5
K-Benzoate	$CDCl_3$	20	—[c]	—
	DMSO-d_6	99	1:12	1:1.2
K-Phenolate	$CDCl_3$	99	1:18	1:1.8
	DMSO-d_6	99	—[c]	—
K-*t*-butoxide	$CDCl_3$	50	1:25	1:2.5
	DMSO-d_6	90	1:10	1:1.0

[a] Molar ratio of acrylate endgroups vs monomer units in the reaction mixture
[b] Molar ratio of acrylate endgroups vs initiator in the reaction mixture
[c] Not measurable because of high viscosity

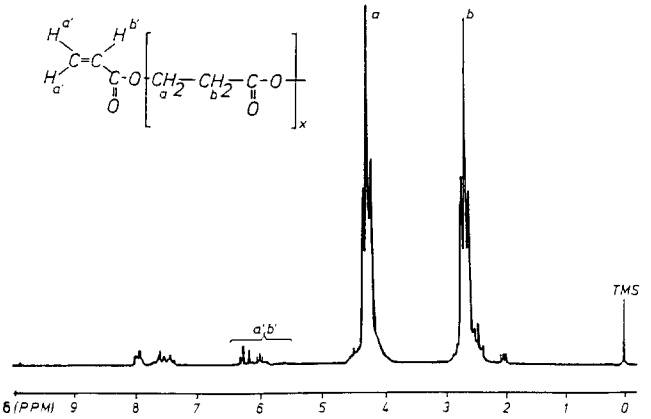


Figure 1 100 MHz ^{1}H n.m.r. spectrum of the reaction mixture obtained by mixing β-propiolactone and potassium benzoate (M/I = 10:1) at 20°C in $CDCl_3$

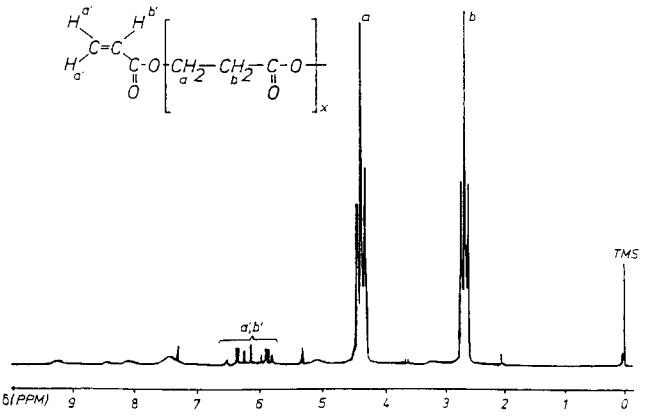


Figure 2 100 MHz ^{1}H n.m.r. spectrum of a poly(β-propiolactone) prepared by bulk polymerization with pyridine (M/I = 50:1) at 20°C (no. 2, *Table 2*), measured in $CDCl_3$

neutral initiators such as triphenylphosphine, the substitution/elimination mechanism outlined for pyridine in equations (2)–(3) is the more likely mechanism. The inductive effect of a positive charge enhances the acidity of the protons in α- and β-position. The elimination is certainly assisted by the attack of a base onto an α-proton. This base may be the initiator, a suitable solvent, such as dimethylsulfoxide, or the anionic chain end. An example of the ^{1}H n.m.r. spectra obtained from the reaction mixtures summarized in *Table 1* is given in *Figure 1*.

N.m.r-analyses of isolated poly(β-propiolactone)s

From the ^{1}H n.m.r. spectra of the reaction mixtures discussed above it is not clear as to what extent the acrylate groups are endgroups of the polylactone or acrylate ions [e.g. equation (3)]. Furthermore, unrealistic reaction conditions were chosen from the viewpoint of a preparative polymerization, because of the low M/I ratios. Moreover, the high initiator concentrations favour rapid exothermic reactions and, thus, deprotonation. Therefore, several additional polymerizations were conducted with M/I ratios of 20:1 or 50:1. Triethylamine, pyridine, triphenylphosphine or tributyltin methoxide were used as initiators and the temperature was maintained at 20–22°C (*Table 2*). The poly(β-propiolactone) resulting from these polymerizations was isolated by

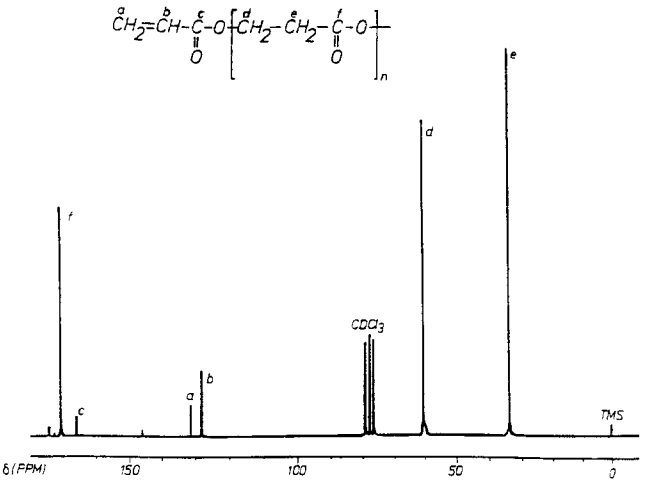


Figure 3 25 MHz ^{13}C n.m.r. spectrum of the pyridine initiated poly(β-propiolactone) no. 2, *Table 2*, measured in $CDCl_3$

precipitation with methanol and characterized by ^{1}H n.m.r. or ^{13}C-n.m.r. spectroscopy (*Figures 2* and *3*). In connection with *Figure 4* it is worth mentioning that the signal intensity of the acrylate groups is enhanced by a favourable nuclear Overhauser effect resulting from the higher mobility of the endgroups.

When the tertiary amines or triphenylphosphine were

Table 2 Bulk polymerizations of β-propiolactone initiated with nonionic initiators

Initiator	M/I[a]	Temperature (°C)	Time (h)	Acrylate[b] Monomer units	Acrylate[c] Initiator
Triphenylphosphine	20:1	20–22	120	1:100	1:5.0
	50:1	20–22	120	1:100	1:2.0
	50:1	−70	48	1:65	1:1.3
Pyridine	20:1	20–22	120	1:15	1:0.7
	50:1	20–22	120	1:20	1:0.4
Triethylamine	20:1	20–22	120	1:22	1:1.1
	50:1	20–22	120	1:26	1:0.5

[a] Initial molar monomer/initiator ratio of monomers vs initiator
[b] Molar ratio of acrylate endgroups and monomer units in the isolated polyesters
[c] Molar ratio of acrylate endgroups vs initiator

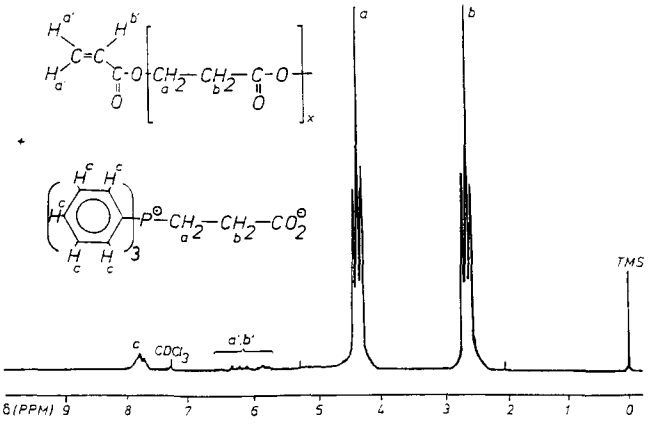


Figure 4 100 MHz ^{1}H n.m.r. spectrum of a poly(β-propiolactone) initiated with triphenylphosphine (M/I = 50:1) in tetrahydrofuran at approx. −70°C

used as initiators, relatively high concentrations of acrylate end-groups were found (*Table 2* and *Figures 2* and *3*). However, the number of acrylate groups produced per mol initiator was significantly lower than in the first series (*Table 1*). The acrylate/initiator ratio is lower for two reasons. First, the precipitation with methanol leads to a fractionation, so that oligomers remain in solution. Second, the low concentration of initiators along with the lower reaction temperature reduces the rate of deprotonation. Another important aspect of these measurements is the detection of initiator fragments as covalently bound endgroups of the isolated poly(β-propiolactone). Interestingly, triethylammonium endgroups were not observable and even pyridinium groups were difficult to detect (*Figure 2*). Obviously, a chain growth via macro-zwitterions is much less likely than is suggested by previous reports of other authors[1–9]. The absence of ammonium endgroups does not exclude the initial formation of betaines which contribute to the initiation process. Yet elimination of these ammonium groups may occur as base-assisted reactions (E_{2B} mechanism) in later stages of the polymerization [e.g. equations (2)–(4)].

In contrast to the amine initiated polymerizations, triphenylphosphonium endgroups were found in triphenylphosphine initiated poly(β-propiolactone)s (*Figure 4*). This finding suggests a certain extent of zwitterionic chain growth. The acrylate endgroups which are also present may result from the initiation process or from base assisted elimination of phosphonium endgroups [compare equations (2)–(3)].

In addition to these bulk polymerizations two triphenylphosphine-initiated polymerization were conducted with an M/I ratio of 50:1 in tetrahydrofuran. In the first case the monomer and initiator solution were mixed at +20°C, in the second case they were mixed at −70°C and slowly warmed up after 1 h. However, the spectroscopic results of both polymerizations were nearly identical: acrylate endgroups were found in addition to phosphonium endgroups (*Figure 4*). These results clearly demonstrate that even a relatively nonbasic initiator of high nucleophilicity generates acrylate endgroups. Therefore, it is obvious that a variation of the nucleophilicity/basicity ratio does not help to avoid unsaturated endgroups, when free anions are generated or when addition elimination reactions such as equations (2) and (3) can occur.

Polymerizations with coordination catalysts

For comparison with the above discussed anionic polymerizations three polymerizations were conducted with tributyltin methoxide as initiator (nos 1–2, *Table 3*). It was demonstrated in a previous part of this series[17] that metal alkoxides with energetically favorable p- or d-orbitals do not react as anionic initiators, but initiate a nonionic insertion mechanism. It is characteristic for this mechanism that the first step is a complexation between lactone and metal followed by ring opening of the acyl–oxygen bond via insertion into the covalent metal–alkoxide bond [equation (6)]. According to this mechanism

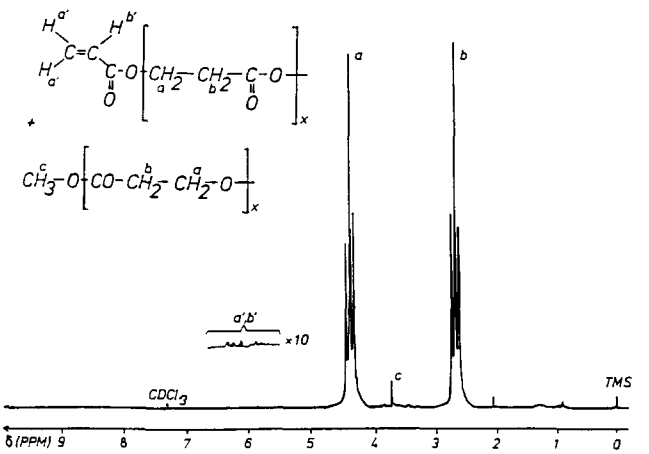


Figure 5 100 MHz ^{1}H n.m.r. spectrum of a poly(β-propiolactone) obtained by bulk-polymerization with tributyltin methoxide (M/I = 50:1) at +60°C

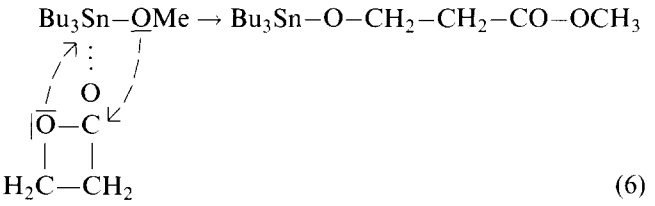
Table 3 Polymerizations of β-propiolactone (in bulk) initiated with coordination initiators

Initiator	M/I[a]	Temperature (°C)	Time (h)	Acrylate[b] Monomer units	Acrylate[c] Initiator
Bu_3SnOMe	50	60	24	>1:800	1:20
Bu_3SnOMe	50	100	24	>1:800	1:20
$Al(iProp)_3$	150	60	96	0	0
$Al(iProp)_3$	150	100	96	0	0

[a] Initial molar monomer initiator ratio
[b] Molar ratio of acrylate endgroups and monomer units in the isolated polyesters
[c] Molar ratio of acrylate endgroups vs initiator

the tributyltin methoxide initiated poly(β-propiolactone) should possess methylester endgroups but no acrylate chain ends. Unfortunately, the initiator was not reactive enough to enable polymerization of β-propiolactone at 20°C. The samples obtained at 60 and 100°C possess the expected methylester endgroups and a low content of acrylate chain ends. However, a comparison of the results listed in *Tables 2* and *3* clearly demonstrates that the concentration of acrylate endgroups formed in the tin methoxide initiated polymerization is much lower than in the case of anionic polymerizations, despite the higher temperature (see *Figures 2* and *5*).

Furthermore, two polymerizations were conducted with aluminium triisopropoxide (nos 3 and 4, *Table 3*). Interestingly the ^{1}H n.m.r. spectra of the resulting poly(β-propiolactone)s did not give any indication of acrylate endgroups. Thus, it is obvious that the absence or low concentration of acrylate groups is a typical feature of insertion mechanisms.



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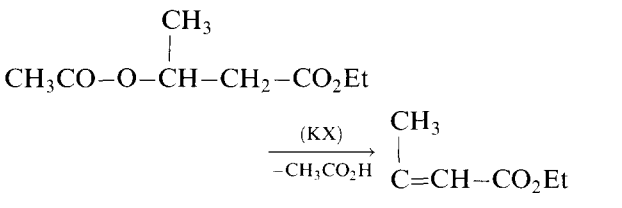

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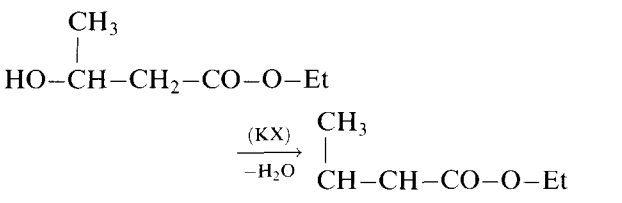

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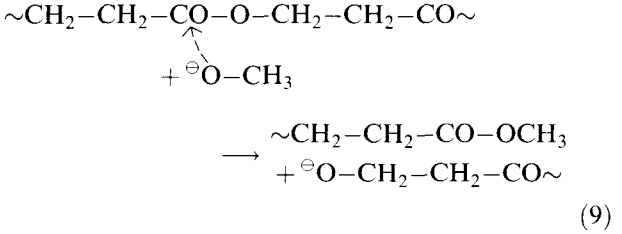

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Model reactions of chain scissions

The formation of unsaturated endgroups, mentioned above and by other authors, was discussed as a direct consequence of the initiation process. Now the question arises, whether the polylactone chains and the initially formed endgroups are stable over the whole course of the anionic polymerization. In order to shed more light on this problem, two series of model reactions were conducted [equations (7) and (8)].

Commercial ethyl β-D,L-hydroxybutyrate was used as a model of a hydroxy endgroup, and its acetyl derivative served as model of an ester group in the oligomers or

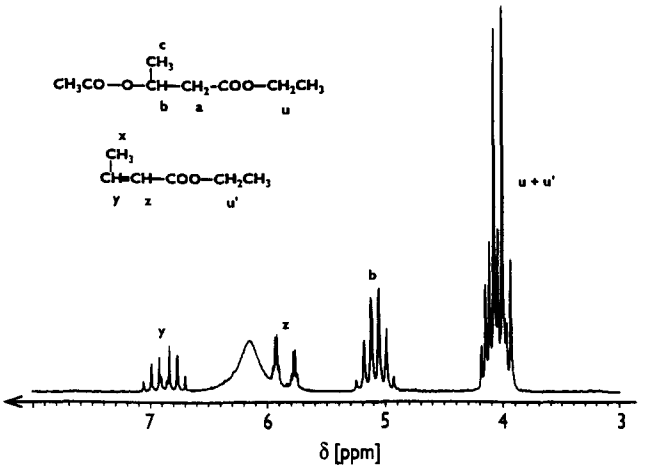

Figure 6 100 MHz ^{1}H n.m.r. spectrum of the reaction mixture of acetylated ethyl β-D,L-hydroxybutyrate and K acetate (molar ratio 1:1) in DMSO-d_6 after 24 h at 60°C

polymers. Both model compounds were shaken with equimolar amounts of K_2CO_3, K-acetate or K-*t*-butoxide in dry DMSO-d_6. The reaction mixtures were directly prepared in n.m.r. sample tubes and the course of the reactions was monitored by ^{1}H n.m.r. spectroscopy. When ethyl β-D,L-hydroxybutyrate was used as substrate, no reaction took place with K_2CO_3 or K-benzoate even at +60°C. With KO-*t*-butoxide, formation of crotonate groups occurred rapidly at 20°C. When the acetate was used as substrate, not only KO-*t*-butoxide but also K_2CO_3 and K-benzoate caused elimination at least at 60°C [equation (7) and *Figure 6*]. These results clearly demonstrate agreement with theory that the elimination of the acetate ion [equation (7)] requires a lower energy of activation than the elimination of water from a hydroxy endgroup [equation (8)]. In consequence it is obvious that the oligo- and polyester chains formed either via alkoxide-propagation or via carboxylate ions [equation (1)] may be the object of base catalysed eliminations reactions.

Finally, a sample of poly(β-propiolactone) and a sample of poly(β-D,L-butyrolactone), both bare of methyl ester endgroups and bare of unsaturated endgroups, were treated with sodium methoxide. The polyesters were dissolved in dry dimethyl formamide and a small amount of a concentrated solution of $NaOCH_3$ in methanol was added. After 2 h or after 24 h the reaction mixture was precipitated into diethylether. As illustrated by *Figure 7* the isolated polyesters contain both methyl ester endgroups and acrylate (or crotonate) endgroups. Thus, the methoxide ion has attacked the polyester chain in two ways, partially by deprotonation elimination [equation (7)] and partially by base-catalysed transesterification [equation (9)]. It is, of course unlikely that this reaction happens when the initiator is completely consumed in the beginning of a polymerization. The formation of acrylate or crotonate groups was also observed when dry sodium methoxide or potassium *t*-butoxide were added to solutions of poly(β-propiolactone) or poly(β-D,L-butyrolactone) in dry DMF at 25°C. No ester endgroups were found under these conditions. Hence, the deprotonation/elimination is the standard reaction which occurs under most circumstances, whereas the transesterification is

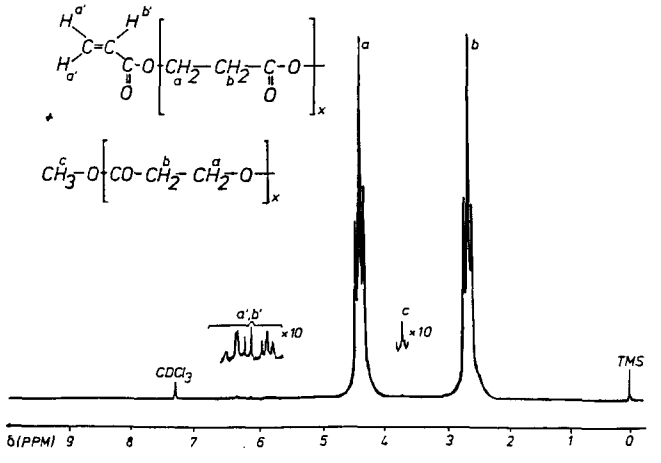

Figure 7 100 MHz ^{1}H n.m.r. spectrum of poly(β-propiolactone) after treatment with sodium methoxide in dioxane at 20°C (monomer unit/methoxide = 10:1)

promoted by the presence of an alcohol. The results confirm the significance of the model reactions discussed above. Obviously, the formation of unsaturated endgroups is not exclusively a direct consequence of the initiation step, but may also occur in later stages of a polymerization.

CONCLUSIONS

The results discussed above allow the conclusion that the anionic polymerization of β-propiolactone is under most circumstances accompanied by deprotonation reactions. The formation of acrylate endgroups may be the consequence of at least four different pathways. The first one consists in the direct basic attack of initiator or anionic chain end onto an α-proton of the lactone [equation (4)] followed by rearrangement to an acrylate (or crotonate) anion. However, convincing evidence for this mechanism has not been published to date. The second pathway involves as first step a nucleophilic attack of the initiator followed by a base support deprotonation of the betain group [equations (2)–(4)]. This reaction sequence may be called the addition-elimination mechanism [equations (3), (4)]. The third mechanism is another addition elimination mechanism resulting from the nucleophilic attack of an alkoxide anion onto the CO-group of a β-lactone[21]. The fourth reaction pathway consists of the deprotonation/elimination of oligo- and polyesters [equations (7) and (9)]. It depends of course, on concentration, temperature and solvent to what extent these individual elimination reactions contribute to the final result. Nonetheless the present and previous studies clearly demonstrate that the preparative usefulness of anionic polymerizations of a β-lactone with proton in α-position is sometimes strongly limited by side reactions, and covalent alkoxides initiating insertion mechanisms are more attractive for preparative purposes.

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