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Preparation of Telechelic Polyester Oligodiols by Chain-Transfer Polymerization of ε-Caprolactone

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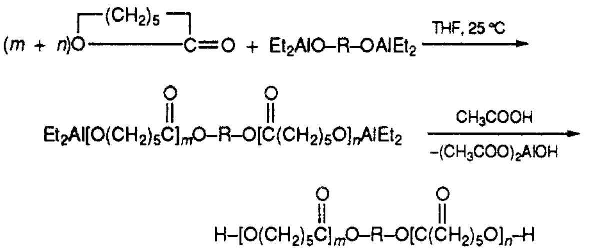
ABSTRACT: α,ω-Dihydroxypoly(ε-caprolactone)s were prepared by polymerization of ε-caprolactone (εCL) initiated with $Al[(OCH(CH_3)_2]_3$ (I) and conducted in the presence of $HO(CH_2)_5OH$ (PD) as a transfer agent. Resulting HO–poly(εCL)–OH had $\bar{M}_n$ = 400–1500, $\bar{M}_w/\bar{M}_n$ = 1.25–1.06, and functionalities f = 1.99–1.93, respectively. GPC traces indicated the complete consumption of the transfer agent. The molecular weights were controlled, at the sufficiently low concentration of the initiator ($[I]_0 \approx 10^{-3}$ mol·L^{-1} vs $[PD]_0 > 10^{-1}$ mol·L^{-1}), by the $[\epsilon CL]_0/[PD]_0$ ratio. The microstructure of oligodiols was characterized using ^1H and $^{13}C\{^1H\}$ NMR spectroscopies. Application of the α,ω-dihydroxypolyethers $HO(CH_2CH_2O)_nH$ and $HO(CH_2CH_2CH_2CH_2O)_nH$ as transfer agents allowed the A–B–A α,ω-dihydroxy block copolymers to be prepared (where A and B are the poly(εCL) and polyether blocks, respectively) having $\bar{M}_n \leq 3 \times 10^3$, $\bar{M}_w/\bar{M}_n$ = 1.08, and f = 1.98. The triblock structure of the copolymers was confirmed by the ^1H and ^{13}C NMR. Kinetic studies revealed that PD inhibits the polymerization of εCL; however, no inhibition was observed in the presence of the macromolecular diols ($\bar{M}_n > 10^3$).

Introduction

One of the possible routes of the synthesis of the telechelic polymers is based on the initiation with the difunctional initiator. This method was recently applied in our[1] and in other laboratories[2] in the preparation of the well-defined α,ω-dihydroxypoly(ε-caprolactone) (HO–poly(εCL)–OH), e.g.:



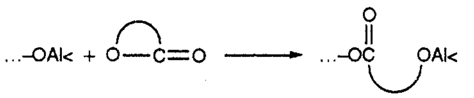
$$(m+n)\,O\!-\!(CH_2)_5\!-\!C\!=\!O + Et_2AlO\!-\!R\!-\!OAlEt_2 \xrightarrow{THF,\ 25\ °C} Et_2Al[O(CH_2)_5\overset{O}{\overset{\|}{C}}]_mO\!-\!R\!-\!O[\overset{O}{\overset{\|}{C}}(CH_2)_5O]_nAlEt_2 \xrightarrow[-(CH_3COO)_2AlOH]{CH_3COOH} H\!-\![O(CH_2)_5\overset{O}{\overset{\|}{C}}]_mO\!-\!R\!-\!O[\overset{O}{\overset{\|}{C}}(CH_2)_5O]_n\!-\!H \quad (1)$$

Although dialkylaluminum alkoxides were already used as initiators in the polymerization of ε-caprolactone (εCL),[3,4] we have shown, for the first time,[5] that this process is a living one and that only a linear, high-molecular-weight poly(εCL) is formed during the time required for the complete monomer consumption (cyclics are absent). The molecular weights and end groups of the obtained polymers could be fully controlled.[6-9]

Preparation of the telechelic poly(εCL) by using typical ionic initiators, sodium dialcoholates, was also attempted,[10] but the resulting difunctional polymers had broad molecular weight distributions and were contaminated by macrocyclic poly(εCL). In contrast, lactides have recently been polymerized with the same initiators, giving a linear, high-molecular-weight α,ω-dihydroxypolylactide.[11]

Application of the difunctional initiator in the synthesis of HO–poly(εCL)–OH is cumbersome, especially for telechelics with low molecular weight. This case requires a high concentration of the initiator to be used, and subsequently the organometallic end groups have to be hydrolyzed and the low-molecular-weight aluminum derivatives should be removed (for example, for the preparation of the HO–poly(εCL)–OH with $\bar{M}_n = 10^3$, 30 wt % of the initiator, with respect to the εCL monomer, should be used).

In the alternative route, polymerization is conducted with an as low as possible initiator concentration in the presence of a transfer agent, carrying the functional groups, e.g.:



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In the case when the transfer agent (ROH) is a diol, difunctional polymers are formed. For the sufficiently low concentrations of initiator and fast and quantitative transfer, the molecular weights of oligodiols are practically determined by the $[monomer]_0/[diol]_0$ ratio. Methods according to this principle have already been used for the preparation of the telechelic polylactides.[12-14] Cationic polymerization in the εCL/diol system led to polymers having broad molecular weight distributions ($\bar{M}_w/\bar{M}_n$ up to 4), apparently due to the transesterification side reactions.[15,16] The so-called "immortal" polymerization with aluminum porphyrins as initiators[17] is based on the same principle. However, in some systems the transfer of the alcohol was not quantitative. This was observed, for example, in the polymerization of εCL, initiated with $Al[OCH(CH_3)_2]_3$ and conducted in the presence of $(CH_3)_2CHOH$[9] or of CH_3CH_2OH.[18]

When the high-molecular-weight diols were used as the transfer agents, the block copolymers were prepared.[19,20]

In the present paper described is the synthesis of HO–poly(εCL)–OH by polymerization of εCL initiated with $Al[OCH(CH_3)_2]_3$ and with 1,5-pentanediol (PD) as the transfer agent.

[●] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

Experimental Section

Substrates and Solvents. **ϵ-Caprolactone** (from Aldrich) after fractionated distillation over CaH_2 under reduced pressure (98 °C at 2 mbar) was kept in vacuo on molecular sieves (4 Å). Then it was finally purified by two consecutive vacuum distillations to ampules with fresh Na mirrors. Purified monomer was distributed by distillation in vacuo into ampules equipped with break-seals and then stored at −12 °C.

Aluminum isopropoxide (from PPH Polskie Odczynniki Chemiczne (POCh), Poland) was purified by vacuum distillation (150 °C at 2 mbar) and distributed into thin-walled glass vials. Then, after breaking the vial, it was dissolved in a known amount of dry THF and finally transferred into calibrated ampules equipped with break-seals and stored at −12 °C.

Titanium isopropoxide (from Jansen Chimica) was purified by vacuum distillation (150 °C at 0.4 mbar) and distributed into thin-walled glass vials.

1,5-Pentanediol (from Aldrich) **and Ispropanol** (from POCh, Poland) were dried by reacting with Na metal and distilled under reduced pressure into thin-walled vials or into ampules equipped with break-seals.

Poly(ethylene glycol) 1000 (from Riedel De Haën, Germany) **and poly(tetramethylene glycol) 1000** (from Blachownia Śląska, Kędzierzyn-Koźle, Poland) were dried under high vacuum at 90–100 °C for 8 h and additionally purified by dissolving in dry (distilled from Na–K alloy) toluene, which thereafter was evaporated at 50 °C under reduced pressure.

THF (from POCh, Poland), after the usual purification, was kept over a Na–K alloy, and from its "blue solution" was distilled via a glass burette, into the reaction vessel.

Procedures. Polymerizations. Polymerizing mixtures were prepared, in sealed glass ampules and dilatometers, using a standard high-vacuum technique. After complete monomer conversion the active centers were deactivated by adding to the reaction mixtures the 3-fold molar excess of the diluted aqueous HCl. Polymers with $\bar{M}_n > 1000$ were precipitated into cold methanol or petroleum ether (−30 °C) and eventually dried under high vacuum for several days. The liquid products, after deactivation, were washed with water. Then their THF solutions were dried with anhydrous $CaCl_2$ and $MgSO_4$, and subsequently solvent was evaporated under high vacuum up to a constant weight of the sample.

Kinetic Measurements. Kinetics of polymerization was monitored using a dilatometric method, according to the procedure described in ref 21.

Gel Permeation Chromatographic (GPC) Analyses. Polymerizing mixtures were frozen in the liquid nitrogen immediately after complete monomer conversion (dilatometric control), and then samples were warmed up just before GPC measurement. GPC analyses were performed using an LKB 2150 HPLC pump, a set of Waters Ultrastyragel columns (10^3, 5×10^2, and 10^2), and a RIDK 102 (Praha, Czechoslovakia) RI detector. THF was used as eluent.

Molecular Weight Measurements. The molecular weight of the high-molecular-weight poly(ϵCL) was measured on a Hewlett Packard 502 high-speed membrane osmometer.

Mass Spectrometry. Mass spectra were recorded on a Finnigan MAT 95 spectrometer using direct chemical ionization with isobutane as the reacting gas.

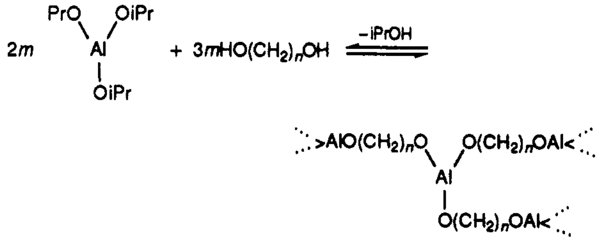
NMR Spectroscopy. ^1H and ^{13}C NMR spectra of HO–poly(ϵCL)–OH were registered in dry $CDCl_3$ on a Bruker AC 200.

Results and Discussion

Synthesis of α,ω-Dihydroxypoly(ϵ-caprolactone) Oligomers. Polymerizations of ϵCL were initiated with $Al[OCH(CH_3)_2]_3$ and carried out in the presence of $HO(CH_2)_5OH$ in THF solvent at 25 or 50 °C. Monomer starting concentrations ($[\epsilon CL]_0$) were close to 2 mol·L^{-1} (if not otherwise stated); those of the initiator ($[I]_0$) were in the range from 3×10^{-3} to 3.5×10^{-3} mol·L^{-1}. The concentration of the 1,5-pentanediol transfer agent ($[PD]_0$) was changed from 1.7×10^{-2} to about 1.0 mol·L^{-1}, depending on the desired molecular weight of the resulting polymer (cf. the equation in footnote *a* of Table 1).

It has to be stressed that attempts to use ethylene glycol ($HO(CH_2)_2OH$) as the transfer agent were unsuccessful. For example, after mixing 0.1 mmol of $[(CH_3)_2CHO]_3Al$ with 1.25 mmol of $HOCH_2CH_2OH$ in 15 mL of a 1 mol·L^{-1} ϵCL/THF solution, the ethylene glycol/aluminum isopropoxide adduct precipitated out and no polymerization was observed for several days (at 25 °C).

The pentamethylene glycol/aluminum isopropoxide reaction products are also sparingly soluble in the polymerizing mixture; however, they were able to initiate the ϵCL polymerization, and the system became homogeneous at the early stages of the process. The order in which substrates are added to the reaction mixture is important. Introduction of the $Al[OCH(CH_3)_2]_3$ initiator into the diol/monomer/solvent mixture governed the homogeneity almost from the very beginning of polymerization. This behavior is apparently due to the polyfunctionality of both aluminum alkoxide and diol:



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This reaction may give the high-molecular-weight networks 1. Substitution of diol for the monofunctional alcohol, e.g., isopropyl alcohol, used in the model studies, resulted in the perfectly homogeneous reaction mixtures.

Concentrations of the initiator $[I]_0 \approx 3 \times 10^{-3}$ mol·L^{-1} ensure operable polymerization times at the temperature range from 25 to 50 °C. The time required for the "complete" (99 mol %) monomer conversion (τ_c) in the absence of diol is equal to 30 min at 25 °C. In the presence of diol the ϵCL polymerization slows down. The higher the $[PD]_0$, the lower is the overall polymerization rate. For example, at $[PD]_0 = 0.763$ mol·L^{-1} τ_c extends to about 15 h. However, an increase of temperature to 50 °C reduces τ_c, at otherwise comparable conditions, to 2.5 h (cf. Table 1).

Starting concentrations of the monomer, initiator, and transfer agent and molecular weights of the resulting HO–poly(ϵCL)–OH, measured by GPC and calculated, assuming that all three isopropoxide groups from each initiator molecule participate in the chain growth and that quantitative chain transfer to the diol molecules occurs, are given in Table 1. There is a reasonably good agreement between measured and calculated $\bar{M}_n$'s. Moreover, the polydispersity indexes ($\bar{M}_w/\bar{M}_n$) are close to values expected for the Poisson distribution. This agrees with observations of Teyssié et al.,[22,23] who first pointed out the living nature of the polymerization of ϵCL initiated with $Al(OiPr)_3$. A narrow MWD indicates also that the rate of exchange of alkoxide ligands at the Al atoms is fast, in comparison with propagation.

HO–poly(ϵCL)–OH oligomers with $\bar{M}_n$ below 800 are, at room temperature, viscous liquids, those with $\bar{M}_n$ of about 1000 are waxy solids, and those with $\bar{M}_n$ of about 1200 and above are white powders (after precipitation from petroleum ether and/or methanol).

Table 1. Polymerization Conditions, Calculated [$\bar{M}_n$(calcd)] and Measured [$\bar{M}_n$(GPC)] Number-Average Molecular Weights, and Polydispersity Indexes ($\bar{M}_w/\bar{M}_n$) of the Resulting ϵCL Oligomers (THF as Solvent)

no.	[ϵCL]$_0$, mol·L^{-1}	[Al(OiPr)$_3$]$_0$ × 10^3, mol·L^{-1}	[HO(CH$_2$)$_5$OH]$_0$ × 10^3, mol·L^{-1}	$\bar{M}_n$(calcd)[a]	$\bar{M}_n$(GPC)[b]	$\bar{M}_w/\bar{M}_n$[d] (calcd)	$\bar{M}_w/\bar{M}_n$[b] (GPC)	*T*, °C	τ_c,[e] min	*f*[f] (calcd)
1	2.05	3.10	0	75480	72500[c]	1.002		25	30	1.000
2	1.89	3.10	17.3	8276	8300	1.01	1.50	25	190	1.350
3	2.00	3.08	120.5	1864	1600	1.06	1.03	25	345	1.930
4	2.06	3.48	120.5	1899	1600	1.05	1.06	50	40	1.920
5	1.99	3.40	133.6	1684	1500	1.06	1.03	50	45	1.930
6	2.05	3.00	201.8	1214	1200	1.08	1.06	25	430	1.960
7	6.75	3.44	1000.5	867	820	1.10	1.15	50	400	1.990
8	3.34	2.98	628.2	702	700	1.12	1.10	50	65	1.986
9	2.10	3.23	736.8	425	400	1.17	1.20	50	150	1.987
10	2.00	3.54	763.2	399	400	1.17	1.20	25	900	1.987

[a] $\bar{M}_n$(calcd) = {[ϵCL]$_0$ × 114.14/(3[Al(OiPr)$_3$]$_0$ + [PD]$_0$)} + [PD]$_0$)} + 104.25, where 114.14 and 104.25 are molecular weights of ϵCL and 1,5-pentanediol, respectively. [b] $\bar{M}_n$(GPC), $\bar{M}_w/\bar{M}_n$ (GPC): molecular weight and its distribution, respectively, measured by gel permeation chromatography calibration on the poly(ϵCL) standards. [c] Measured by membrane osmometry. [d] $\bar{M}_w/\bar{M}_n$ calculated according to eq 5. [e] τ_c: time required for the complete ϵCL conversion, determined by dilatometry and checked by GPC. [f] *f*: functionalities calculated according to eq 7.

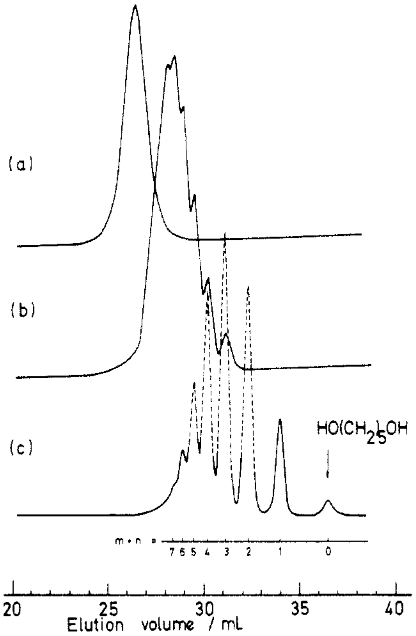


Figure 1. GPC traces of the ϵCL/HO(CH$_2$)$_5$OH/Al(OiPr)$_3$ polymerizing mixtures recorded after complete ϵCL consumption. Polymerization conditions are given in Table 1: (a) sample 5; (b) sample 7; (c) sample 10. Waters Ultrastyragel columns: 10^3, 5 × 10^2, and 10^2. Eluent: THF. Flow rate: 0.7 mL·min^{-1}.

Yields of the crude products, before removing the residues of the aluminum alkoxide initiator, were quantitative.

Characterization of HO-poly(ϵCL)-OH. Gel Permeation Chromatography (GPC). The representative GPC traces of the polymerizing mixtures, recorded after the complete monomer conversion, are given in Figure 1. Trace a clearly shows that macrocyclic oligomers are practically not formed during the time required for the complete conversion of ϵCL. In traces a and b the peaks due to the 1,5-pentanediol (elution volume: 36.4 mL) are absent, indicating complete consumption of this transfer agent. Only for the sufficiently low [monomer]$_0$/[diol]$_0$ ratios can the unreacted diol be detected. This is seen in Figure 1c.

Chromatograms in parts b and c of Figure 1 can be, at least, partially resolved into individual peaks, corresponding to the first 7-8 products of the polyaddition. Thus, we have tentatively correlated structures of the consecutive *n*-mers with their elution volumes (Table 2).

For samples 7 and 10 the mass spectroscopic measurements with chemical ionization confirmed the presence of the individual compounds with molecular weights 218, 332, 446, 560, and 675 (219, 333, 447, 561, and 676 of the *m*/*z* series were obtained).

Table 2. Structures, Formula Weights (FW), and the Elution Volumes of the Individual HO-poly(ϵCL)-OH Oligomers

m + *n* in H[O(CH$_2$)$_5$C(O)]$_m$O(CH$_2$)$_5$O[C(O)(CH$_2$)$_5$O]$_n$H	FW	elution vol., mL
0	104.15	36.43
1	218.29	34.85
2	332.43	32.25
3	446.57	31.00
4	560.71	30.10
5	674.85	29.40
6	788.99	28.89
7	903.13	28.44

Data in Table 2 were used eventually for the "self-calibration" of GPC traces in the low-molecular-weight range ($\bar{M}_n$ < 900). For polymers with higher molecular weights calibration was performed, using poly(ϵCL) standards, prepared as described in ref 6. The $\bar{M}_n$(GPC) values given in Table 1 are based on these calibrations.

GPC traces also allowed the determination of the polydispersity indexes ($\bar{M}_w/\bar{M}_n$). It is worthwhile to stress that $\bar{M}_w/\bar{M}_n$, for the Poisson distribution, depends on the average degree of the polymerization ($\bar{n}$) of the resulting polymer:[24]

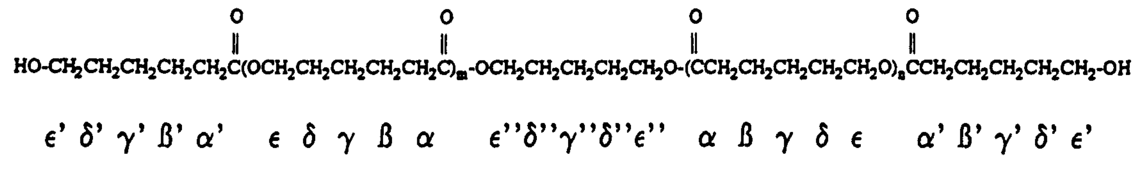
$$\bar{M}_w/\bar{M}_n = 1 + \bar{n}/(1 + \bar{n})^2 \qquad (5)$$

Respective values, calculated for samples 1-10 given in Table 1, are close to these obtained experimentally.

^{1}H NMR Spectroscopy. In the ^{1}H NMR spectra of poly(ϵCL) obtained with Al(OiPr)$_3$ and HO(CH$_2$)$_5$OH (Figure 2), besides signals due to the main-chain atoms, the signal related to the -CH$_2$OH end groups was also detected as a triplet at δ 3.64 (at the ϵ′ position in structure 2). The signals due to -CH$_2$- protons at the ϵ″, δ″, and γ″ positions, derived from the transfer agent, overlapped with those due to the ϵ, δ, and γ -CH$_2$- protons of the main chain.

Chemical shifts of the -CH$_2$- main-chain protons are as follows: δ 2.30 (α, t), 1.65 (β + δ, m), 1.39 (γ, m), and 4.06 (ϵ, t) (cf. also refs 6 and 25).

Assignment of the triplet at δ 3.64 has been additionally confirmed by the reaction of the oligodiol with (CF$_3$SO$_2$)$_2$O. The spectrum of the resulting product showed a new triplet at δ 4.64, whereas a triplet at δ 3.64 completely disappeared. This was due to the reaction:



$$HO\text{-}CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}(OCH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}})_m\text{-}OCH_2CH_2CH_2CH_2CH_2O\text{-}(\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2CH_2O)_n\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2CH_2\text{-}OH$$

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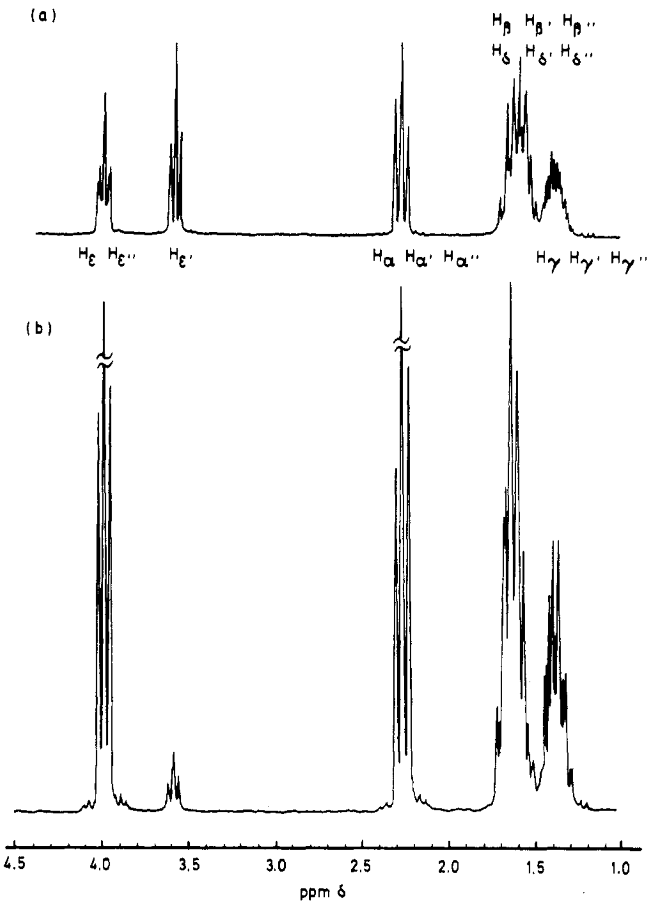


Figure 2. ^{1}H NMR spectra (measured in $CDCl_3$, 200 MHz) of HO–poly(εCL)–OH oligomers. Polymerization conditions are given in Table 1: (a) sample 10; (b) sample 5.

$$\underset{\delta\,1.65\;\delta\,3.64}{\ldots\text{–}CH_2CH_2CH_2CH_2CH_2OH} + (CF_3SO_2)_2O \xrightarrow[-CF_3SO_3H]{CDCl_3,\ rt} \underset{\delta\,1.85\;\delta\,4.64}{\ldots\text{–}CH_2CH_2CH_2CH_2CH_2OSO_2CF_3} \qquad (6)$$

After esterification, the multiplet due the ...–CH_2CH_2-OSO_2CF_3 protons also shifts to the low field and appears at δ 1.85, the same downfield shift we observed for the esterified 1,5-pentanediol $CF_3SO_2O(CH_2)_5OSO_2CF_3$.

The relative intensity of the absorption of ...–CH_2OH protons decreases with increasing molecular weight of the oligodiol. This is clearly seen in parts a and b of Figure 2, from comparison of the spectra of oligodiols with $\bar{M}_n$(GPC) = 400 and 1500, respectively.

^{13}C NMR Spectroscopy. $^{13}C\{^1H\}$NMR spectra of HO–poly(εCL)–OH are shown in Figure 3. Signals in these spectra were assigned in the following way. Chemical shifts of the carbon atoms of the end groups: δ 34.09 ($C_{\alpha'}$), 25.20 ($C_{\beta'}$), 24.57 ($C_{\gamma'}$), 32.22 ($C_{\delta'}$), 62.38 ($C_{\epsilon'}$), 173.60 (>C=O). $C_{\gamma''}$ absorbing at δ 22.32 and 22.12 is derived from 1,5-pentanediol and linked at both sides and at one side only of the εCL repeating unit, respectively. Poly(εCL) main-chain carbon atoms absorb at δ 33.99 (C_α), 25.40 (C_β), 24.45 (C_γ), 28.21 (C_δ), 63.39 (C_ϵ), and 173.40 (C=O).

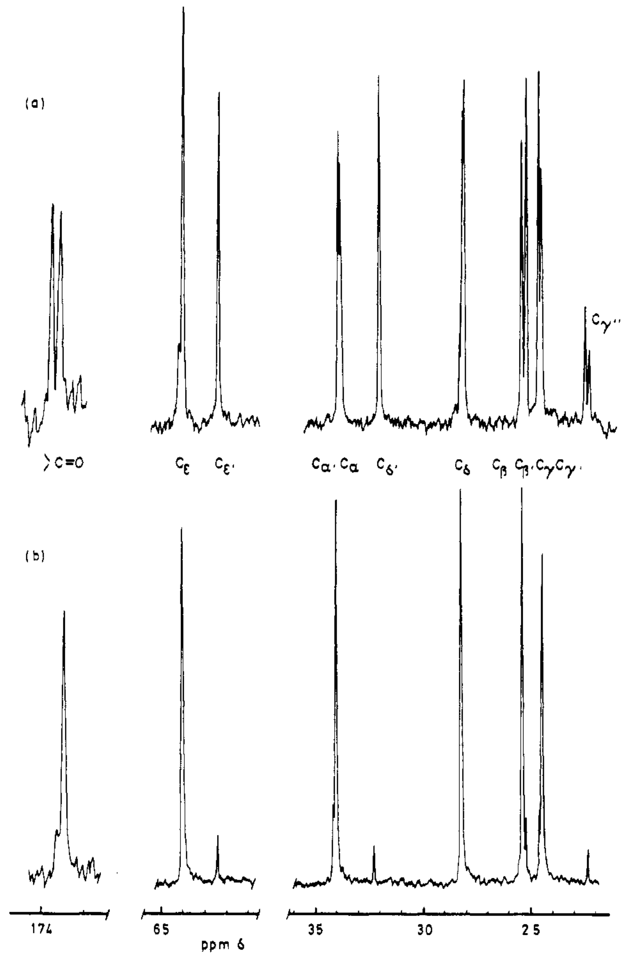


Figure 3. $^{13}C\{^1H\}$ NMR spectra (measured in $CDCl_3$, 50.3 MHz) of HO–poly(εCL)–OH oligomers. Polymerization conditions given in Table 1: (a) sample 10; (b) sample 5.

Functionalities of HO–poly(εCL)–OH. Oligodiols prepared in the system εCL/Al(OiPr)$_3$/HO(CH$_2$)$_5$OH may, in principle, contain, apart from the ...–CH_2OH end groups derived from the transfer agent, also the ...–OiPr end groups derived from the initiator. The functionality (*f*) of these oligodiols, i.e., the average number of hydroxyl end groups per one macromolecule, can be calculated from the feed composition, assuming that all isopropoxide and hydroxyl groups are quantitatively transferred into the macromolecules and that, after hydrolysis, the >AlO–... active centers are converted quantitatively into the hydroxyl end groups:

$$f = \frac{[PD]_0}{3[Al(OiPr)_3]_0 + [PD]_0} + 1 \qquad (7)$$

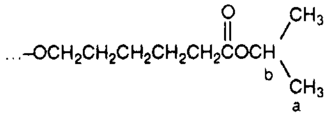
Due to the high ratio of $[PD]_0/[I]_0$, the respective values (given in Table 1) show that functionalities of HO–poly(εCL)–OH having $\bar{M}_n < 1000$ should be close to 1.99. The analysis of the ^{1}H NMR spectra, presented below, con-

Table 3. Polymerization of ϵCL with Various Diols as Transfer Agents (Solvent: THF)

no.	[ϵCL]$_0$, mol·L^{-1}	[Al(OiPr)$_3$]$_0$ × 10^3, mol·L^{-1}	diol	[diol]$_0$ × 10^3, mol·L^{-1}	$\bar{M}_n$(calcd)[a]	$\bar{M}_n$(GPC)[b]	$\bar{M}_w/\bar{M}_n$[b] (GPC)	T, °C	τ_c, min	f[d]
11	2.00	3.70	HO(CH$_2$)$_5$OH	159	1423	1300	1.07	25	390	1.94
12	2.09	3.73	HO–poly(ϵCL)–OH ($\bar{M}_n$ = 1300, $\bar{M}_w/\bar{M}_n$ = 1.06)[b]	162	2717	3000	1.20	25	100	1.94
13	2.02	1.01	HO(CH$_2$CH$_2$O)$_n$H ($\bar{M}_n$ = 900, $\bar{M}_w/\bar{M}_n$ = 1.03)[c]	140	2411	2200[c] 2700	1.07[c] 1.08	50	<400	1.98
14	2.14	1.03	HO[(CH$_2$)$_4$O]$_n$H ($\bar{M}_n$ = 1200, $\bar{M}_w/\bar{M}_n$ = 1.50)[c]	123.6	3168	2800[c] 3300	1.20[c] 1.20	50	<400	1.98

[a] $\bar{M}_n$(calcd) = {[ϵCL]$_0$ × 114.14/(3[Al(OiPr)$_3$]$_0$ + [diol]$_0$)} + $\bar{M}_n$(diol). [b] $\bar{M}_n$(GPC), $\bar{M}_w/\bar{M}_n$(GPC): molecular weight and its distribution, respectively, measured by gel permeation chromatography calibration on the poly(ϵCL) standards. [c] Calibration on the HO(CH$_2$CH$_2$O)$_n$H standards. [d] f = {[diol]$_0$/(3[Al(OiPr)$_3$]$_0$ + [diol]$_0$} + 1.

firmed this conclusion.



$$\ldots\text{-OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O}\underset{\text{b}}{\text{CH}}(\underset{\text{a}}{\text{CH}_3})_2$$

3

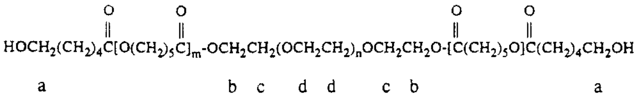
Protons in the end groups derived from the Al(OiPr)$_3$ initiator (cf. structure **3**) absorb at δ 1.23 (H$_a$, d) and 5.00 (H$_b$, m).[22,25] Spectra of polymers shown in Figure 2 contain small, but distinct, doublets at δ 1.23. For the methine protons, the signal-to-noise ratio is low, and the multiplet at δ 5.00 overlaps with the base line. Nevertheless, it is possible to estimate the functionalities, on the basis of the ^{1}H NMR spectra, by comparing intensities of the signals at δ 1.23 (...–CH$_2$C(O)OCH(C**H**$_3$) protons) and at δ 3.65 (...–C**H**$_2$OH protons). For the spectra given in Figure 2 we have obtained (a) f = 1.99 and (b) f = 1.98 compared with 1.987 and 1.93, calculated from the feed composition, respectively (accuracy of the integration equals ±5%).

Application of Oligodiols as Transfer Agents. The method of the synthesis of telechelic poly(ϵCL), described in the present paper, may be used for preparation of the A–B–A triblock copolymers, where A is the poly(ϵCL) block.

In a model polymerization, we used HO–poly(ϵCL)–OH ($\bar{M}_n$ = 1300) as the transfer agent. Concentrations of substrates are given in Table 3. $\bar{M}_n$(calcd) and $\bar{M}_n$(GPC) of the resulting polymer are in good agreement. It has to be stressed that the polymerization time is considerably shorter for the process with the oligodiol compared with that with HO(CH$_2$)$_5$OH as the transfer agent; the respective values are 100 vs 390 min at 25 °C. Thus, it is possible to further decrease [Al(OiPr)$_3$]$_0$ and still have operable reaction times.

Application of poly(ethylene glycol) (PEG) with $\bar{M}_n$ = 900, as the starting oligodiol, allowed the synthesis of the HO–poly(ϵCL)-*b*-PEG-*b*-poly(ϵCL)–OH triblock copolymer with $\bar{M}_n$ = 2400, $\bar{M}_w/\bar{M}_n$ = 1.08, and functionality f = 1.98. In Figure 4 are compared GPC traces of the starting PEG and that of the polymerization mixture, after complete ϵCL consumption. A signal due to the starting PEG is absent in the chromatogram of the polymerization products.

Analysis of the ^{1}H NMR and ^{13}C NMR spectra of the isolated products (Figures 5 and 6) indicates the presence of both PEG and poly(ϵCL) blocks in the required proportions.



$$\underset{\text{a}}{\text{HOCH}_2}(\text{CH}_2)_4\overset{\overset{\text{O}}{\|}}{\text{C}}[\text{O(CH}_2)_5\overset{\overset{\text{O}}{\|}}{\text{C}}]_m\text{-O}\underset{\text{b}}{\text{CH}_2}\underset{\text{c}}{\text{CH}_2}(\text{O}\underset{\text{d}}{\text{CH}_2}\underset{\text{d}}{\text{CH}_2})_n\text{O}\underset{\text{c}}{\text{CH}_2}\underset{\text{b}}{\text{CH}_2}\text{O-}[\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_5\text{O}]\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_4\underset{\text{a}}{\text{CH}_2\text{OH}}$$

5

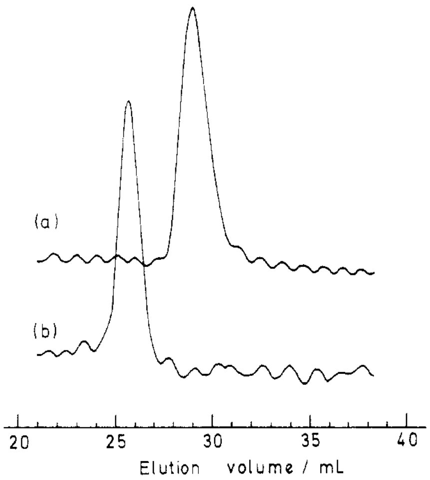


Figure 4. GPC traces of (a) H(OCH$_2$CH$_2$)$_n$OH, $\bar{M}_n$ = 900, and (b) a ϵCL/HO(OCH$_2$CH$_2$)$_n$OH/Al(OiPr)$_3$ polymerizing mixture recorded after complete ϵCL consumption. Polymerization conditions are given in Table 3 (sample 13). Waters Ultrastyragel columns: 10^3, 5 × 10^2, and 10^2. Eluent: THF. Flow rate: 0.7 mL·min^{-1}.

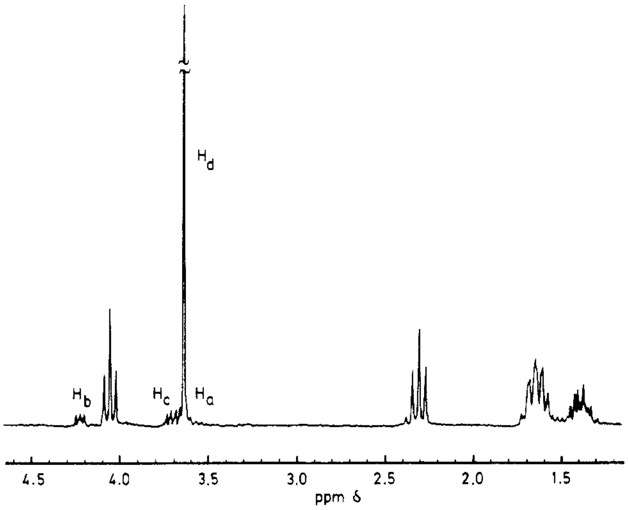


Figure 5. ^{1}H NMR spectrum (measured in CDCl$_3$, 200 MHz) of a HO–poly(ϵCL)-*b*-PEG-*b*-poly(ϵCL)–OH copolymer. Polymerization conditions are given in Table 3 (sample 13).

Protons of the PEG block absorb at δ 3.64 (H$_d$). Triplets at δ 4.23 and 3.71 are due to the methylene protons in the PEG repeating unit linked with the poly(ϵCL) block (H$_b$ and H$_c$, respectively). The signal of the –CH$_2$OH end group (H$_a$) is overlapped with that of the main-chain PEG protons (Figure 5). Respective chemical shifts in the ^{13}C{^{1}H} NMR spectrum (Figure 6) are as follows: δ 70.4 (C$_d$), 69.01 (C$_b$), 63.29 (C$_c$), 62.35 (C$_a$). The remaining signals are due to the poly(ϵCL) block (cf. the preceding section).

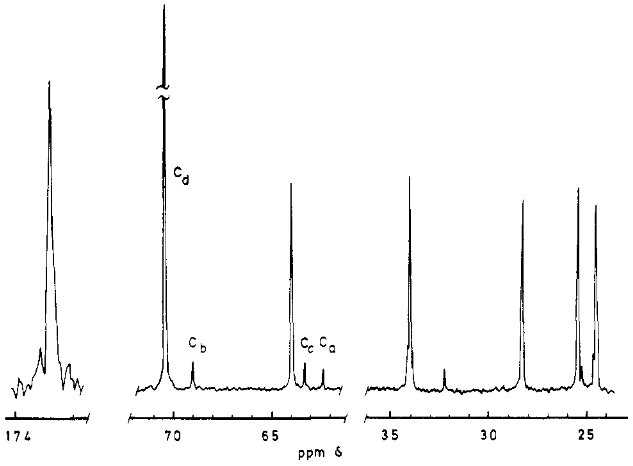


Figure 6. $^{13}C\{^1H\}$ NMR spectrum (measured in $CDCl_3$, 50.3 MHz) of a HO–poly(ϵCL)-*b*-PEG-*b*-poly(ϵCL)–OH copolymer. Polymerization conditions are given in Table 3 (sample 13).

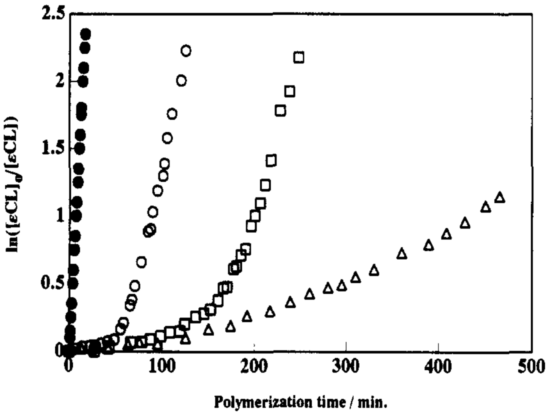


Figure 7. Kinetics of ϵCL polymerization initiated with $Al(OiPr)_3$ and conducted in the presence of $HO(CH_2)_5OH$. Polymerization conditions: $10^3[Al(OiPr)_3]_0$/mol·L^{-1} = 3.2 (●), 3.1 (○), 3.08 (□), 3.5 (△); $10^3[HO(CH_2)_5OH]_0$/mol·L^{-1} = 0 (●), 17.3 (○), 120.5 (□), 763 (△); $[\epsilon CL]_0$ = 2 mol·L^{-1}, THF as a solvent, 25 °C.

The absence of signals related to the end groups ...–OCH_2CH_2OH of PEG (δ 61.5 and 72.5) indicates the formation of the triblock A–B–A copolymer.

In ref 16 synthesis of PEG-*b*-poly(ϵCL) diblock copolymer was reported with $Ti(OiPr)_4$ as the initiator. Polymerization was carried out at 160 °C, for 8 h. Unfortunately, the GPC spectra of the polymerization products were not reported. We have repeated polymerization of ϵCL under comparable conditions; i.e., $[\epsilon CL]_0$ = 6.70 mol·L^{-1}, $[Ti(OiPr)_4]_0 = 2.5 \times 10^{-3}$ mol·L^{-1}, $[PD]_0$ = 0.784 mol·L^{-1}, and thus $\bar{M}_n$(calcd) = 1067. $\bar{M}_n$(GPC) = 1200 of the resulting poly(ϵCL) agreed satisfactory with the calculated value, but the molecular weight distribution was rather broad, $\bar{M}_w/\bar{M}_n = 1.60$, and signals related to the undesired cyclic oligomers were also present; the concentration of the cyclic dimer in the polymerizing mixture was equal to 5×10^{-2} mol·L^{-1} (in the ϵCL units).

We have also prepared the A–B–A copolymer based on poly(tetramethylene glycol) (PTMG). Respective data are given in Table 3 (sample 14).

Kinetics and Mechanism of ϵCL Polymerization in the Presence of Diols. Figures 7 and 8 show results of the dilatometric measurements, represented in the semilogarithmic coordinates. For the process without diol the straight line was obtained, indicating the internal first-order kinetics with respect to ϵCL (Figure 7). As we have already reported, k_p^{app} = 0.79 L·mol^{-1}·s^{-1} (THF, 25 °C).[26] Polymerization, conducted in the presence of 1,5-pentanediol, is almost completely inhibited, at its early stages, then the rate gradually increases, and eventually it becomes first order with respect to ϵCL. The slopes of the linear parts of semilogarithmic anamorphoses of kinetic curves decrease with increasing concentration of the diol in the feed (Figure 7). It is evident that diols retard considerably polymerization in the ϵCL/$Al(OiPr)_3$ system. A similar phenomenon was already observed in the polymerization ϵCL initiated with bimetallic aluminum μ-oxoalkoxides and carried out in the presence of $(CH_3)_2CHOH$.[27]

On the other hand, when polymerization was conducted with HO–poly(ϵCL)–OH ($\bar{M}_n$ = 1300) as a transfer agent, almost perfectly first-order kinetics, without an induction period, was observed (Figure 8a). This process was relatively fast, with k_p^{app} = 0.2 L·mol^{-1}·s^{-1} (25 °C, THF). At higher temperature the curvature of the semilogarithmic kinetic runs still remains (Figure 8b).

This kinetic behavior can be related to the complexation of the aluminum alkoxide active species by the PD molecules, hindering the approach of the monomer molecules and slowing down the propagation. PD transforms during polymerization into the high-molecular-weight diol. The alkoxide ligands at the Al atoms also increase their molecular weight. Thus, at the higher monomer conversion degrees, the complexation of the ...–OAl< centers becomes prohibited due to the steric hindrance created by the macromolecules. The monomer molecules, in contrast, are still able to approach the active center, which leads eventually to an increase of the propagation rate. The ^{27}Al NMR spectra of the polymerizing mixtures indicate that the tetrameric aluminum trialkoxide active species are

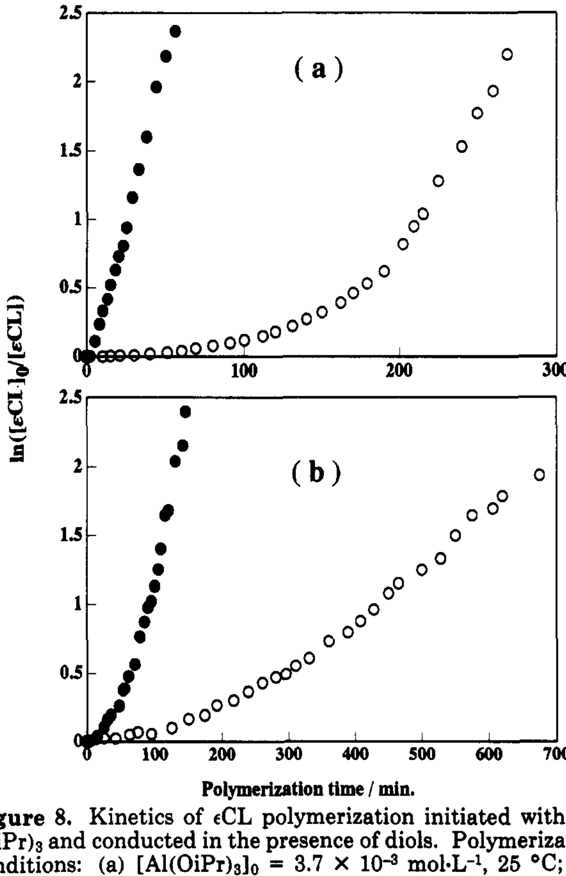


Figure 8. Kinetics of ϵCL polymerization initiated with $Al(OiPr)_3$ and conducted in the presence of diols. Polymerization conditions: (a) $[Al(OiPr)_3]_0 = 3.7 \times 10^{-3}$ mol·L^{-1}, 25 °C; (○) $[HO(CH_2)_5OH]_0$ = 0.159 mol·L^{-1}, (●) [HO–poly(ϵCL)–OH]$_0$ = 0.162 mol·L^{-1}, $\bar{M}_n$ = 1340; (b) (○) $[Al(OiPr)_3]_0 = 3.54 \times 10^{-3}$ mol·L^{-1}, $[HO(CH_2)_5OH]_0$ = 0.763 mol·L^{-1}, 25 °C; (●) $[Al(OiPr)_3]_0 = 3.23 \times 10^{-3}$ mol·L^{-1}, $[HO(CH_2)_5OH]_0$ = 0.737 mol·L^{-1}, 50 °C; $[\epsilon CL]_0$ = 2 mol·L^{-1}, THF as a solvent.

disassembled by the alcohol and/or oligoalcohol molecules.[28] More detailed analyses of the kinetics of εCL polymerization in the presence of alcohols and of the structure of pertinent propagating active species will be published elsewhere.[18]

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