Polycaprolactone-Based Block Copolymers. 1. Synthesis by Anionic Coordination Type Catalysts

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ABSTRACT: Bimetallic μ-oxo alkoxides are very active anionic coordination type catalysts in the living polymerization of ϵ-caprolactone. These compounds have a well-defined composition which can be systematically modified. It is proposed that at least half the alkoxy groups of these catalysts are replaced by carboxylate ones and the remaining alkoxy groups by any hydroxyl-terminated polymer PX. These new polymer PX-supported catalysts are powerful tools in tailoring poly(ϵ-caprolactone) block copolymers with well-controlled molecular parameters.

Introduction

Multiphase polymer systems have been of great scientific and technological interest in the past 2 decades.[1-4] These systems represent indeed the best means of combining the useful properties of different molecular species. In addition, they often have special properties, examples being the high-impact thermoplastics and the thermoplastic elastomers.[5,6]

Multiphase polymer systems can be prepared by two different routes: incompatible polymer blending or block and graft copolymerization.[1-4] Block and graft copolymers are the most attractive systems; they exhibit the best balance of properties because of optimum interfacial adhesion. They can also be used as emulsifiers in polymer blends.[4]

Interest in poly(ϵ-caprolactone) (PCL) is mainly due to its miscibility with different commercial polymers (SAN, ABS, PVC, nitrocellulose),[7-10] its biodegradability,[7,11] its ability to disperse pigments, and its low-temperature adhesiveness.[7]

Several patents and scientific papers have dealt with the synthesis and applications of block and graft copolymers based on PCL. ϵ-Caprolactone (ϵ-CL) has been grafted onto polymeric backbones carrying hydroxyl pendant groups.[12] It has also been polymerized by living macromolecular carbanions or alcoholates:[13,14] the copolymerization yields are, however, low and the molecular parameters poorly controlled. The block copolymers so obtained have been evaluated to improve the impact strength of SAN,[15] the ozone resistance of SBR elastomers, or the adhesion of styrene, butadiene, and vinyl chloride containing polymers.[16]

The difficulties encountered in ϵ-caprolactone block copolymerization have prompted us to explore a more suitable catalytic pathway. Several papers from this laboratory have established the perfectly "living" character of the ϵ-caprolactone polymerization initiated by bimetallic μ-oxo alkoxides under mild conditions;[17,18] the aim of this paper is to report the application of these anionic coordinative type catalysts to the block copolymerization of ϵ-caprolactone.

Experimental Section

Reagents. Benzene, toluene, and chlorobenzene were dried by refluxing over CaH_2 or $LiAlH_4$ for at least 48 h and distilled under an argon atmosphere.

ϵ-Caprolactone and styrene were dried over CaH_2 at room temperature and purified by distillation under reduced pressure (10^{-2} mmHg).

Butadiene was passed through columns containing desiccated barium oxide, Drierite, and 3-Å molecular sieves; it was then condensed at −80 °C into a vessel containing *n*-butyllithium and finally distilled into the polymerization flask.

2-Ethylhexanoic acid was dried over 3-Å molecular sieves and distilled under reduced pressure.

Hydroxyl-terminated polystyrene (PST) and polybutadiene (PBD) (prepared as indicated below) were dried by azeotropic distillation of benzene. The polymer was dissolved in dried benzene, which was then distilled off the flask (three times); after a final addition of fresh dried benzene, the flask was connected to another one containing styryllithium oligomers, and benzene was distilled under reduced pressure from one flask to the other and back four times.

Bimetallic μ-Oxo Alkoxides. Di-μ-oxo-bis[bis(1-methylethoxy)aluminum]zinc, referred to as aluminum zinc μ-oxo isopropoxide, was prepared by thermal condensation between aluminum isopropoxide and zinc acetate in a 2/1 molar ratio at about 200 °C as previously described.[19]

Replacement of the isopropoxy groups of Al_2Zn μ-oxo isopropoxide by 2-ethylhexanoate ones was carried out under an argon atmosphere and dry conditions. A 5×10^{-2} mol/L solution of 2-ethylhexanoic acid in benzene was added dropwise into an Al_2Zn μ-oxo isopropoxide solution in toluene (10^{-1} mol/L) warmed to 110 °C; the benzene/isopropyl alcohol azeotrope was regularly distilled off (T_{eb} = 71.5 °C).

The substitution of the isopropoxy groups of the bimetallic compounds by hydroxyl-terminated polymers was similarly carried out. The dried solution of polymer in benzene was added into the dried solution of the bimetallic compound in toluene; benzene/isopropyl alcohol azeotrope was then distilled off continuously.

The concentration of the bimetallic compound solutions was determined by complexometric titration of Zn by EDTA.[19] The isopropoxy group content was determined by quantitative analysis of the isopropyl alcohol resulting from its hydrolysis by chlorohydric acid: the amount of isopropyl alcohol was determined by GLC (Intersmat IGC 15), using *tert*-butyl alcohol as internal reference.

Synthesis of ω-Hydroxy-PST and -PBD. A 1 mol/L solution of *sec*-butyllithium (obtained from Metall Gesellschaft, West Germany) was added dropwise under stirring into a solution of styrene in toluene at 0 °C. Once the color corresponding to styryl anions persisted, the amount of *sec*-BuLi corresponding to the required [monomer]:[catalyst] ratio was added, the polymerization glass flask was sealed off under vacuum, and the solution was stirred overnight at room temperature. Into a second flask connected to the polymerization flask through a break seal were successively introduced a solution of *n*-BuLi and a previously dried (over CaH_2) solution of ethylene oxide in benzene (20%). This monomer does not anionically polymerize in the presence of a Li counterion. After the second vessel was sealed off, the break seal was broken and the ethylene oxide (a fivefold excess) was distilled into the poly(styryllithium) solution cooled at 0 °C.

For preparation of ω-hydroxy-PBD, three glass flasks (F_1, F_2, and F_3) were connected to the glass polymerization flask (PF) through break seals (except for F_1). PF was rinsed with a solution of styryllithium oligomers in benzene; once this solution was collected into F_1, the required amount of benzene was distilled from F_1 into PF and F_1 was sealed off. A suitable amount of *sec*-BuLi was added into PF through a self-sealing device, which

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was also sealed off. Butadiene was condensed into F_2 as explained above; after it was distilled into PF, F_2 was also sealed off. The butadiene polymerization was conducted for 2 h at 0 °C and 16 h at 50 °C. F_3 was used to introduce the ethylene oxide as previously explained.

PST and PBD were recovered by precipitation into acidified methanol and washed with methanol before drying. The hydroxyl functionality was determined by acetylating the hydroxyl groups with acetic anhydride in pyridine. The acetate groups were analyzed by infrared spectroscopy: their absorbance at 1737 cm^{-1} was compared to the absorbance of the aromatic unsaturations at 1600 cm^{-1} and related to a preliminary established calibration curve based on ethyl acetate–polystyrene mixtures of known composition.

Copolymerization Procedure and Characterization of Copolymers. Copolymerizations were carried out under stirring and an argon atmosphere in a previously dried flask. Solvent (benzene or toluene), ϵ-caprolactone, and catalyst were successively added through a self-sealing device, which was then sealed off. The monomer concentration was 1 mol/L, and the copolymerization took place at room temperature, except for [monomer]:[catalyst] ratios higher than 300, for which the temperature was 50 °C. The copolymer was precipitated into acidified methanol; 5% antioxidant (Irganox 1010) was added to methanol before precipitating PBD-based copolymers.

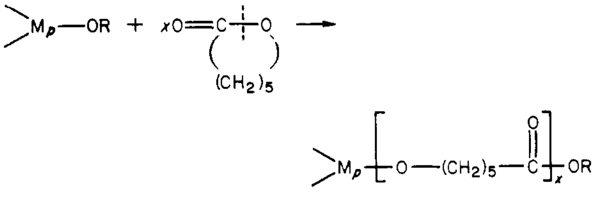
Molecular weights were determined with a vapor pressure osmometer (Knauer) or a membrane osmometer (Hewlett-Packard, Model 502) in toluene at 45 °C. A gel permeation chromatograph (Waters 200), equipped with columns filled with 3×10^3, 3×10^4, 3×10^5, and 10^7 Å Styragels, was also used in tetrahydrofuran (THF) at 25 °C. Thanks to the viscometric relations in THF at 25 °C for PST ($[\eta] = 1.25 \times 10^{-4}M^{0.717}$[20]), PBD ($[\eta] = 4.57 \times 10^{-4}M^{0.693}$[20]), and PCL ($[\eta] = 1.09 \times 10^{-3}M^{0.60}$[21]), the universal calibration method could be applied, using polystyrene standards (Pressure Chemical Co). The samples' polydispersity was determined by Pickett's calculation method.[22]

The copolymer composition was determined by elemental analysis or from ^{1}H NMR spectra recorded on a Varian HA-100 spectrometer.

PBD Degradation. To a solution of PBD (0.5%) in chlorobenzene were added, per gram of PBD, 2 mL of a solution of OsO_4 (5%) in benzene, 20 mL of a solution of *tert*-butyl hydroperoxide in *tert*-butyl alcohol, and 1 mL of benzaldehyde when PBD and PCL were simultaneously present. The solution was refluxed at 90 °C for 15 min; after cooling, it was concentrated under reduced pressure and finally poured into methanol. The degradation products of PBD were soluble in methanol; those of PCL were not.

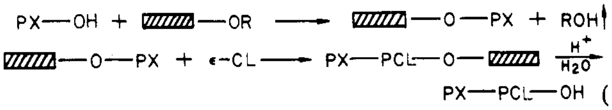
Results and Discussion

Principle of the ϵ-Caprolactone (ϵ-CL) Block Copolymerization. The μ-oxo alkoxides have the general formula $M_d-[O-M_p(OR)_{p-1}]_d$, where M_d and M_p are di- and tri- or tetravalent metals, respectively, and OR is an alcoholate group with at least three carbon atoms; the aluminum zinc μ-oxo isopropoxide is, among others, a very attractive catalyst in the ϵ-CL polymerization.[17,18,23-25] The propagation has a perfectly living character and proceeds through a selective acyl-oxygen cleavage of the lactone with insertion into the M_p–OR bond of the catalyst (eq 1). The kinetic and mechanistic details of this homopolymerization have been reported elsewhere,[18,23] and (ϵ-caprolactone-*b*-β-propiolactone) copolymers have been synthesized, thanks to the living character of the propagation process.[26] It is of prime importance to note that the alcoholate group of the catalyst is present as an end group in the polyester formed (eq 1). Furthermore, the alcoholate group can be exchanged for another one according to eq 2. R'OH must be a more acidic and less volatile alcohol than ROH. It is therefore attractive to substitute the alkoxy groups of the bimetallic μ-oxo alkoxides by a hydroxyl-terminated polymer PX (since many of them are presently available) and to evaluate the so modified bimetallic compounds as initiators of ϵ-CL polymerization. The proposed scheme of ϵ-CL block copolymerization can accordingly be summarized as in eq 3, where the shaded box represents a polymerization site of a bimetallic catalyst and PX–OH any ω-hydroxyl-terminated polymer.



(1)

$$M_d-[O-M_p(OR)_{p-1}]_d + d(p-1)R'OH \rightarrow M_d-[O-M_p(OR')_{p-1}]_d + d(p-1)ROH\uparrow \quad (2)$$



(3)

Substitution of the Alkoxy Groups of the Bimetallic Oxo Alkoxides by Hydroxyl-Terminated Polymers. When aluminum zinc μ-oxo isopropoxide is used, a secondary and volatile alcohol (T_{eb} of isopropyl alcohol: 71.5 °C) is formed and the equilibrium of the substitution reaction (eq 2) can accordingly be completely displaced in the presence of a primary alcohol terminated polymer.

The association of the bimetallic μ-oxo alkoxides in a nonpolar solvent is already well-documented;[23,27] a deassociating solvent (chlorobenzene) has been therefore selected to favor the completeness of the substitution. The OR/OH stoichiometry is also carefully adjusted to 1/1. With an ω-hydroxyl-terminated polystyrene (PST) with a number-average molecular weight ($\bar{M}_n$) of 6000 and an experimental hydroxyl functionality (f_{OH}) of 1.03, only a partial substitution of the alkoxy groups of the catalyst is observed (72%). That kind of dissapointing result has been systemically observed, and the addition of ϵ-CL leads exclusively to the formation of a mixture of homopolymers PCL and PST. That indicates that, whereas it is not possible to completely substitute the alkoxy groups of the catalyst, the unsubstituted groups preferably initiate the ϵ-CL homopolymerization.

To avoid the above-mentioned difficulties, we have considered systematic modifications of the catalyst; it should be possible to completely substitute the remaining Al–OR sites by a macromolecular alcohol by reducing the number of polymerization sites per catalyst mole. An exploratory investigation has established that the complete substitution of the alkoxy groups of the catalyst by carboxylate ones (eq 4) is responsible for the total inactivation of the bimetallic compound: no polyester is formed when ϵ-CL is added to μ-oxo-(2-ethylhexanoato)$_4Al_2O_2Zn$ (I) for 20 days at 50 °C. The choice of 2-ethylhexanoic acid has been prompted by its low reactivity toward the Al–O–Zn bonds ($pK_a = 5.2$) and its hydrocarbon backbone which enhances the solubility of the final bimetallic compound in organic media. Accordingly a partial substitution of the alkoxy groups of the catalyst by low molecular weight carboxylates can be proposed to reduce the number of potential insertion sites per catalyst molecule; details of the structural and kinetic characteristics of these new entities will be published elsewhere.[28]

$$Zn-[O-Al(OR)_2]_2 + 4R'COOH \rightarrow Zn-[O-Al(OOCR')_2]_2 + 4ROH\uparrow \quad (4)$$

$$R = \text{isopropyl};\ R' = CH(CH_2CH_3)(CH_2)_3CH_3$$

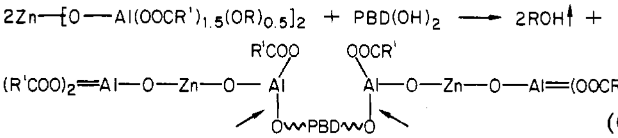
Table I
Results of Koltoff's Degradation Method Applied to Polybutadiene (PBD) and Poly(ϵ-caprolactone) (PCL)

sample	$\bar{M}_n$ initial	$\bar{M}_n$ after degradation	polymer recovd after degradation, %
$PBD(OH)_2$	4 400		0
PCL-1	10 500	5 700	92
PCL-2	30 500	8 200	88
PCL-3[a]	14 500	14 000	98

[a] Sample previously extracted with EDTA.

Use of Modified Bimetallic Compounds to Prepare Poly(ϵ-caprolactone-*b*-butadiene-*b*-ϵ-caprolactone) Copolymer. Three of the four isopropoxy groups of Al_2Zn μ-oxo isopropoxide are first substituted by slow addition of a stoichiometric amount of 2-ethylhexanoic acid (eq 5). The so modified bimetallic catalyst (II) is then added to α,ω-dihydroxypolybutadiene (PBD) in a 1:2 [PBD]:[catalyst] ratio (eq 6). PBD is by now end-capped by two bimetallic entities, each of them carrying one potential insertion site for the lactone (marked by an arrow in eq 6), all other Al–O bonds being inactive.

$$Zn-[O-Al(OR)_2]_2 + 3R'COOH \longrightarrow \underset{\text{II}}{Zn-[O-Al(OOCR')_{1.5}(OR)_{0.5}]_2} + 3ROH\uparrow \quad (5)$$



$$2Zn-[O-Al(OOCR')_{1.5}(OR)_{0.5}]_2 + PBD(OH)_2 \longrightarrow 2ROH\uparrow + \underset{\text{III}}{(R'COO)_2{=}Al-O-Zn-O-\overset{R'COO}{\underset{O\sim PBD\sim O}{Al\quad\quad Al}}-O-Zn-O-Al{=}(OOCR')_2} \quad (6)$$

III

These two successive substitution steps proceed in toluene and are practically quantitative, as proved by the experimental amount of isopropyl alcohol recovered (GLC analysis); it is to be noted that the functionality of the α,ω-dihydroxy-PBD used amounts to 1.8, its $\bar{M}_n$ to 4400, and its $\bar{M}_w/\bar{M}_n$ to 1.6 (Butarez HTS from Phillips Petroleum Co). ϵ-CL is then added to a toluene solution of catalyst III at 25 °C; the [monomer] (M) to [catalyst] ratio or [M]/0.9[III] is 300 and the initial monomer concentration $[M]_0$ is 1 mol/L. After 72 h, the ϵ-CL conversion is as high as 98%. The extraction of the crude polymer with hexane at -20 °C indicates the absence of homopolybutadiene; the $\bar{M}_n$ of this product is 35 000, in accordance with the theoretical value expected from the [M]/0.9[III] ratio (34 200). The structure of the copolymer obtained has, however, to be determined to establish whether every Al–O–PBD bond really initiates ϵ-CL polymerization or not. It is necessary to selectively degrade the PBD sequence and to analyze recovered polyester sequences to establish if this copolymer is a diblock or a triblock or a mixture of these two species. Koltoff's method, based on the action of hydroperoxides in the presence of osmium tetraoxide was selected to degrade the polydiene block.[29] Preliminary tests on homopolybutadiene and homopolyester (obtained with bimetallic oxo alkoxides) established the efficiency and the selectivity of this method. The results gathered in Table I agree with a total degradation of PBD and complete integrity of PCL when previously extracted with EDTA (to completely eliminate any trace of metals). Once mixtures of PBD and carefully purified PCL are submitted to the same treatment, PCL is only slightly modified (Table II); addition of benzaldehyde as a radical inhibitor would seem to be beneficial (Table II). By applying to the copolymer the above-defined degradation method, we recovered PCL sequences with an $\bar{M}_n$ of 17 000; this $\bar{M}_n$ is to be compared to the expected values for pure diblock (30 600) and triblock (15 300) copolymers.

Table II
Results of Koltoff's Degradation Method, Modified by the Addition of Benzaldehyde and Applied to a Mixture of PBD and PCL[a]

initial % of PBD	benzaldehyde	PCL recovd after degradation, %	$\bar{M}_n$ of PCL initial	$\bar{M}_n$ of PCL after degradation
10	no	97	14 500	13 500
20	no	95	14 500	13 500
10	yes	98	14 500	14 000
20	yes	97	14 500	14 000

[a] Previously extracted with EDTA.

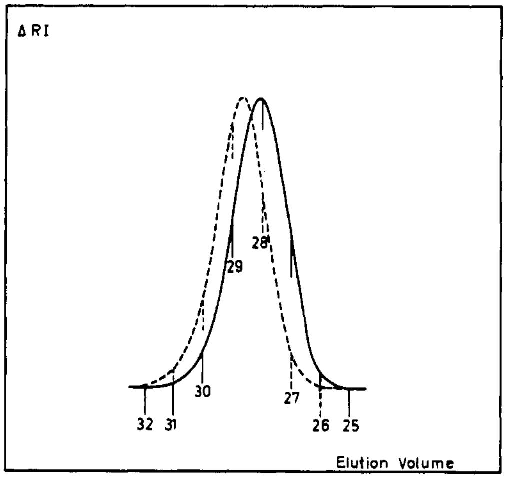


Figure 1. Gel permeation chromatograms of (ϵ-caprolactone-*b*-butadiene-β-ϵ-caprolactone) copolymer (—) and its corresponding PCL blocks (- - -).

Figure 1 compares the gel permeation chromatograms of the copolymer (PI = $\bar{M}_w/\bar{M}_n$ = 1.5) and the PCL sequences (PI = 1.4). The results obtained agree essentially with the triblock copolymer formation, in spite of the very slight discrepancy between theoretical and experimental $\bar{M}_n$ values. The formation of a small amount of diblock copolymer is, however, to be expected on the basis of the imperfect functionality (1.8) of the starting α,ω-dihydroxy-PBD. From the experimental $\bar{M}_n$ value of the PCL sequences (17 000) and their theoretical value in diblock (30 600) and triblock (15 300) copolymers, the mole fraction of triblock is calculated to be 0.89. It is accordingly evident that both PBD end groups of entity II are active catalytic sites for ϵ-CL polymerization.

In conclusion, the use of isopropoxy-(2-ethyl-hexanoate)$_3Al_2O_2Zn$ (II) as a modified catalyst is a very efficient method to prepare triblock copolymers with two external PCL sequences.

Synthesis of Poly(styrene-*b*-ϵ-caprolactone) and Poly(butadiene-*b*-ϵ-caprolactone) Copolymers from Modified Bimetallic Catalysts. Al_2Zn μ-oxo isopropoxide is modified by substituing either two or three of its isopropoxy groups by 2-ethylhexanoate ones; the remaining isopropoxy groups are then substituted by ω-hydroxy-PST ($\bar{M}_n$ = 6000; f_{OH} = 1.03) and two new catalytic species: i.e., $(PST)_2$-(2-ethylhexanoate)$_2Al_2O_2Zn$ (IV) and PST-(2-ethylhexanoate)$_3Al_2O_2Zn$ (V) are obtained. In both cases, the substitution reactions are complete as established by the absence of isopropyl alcohol in the hydrolysis products of IV and V. Catalysts IV and V polymerize ϵ-CL (1 mol/L

Table III
ϵ-Caprolactone Block Copolymerization Initiated by $(PST)_2$-(2-ethylhexanoato)$_2Al_2O_2Zn$

fractions[a]		theor copol comp, %	comp of crude product, %	% vs. initial PST
PCL homo	I	—	—	—
PCL block	II	52.5	49	87
PST block		47.5	44.5	
PST homo	III	—	6.5	13

[a] I and II are insoluble in 70/23/7 cyclohexane/hexane/toluene; I is soluble in acetic acid while II is not. III is soluble in 70/23/7 cyclohexane/hexane/toluene.

Table IV
ϵ-Caprolactone Block Copolymerization Initiated by PST-(2-ethylhexanoato)$_3Al_2O_2Zn$

fractions[a]		theor copol comp, %	comp of crude product, %	% vs. initial PST
PCL homo	I	—	—	—
PCL block	II	30	28	90
PST block		70	65	
PST homo	III	—	7	10

[a] See Table III footnote.

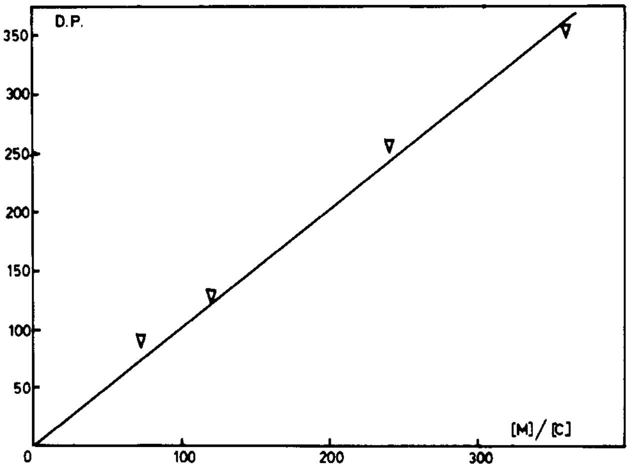


Figure 2. Relationship between experimental and theoretical degree of polymerization (DP) of the poly(ϵ-caprolactone) sequences initiated by $(PST)_2$-(2-ethylhexanoato)$_2Al_2O_2Zn$ in toluene at 25 °C: (—) theoretical; (▽) experimental points.

solution in toluene) at 25 °C; the [M]:[Al–O–PST] ratio is fixed to 60. After 17 h, the ϵ-CL conversion reaches 84% with catalyst IV and 35% with V. The crude product is extracted with selective solvents of PCL (acetic acid) and PST (a 70/23/7 mixture of cyclohexane/hexane/toluene), respectively. The absence of any trace of homo-PCL is clearly put in evidence, whereas small amounts of homo-PST are present as reported in Tables III and IV. In both cases, the percentage of noncopolymerized PST is very similar (10% and 13%); this percentage is strongly related to the dryness of solvent and reagents, as it can reach 33% (catalyst IV) or 43% (catalyst V) when the products used are only dried by azeotropic distillation of benzene. The ϵ-CL block copolymerization is a living propagation mechanism (Figure 2), that is, first order in monomer (Figure 3) and second order in catalyst (Figure 4), as established on the basis of the kinetic equation

$$\ln([M]_0/[M]) = k_0[C]^{\alpha}t \qquad (7)$$

with [C] the catalyst concentration and α the order in catalyst. Once attached to the bimetallic catalyst, the PST chains have, therefore, no effect on the polymerization mechanism of ϵ-CL;[23] they, however, decrease the absolute polymerization rate, as seen in Table V. This clearly illustrated influence seems rather unexpected in terms of a possible steric hindrance by the polymer chain to the approach of the monomer and might be due more probably to a back-biting interaction of this polymer's π electrons to the catalyst coordination sites.

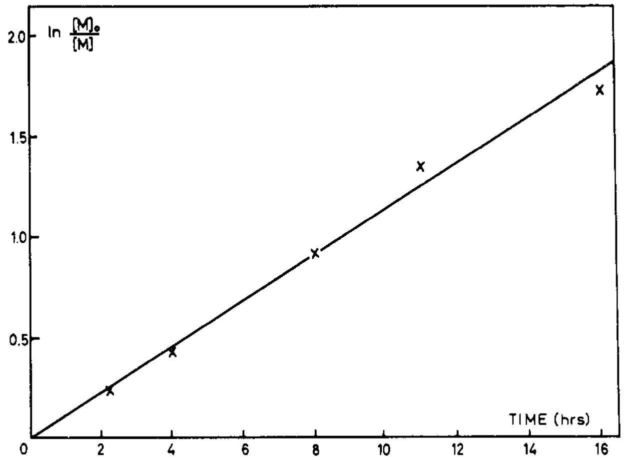


Figure 3. Kinetics of ϵ-caprolactone copolymerization initiated by $(PST)_2$-(2-ethylhexanoato)$_2Al_2O_2Zn$ in toluene at 25 °C.

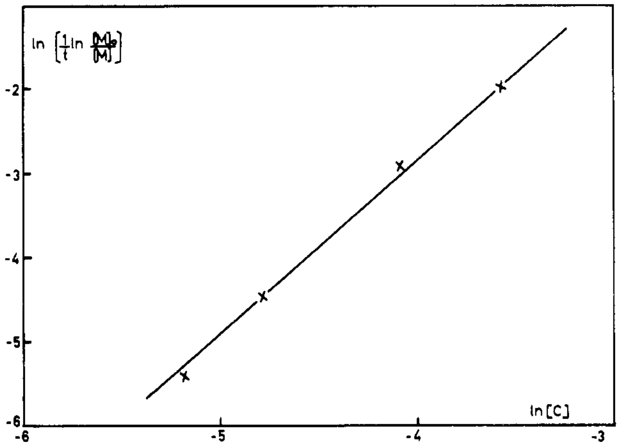


Figure 4. Determination of the order in catalyst in the ϵ-caprolactone copolymerization initiated by $(PST)_2$-(2-ethylhexanoato)$_2Al_2O_2Zn$ in toluene at 25 °C.

Table V
Substitution of the Isopropoxy (OR) Groups of Al,Zn μ-Oxo Isopropoxide by 2-Ethylhexanoate (OOCR') and Poly(styreneoxy) (OPST) Ones and Its Effect on ϵ-Caprolactone Polymerization Rate

no. of OR per catalyst	no. of OOCR per catalyst	no. of OPST per catalyst	$t_{1/2}$,[a] h
2	2	0	6
0	2	2	10
1	3	0	25
0	3	1	70

[a] $t_{1/2}$ is the half-polymerization time of ϵ-caprolactone in toluene (1 mol/L) at 25 °C; [monomer]/[catalyst] = 140.

High molecular weight PST- and/or PBD-based block copolymers ($\bar{M}_n$ up to 3 × 10^5) have been prepared from isopropoxy-(2-ethylhexanoate)$_3Al_2O_2Zn$ or compound II. In these cases, only one polymeric chain (PST or PBD) was bound per catalyst molecule in order to limit the viscosity of the copolymerization medium without significant reduction of the initial concentration of the polymer-supported catalyst. The amount of noncopolymerized PST or PBD ($\bar{M}_n \simeq$ (1–1.5) × 10^5) is around 10% when the polymerization medium is carefully dried; a correct stoichiometry (catalyst/ω-hydroxyl polymer) and a complete hydroxyl functionalization are, of course, important factors to avoid the presence of homopolymers. Generally, the polydispersity of the block copolymers prepared in that way is around 1.2. Alternatively, the coupling of these OH-terminated diblock copolymers by means of classical methods (diisocyanates, phosgene) can lead to the preparation of the corresponding PX–PCL–PX triblock materials.

In conclusion, the new polymer-supported bimetallic compounds herein described provide pathways to the synthesis of numerous PCL-based diblock and triblock copolymers. When the hydroxyl-terminated preformed block is prepared by living anionic polymerization, this technique further enables one to tailor a whole set of new materials with a broad range of accurately controlled molecular parameters. Several series of various copolymers have been prepared by applying this new synthetic method; their physico-mechanical behavior,[21,24] their liquid crystalline structures in the presence of a preferential solvent of one block,[30-32] and their role as additives in polymer blends[21,24,33] have been studied and are published elsewhere.

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References and Notes

(1) Aggarwal, S. L. *Polymer* **1976**, *17*, 938.
(2) Schmitt, B. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 273.
(3) Cooper, S. L.; Estes, G. E. *Adv. Chem. Ser.* **1979**, *No. 176.*
(4) Paul, D. R.; Newman, S. *Polym. Blends* **1978**, *1*, *2.*
(5) Bucknall, C. B. "Toughened Plastics"; Applied Science Publishers Ltd.: London, 1977.
(6) Holden, G.; Bishop, E. T.; Legge, N. R. *J. Polym. Sci., Part C* **1969**, *26*, 37.
(7) Union Carbide, Bulletin F 42501, 1969.
(8) Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1109.
(9) Koleske, J. V.; Lundberg, R. D. *J. Polym. Sci., Part A-2* **1969**, *7*, 795.
(10) Seefried, C. G., Jr.; Koleske, J. V. *J. Test. Eval.* **1976**, *4*, 220.
(11) Potts, J. E.; Clendinning, R. A.; Ackart, W. B.; Niegisch, W. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1972**, *13*, 629.
(12) Union Carbide, U.S. Patents 3 855 357 (1973) and 3 816 566 (1974). Pilato, L. A.; Koleske, J. V.; Joesten, B. L.; Robeson, L. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1976**, *17*, 824.
(13) Hsieh, H. L. *J. Appl. Polym. Sci.* **1978**, *22*, 1119.
(14) Nobutoki, K.; Sumimoto, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1741.
(15) Clark, E.; Childers, C. W. *J. Appl. Polym. Sci.* **1978**, *22*, 1081.
(16) Phillips Petroleum Co., U.S. Patents 3 652 720 (1972) and 3 666 701 (1972).
(17) Hamitou, A.; Jerome, R.; Hubert, A. J.; Teyssie, Ph. *Macromolecules* **1973**, *6*, 651.
(18) Hamitou, A.; Ouhadi, T.; Jerome, R.; Teyssie, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865.
(19) Ouhadi, T. Ph.D. Thesis, University of Liège, 1973.
(20) Kraus, G.; Stacy, C. J. *J. Polym. Sci., Part A-2* **1972**, *10*, 657.
(21) Heuschen, J. Ph.D. Thesis, University of Liège, 1977.
(22) Balke, S.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1969**, *13*, 1391.
(23) Ouhadi, T.; Hamitou, A.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1976**, *9*, 927.
(24) Teyssie, Ph.; Bioul, J. P.; Hamitou, A.; Heuschen, J.; Hocks, L.; Jerome, R.; Ouhadi, T. *ACS Symp. Ser.* **1977**, *No. 59*, 165.
(25) Ouhadi, T.; Heuschen, J. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1183.
(26) Hamitou, A.; Jerome, R.; Teyssie, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1035.
(27) Ouhadi, T.; Bioul, J. P.; Stevens, C.; Warin, R.; Hocks, L.; Teyssie, Ph. *Inorg. Chim. Acta* **1976**, *19*, 203.
(28) Heuschen, J.; Jerome, R.; Teyssie, Ph., to be submitted for publication.
(29) Koltoff, J. M.; Lee, T. S. *J. Polym. Sci.* **1946**, *1*, 429.
(30) Herman, J. J. Ph.D. Thesis, University of Liège, 1978.
(31) Herman, J. J.; Jerome, R.; Teyssie, Ph.; Gervais, M.; Gallot, B. *Makromol. Chem.* **1978**, *179*, 1111.
(32) Herman, J. J.; Jerome, R.; Teyssie, Ph.; Gervais, M.; Gallot, B. *Makromol. Chem.*, submitted for publication.
(33) Heuschen, J.; Jerome, R.; Teyssie, Ph. French Patent 77-08098 (Mar 11, 1977).

Polymerization of 1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose, a Substituted 2,6-Dioxabicyclo[3.1.1]heptane

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ABSTRACT: The polymerization of 1,3-anhydro-2,4,6-tri-*O*-benzyl-β-D-glucopyranose has been studied under a variety of conditions. Cationic and some coordination catalysts caused polymerization; anionic initiators did not. Stereoselectivity and yields were variable and the products were polymers of low viscosity and oligomers. Phosphorus pentafluoride produced good yields of polymer, rich in α-D configuration. Triethylaluminum–water catalyzed production of polymer with a high proportion of β-D configuration. None of the catalysts tested gave completely stereoregular products. The polymerization mechanism and possible causes of low molecular weight are discussed.

Polymerization of bicyclic acetals to produce stereoregular polysaccharides and related polyacetals has been investigated in a number of centers[1-5] and the subject has been recently reviewed.[1-3] Because of the ubiquitous nature of polysaccharides and their important physiological functions, especially involving information transport, the products of these ring-opening polymerizations have been useful model substrates for investigating immunological and allergic reactions, enzyme function, and protein (lectin)–carbohydrate interactions.[3]

Although the structure of the monomers used appears complex, there are a number of simplifying features which make these ring-opening polymerizations amenable to rigorous analysis. Since one uses optically pure monomers, the structural complexities introduced with racemic monomers are avoided, and stereoselectivity can be simply monitored in a series of polymerizations by polarimetry, as well as by NMR spectroscopy. Bond breaking has been

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