

Poly lactones. 35. Macrocyclic and Stereoselective Polymerization of β -D,L-Butyrolactone with Cyclic Dibutyltin Initiators

Hans R. Kricheldorf* and Soo-Ran Lee

Institut für Technische und Makromolekulare Chemie der Universität Hamburg, Bundesstrasse 45, D-20146 Hamburg, FRG

Received March 28, 1995; Revised Manuscript Received July 11, 1995*

ABSTRACT: 2,2-Dibutyl-1,3-dioxo-2-stannanes prepared from dibutyltin oxide and 1,3-propanediol or neopentandiol were used as cyclic initiators for polymerizations of β -D,L-butyrolactone. Because these initiators were not reactive below 50 °C, all polymerizations were conducted in bulk at temperatures ≥ 50 °C. As evidenced by ^{13}C NMR spectroscopy, the resulting poly(β -D,L-butyrolactone) is preferentially syndiotactic, but the percentage of syndiotactic diads decreases with increasing reaction temperature. ^1H NMR spectra proved that the insertion of lactones occurred at both Sn–O bonds of the cyclic initiators, and thus, the propagation yields automatically macrocyclic esters. The ring size increases with increasing monomer/initiator ratio and higher conversions. Selective ring opening with 1,2-dimercaptoethane produces linear polyesters with shorter elution times in GPC measurements than the corresponding macrocycles of the same molecular weight. Batchwise copolymerizations with ϵ -caprolactone yielded macrocyclic block copolymers which after ring-opening with dimercaptoethane turned into linear A–B–A triblock copolymers. However, when mixtures of both lactones were copolymerized at 100 °C, random copolymers were obtained.

Introduction

Poly(β -D-hydroxybutyrate) is a highly crystalline biopolymer produced by various types of bacteria.¹ Biotechnically produced copolymers of β -D-hydroxybutyric acid containing small amounts of other β -hydroxy acids were commercialized by ICI as biodegradable engineering plastic.^{1,2} The homopolymer itself has the disadvantage of a high melting point (around 180 °C) and a low thermostability, so that processing from the melt is difficult. Furthermore, its insolubility in most common solvents prevents an easy processing from solution.

An alternative approach to a production of biodegradable homo- or copolymers of β -hydroxybutyric acid consists of homo- and copolymerizations of β -D,L-butyrolactone, β -D,L-BL which is technically produced from diketene. In recent years synthesis and characterization of preferentially syndiotactic poly(β -D,L-butyrolactone), poly(β -D,L-Hbu), has found increasing interest.^{3–10} A 100% syndiotactic poly(β -D,L-Hbu) should possess a melting temperature (T_m) in the range 140–150 °C and a good solubility in several common solvents. However, the synthesis of a nearly 100% syndiotactic poly(β -D,L-Hbu) with a high molecular weight is yet an unsolved problem. The best result, a sample with >90% syndiotactic diads but low molecular weight ($M_n \leq 5000$), was obtained from a $\text{Bu}_2\text{Sn}(\text{OMe})_2$ -initiated polymerization.⁸ Therefore, it was one purpose of this work to study the usefulness of the cyclic dibutyltin compounds **1a** and **1b** as initiators for a stereoselective poly-

merization of β -D,L-BL. Preliminary results of this study were briefly described in a recent conference report.¹⁰

Experimental Section

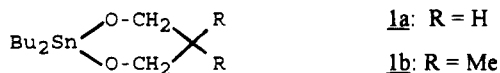
Materials. β -D,L-Butyrolactone and ϵ -caprolactone were purchased from Aldrich Chemical Co. (Milwaukee, WI) and dried by distillation over freshly powdered calcium hydride. Dibutyltin oxide, 1,3-propanediol, and neopentandiol were also purchased from Aldrich Co., but used without additional purification.

2,2-Dibutyl-1,3-dioxo-2-stannane (1a). Dibutyltin oxide (0.1 mol) and 1,3-propanediol were refluxed in dry toluene (250 mL). The liberated water was removed by azeotropic distillation over a period of 8 h. Finally, the toluene solution was concentrated in vacuo and the crystallized product was isolated by filtration. Yield: 75%. Mp: 85–86 (mp 88 °C in ref 11).

2,2-Dibutyl-5,5-dimethyl-1,3-dioxo-2-stannane (1b). Potassium *tert*-butoxide (0.4 mol) was dissolved in hot *tert*-butanol (400 mL), neopentandiol (0.2 mol) was added, and afterward Bu_2SnCl_2 (0.2 mol) was added in three portions. The reaction mixture was stirred at 60 °C for 0.5 h. The warm reaction mixture was diluted with ethyl acetate (200 mL), cooled with ice, and filtered from the precipitated KCl. The filtrate was concentrated in vacuo, and the product was isolated by distillation over a short-path apparatus in vacuum. Yield: 50 mg. Mp: 165–175 °C (no melting point was given in ref 12).

Homopolymerizations. (A) Polymerizations of Tables 1–3. β -D,L-Butyrolactone (50 mmol) was weighed into a 25 mL Erlenmeyer flask with silanized glass walls (pretreatment with Me_2SiCl_2), and initiator **1a** was added in the form of a 0.5 M solution in hot toluene or chloroform. Initiator **1b** was added as a suspension in dry CH_2Cl_2 . The reaction vessel was closed with a glass stopper and steel spring and thermostated at 50 or 75 °C. Finally, the reaction product was dissolved in CH_2Cl_2 (30 mL) and precipitated into Et_2O .

(B) Polymerizations of Table 5. The neat initiator **1a** (or $\text{Bu}_2\text{Sn}(\text{OMe})_2$) was added to neat β -D,L-butyrolactone in a 50 mL Erlenmeyer flask. The reaction mixture was thermostated at 75 °C and finally dissolved in CH_2Cl_2 so that a total volume of 75 mL was obtained. This solution was divided into three portions of 25 mL. One portion was directly precipitated into dry Et_2O at 20 °C. Dimercaptoethane (25 mmol) was added to the second portion, and this solution was precipitated



merization of β -D,L-BL. Furthermore, it was intended to elucidate the formation of macrocycles and their regioselective cleavage to yield linear poly(β -D,L-Hbu)

* Abstract published in *Advance ACS Abstracts*, August 15, 1995.

Table 1. Polymerizations of β -D,L-Butyrolactone Initiated with 2,2-Dibutyl-5,5-dimethyl-1,3-dioxo-2-stannane (1b)^a

polym no.	monom init	temp (°C)	time (days)	yield (%)	η_{inh}^b (dL/g)	i/s ^c	% syndiotactic diads	T_g^d (°C)	T_m^d (°C)
1	50	50	10	77	0.10	0.6/10	62	-1	65/72
2	100	50	10	80	0.11	0.6/1.0	62	+6	69
3	400	50	10	0					
4	100	75	6	85	0.16				
5	200	75	6	93	0.25	0.8/1.0	55	8	73
6	400	75	6	89	0.34	0.8/1.0	55	6	66
7	800	75	6	94	0.35	0.8/1.0	55	7	68

^a Added as suspension in CH₂Cl₂. ^b Measured at 25 °C in CH₂Cl₂. ^c Ratio of isotactic and syndiotactic CO diads. ^d From DSC measurements at a heating rate of 20 °C/min.

Table 2. Polymerization of β -D,L-Butyrolactone Initiated with 2,2-Dibutyl-1,3-dioxo-2-stannane (0.5 M in Hot CHCl₃)

polym no.	monom init	temp (°C)	time (days)	yield (%)	η_{inh}^a (dL/g)	i/s ^b	% syndiotactic diads	T_g^c (°C)	T_m^c (°C)
1	50	50	6	81	0.12	0.5/1.0	67	5	66 and 110
2	100	50	7	80	0.1	0.5/1.0	67		
3	200	50	30	0					
4	100	75	6	77	0.16	0.6/1.0	62	7	67 and 72
5	200	75	6	84	0.28	0.7/1.0	58	9	70
6 ^d	400	75	6	95	0.44 ^d	0.7/1.0	58	11	70

^a Measured at 25 °C in CH₂Cl₂. ^b Ratio of isotactic and syndiotactic diads (CO signal). ^c From DSC measurements at a heating rate of 20 °C/min. ^d $M_w \sim 32\,000$ and $M_w/M_n \sim 1.7$ from GPC measurements using polystyrene standards and the universal calibration method.

into Et₂O after a storage of 20 h at 20 °C. Dimercaptoethane (50 mmol) was also added to the third portion, which was precipitated after 1 h storage at 20 °C. The precipitated polyesters were isolated by filtration and dried at 40 °C in vacuo.

Copolymerizations. (A) Polymerizations of Table 6. ϵ -Caprolactone (50 mmol) was weighed into a 50 mL Erlenmeyer flask (with silanized glass walls), initiator **1a** (1 mmol) was added, and the reaction mixture was thermostated at 75 °C for 24 h. Afterward β -D,L-butyrolactone (50 mmol) was added and the reaction vessel was shaken until a homogeneous solution was obtained, which was thermostated again at 75 °C. Finally, the product was dissolved in CH₂Cl₂ (60 mL) and precipitated into Et₂O.

(B) Polymerizations of Table 7. Neat β -D,L-butyrolactone (100 mol) was polymerized for 6 days in bulk at 75 °C with initiator **1a** (10 mmol). The resulting macrocyclic poly(β -D,L-Hbu) was precipitated into dry Et₂O, isolated, and dried at 40 °C in vacuo (yield 81%).

The isolated poly(β -D,L-Hbu) was divided into four portions. One portion was dissolved in ϵ -caprolactone (25 mmol), and the polymerization was continued for 5 days at 75 °C. The resulting copolyesters were dissolved in CH₂Cl₂ and precipitated into Et₂O. Analogous polymerizations of ϵ -caprolactone were conducted over a period of 9 days. Two more polymerizations were conducted with 50 mmol portions of ϵ -caprolactone.

(C) Random Copolymerization. ϵ -Caprolactone (25 mmol) and β -D,L-butyrolactone (25 mmol) were weighed into a 25 mL Erlenmeyer flask, and initiator **1a** (0.5 mmol or 0.25 mmol) dissolved in hot toluene was added. The reaction mixture was thermostated at 100 °C for 72 h, afterward dissolved in CH₂Cl₂ (40 mL), and precipitated into Et₂O. The diethyl ether was decanted from the precipitated syrupy copolyester which was dried at 20 °C in vacuo. Yields: 30% and 32%, respectively. Molar composition (¹H NMR) of ϵ -Cap/ β -D,L-Hbu: 0.9/1.0.

Model Reaction of Bu₂Sn(OMe)₂ and DME. Dibutyl-dimethoxytin (20 mmol) and 1,2-dimercaptoethane (20 mmol) were dissolved in CH₂Cl₂ (25 mL) and allowed to stand for 24 h at 25 °C. Afterward the reaction mixture was concentrated in vacuo, and the solid residue was characterized by melting point and IR and ¹H NMR spectroscopy. It was identical with product prepared from dibutyltin oxide and DME according to the literature.¹¹

Measurements. The viscosities were measured with an automated Ubbelohde viscometer thermostated at 25 °C. The DSC curves were recorded with a Perkin-Elmer DSC-7 in aluminum pans under nitrogen. The 100 MHz ¹H NMR spectra were recorded with a Bruker AC-100 FT NMR spectrometer in 5 mm o.d. sample tubes. The 25.4 MHz ¹³C

NMR spectra were measured with the same spectrometer in 10 mm o.d. sample tubes. CDCl₃ containing TMS served as the solvent for all NMR measurements. The GPC measurements were conducted with a Kontron HPLC 420 equipped with a Waters differential refractometer 410. Four Ultra-styragel columns with pore sizes of 10², 10³, 10⁴, and 10⁵ Å were used, and tetrahydrofuran served as the eluent.

Results and Discussion

Homopolymerization of β -D,L-Butyrolactone. The 1,3-dioxo-2-stannanes **1a** and **1b** are known in the literature,^{11–13} but without NMR spectroscopic characterization. In the present work three different synthetic methods were tested and compared. The most convenient proved to be the reaction of dibutyltin oxide with the corresponding 1,3-diols in an inert solvent. The cyclic initiators are poorly soluble in organic solvents owing to the association via the energetically favorable free d-orbitals of the Sn atoms and the free *n*-electrons of the oxygens. Whereas **1b** was found to be almost insoluble in typical NMR solvents, dilute solutions of **1a** were obtained in hot chloroform or toluene, which allowed measurements of NMR spectra and addition of the dissolved initiator to the monomer.

Due to the poor solubility of **1b** only a few polymerizations were conducted with this initiator. In all experiments the initiator was added in the form of a fine powder to the neat β -D,L-BL. All attempts to initiate a polymerization at temperatures below 50 °C failed despite reaction times up to 4 weeks. Even at 50 °C satisfactory yields required reaction times of at least 10 days, and no polymerization occurred at monomer/initiator (M/I) ratios ≥ 400 (Table 1). In order to obtain higher molecular weights the temperature was raised to 75 °C (nos. 4–7, Table 1). Now high yields and higher inherent viscosities were found even at M/I ratios of 400 and 800. However, the viscosity data indicate that the molecular weights do not increase, when the M/I is varied from 400 to 800. Higher temperatures were not applied because it was learned from previous studies^{8,9} that increasing temperature favors an atactic stereo-sequence.

The tacticities of the isolated poly(β -D,L-Hbu) were analyzed by means of ¹³C NMR spectroscopy, as de-

Table 3. Polymerization of β -D,L-Butyrolactone Initiated with 2,2-Dibutyl-1,3-dioxane-2-stannane (1a) (0.5 M in Hot Toluene)

polym no.	monom init	temp (°C)	time (days)	yield (%)	η_{inh}^a (dL/g)	i/s	% syndiotactic diads	T_g^c (°C)	T_m^c (°C)
1	50	50	6	70	0.10	0.6/1.0	62	2	61 and 123
2	100	50	6	84	0.11	0.6/1.0	62	4	72
3	200	50	6	0					
4	100	75	3	70	0.17	0.6/1.0	62	8	73
5	200	75	3	81	0.26	0.7/1.0	58	10	74
6	400	75	6	92	0.37	0.8/1.0	55	9	69
7	800	75	6	30	0.18	0.6/1.0	62	8	64

^a Measured at 25 °C in CH₂Cl₂. ^b Ratio of isotactic and syndiotactic diads. ^c From DSC measurements with a heating rate of 20 °C/min.

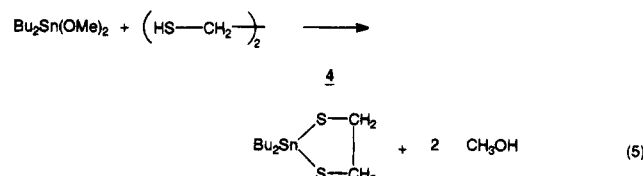
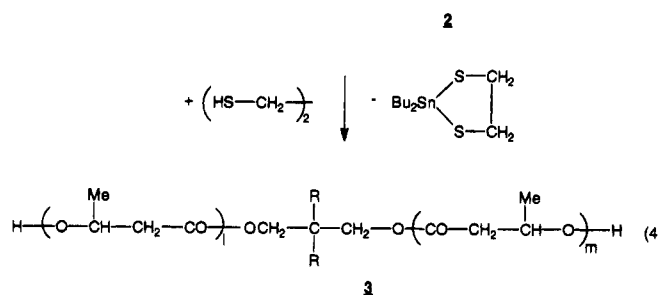
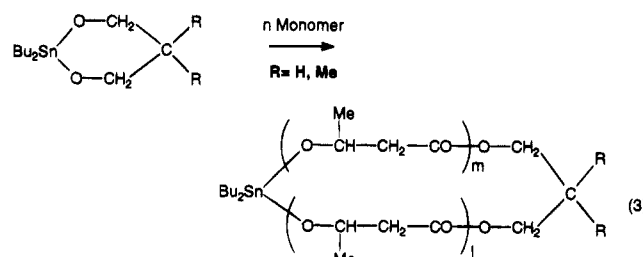
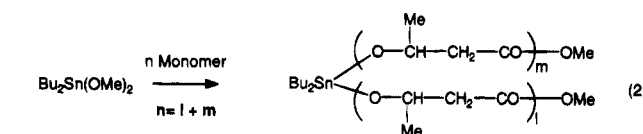
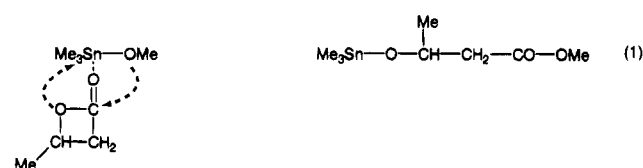
scribed previously.³⁻⁹ The syndiotactic diads were predominant in all cases, but their percentage was relatively low, when compared to the values obtained from Bu₂Sn(OMe)₂-initiated polymerizations.⁶⁻⁹ In agreement with this rather low level of regular stereo-sequences, the DSC measurements revealed melting endotherms which were all below 75 °C (Table 1).

When an analogous series of polymerizations was conducted with **1a** dissolved in chloroform, somewhat better results were found (Table 2). Again no polymerization took place below +50 °C. However, the percentage of syndiotactic diads was slightly higher. When **1a** was dissolved in toluene prior to the addition to the monomer, the yields, viscosities, and tacticities were comparable with those observed for **1b**-initiated polymerizations (Table 3). Nonetheless, the **1a**-initiated polymerizations are remarkable, because the DSC measurements revealed that samples prepared at 50 °C show two melting endotherms: one endotherm in the range 60–70 °C and second one in the range 110–125 °C (Tables 2 and 3 and Figure 1). Obviously, these samples possess a bimodal distribution of syndiotactic blocks. The main fraction of polyester chains contains relatively short blocks comparable to those produced by initiator **1b**. Yet, in addition to that a smaller fraction of chains with relatively long syndiotactic blocks is present, when **1a** is used as initiator at 50 °C. A quite analogous bimodal distribution of the lengths of the syndiotactic block was found for Bu₂Sn(OMe)₂-initiated poly(β -D,L-HBu)⁸ at temperatures ≤ 50 °C. This finding suggests that two different stereoselection mechanisms were operating when Bu₂Sn(OMe)₂ or **1a** was used as initiator. A hypothetical mechanism explaining this phenomenon has recently been discussed.⁸

Finally, it should be mentioned that the initiation with **1a** or **1b** gave slightly higher molecular weights than initiation with other previously studied tin catalysts. In the case of sample no. 6, Table 2, which has the highest inherent viscosity, GPC measurements indicate a weight average molecular weight (M_w) of 32 000 and a M_w/M_n ratio of 1.7. These measurements were evaluated by means of the universal calibration method using commercial polystyrene standards for calibration and by means of the a and K values of the Mark–Houwink equation of polystyrene in tetrahydrofuran.¹⁴ This sample possesses the highest molecular weight of syndiotactic poly(β -D,L-HBu) synthesized by this research group so far.^{3,4} Obviously, this positive result, although not yet satisfactory, is an advantage of the bifunctional initiator.

Mechanistic Aspects. In previous parts of this series Bu₃SnOMe- and Bu₂Sn(OMe)₂-initiated polymerizations of β -lactones and higher membered lactones were reported. It was demonstrated that these tin methoxides like other covalent metal alkoxides initiate an insertion mechanism which involves at least the

following two reaction steps: (a) complexation of the monomer by the initiator via free d-orbitals; (b) “insertion” of the monomer into the metal–O bond (eq 1). In



this connection it was demonstrated that in the case of Bu₂Sn(OMe)₂ both methoxide groups are active, so that two polyester chains grow from one tin atom (eq 2). If the same mechanism is operating in the case of **1a** and **1b**, the consequence is a macrocyclic chain growth according to eq 3. Precipitation of the crude reaction product into an inert nonsolvent, such as diethyl ether, should allow the isolation of the macrocycles thus obtained.

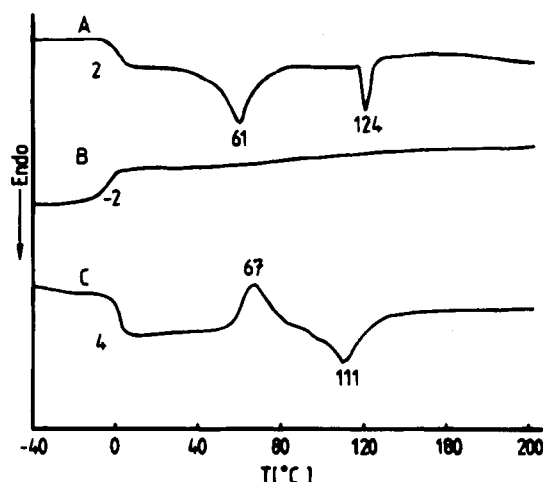


Figure 1. DSC measurements of poly(β -D,L-Hbu) (no. 1, Table 3): (A) first heating; (B) first cooling; (C) second heating (heating/cooling rate 20 °C/min).

Table 4. ^1H NMR Chemical Shifts of 1,3-Propanediol and Some Neopentanediol Derivatives

compd	δ in ppm relative to TMS		
	$-\text{OCH}_2-$	CH_2	CMe_2
$(\text{HOCH}_2)_2\text{CH}_2$	3.84	1.81	
$\text{Bu}_2\text{Sn}(\text{OCH}_2)_2\text{CH}_2$	4.00		
$(\text{CH}_3\text{COOCH}_2)_2\text{CH}_2$	4.13	1.90	
$(\text{HOCH}_2)_2\text{CMe}_2$	3.45		0.88
$\text{Bu}_2\text{Sn}(\text{OCH}_2)_2\text{CMe}_2$	3.61		
$(\text{CH}_3\text{COOCH}_2)_2\text{CMe}_2$	3.88		0.97

Experimental evidence for the assumed macrocyclic chain growth was obtained by ^1H NMR spectroscopy. As illustrated by the data compiled in Table 4, esterification of the OH groups of 1,3-propanediol or neopentanediol shifts the signal of the neighboring CH_2 protons 0.4–0.5 ppm downfield. As illustrated by Figures 2 and 3, the ^1H NMR spectra of poly(β -D,L-Hbu) samples isolated from diethyl ether display the signals of the diol units in exactly those positions expected for a symmetrical esterification of both diol groups. Furthermore, the signals of the Bu_2Sn group show up in an equimolar ratio compared to the diol units.

Additional evidence was obtained from a treatment of the macrocycles with dimercaptoethane (DME), at 25 °C in CH_2Cl_2 solution. Under these conditions a regioselective ring cleavage takes place, so that the Bu_2Sn group is removed in the form of a five-membered heterocycle (eq 4). The fact that Sn–S bonds are more stable than Sn–O bonds is responsible for the success of this cleavage. A model reaction between $\text{Bu}_2\text{Sn}(\text{OMe})_2$ and DME (eq 5) again conducted at 25 °C in CH_2Cl_2 confirms this reaction pathway. The conversion of $\text{Bu}_2\text{Sn}(\text{OMe})_2$ was almost quantitative despite the mild reaction conditions. Treatment of poly(β -D,L-Hbu) with DME yielded ^1H NMR spectra without the signals of the Bu_2Sn group, whereas the signals of the diol units were still there. The quantitative removal of the Bu_2Sn group requires a slight excess of DME in combination with a long reaction time (≥ 24 h) when conducted at 25 °C. With an equimolar amount of DME and a reaction time ≤ 24 h the conversion is incomplete (ca. 90%), either because the reaction is too slow due to the extremely low concentrations of the reactants or because a small amount of DME is lost by oxidation (the reaction mixtures were not deoxygenated). Nonetheless, the treatment of the macrocyclic polyesters with DME has two interesting consequences. Firstly, it is helpful from

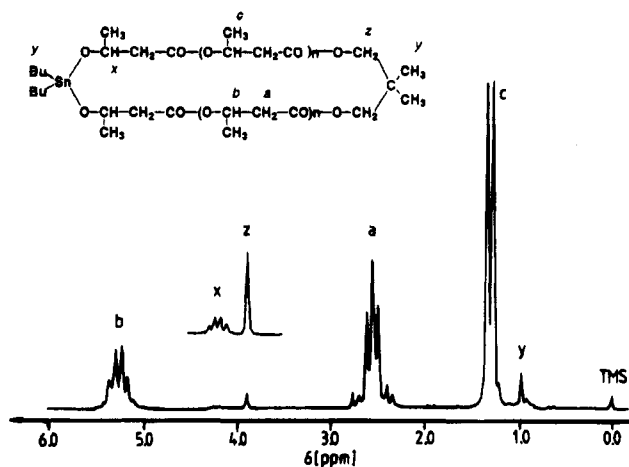


Figure 2. 100 MHz ^1H NMR spectrum of **1b** initiated poly(β -D,L-Hbu) (no. 4, Table 1) and precipitated into Et_2O .

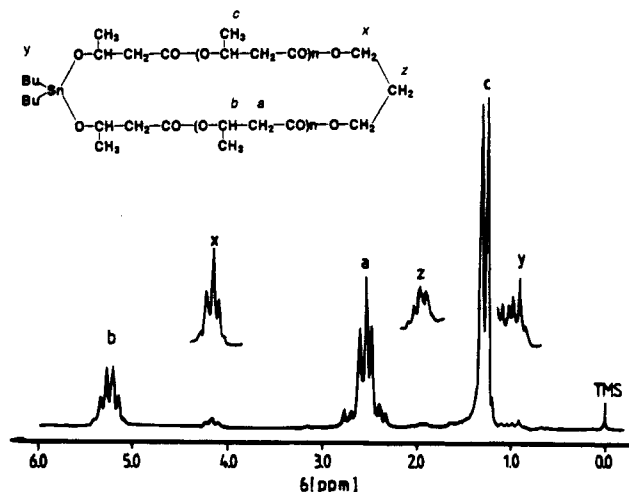


Figure 3. 100 MHz ^1H NMR spectrum of **1a** initiated poly(β -D,L-Hbu) (no. 2, Table 5) isolated after precipitation into Et_2O .

an analytical point of view, and secondly, it enables the synthesis of polyester diols. These polyester diols are in turn useful for a variety of modifications, particularly for chain extension and for the synthesis of triblock or multiblock copolymers.

The selective ring-cleavage of a macrocycle yielding a linear polymer should slightly increase its hydrodynamic volume. Hence the elution time in GPC measurements should slightly decrease provided that the ring-opening is selective enough to avoid additional degradation steps. A series of three poly(β -D,L-Hbu) samples was subjected to GPC measurements with and without treatment with DME. The data listed in Table 5 shows that treatment with DME indeed reduces the elution time. A comparison with three $\text{Bu}_2\text{Sn}(\text{OMe})_2$ -initiated samples confirms our interpretation. In the case of $\text{Bu}_2\text{Sn}(\text{OMe})_2$ -initiated polyesters (eq 2) treatment with DME should lower the molecular weights by half and, thus, increase the elution time. Exactly this result was obtained in all three cases. Taken together, all NMR spectroscopic results, GPC measurements, and model reactions agree in that originally macrocycles are formed which upon treatment with DME yield linear polyester diols.

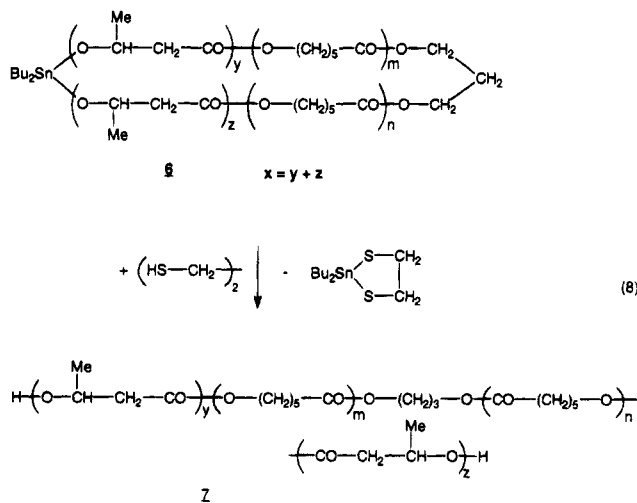
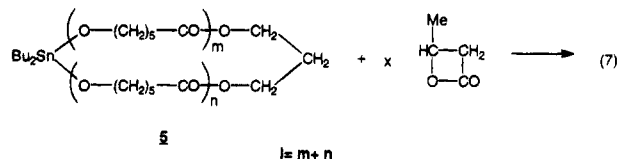
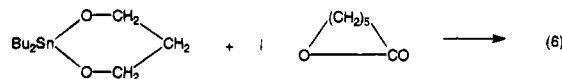
Copolymerizations with ϵ -Caprolactone. The successful homopolymerization of β -D,L-BI with initiator **1a** raised the question, to what extent is this initiator useful for copolymerizations. For analytical reasons

Table 5. Bu₂Sn(OCH₂)₂CH₂-Initiated Polymerizations (Nos. 1–3) and Bu₂Sn(OMe)₂-Initiated Polymerization of β-D,L-Butyrolactone at 75 °C in Bulk

pol	M/I	time (days)	GPC elution times (min)		
			direct precipitation into Et ₂ O ^a	treatment with (HSCH ₂) ₂ 1/1 for 20 h ^b	treatment with (HSCH ₂) ₂ 2/1 for 1 h ^c
1	25/1	1	35.34	35.20	35.26
2	50/1	2	34.10	33.88	33.91
3	100/1	3	32.03	31.59	32.00
4	25/1	1	33.81	34.37	34.05
5	50/1	2	31.74	32.11	32.80
6	100/1	3	30.95	32.06	31.70

^a The reaction product was dissolved in CH₂Cl₂ before precipitation. ^b (HSCH₂)₂ was added to the CH₂Cl₂ solution of the polymerization product (molar ratio 1/1 relative to the initiator) prior to the precipitation into Et₂O. ^c (HSCH₂)₂ was added to the CH₂Cl₂ solution of the polymerization product (molar ratio 2/1 relative to initiator) prior to the precipitation into Et₂O.

(evaluation of NMR spectra) the present work concentrated on copolymerizations of ε-caprolactone (ε-Cap). A first series of copolymerizations, designed to yield block copolymers, was conducted in such a way that ε-Cap was polymerized first (eq 6) and β-D,L-BI was



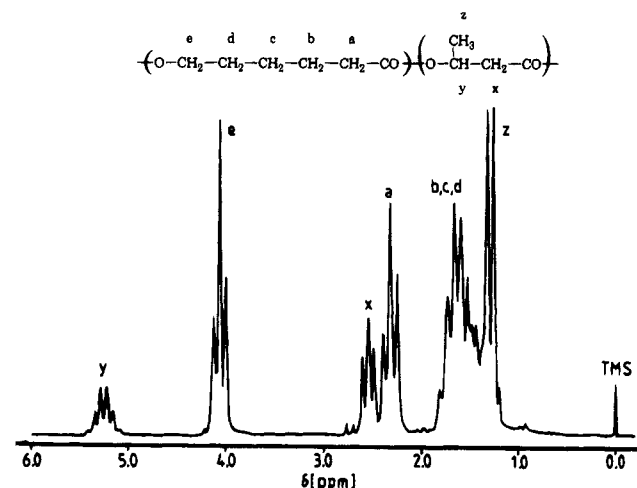
added to the living poly(ε-Cap) 5 (eq 7). The homopolymerizations of ε-Cap (eq 6) were conducted in bulk at 75 °C using M/I ratios of 50/1, 100/1, and 200/1 (Table 6). When the ¹H NMR spectra of the reaction mixture indicated ≥ 95% conversion (after 24 h) the β-D,L-BI was added. Preliminary experiments with reaction times of 1d or 3d (not listed in Table 6) showed that longer reaction times were needed for significant conversion of the less reactive β-D,L-BI. Therefore, all copolymerizations of this series were extended over a period of 12 days.

When the reaction mixtures were analyzed by GPC measurements over the whole reaction time, a slow

Table 6. Batchwise Block Copolymerization of ε-Caprolactone (ε-Cl) and β-D,L-Butyrolactone (β-BI) by Means of Initiator 1a at 75 °C in Bulk

exp no.	ε-Cl ^a /init	time (days)	ε-Cl ^b /β-BI	time (days)	yield (%)	ε-Cl ^c /β-BI	η _{inh} ^d (dL/g)	T _m ^e (°C)	T _c ^f (°C)
1	50/1	1	1/1	12	71	1.7/1	0.58	60	12
2	100/1	1	1/1	12	56	7/1	0.38	63	22
3	200/1	1	1/1	12	45	20/1	0.45	64	25
4	50/1	1	5/1	12	88	6/1	0.21	64	14
5	100/1	1	5/1	12	91	9/1	0.60	64	18
6	200/1	1	5/1	12	87	17/1	0.75	63	23

^a Initial molar monomer/initiator ratio. ^b Molar feed ratio: ε-caprolactone/β-D,L-butyrolactone. ^c Molar composition of the isolated copolymers as determined by ¹H NMR spectroscopy. ^d Measured at 25 °C with c = 2 g/L in CH₂Cl₂. ^e DSC measurements with a heating rate of 20 °C/min. ^f DSC measurements with a heating rate of 20 °C/min.

**Figure 4.** 100 MHz ¹H NMR spectrum of the triblock copolyester 7 (no. 1, Table 6).

decrease of the average molecular weights was found for the first 6 days. The reason for this unexpected observation was detected when the 1a-initiated polymerization of neat ε-caprolactone was studied (in bulk at 75 °C). After the fast polymerization of this monomer, which was almost complete after 24 h, a permanent degradation was found for the following period of 12 days. Obviously, the initially formed high molecular weight poly(ε-caprolactone) is a kinetically controlled product, and the slower “back-biting degradation” drives the entire process in the direction of the thermodynamically controlled equilibrium containing a higher fraction of linear and cyclic oligomers. The high reactivity of dibutyltin alkoxides in such equilibration processes has been demonstrated previously.¹⁵ Thus, the block copolymerization according to eq 7 involves two parallel reactions: firstly, the “back-biting degradation” of Sn–O–caprolactone “chain ends”, and secondly, the polymerizations of β-D,L-BI. Obviously, the degradation process is predominant during the first half of the reaction time.

Nonetheless, block copolymers were isolated after a total reaction time of 13 days, but the ¹H NMR spectra clearly proved (e.g. Figure 4) that the content of β-D,L-Hbu units was in all cases lower than expected from the feed ratio. The ¹³C NMR spectra (e.g. Figure 5A) clearly indicate the blocky sequence. The two CO signals of the blocks are strong, whereas the signals of the “crossover steps” (ε-Cap → β-D,L-Hbu and β-D,L-Hbu → ε-Cap) are weak (for assignments see Figure 9). The CO signal of β-D,L-Hbu blocks exhibits a splitting resulting from isotactic and syndiotactic diads. The

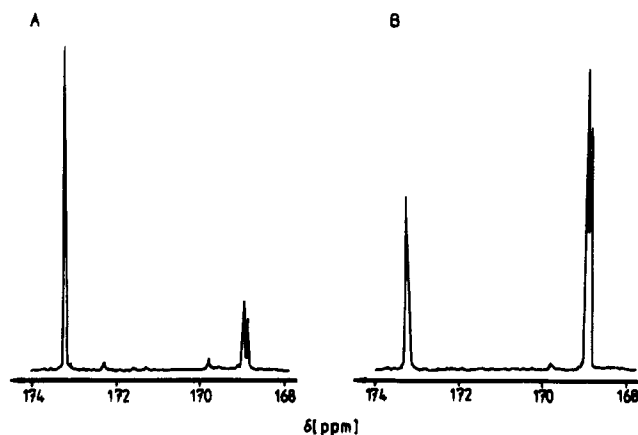


Figure 5. 25.4 MHz ^{13}C NMR spectrum (CO signal): (A) A-B-A triblock copolyester **7** (no. 1, Table 6); (B) A-B-A triblock copolyester **9** (no. 1, Table 7).

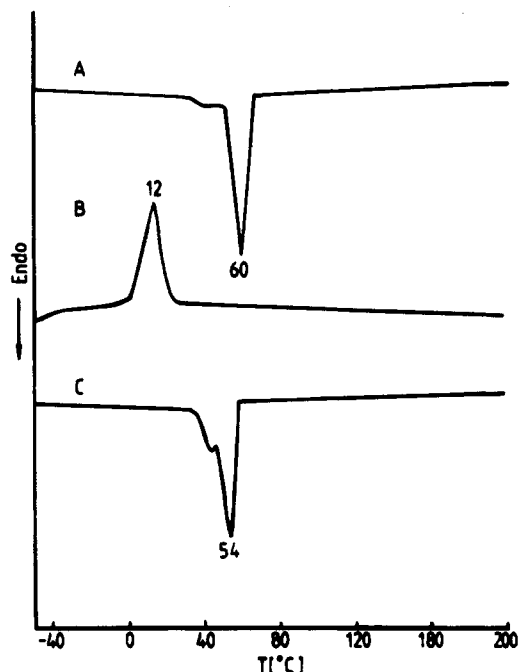


Figure 6. DSC measurements of triblock copolyester **7** (no. 1, Table 6): (A) first heating; (B) first cooling; (C) second heating.

syndiotactic diads prevail with approximately 60%. The particular usefulness of the ^{13}C NMR CO signals for sequence analyses has previously been demonstrated for a broad variety of copolyesters and copoly lactones¹⁶⁻¹⁸ and the results obtained in this work (including Figure 9) agree well with this experience. Finally, the blockiness of the isolated copolyesters of structure **7** and **8** was confirmed by DSC measurements in combination with WAXD powder patterns. As exemplified by Figure 6, all the copolyesters listed in Table 6 contain crystalline blocks of ϵ -caprolactone units. The WAXD powder patterns exclusively display reflections of crystalline poly(ϵ -caprolactone).

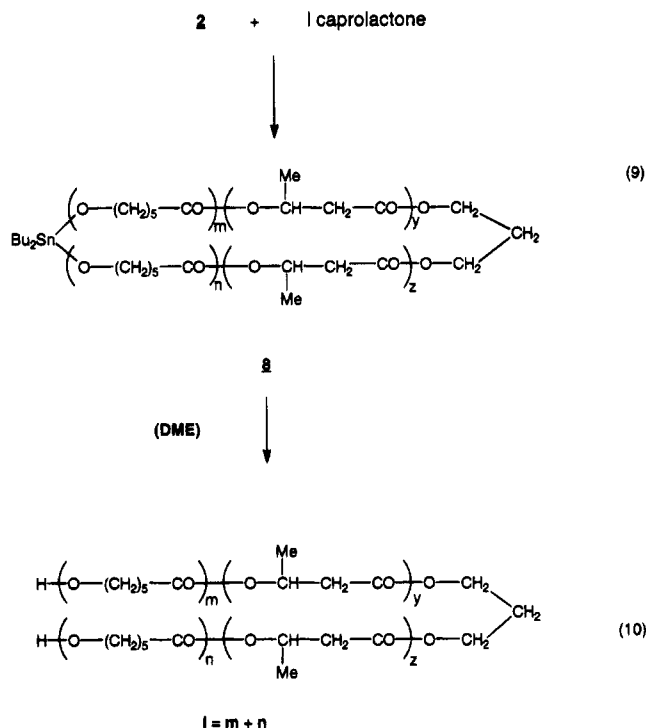
Four more syntheses of block copolyesters were conducted in such a way that macrocyclic poly(β -D,L-Hbu) was prepared by means of **1a** as described above. The isolated cyclic polyester of structure **2** was then dissolved in ϵ -caprolactone (two different quantities; see experimental and Table 7), and the reaction mixtures were thermostated at 75 °C for 5 or 9 days. In this case inherent viscosities and GPC analyses of the reaction

Table 7. Polymerizations of Neat ϵ -Caprolactone in Bulk at 75 °C Initiated with Preformed Macrocyclic Poly(β -D,L-butyrolactone)^a

exp no.	quantity of ϵ -caprolactone (mmol)	time (days)	yield (%)	ϵ -Cap ^b / β -Hbu	η_{inh}^c (dL/g)	GPC retention (min)
1	25	5	59	0.45	0.24	30.2
2	25	9	85	0.60	0.30	30.2
3	50	5	66	0.78	0.25	30.4
4	50	9	82	1.22	0.29	30.0

^a η_{inh} 0.16 dL/g (in CH_2Cl_2 at 20 °C, GPC retention time 31.7 min). ^b Molar composition of the isolated copolyester as determined by ^1H NMR spectroscopy. ^c Measured at 25 °C with $c = 2$ g/L in CH_2Cl_2 .

products revealed that the average molecular weight increased with the conversion of ϵ -caprolactone (Table 7). The precipitated copolyesters of structure **8** (or **9**) possessed a perfect block structure, as evidenced by the ^{13}C NMR spectrum of Figure 5B. Furthermore, both DSC measurements and WAXD powder patterns confirmed the presence of crystalline blocks of poly(ϵ -caprolactone) (Figure 7). Yet, in contrast to the block copolyester **6** or **7** the WAXD powder patterns of copolyesters **8** or **9** also exhibit reflections of crystalline syndiotactic poly(β -D,L-Hbu) blocks. This finding is obviously the result of a more perfect blockiness of the sequence and of a higher molar fraction of the β -D,L-Hbu units. Hence, from a preparative point of view the strategy outlined in eqs 9 and 10 is more satisfactory for the synthesis of perfect block copolyesters than the approach described by eqs 6 and 7.



The triblock copolyesters of structures **8** and **9** are also well suited to demonstrate the role of DME as a "ring-opening agent". When a sample of structure **8** (no. 2, Table 7) was treated with DME (10% molar excess), the elution time of the GPC measurements was reduced from 30.3 to 29.9 min, indicating an increase of the hydrodynamic volume. The ^1H NMR spectra of the precipitated, isolated sample with structure **9** exhibits in the range 3.0–4.0 ppm only one triplet signal at 3.63 ppm, resulting from the CH_2OH end group of the

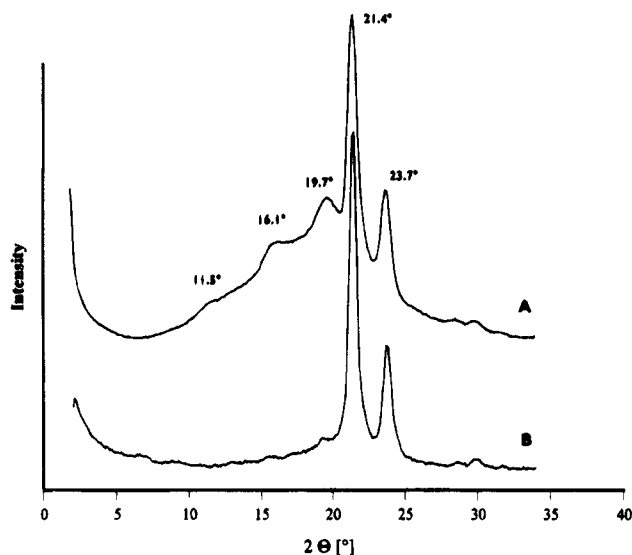


Figure 7. WAXD powder patterns of (A) A-B-A triblock copolyester of structure **9** (no. 1, Table 7) and (B) neat poly(ϵ -caprolactone).

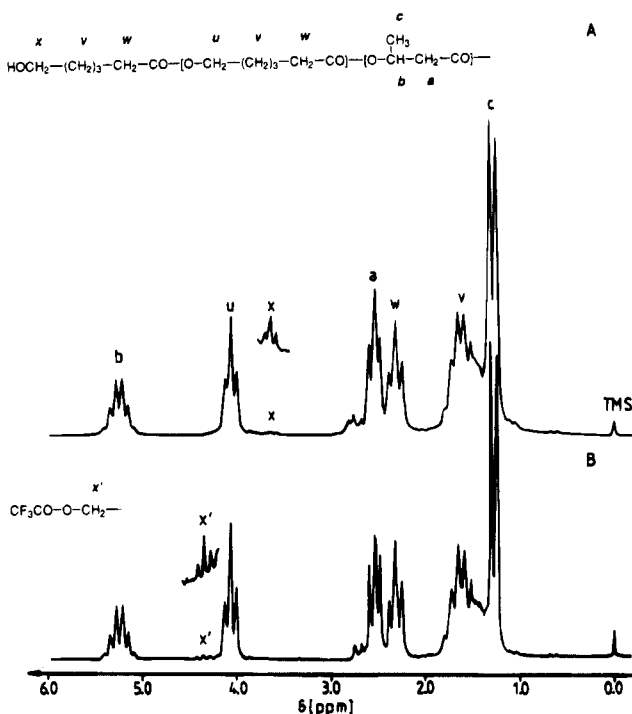


Figure 8. 100 MHz ^1H NMR spectra (in CDCl_3): (A) linear A-B-A triblock copolyester of structure **9** (no. 2, Table 7 after treatment with DME); (B) the same solution after addition of one drop of trifluoroacetic anhydride.

caprolactone A blocks (signal x in Figure 8A). Addition of trifluoroacetic anhydride (one drop) to this solution in CDCl_3 causes rapid esterification and shifts the signal of the $\text{CH}_2\text{OCOCF}_3$ end group ca. 0.5 ppm downfield (x' in Figure 8B). Thus all these results are in perfect agreement with the reactions and the structures outlined in eqs 3, 9, and 10.

Finally, two copolymerizations were conducted with the purpose of synthesizing random copolyesters. The initiator **1a** ($M/I = 100$ or 200) was added to an equimolar mixture of ϵ -Cap and β -D,L-BI, and this reaction mixture was kept at 100°C for 3 days. Both copolymerizations yielded an amorphous syrupy material upon precipitation into diethyl ether. The ^1H NMR spectra indicated a composition close to the feed

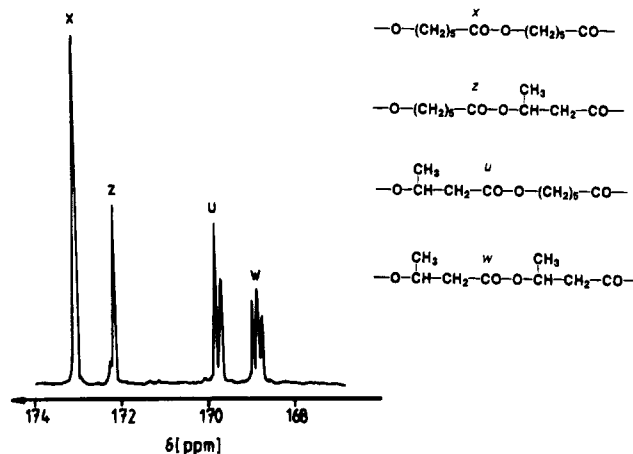


Figure 9. 25.4 MHz ^{13}C NMR spectrum (CO signals) of the random copolyester obtained by **1a** initiated copolymerization of ϵ -Cap and β -D,L-Hbu in bulk at 100°C ($M/I = 200/1$).

ratio, and the ^{13}C NMR spectra proved the formation of a perfectly random sequence (Figure 9) in agreement with the amorphous character of both samples. This result is somewhat surprising, when composition and sequence are exclusively considered as a consequence of a kinetically controlled copolymerization, because β -D,L-butyrolactone is less reactive than ϵ -caprolactone in homopolymerizations. Possibly, transesterification reactions initiated by the active chain ends were involved. However, ester interchange reactions between two polyester chains can be excluded. When a molecular blend of preformed poly(ϵ -caprolactone) and poly(β -D,L-butyrolactone) was doped with initiator **1a**, no transesterification was detectable after 3 or 6 days at 100°C . Taken together, the present study of copolymerization demonstrates that initiator **1a** may be useful for syntheses of both block and random copolyesters, when the reaction conditions are accordingly optimized.

Conclusions

The present work demonstrates that the dioxastannanes **1a** and **1b** are useful initiators for the homo- and copolymerization of β -D,L-Hbu and ϵ -Cap. The results indicate the initial formation of macrocycles by insertion of lactones into both Sn-O bonds. Obviously, the ring-opening polymerization with cyclic initiators provides a particularly easy access to the synthesis of macrocycles in high yields and with controlled molecular weight. The versatility of the initiator **1a** (in combination with DME) is demonstrated by the synthesis of (1) macrocyclic homopolyesters, (2) linear difunctional homopolyesters, (3) macrocyclic block copolyesters, (4) linear triblock copolyesters, (5) macrocyclic random copolyester, (6) linear random copolyester, and (7) variation of the tacticity of poly(β -D,L-Hbu). Further examples for molecular engineering with cyclic initiators will be published in future parts of this series.

References and Notes

- Holmes, P. A. In *Biologically Produced (R)-3-Hydroxyalkane Polymers and Copolymers*; Bassett, D. C., Ed.; Developments in Crystalline Polymers; Elsevier: NY, 1988; Vol. 2, pp 1-65.
- Mobley, D. P. *Plastics from Microbs*; Hanser Publishing: München, New York, 1994; Chapter 2.
- Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *1*, 286.
- Kricheldorf, H. R.; Kreiser-Saunders, J.; Scharnagl, N. *Makromol. Chem. Macromol. Symp.* **1990**, *32*, 285.

- (5) Hocking, P. J.; Marchessault, R. H. *Polym. Bull.* **1993**, *30*, 163.
- (6) Kemnitzer, J. E.; McCarthy, S. P.; Gross, A. *Macromolecules* **1993**, *26*, 1221.
- (7) Kemnitzer, J. E.; McCarthy, S. P.; Gross, A. *Macromolecules* **1993**, *26*, 6144.
- (8) Kricheldorf, H. R.; Lee, S.-R.; Scharnagl, N. *Macromolecules* **1994**, *27*, 3139.
- (9) Kricheldorf, H. R.; Lee, S.-R. *Macromol. Chem. Phys.* **1994**, *195*, 2299.
- (10) Kricheldorf, H. R.; Lee, S.-R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 502.
- (11) Pommier, J. C.; Valade, J. *J. Organomet. Chem.* **1968**, *12*, 433.
- (12) Mehrotra, R. C.; Gupta, V. D. *J. Organomet. Chem.* **1965**, *4*, 145.
- (13) Smith, P. J.; White, R. F. M. *J. Organomet. Chem.* **1972**, *40*, 341.
- (14) van Dijk, J. A. P. P.; Smith, J. A. M.; Kohn, F. E.; Feijen, J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 197.
- (15) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286.
- (16) Kricheldorf, H. R. *Makromol. Chem.* **1978**, *179*, 2133.
- (17) Kricheldorf, H. R.; Mang, T.; Jonte, M. *Makromol. Chem.* **1983**, *196*, 955.
- (18) Kricheldorf, H. R.; Kreiser-Saunders, I. *Makromol. Chem.* **1987**, *188*, 1861.

MA950416A