6832 *Macromolecules* **2006,** *39,* 6832−6837

C−O and Not C−C Bond Cleavage Starts the Polymerization of β-Butyrolactone with Potassium Anions of Alkalide

Zbigniew Grobelny,* Andrzej Stolarzewicz, Barbara Morejko, and Wojciech Pisarski

Institute of Materials Science, University of Silesia, 40-007 Katowice, Poland

Adalbert Maercker

Institut für Organische Chemie, Universität Siegen, D-57068 Siegen, Germany

Andrzej Skibiński

Department of Organic Chemistry, Biochemistry and Biotechnology, Silesian University of Technology, 44-101 Gliwice, Poland

Stanisław Krompiec and Józef Rzepa

Institute of Chemistry, University of Silesia, 40-006 Katowice, Poland

Received November 24, 2005; Revised Manuscript Received July 21, 2006

ABSTRACT: The mechanism of the initiation step of β-lactones polymerization with potassium anions of alkalide is verified, as had been suggested by Szwarc [Szwarc, M. *Ionic Polymerization Fundamentals*; Carl Hanser Verlag: Munich, 1996; p 69]. Contrary to previous papers, the carbon−carbon bond scission is not observed. It is shown that indeed this kind of bond rupture does not occur, at least in β-butyrolactone. In fact, the acyl−oxygen bond is mainly cleaved in this lactone by potassium anions. The reaction proceeds by lactone dianion as an intermediate succeeding formation of the radical anion. The latter decomposes by the alkyl−oxygen bond cleavage in a side reaction. Finally, potassium crotonate and potassium 3-hydroxybutyrate are mainly formed, and potassium butyrate is a side product. They become the real initiators of the polymerization. The same results are observed with alkalide K^-, $K^+(15\text{-crown-}5)_2$, and $K^-,K^+(18\text{-crown-}6)$.

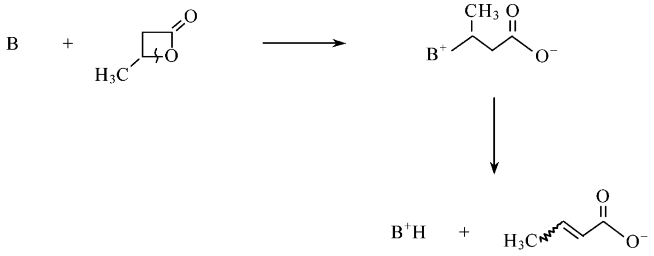
Introduction

Anionic polymerization of β-lactones was described in several works.[1−16] Some of them concerned the polymerization of β-butyrolactone.[5,6,8−16] Biodegradable and bioresorbable materials could be obtained in such a way. The course of initiation step of that process depended on the kind of initiator used.

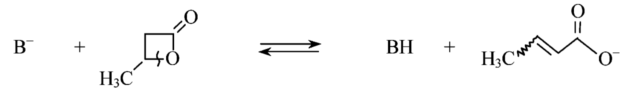
Kricheldorf[5] investigated two classes of initiators, namely neutral bases such as tertiary amines or triphenylphosphine and ionic ones as potassium alkoxides, phenoxides, and carboxylates. Formation of crotonate starting groups was detected in almost all the polymerizations. The presence of those groups resulted from deprotonation of the monomer. It could occur according to two different mechanisms. The first one concerned the nucleophilic attack at C3 of the monomer with the alkyl−oxygen ring opening followed by elimination of the protonated base (Scheme 1). The second mechanism showed direct deprotonation of the monomer (Scheme 2). The nucleophilicity/basicity ratio of the initiator determined which mechanism prevailed. In both cases the crotonate anion was formed, and that initiated the polymerization with alkyl−oxygen bond cleavage. The active polymer chain end should also be capable of undergoing transfer reaction to the monomer.

Deprotonation of β-butyrolactone was also observed by Jedliński in the polymerization with potassium naphthalenide[8] and potassium hydride[9] both activated by 18-crown-6. The polymers had crotonate starting groups.

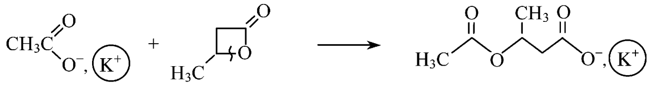
Scheme 1. Alkyl−Oxygen Bond Cleavage before Deprotonation[5]



Scheme 2. Alkyl−Oxygen Bond Cleavage after Deprotonation[5]



Scheme 3. Alkyl−Oxygen Bond Cleavage[15]



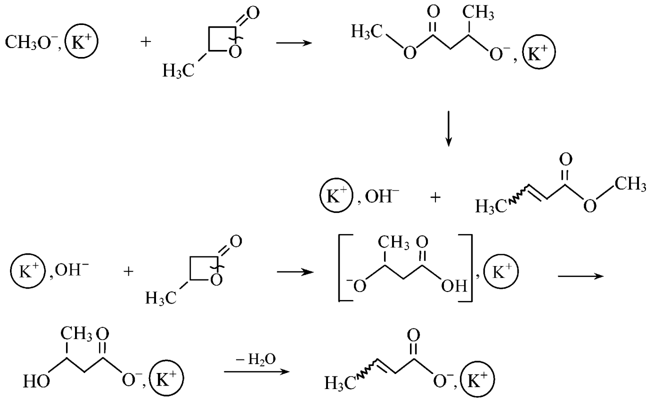
where K^+ denotes a complex of K^+ with dibenzo-18-crown-6

Duda[15] stated that the polymer of β-butyrolactone obtained with potassium acetate activated by dibenzo-18-crown-6 possessed the acetate starting group coming from the carboxylate anion of the initiator. In that polymerization the lactone ring was opened in the alkyl−oxygen position (Scheme 3). The crotonate starting groups were also detected. Those were formed in the chain transfer reaction to the monomer. Penczek[16] concluded that usually both the initiation by addition and transfer coexisted, and their relative importance depended on the ionic initiator used: more important for alkoxides, less important for carboxylates.

Słomkowski[17] and Boileau[18] were the first ones that prepared poly(β-propiolactone) at the living conditions, and that β-bu-

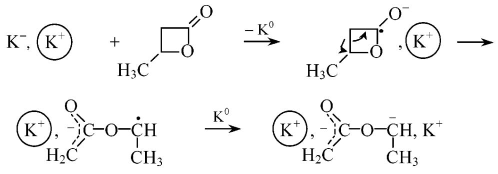
10.1021/ma052511h CCC: $33.50 © 2006 American Chemical Society
Published on Web 09/07/2006

Scheme 4. Acyl−Oxygen Bond Cleavage[6]



where K^+ denotes a complex of K^+ with 18-crown-6

Scheme 5. Carbon−Carbon Bond Cleavage[14]



where K^+ denotes a complex of K^+ with 18-crown-6

tyrolactone differed, since the ratios of the rate constant of chain transfer to the rate constant of propagation varied substantially.[15]

In the polymerization of β-butyrolactone with potassium methoxide activated by 18-crown-6 the scission of the acyl−oxygen bond was reported,[6] giving unstable potassium β-alkoxide ester (Scheme 4). That decomposed to potassium hydroxide and unsaturated ester. The former opened the next monomer molecule with the acyl−oxygen bond cleavage. Potassium 3-hydroxybutyrate and, after water elimination, potassium crotonate were the final products of the initiation step.

Another mechanism was presented for the β-propiolactone[10,11] and β-butyrolactone[11] polymerization with alkalide K^-,K^+(18-crown-6) as two-electron-transfer reagent. The homolytic carbon−carbon bond cleavage was assumed for that system succeeding the formation of lactone radical anion (Scheme 5).[11,19] It was proposed that the further reaction with K^0 deriving from K^- led to enolate carbanion stabilized by resonance and that enolate possessed two kinds of anionic centers, i.e., enolic and carbanionic ones. The former was assumed to be inactive whereas the latter opened the monomer ring and starting the polymerization. That mechanism was then proposed also for other β-lactones and reviewed repeatedly in several papers.[12−14,19,20]

However, such a course of the reaction seems to be improbable. The postulated organopotassium enolate should rather deprotonate the lactone molecule similarly to potassium naphthalenide[8] and not open the lactone ring. Moreover, in the model reaction carried out at the equimolar ratio of the reagents,[20] the organopotassium enolate, due to its expected extreme reactivity, should rapidly deprotonate crown ether before the reaction with hydrogen chloride or methyl iodide added as a quenching agent.[21]

Szwarc,[22] analyzing the mechanism of K^- reaction with β-lactones proposed by Jedliński,[10] stated: "Interaction of K^- solvated by crown ether with β-propiolactone leads to the rupture of the C−C bond instead of the expected opening of the CO−O or O−CH_2 bonds, yielding eventually ethyl acetate. This result calls for verification." It means that the reaction involved would rather favor heterolytic than homolytic bond scission.

Thus, we decided to reinvestigate the unusual ring-opening mechanism of β-lactones. β-Butyrolactone and alkalide K^-,K^+-(15-crown-5)$_2$ **1** in tetrahydrofuran solution were selected for that purpose as the most suitable model reagents. The latter had been found to be much more stable than K^-,K^+(18-crown-6) at ambient temperature.[23] The concentration of potassium anions in tetrahydrofuran solution of **1** does not change for 1 h after their generation, whereas alkalide K^-,K^+(18-crown-6) in the same solvent decomposes autocatalytically to a large extent already during its preparation. A mixture of dipotassium alkoxides derived from the crown ether destruction by K^- is formed in this case.[24] Moreover, **1** was successfully employed in the study of the ring opening reaction in several monosubstituted oxiranes[25−29] and other cyclic ethers.[30,31] Organometallic compounds were formed in all those processes as intermediates of an extreme reactivity.[21,29]

Results and Discussion

Benzyl bromide had been applied as a convenient quenching agent to determine the course of the reaction of **1** with β-butyrolactone. That had been added to the reaction mixture immediately after mixing of the reagents. Four main signals were then observed in GC-MS chromatogram of the benzylated sample. The first two signals were identified as benzyl 3-hydroxybutyrate (in 7% yield) and benzyl crotonate (2%). It indicated that two salts were initially formed in the reaction, i.e., potassium 3-hydroxybutyrate and potassium crotonate. They were the same products as those found earlier in the process initiated with potassium methoxide.[6] The other two signals were assigned to benzyl derivatives of the products formed by the addition of one monomer molecule to each of the potassium salts (in 10% and 16% yield, respectively). Propylene and carbon dioxide were found in the gaseous phase over the reaction mixture. Propylene was also found in the liquid phase. Hydrogen and carbon monoxide were not detected.

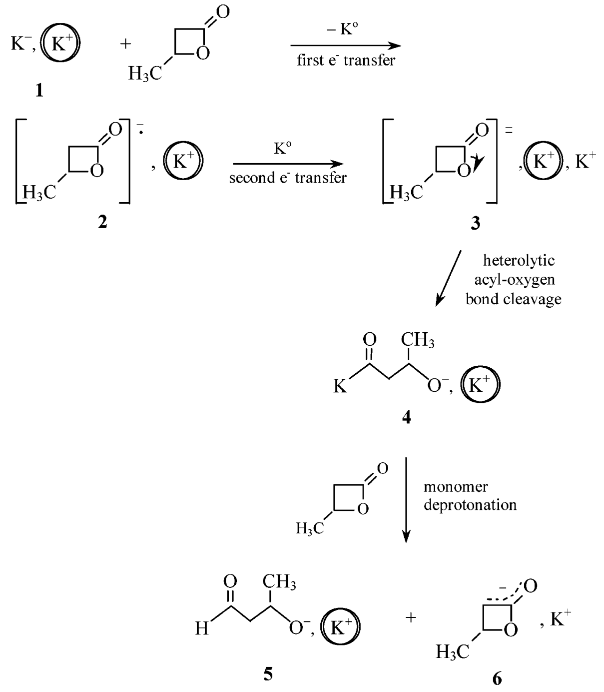
Two signals of a low intensity were identified as 3-benzyloxybutyric acid (2%) and benzyl butyrate (1%). Thus, potassium 3-carboxy-2-propoxide and potassium butyrate were formed in the initiation process in small amounts, too.

Yields of all reactions were low because β-butyrolactone was used in 10-fold excess in relation to potassium anions.

The potassium anion is known to react as two-electron-transfer reagent in two steps.[32] It becomes K^0 after the first electron transfer to an acceptor molecule. The potassium cation is formed in the second step of the reaction. Therefore, it is assumed that the process under study starts with one electron transfer from K^- of **1** to the LUMO orbital localized mainly between carbon and oxygen atoms of the lactone carbonyl group. It gives K^0 and lactone radical anion **2** (Scheme 6). Then, K^0 transfers the second electron to **2**. It results in lactone dianion **3**, which decomposes to **4** with the heterolytic cleavage of the acyl−oxygen bond. The latter deprotonates the monomer, giving potassium β-alkoxide aldehyde **5** and potassium enolate **6**.

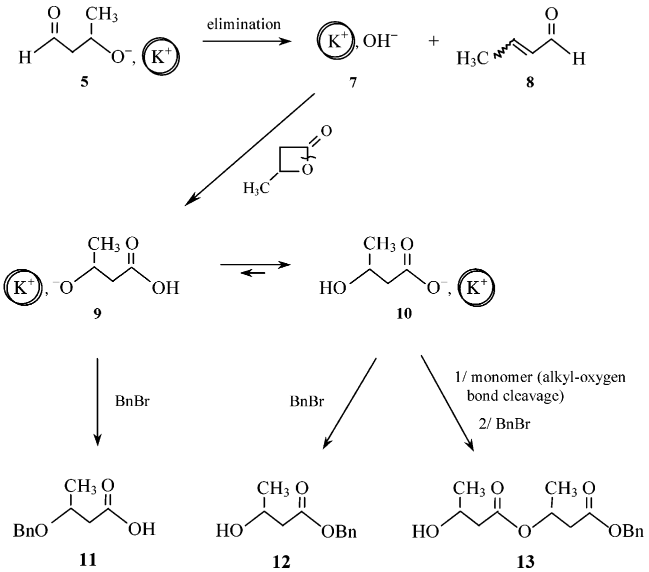
This reaction needs some comments. Organopotassium intermediate **4** could deprotonate not only the monomer but also crown ether or the solvent. It is known that deprotonation of 15-crown-5 with an organometallic compound results in potassium tetraethylene glycoxide vinyl ether as the product of crown ring opening.[21,29] That compound was not found in the reaction mixture. Products of the expected reaction of **4** with tetrahydrofuran, i.e., ethylene and potassium enolate of acetaldehyde,[33] were also not detected. Moreover, the lack of carbon monoxide in the gaseous reaction products showed that **4** did not undergo decarbonylation. Thus, only deprotonation of the monomer can be taken into account in the studied system.

Scheme 6



where K^+ denotes a complex of K^+ with two 15-crown-5 molecules.

Scheme 7

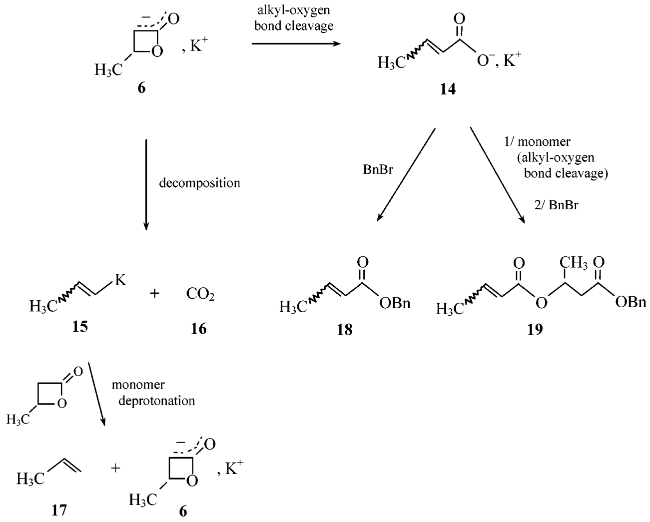


We assume that **5** is unstable similarly to potassium β-alkoxide ester (Scheme 4) and decomposes by elimination to potassium hydroxide **7** and crotonaldehyde **8** (Scheme 7).

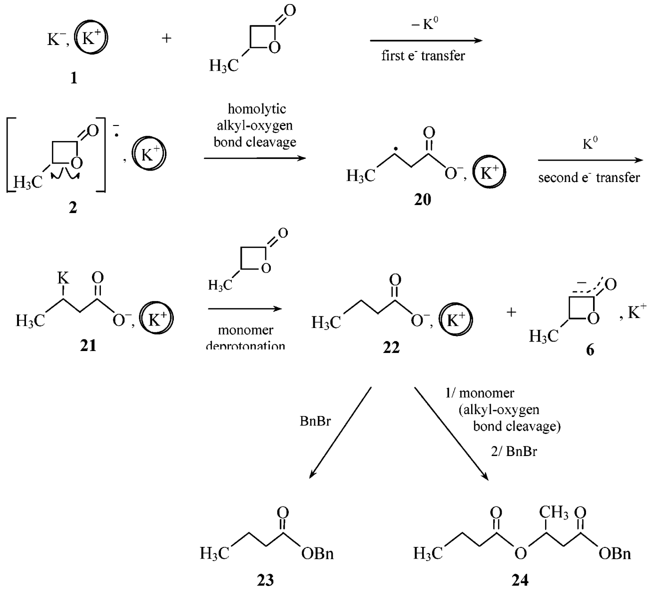
Then, **7** reacts with the next monomer molecule. The opening of the acyl−oxygen bond takes place in this reaction, resulting in unstable potassium 3-carboxy-2-propoxide (**9**) as proposed in ref 6 (Scheme 4). It exists in an equilibrium with potassium 3-hydroxybutyrate (**10**). This equilibrium is shifted to the right, but only weak signals of benzyl derivatives of **9** and **10**, i.e., **11** and **12**, respectively, are present in the GC-MS spectrum. The main signal represents benzylated product **13** of the reaction of **10** with one monomer molecule.

It should be stressed in this point that the percentage of the benzylated species **11** and **12** as found by GC is not necessarily identical with the percentage of the parent reactive species **9** and **10** in the reaction mixture. If two nucleophiles in an equilibrium compete for one electrophile, the main product results from the fastest reaction, i.e., from the most nucleophilic species.

Scheme 8



Scheme 9



Crotonaldehyde was not detected in the reaction mixture presumably due to its decomposition during gas chromatography analysis (see Experimental Section). Therefore, the mechanism according to Scheme 7 has to be taken only as tentative.

The rearrangement of **6** leads to potassium crotonate **14**, as suggested in refs 8 and 9 (Scheme 8). Compound **6** also undergoes a destruction leading to propenylpotassium (**15**) and carbon dioxide (**16**). Then, **15** deprotonates the monomer, giving propylene (**17**) and enolate (**6**). That course of reaction was established by us in a separate experiment described in Experimental Section.

Compound **14** produces **18** after benzylation. However, most of **14** decays in the reaction with one monomer molecule. Compound **19** is the benzylated product of this reaction.

A homolytic alkyl−oxygen bond cleavage of β-lactone radical anion **2** occurring in a side reaction shows Scheme 9. Potassium butyrate (**22**) is the product of this cleavage found after benzylation as **23**. Compound **22** similarly to **10** and **14** can add one monomer molecule; however, the benzylated product of this reaction, **24**, is obtained in a very low yield (<1%).

Thus, two main products, i.e., potassium 3-hydroxybutyrate (**10**) and potassium crotonate (**14**), and one side product, i.e., potassium butyrate (**22**), are formed in the studied process as the real initiators of the β-butyrolactone polymerization.

These results differ strongly from those presented earlier for the reaction of β-butyrolactone with K^-,K^+(18-crown-6).[11−14,19] Therefore, we repeated the experiments using K^-,K^+(18-crown-6). Tetrahydrofuran solution of this alkalide was introduced into the excess of the monomer. However, the same reaction products were identified after benzylation as by the use of **1**. The formation of dibenzyl derivative of enolate carbanion postulated for the C−C bond cleavage as well as its reaction product with the monomer were not observed. Methylation or protonation of the reaction mixture also did not produce the appropriate derivatives. Those compounds were not found in GC-MS as well as in NMR spectra. Evidently, the reaction course did not depend on the kind of crown ether of alkalide.

Thus, the question is why the results of this and the earlier works are different. There could be several reasons for that, but two of them seem to be obvious.

At first, as reported in ref 20, the monomer was purified by distillation with metallic sodium, whereas we have found that β-butyrolactone reacts with this metal during distillation. The ^{13}C NMR spectrum of the distillate obtained in such a way reveals, besides carbon signals of the monomer, also signals of the carbon−carbon double bond at 123.5 and 145.5 ppm and the methyl group at 17.6 ppm. The same groups are identified in ^1H NMR spectrum at 5.85, 6.95, and 1.80 ppm, respectively. These signals are characteristic of crotonic acid and its esters. It means that the monomer used in earlier works was not pure enough for examination of the reaction mechanism and potassium anions could react also with its impurities.

Second, the model experiments of β-butyrolactone with alkalide K^-,K^+(18-crown-6) were generally carried out at the equimolar ratio of the reagents.[20] The blue solution of alkalide was titrated with the monomer until discoloration of the reaction mixture, i.e., until decay of K^-. It means that K^- was in the excess during the reaction. That could lead to wrong conclusions because of possible side reactions between potassium anions and primary reaction products.[25−30] In fact, the benzylated derivative of potassium tetraethylene glycoxide vinyl ether is, for example, identified in the reaction mixture when β-butyrolactone was dropped into the solution of **1**, i.e., at the excess of potassium anions.

The sum of these and other unknown until now effects may be responsible for the disagreements found. However, which kind of them prevails is difficult to estimate.

It is noteworthy that the acyl−oxygen bond cleavage induced by K^- has been observed in linear aromatic esters,[34] whereas aliphatic esters were reduced in the presence of K^- with the scission of the alkyl−oxygen bond.[35,36] The question why the acyl−oxygen bond opening is preferred in the system containing β-butyrolactone remains without answer.

Conclusions

The results of this work show that the postulated earlier ring-opening mechanism of the C−C bond cleavage in β-butyrolactone by alkalide does not take place. The C−O bond is opened in the presence of potassium anions, and it is mainly the acyl−oxygen bond. Potassium 3-hydroxybutyrate and potassium crotonate are products of this reaction and real initiators of the β-butyrolactone polymerization. Potassium butyrate, being the product of the side reaction with the alkyl−oxygen bond scission, also participates in the initiation.

Experimental Section

Analyses. Gas chromatography−mass spectrometry (GC-MS) analysis of liquids was performed on a GC Trace 2000 gas chromatograph equipped with a Finnigan Trace MS detector. GC conditions: capillary column Equity-5, 30 m × 0.25 mm × 0.5 μm (Supelco); carrier gas He 80 kPa, constant pressure; oven temperature 60 °C (3 min), 60−250 °C (12 °C/min), 250 °C (25 min); injector SSL 250 °C; GC interface 250 °C. MS conditions: source 200 °C; e^- energy 40 eV; emission 70 μA; detector 350 V. Diethylene glycol was used as an internal standard for the yield measurements. Gaseous compounds were determined with a Chromatron GCHF chromatograph at ambient temperature on a 2 m metal column filled with modified alumina. NMR spectra were recorded in $CDCl_3$ with a Varian-Inova-300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) at 20 °C. Chemical shifts were expressed in ppm downfield from TMS.

Materials. β-Butyrolactone (Aldrich) was heated over CaH_2 for 6 h and then distilled under a dry argon atmosphere; the fraction boiling at 47 °C/5 mmHg was collected (purity 99.6%). Distillation over metallic sodium carried out in ref 20 is not recommended because the metal reacted with lactone. A new product or products with the double bond are observed in this case in the distillate. Tetrahydrofuran (POCH) was boiled over CuCl to decompose peroxides and then over CaH_2 for 10 h, and finally it was distilled at 66 °C. This fraction was dried over metallic potassium for 20 h and redistilled prior to use (purity 99.9%). Potassium (Aldrich, 99.95%) (1 g) was distilled under high vacuum to obtain a metal mirror in a reactor described in ref 23. 0.1 M K^-,K^+(15-crown-5)$_2$ dark blue solution was obtained by dissolution of the metal in 0.2 M 15-crown-5 tetrahydrofuran solution (10 cm^3). After ultrasonic mixing (25 min) the solution was filtered off through a glass frit and then used as the reagent. Similarly, 0.1 M K^-,K^+(18-crown-6) blue solution was obtained using 0.1 M 18-crown-6 tetrahydrofuran solution (10 cm^3) at the contact time equal to 15 min. Butyryl chloride (a substrate for the synthesis of **24**) was prepared by a standard procedure from butyric acid and thionyl chloride. Methyl crotonate, *trans*-crotonic acid, *trans*-crotonyl chloride (90%), and thionyl chloride were purchased from Acros. Butyric anhydride and tetrabutylammonium hydrogen sulfate were purchased from Sigma-Aldrich. Silica gel 60 (40−63 μm) was supplied from Merck. Other chemicals for synthesis were purchased from POCH.

Reaction of K^-,K^+(15-Crown-5)$_2$ or K^-,K^+(18-Crown-6) with β-Butyrolactone. 0.1 M alkalide tetrahydrofuran solution (10 cm^3) was dropped for 0.5 min into 1.0 M β-butyrolactone tetrahydrofuran solution (10 cm^3) while mixing under a dry argon atmosphere. Thus, the molar ratio of reagents was equal to 1:10, and β-butyrolactone was still in the excess. The reaction mixture was then immediately treated with 10% excess of benzyl bromide. All experiments were conducted at 25 °C.

The products obtained were identified matching their mass spectra, retention times, and NMR spectra with those of authentic compounds, except for crotonaldehyde. Its GC-MS analysis was unsuccessful presumably because of its decomposition or polymerization on the chromatographic column. The analysis of the pure compound gave no signal in the spectrum.

Reaction of potassium hydride with β-butyrolactone was carried out in the presence of 18-crown-6 at 25 °C using equimolar amounts of the reagents in order to generate potassium lactone enolate.[10] A solution of β-butyrolactone (0.086 g, 1 mmol) and 18-crown-6 (0.264 g, 1 mmol) in tetrahydrofuran (5 cm^3) was dropped into KH (0.04 g, 1 mmol) suspended in tetrahydrofuran (5 cm^3) while mixing. Gaseous products (19 cm^3) evolved for 15 min. They involved hydrogen, propylene, and carbon dioxide. The former was obtained by deprotonation of β-butyrolactone, whereas two further compounds were formed during the decomposition of potassium β-butyrolactone enolate.

Benzyl (*R,S*)-3-(benzyloxy)butyrate (a substrate for the synthesis of **11**) was prepared by the method of Antonov[37] from freshly distilled benzyl alcohol (35.5 cm^3, 343 mmol), sodium (0.50 g, 22 mmol), and methyl crotonate (16.4 cm^3, 155 mmol). The yield of the pale yellow product was 7.30 g (16.6%); bp 150−158 °C/0.5 mmHg, lit. bp 150−153 °C/0.1 mmHg.[37]

^{1}H NMR (300 MHz): 1.30 (d, 3H, $J = 6.3$ Hz, C*H*$_3$), 2.53 (dd, A of ABX system, 1H, $J_{AX} = 5.4$ Hz, $J_{AB} = 15.0$ Hz, C*H*$_2$−O), 2.74 (dd, B of ABX system, 1H, $J_{BX} = 7.2$ Hz, $J_{AB} = 15.0$ Hz, C*H*$_2$−O), 4.03−4.13 (m, X of ABXM$_3$ system, 1H, C*H*−O), 4.51 (d, A of AB system, 1H, $J_{AB} = 11.7$ Hz, PhC*H*H−O), 4.59 (d, B of AB system, 1H, $J_{AB} = 11.7$ Hz, PhC*H*H−O), 5.17 (m, AB system, 2H, PhC*H*$_2$−O), 7.30−7.41 (m, 10H, 2 *Ph*).

^{13}C NMR (75 MHz): 19.81, 42.07, 66.22, 70.81, 71.97, 127.49, 127.60, 128.16, 128.20, 128.30, 128.50, 135.91, 138.46, 171.25.

(*R*,*S*)-3-(Benzyloxy)butyric acid (11) was prepared by the method of Bachmann and Seebach.[38] The solution of benzyl 3-benzyloxybutyrate (5.69 g, 20 mmol) in methanol (25 cm^3) was added to 12% aqueous sodium hydroxide (25 cm^3), and the resulting emulsion was stirred vigorously. Slight exothermic reaction occurred, and after ca. 2 h the mixture became homogeneous. Stirring was continued at room temperature for 2 days. After evaporation of methanol at room temperature under reduced pressure, the resulting mixture was first extracted with diethyl ether (5 × 15 cm^3), and ethereal extracts were discarded. Next, the pH of the aqueous phase was adjusted under cooling with concentrated hydrochloric acid (7.5 cm^3) to about 1, and the obtained mixture was extracted with diethyl ether (5 × 15 cm^3). The combined ethereal extracts were washed with water (3 × 10 cm^3), dried over anhydrous magnesium sulfate, and filtered. After evaporation of the solvents, the residual yellow oil was distilled under reduced pressure, affording 2.30 g (59%) a colorless liquid; bp 138−141 °C/0.4 mmHg, lit. bp 138−140 °C/0.1 mmHg,[37] 115 °C/0.01 mmHg,[38] 107 °C/0.02 mmHg.[39]

^{1}H NMR (300 MHz): 1.28 (d, 3H, $J = 6.3$ Hz, C*H*$_3$), 2.48 (dd, A of ABX system, 1H, $J_{AX} = 5.7$ Hz, $J_{AB} = 15.3$ Hz, C*H*$_2$−O), 2.68 (dd, B of ABX system, 1H, $J_{BX} = 6.9$ Hz, $J_{AB} = 15.3$ Hz, C*H*$_2$−O), 3.95−4.06 (m, X of ABXM$_3$ system, 1H, C*H*−O), 4.51 (d, A of AB system, 1H, $J_{AB} = 11.7$ Hz, PhC*H*H−O), 4.59 (d, B of AB system, 1H, $J_{AB} = 11.7$ Hz, PhC*H*H−O), 7.24−7.36 (m, 5H, *Ph*), 11.27 (br, 1H, COO*H*).

^{13}C NMR (75 MHz): 19.81, 41.89, 70.96, 71.70, 127.74, 127.80, 128.46, 138.27, 177.88. NMR data are in agreement with ref 39.

MS *m*/*e* (rel int): 194 (48, M$^+$), 166 (34), 148 (27), 108 (29), 107 (50), 91 (100), 79 (16), 77 (16), 65 (13), 45 (35), 43 (27).

Benzyl (*R*,*S*)-3-Hydroxybutyrate (12). The solution of β-butyrolactone (5.0 cm^3, 61 mmol), freshly distilled benzyl alcohol (21.0 cm^3, 203 mmol), and *p*-toluenesulfonic acid monohydrate (0.1 g) was stirred at room temperature for 3 days under a nitrogen atmosphere. Then, the finely powdered anhydrous CaCO$_3$ (1.1 g) was added, and stirring of the suspension was continued for an additional day at room temperature. The solid was filtered off, and the excess benzyl alcohol was evaporated at 70−75 °C/1.5 mmHg. The remaining oil was dissolved in diethyl ether (40 cm^3), the ethereal solution was washed with 5% aqueous sodium bicarbonate (3 × 7 cm^3) and water (3 × 7 cm^3), dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness giving a pale yellow oil. The crude product was distilled under reduced pressure, affording 5.58 g (47%) of 3-hydroxybutyric acid benzyl ester as a colorless liquid; bp 111−114 °C/0.8 mmHg, lit. bp 105−115 °C/0.05 mmHg,[40] 90 °C/0.001 mmHg.[41]

^{1}H NMR (300 MHz): 1.20 (d, 3H, $J = 6.3$ Hz, C*H*$_3$), 2.42−2.54 (m, AB of ABX system, 2H, C*H*$_2$−C(=O)), 3.14 (s, 1H, O*H*), 4.15−4.25 (m, X of ABXM$_3$ system, 1H, C*H*−O), 5,13 (s, 2H, PhC*H*$_2$−O), 7.31−7.35 (m, 5H, *Ph*).

^{13}C NMR (75 MHz): 22.52, 42.95, 64.24, 66.41, 128.24, 128.34, 128.60, 135.64, 172.55. NMR data are in agreement with refs 40 and 41.

MS *m*/*e* (rel int): 194 (14, M$^+$), 166 (12), 148 (12), 108 (23), 107 (39), 91 (100), 79 (14), 77 (20), 65 (13), 45 (48), 43 (45).

Benzyl 3-((3′-hydroxybutanoyl)oxy)butyrate (13)—the equimolecular mixture of (3*R*, 3′*R*), (3*S*, 3′*S*), (3*R*, 3′*S*), and (3*S*, 3′*R*) isomers. A solution of racemic benzyl 3-hydroxybutyrate (**12**) (0.51 g, 2.6 mmol), racemic β-butyrolactone (0.27 g, 0.26 cm^3, 3.8 mmol), *p*-toluenesulfonic acid monohydrate (0.024 g), and 1.0 cm^3 dichloromethane was stirred at room temperature for 5 days under a nitrogen atmosphere. The reaction mixture was diluted with diethyl ether, washed successively with 5% aqueous NaHCO$_3$ solution and water, then dried over anhydrous MgSO$_4$, and the solvents were evaporated. Flash chromatography on 6.5 g of silica gel 60 using diethyl ether/hexane (1:3) eluent gave unreacted benzyl 3-hydroxybutyrate (0.30 g, 1.5 mmol) and followed by diethyl ether/hexane (1:2) eluent gave 0.15 g (48% yield) of colorless oil.

^{1}H NMR (300 MHz): 1.18 (d, 3H, $J = 6.3$ Hz, C*H*$_3$CH), 1.20 (d, 3H, $J = 6.3$ Hz, C*H*$_3$CH), 1.30 (d, 3H, $J = 6.3$ Hz, C*H*$_3$CH), 1.31 (d, 3H, $J = 6.3$ Hz, C*H*$_3$CH), 2.27−2.43 (m, 4H, 2 AB of 2 ABX systems, 2 CHC*H*$_2$COO), 2.57 (dd, 1H, A of ABX system, $J = 4.5$ Hz, $J = 15.6$ Hz, CHC*H*H−COO), 2.59 (dd, 1H, A of ABX system, $J = 4.9$ Hz, $J = 15.6$ Hz, CHCH*H*−COO), 2.68 (dd, 1H, B of ABX system, $J = 7.9$ Hz, $J = 15.6$ Hz, CHC*H*H−COO), 2.69 (dd, 1H, B of ABX system, $J = 7.8$ Hz, $J = 15.6$ Hz, CHC*H*H−COO), 2.83 (br s, 2H, 2 O*H*), 4.07−4.20 (m, 2H, 2 CH$_3$C*H*−OH), 5.12 (s, 4H, 2 PhC*H*$_2$−O), 5.16−5.40 (m, 2H, 2 COOC*H*CH$_3$), 7.29−7.40 (m, 10H, 2 *Ph*).

^{13}C NMR (75 MHz): 19.98 (*C*H$_3$), 20.00 (*C*H$_3$), 22.39 (*C*H$_3$), 22.55 (*C*H$_3$), 40.71 (CH*C*H$_2$COO), 40.76 (CH$_2$*C*H$_2$COO), 43.22 (CH*C*H$_2$COO), 43,32 (CH*C*H$_2$COO), 64.21 (H*C*-O), 64.45 (H*C*−O), 66.70 (2 H*C*-O), 67.60 (H*C*-O), 67.68 (H*C*-O), 128.48 (*C*H in *Ph*), 128.50 (*C*H in *Ph*), 128.67 (*C*H in *Ph*), 135.66 (2 *C* in *Ph*), 170.26 (*C*OO), 170.35 (*C*OO), 171.87 (*C*OO), 172.14 (*C*OO).

The chemical shifts of (3*R*, 3′*R*) and (3*S*, 3′*S*) isomers are in agreement with data for (3*R*, 3′*R*) isomer reported by Lengweiler.[40]

MS *m*/*e* (rel int): 280 (3, M$^+$), 194 (32), 173 (48), 146 (12), 107 (36), 105 (17), 91 (100), 87 (42), 77 (10), 69 (14), 65 (10), 45 (26), 43 (18).

Benzyl *trans*-Crotonate (18). *trans*-Crotonic acid (8.60 g, 100 mmol), finely powdered KOH (5.63 g, 100 mmol), and anhydrous K$_2$CO$_3$ (13.85 g, 100 mmol) were mixed at ca. 75 °C. After foaming had ceased, solids were cooled to room temperature, and the solution of freshly distilled benzyl bromide (5.9 cm^3, 50 mmol) and tetrabutylammonium hydrogen sulfate (0.8 g) in benzene (50 cm^3) was added. The resulting suspension was vigorously stirred at room temperature for 12 h. Next, the solids were filtered off and washed with benzene (2 × 25 cm^3). The combined filtrates were washed with saturated sodium bicarbonate solution (2 × 15 cm^3) and water (3 × 15 cm^3), dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated. Distillation under reduced pressure of residue afforded 5.75 g (65%) the product as a colorless liquid; bp 84−86 °C/0.8 mmHg, lit. bp 125 °C/5 mmHg.[42]

^{1}H NMR (300 MHz): 1.79 (dd, 3H, $J = 6.9$ Hz, $J = 1.7$ Hz, C*H*$_3$), 5.13 (s, 3H, C*H*$_2$−O), 5.86 (dq, 1H, $J = 1.7$ Hz, $J = 15.5$ Hz, C*H*=), 6.98 (dq, 1H, $J = 6.9$ Hz, $J = 15.5$ Hz, C*H*=), 7.23−7.35 (m, 5H, *Ph*).

^{13}C NMR (75 MHz): 17.62, 65.58, 122.24, 127.80, 127.94, 128.21, 135.97, 144.75, 165.84. NMR data are in agreement with ref 43.

MS *m*/*e* (rel int): 176 (47, M$^+$), 158 (38), 131 (53), 107 (13), 91 (100), 69 (96), 64 (20), 50 (10), 39 (28).

(*R*,*S*)-Benzyl 3-((But-2-enoyl)oxy)butyrate (19). A solution of *trans*-crotonyl chloride (90%) (1.22 g, 10.5 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added dropwise to a solution of benzyl 3-hydroxybutyrate (1.02 g, 5.2 mmol) and anhydrous pyridine (1.04 cm^3, 12.9 mmol) in CH$_2$Cl$_2$ (10 cm^3) at 0 °C. The mixture was stirred 3 days at room temperature, poured onto a mixture of ice and 5% sodium bicarbonate solution, diluted with CH$_2$Cl$_2$, and stirred 2 h. The organic phase was separated, washed with cold water, 2% hydrochloric acid, 5% sodium bicarbonate solution, again with water, then dried, and evaporated. The crude product (0.58 g) was purified by flash chromatography on silica gel 60 column using dichloromethane as an eluent. Yield 0.51 g (1.9 mmol, 37%).

^{1}H NMR (300 MHz): 1.31 (d, 3H, $J = 6.0$ Hz, C*H*$_3$CH), 1.79 (dd, 3H, $J = 6.9$ Hz, $J = 1.8$ Hz, C*H*$_3$CH=), 2.57 (dd, 1H, $J = 5.7$ Hz, $J = 15.3$ Hz, CHC*H*H−COO), 2.72 (dd, 1H, $J = 7.5$ Hz, $J = 15.3$ Hz, CHCH*H*−COO), 5.12 (s, 2H, PhC*H*$_2$−O), 5.30−5.38 (m, 1H, $CH_3C\mathit{H}$-O), 5.76 (dq, 1H, $J = 1.8$ Hz, $J = 15.6$ Hz,), 6.92 (dq, 1H, $J = 6.9$ Hz, $J = 15.6$ Hz, $CH_3C\mathit{H}{=}$), 7.32−7.35 (m, 5H, *Ph*).

^{13}C NMR (75 MHz): 18.05 ($\mathit{C}H_3CH{=}$), 20.06 ($\mathit{C}H_3CH$), 41.05 ($CH\mathit{C}H_2COO$), 66.53 (H*C*-O), 67.16 (H*C*-O), 122.80 (${=}\mathit{C}HCOO$), 128.35 (*C*H of *Ph*), 128.39 (2*C*H of *Ph*), 128.64 (2*C*H of *Ph*), 135.84 (*C* in *Ph*), 144.91 ($CH_3\mathit{C}H{=}$), 165.72 (${=}CH\mathit{C}OO$), 170.23 (*C*OO).

MS *m*/*e* (rel int): 262 (9, M^+), 193 (9), 176 (14), 155 (100), 107 (40), 91 (56), 86 (16), 69 (55), 39 (16).

Benzyl Butyrate (23). Concentrated H_2SO_4 (0.1 cm^3) was added to a stirred solution of butyric anhydride (15.5 cm^3, 101 mmol) and benzyl alcohol (10.3 cm^3, 100 mmol). After exothermic reaction had ceased, the mixture was heated at 120 °C for 2.5 h. The resulting reaction mixture was cooled to room temperature and poured into ice water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×25 cm^3). The combined organic layers were washed with a cold saturated sodium bicarbonate solution (until butyric acid was removed), cold water, dried over anhydrous magnesium sulfate, and filtered. After evaporation of the solvent, the residual oil was distilled under reduced pressure, affording 14.21 g (80%) of benzyl butyrate as colorless liquid; bp 127−128 °C/16 mmHg, lit. bp 91−92 °C/3 mmHg.[44]

^{1}H NMR (300 MHz): 0.92 (t, 3H, $J = 7.4$ Hz, $C\mathit{H}_3$), 1.65 (sextet, 2H, $J = 7.4$ Hz, $C\mathit{H}_2$), 2.29 (t, 2H, $J = 7.4$ Hz, $C\mathit{H}_2$), 5.08 (s, 2H, $C\mathit{H}_2$−O), 7.25−7.33 (m, 5H, *Ph*).

^{13}C NMR (75 MHz): 13.51, 18.31, 36.00, 65.82, 127.98, 128.02, 128.38, 136.14, 173.13. NMR data are in agreement with ref 43.

MS *m*/*e* (rel int): 178 (78, M^+), 108 (68), 91 (100), 68 (14), 71 (18), 65 (13), 52 (13).

(*R*,*S*)-Benzyl 3-((Butanoyl)oxy)butyrate (24). A solution of butyryl chloride (1.10 g, 10.4 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a solution of benzyl 3-hydroxybutyrate (1.02 g, 5.2 mmol) and anhydrous pyridine (1.04 cm^3, 12.9 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C. The mixture was stirred 3 days at room temperature, poured onto the mixture of ice and 5% sodium bicarbonate solution, diluted with CH_2Cl_2, and stirred for 2 h. The organic phase was separated, washed with cold water, 2% hydrochloric acid, 5% sodium bicarbonate solution, again with water, then dried, and evaporated. The crude product (1.07 g) was purified by flash chromatography on silica gel 60 column using diethyl ether/hexane (1:4) eluent. Yield 0.59 g (2.2 mmol, 38%).

^{1}H NMR (300 MHz): 0.90 (t, 3H, $J = 7.4$ Hz, $C\mathit{H}_3CH_2$), 1.29 (d, 3H, $J = 6.3$ Hz, $C\mathit{H}_3CH$), 1.59 (sextet, 2H, $J = 7.4$ Hz, $CH_3C\mathit{H}_2$), 2.15−2.21 (m (similar to AB of ABX_2 system), 2H, $CH_2C\mathit{H}_2COO$), 2.55 (dd, 1H, $J = 5.5$ Hz, $J = 15.4$ Hz, $CHC\mathit{H}H$−COO), 2.68 (dd, 1H, $J = 7.7$ Hz, $J = 15.4$ Hz, $CHCH\mathit{H}$−COO), 5.12 (s, 2H, $PhC\mathit{H}_2$−O), 5.30 (ddq, 1H, $J = 5.5$ Hz, $J = 7.7$ Hz, $J = 6.3$ Hz, $CH_3C\mathit{H}$-O), 7.33−7.35 (m, 5H, *Ph*).

^{13}C NMR (75 MHz): 13.70 ($\mathit{C}H_3CH_2$), 18.51 ($CH_3\mathit{C}H_2$), 20.06 ($\mathit{C}H_3CH$), 36.41 ($CH_2\mathit{C}H_2COO$), 41.03 ($CH\mathit{C}H_2COO$), 66.55 (H*C*-O), 67.17 (H*C*-O), 128.42 (*C*H in *Ph*), 128.68 (*C*H in *Ph*), 135.88 (*C* in *Ph*), 170.20 (*C*OO), 172.93 (*C*OO).

MS *m*/*e* (rel int): 264 (50, M^+), 193 (26), 179 (36), 178 (36), 157 (100), 148 (22), 107 (75), 91 (86), 69 (39), 41 (27).

Acknowledgment. The authors are indebted to Dr. Krzysztof Skutil for GC analysis of gaseous reaction products.

References and Notes

(1) Hall, H. K. *Macromolecules* **1969**, *2*, 488−497.
(2) Gross, R. A.; Zhang, G.; Konrad, G.; Lenz, R. W. *Macromolecules* **1988**, *21*, 2657−2668.
(3) Hofman, A.; Słomkowski, S.; Penczek, S. *Makromol. Chem.* **1984**, *185*, 91−101.
(4) Dale, J.; Schwartz, J. E. *Acta Chim. Scand.* **1986**, *B40*, 559−567.
(5) Kricheldorf, H. R.; Scharnagl, N. *J. Macromol. Sci., Chem.* **1989**, *A26*, 951−968.
(6) Jedliński, Z.; Kowalczuk, M.; Kurcok, P. *Macromolecules* **1991**, *24*, 1218−1219.
(7) Kurcok, P.; Kowalczuk, M.; Hennek, K.; Jedliński, Z. *Macromolecules* **1992**, *7*, 2017−2020.
(8) Jedliński, Z.; Kowalczuk, M.; Główkowski, W.; Grobelny, J.; Szwarc, M. *Macromolecules* **1991**, *24*, 349−352.
(9) Kurcok, P.; Matuszowicz, A.; Jedliński, Z. *Macromol. Rapid Commun.* **1995**, *16*, 201−206.
(10) Jedliński, Z.; Kurcok, P.; Kowalczuk, M. *Macromolecules* **1985**, *18*, 2679−2683.
(11) Jedliński, Z.; Kowalczuk, M. *Macromolecules* **1989**, *22*, 3244−3250.
(12) Jedliński, Z.; Kowalczuk, M.; Kurcok, P. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 277−293.
(13) Jedliński, Z. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 235−245.
(14) Jedliński, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2158−2165.
(15) Duda, A. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 21−29.
(16) Sosnowski, S.; Słomkowski, S.; Penczek, S. *Macromolecules* **1993**, *26*, 5526−5527.
(17) Słomkowski, S.; Penczek, S. *Macromolecules* **1976**, *9*, 367−368.
(18) Deffieux, A.; Boileau, S. *Macromolecules* **1976**, *9*, 369−381.
(19) Jedliński, Z. *Acc. Chem. Res.* **1998**, *31*, 55−61 and references therein.
(20) Jedliński, Z.; Misiołek, A.; Kurcok, P. *J. Org. Chem.* **1989**, *54*, 1500−1501.
(21) Stolarzewicz, A.; Grobelny, Z.; Maercker, A. Organometallic Intermediates Formed in the Reaction of Ethers with Potassium Anions. In *Focus on Organometallic Chemistry Research*; Cato M. A., Ed.; Nova Science Publishers: Hauppauge, NY, 2005; Chapter 2, and references therein.
(22) Szwarc, M. *Ionic Polymerization Fundamentals*; Carl Hanser Verlag: Munich, 1996; p 69.
(23) Grobelny, Z.; Stolarzewicz, A.; Sokół, M.; Grobelny, J.; Janeczek, H. *J. Phys. Chem.* **1992**, *96*, 5193−5196.
(24) Jedliński, Z.; Stolarzewicz, A.; Grobelny, Z. *Makromol. Chem.* **1986**, *187*, 795−799.
(25) Grobelny, Z.; Stolarzewicz, A.; Maercker, A.; Demuth, W. *J. Organomet. Chem.* **1999**, *590*, 153−157.
(26) Grobelny, Z.; Stolarzewicz, A.; Morejko-Buż, B.; Guika, G.; Gražulevičius, J. V. *Eur. Polym. J.* **2002**, *38*, 2359−2363.
(27) Grobelny, Z.; Stolarzewicz, A.; Morejko-Buż, B.; Maercker, A. *J. Organomet. Chem.* **2002**, *660*, 6−13.
(28) Grobelny, Z.; Stolarzewicz, A.; Maercker, A.; Krompiec, S.; Bieg, T. *J. Organomet. Chem.* **2002**, *660*, 133−138.
(29) Grobelny, Z. *J. Organomet. Chem.* **2003**, *677*, 118−124 and references therein.
(30) Grobelny, Z.; Stolarzewicz, A.; Maercker, A. *J. Organomet. Chem.* **2000**, *604*, 283−286.
(31) Grobelny, Z. *Eur. J. Org. Chem.* **2004**, 2973−2982 and references therein.
(32) Perrin, Ch. L.; Wang, J.; Szwarc, M. *J. Am. Chem. Soc.* **2000**, *122*, 4569−4572.
(33) Lehmann, R.; Schlosser, M. *Tetrahedron Lett.* **1984**, *25*, 745−748.
(34) Fish, R. H.; Dupon, J. W. *J. Org. Chem.* **1988**, *53*, 5230−5234.
(35) Barrett, A. G. M.; Godfrey, Ch. R. A.; Hollinshead, D. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; Joukhadar, L.; McGhie, J. F.; Misra, S. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1501−1509.
(36) Barrett, A. G. M.; Prokopiou, P. A.; Barton, D. H. R.; Boar, R. B.; McGhie, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 1173−1174.
(37) Antonov, V. K.; Shchelokov, V. I.; Shemyakin, M. M. *Zh. Obshch. Khim.* **1965**, *35*, 2239−2246.
(38) Bachmann, B. M.; Seebach, D. *Helv. Chim. Acta* **1998**, *81*, 2430−2461.
(39) Plattner, D. A.; Brunner, A.; Dobler, M.; Müller, H. M.; Petter, W.; Zbinden, P.; Seebach, D. *Helv. Chim. Acta* **1993**, *76*, 2004−2033.
(40) Lengweiler, U. D.; Fritz, M. G.; Seebach, D. *Helv. Chim. Acta* **1996**, *79*, 670−701.
(41) Zhang, Y.; Gross, R. A.; Lenz, R. W. *Macromolecules* **1990**, *23*, 3206−3212.
(42) Plisow, A. K.; Bogatskii, A. V. *Zh. Obshch. Khim.* **1957**, *27*, 360−364.
(43) Sun, S.; Edwards, L.; Harrison, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 437−448.
(44) Zeinalov, B. K.; Magerramova, A. K. *Azerb. Khim. Zh.* **1962**, *6*, 15−21 (*Chem. Abstr.* **1963**, *59*, 8647g).

MA052511H