Synthesis of Low Molecular Weight-Hydroxy Polycaprolactone Macromonomers by Coordinated Anionic Polymerization in Protic Conditions

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ABSTRACT: This article reports the development of a new catalytic process that takes advantage of the exchange reaction between aluminium alkoxides and alcohols to obtain functionalized low molecular weight oligomers by anionic ring-opening polymerization. The aluminium alkoxides can be used in homogeneous medium or grafted on a porous support to make possible a heterogeneous process. ω-Hydroxy oligo polycaprolactones macromonomers with 2-hydroxyethylmethacrylate or hydroxymethylstyrene as polymerizable end groups have been synthesized and characterized by NMR and SEC. Mass spectrometry (LSIMS) has been used in an attempt to determine the MWD. These macromonomers have been engaged in copolymerization with styrene and the reactivity ratios have been approached. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2357–2372, 1997

Key words: polycaprolactone; macromonomer; aluminium alkoxides; anionic ring-opening polymerization; heterogeneous polymerization

INTRODUCTION

Macromonomers constitute a very interesting class of functionalized polymers because they offer an easy access to graft polymers by copolymerization of the macromonomer with other monomers.[1,2] Among the most interesting grafts are those, the chemical nature of which is different from the polymer backbone. Due to the hydrophobic character of many backbones, the polar polyether and polyester grafts appear as quite versatile grafts. This feature noticeably enlarges the field of their potential uses in domains such as emulsifiers, compatibilizers, coatings, or adhesives; because of parameters such as the chemical nature, length, and grafting density of the segments, molecular weight of the backbone can be designed for specific applications.

The synthesis of polyether macromonomers is now well documented and it is possible to get tailor-made macromonomers according to many strategies.[1–4] Polyesters macromonomers are other versatile compounds and can easily be obtained from lactones and lactides anionic ring-opening polymerization. These products are interesting because of their economical interest, such as biodegradability, miscibility with some other polymers, soft segments in polyurethane synthesis, and drug release. For tensioactive applications, the hydrophilicity of the ester group can be balanced by the hydrophobicity of the methylene groups, so that the HLB of these macromonomers can be easily modulated by the ring size.

From the macromolecular engineering point of view, macromonomers can be seen as difunctionalized oligomers with two different functionalities. Their further behavior in copolymerization and

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then the possible applications of the derived materials will depend at least on the following parameters, namely (a) the chemical nature of the oligomer chain; (b) the degree of polymerization as well as the molecular weight distribution of the polymer chain; (c) the nature of the functionalization of both end groups: first, the polymerizable end group (also called α-end group), second, the chemical nature of the other end group (ω-end group). Each of these parameters depends on the other ones, and it is difficult to control each of them separately.

As far as we are concerned with the synthesis of well-defined macromonomers, anionic polymerization is the best method for that aim because one of the more versatile feature of this polymerization technique is the living character that allows to control the degree of polymerization with a narrow molecular weight distribution. The further reactivity of these macromonomers will depend on their degree of polymerization, and generally decreases as the chain length increases.[4] On the other hand, the behavior and applications of the derived copolymers will also depend on the length of the grafts.

Lactones and lactides can effectively be polymerized using ionic as well as based on Lewis acid salts initiators.[5] Typical anionic initiators generally lead to broad molecular distributions because of inter- and intramolecular transesterifications and formation of cyclic molecules by back-biting reactions[6] when using too strong nucleophiles as initiators. The initiators based on aluminium alkoxides[7–9] and alkylaluminium alkoxides[10,11] give rise to polymerizations displaying a perfectly living character while those based on other alkoxides metal such as titanium or zirconium propoxides and butyltin methoxide yield some macrocyclic oligomers.[12]

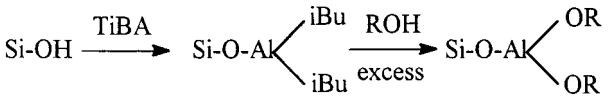
In the anionic polymerization framework, the most usual way to bring polymerizable α-end groups is to take advantage of the living character and to deactivate the macroanion by the adequate insaturated reagent. The ω-end group will therefore the aprotic moity issued from the initiator. Should we follow this procedure, ω-hydroxy macromonomers will be obtained from initiators displaying masked hydroxyl groups with protecting groups.[13] In the same way, functionalized initiators with phtalimides will be used to get ω-aminated macromonomers.[14] Conversely, insaturated initiators can be used provided the initiation step is quantitative and fast enough with respect to the propagation steps to assure a narrow MWD. In that case, hydroxyl groups are easily recovered by hydrolysis of the active centers.

The anionic polymerization is usually restricted to stoichiometric conditions as far as a functionalized initiator molecule is needed for each polymer chain. In the anionic coordinated polymerization field, Teyssié reported the polymerization of caprolactone by aluminium triisopropoxide for which polymers with isopropylester end groups are obtained.[15,16] In the same way, the μ-oxo bimetallic alkoxides display high activities for the polymerization of lactones.[17] Convenient procedures have been proposed by the same group using either a functional aluminium alkoxide bearing a methacrylic double bond as initiator or reacting methacryloyl chloride onto the aluminium alkoxide end groups.[18,19]

These initiators are generally used in apolar or low polar media, so that aggregates take place, which influence the initiation process by decreasing the number of the active centers, modifying their environment, and then their intrinsic activity. Polar aprotic solvents may be used to dissociate the ion pairs or to decrease the aggregation state to a significative extent. Nevertheless, exchange reactions between the grafted alkoxide and the alcohol molecules occur, leading to a competition between the chain growth and the transfer reaction that explains the decrease of the molecular weights. Teyssié found that the number of active centers was the sum of the aluminium isopropoxide and the alcohol molecules, so that the molecular weights decrease as the amount of alcohol increases.[20] Kricheldorf prepared initiators by mixing various alcohols with equimolar amounts of $AlEt_3$.[21,22]

Another way to limit aggregation is to make use of bulky substituents. This way was fully proposed by Inoue[23] who developed aluminium porphyrins, in which the aluminium atoms are located in the middle of the porphin nucleus so that their steric hindrance impedes any interaction between two active centers. The influence of alcohols on the molecular weights was also noticed by Inoue with the aluminium porphyrins.[24]

It was stated above that the drastic molecular weight decrease owing to the exchange reaction might be seen as a major drawback if dealing with the synthesis of high molecular weight polymers. This point of view may be totally changed if one considers this process allows one to extend the field of synthesis of the functionalized oligomers because any polymer chain is end-capped by the radical coming from the alcohol. It must be high-



Scheme 1 Formation of the active centers with triisobutylaluminium as trialkylaluminium.

lighted that one of the main features of this procedure is that many more polymer chains than metal atoms involved in the reaction are finally recovered.

Another interesting point is the ability to graft the active centers on a porous inert support to develop a heterogeneous process working in protic conditions.[25,26] This system turns to account the combination of a solid support and the use of alcohols in excess and enables one to produce materials free of metal atoms and can be easily recycling. We reported the great versatility of this catalytic system for functionalized oligomers[27–29] and copolymers[30,31] synthesis.

In this article we report some results about the preparation of ω-hydroxy polycaprolactone macromonomers by using aluminium alkoxides either in heterogeneous or homogeneous medium, with alcohol molecules in excess. Hydroxyethyl methacrylate (HEMA) and hydroxymethylstyrene (HMS) have been used as starting alcohols to bring either methacrylate or styrene moieties as polymerizable end groups. These macromonomers have been characterized by NMR, SEC, MS, and engaged in copolymerization with styrene.

RESULTS AND DISCUSSION

Polymerization with the Heterogeneous Catalytic System

The active centers are obtained by reaction of trialkylaluminium on porous silica to convert the silanol functions to Si—O—AlR_2 groups (Scheme 1). The number of silanols grafted on the silica can be fixed by a thermic treatment under vacuum. After heating silica at 450°C, the residual amount of silanols is around 1.2 10^{-3} mol/g silanols. The remaining Al—C bonds are hydrolyzed by an alcohol in excess to give the desired aluminium alkoxides.

The kinetics of monomer consumption has been studied by gas chromatography. Figure 1 displays a characteristic curve of the monomer consumption as a function of time. After an induction period, the polymerization is first order in the monomer. An induction period has already been observed by Teyssié et al. with aluminium isopropoxide as the initiator in stoichiometric conditions.[32] The authors interpreted this behavior in terms of a rearrangement of the aggregates. It must be stressed here that both grafting the active centers on silica and the presence of protic molecules would assure single active centers. Another explanation based on a possible difference in the reaction rates after the first insertion is also questionable because the chemical environment of the active centers is not noticeably affected (Scheme 2).

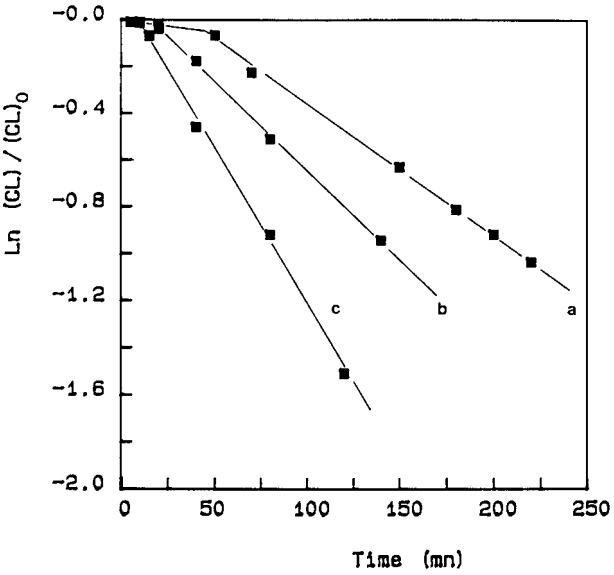
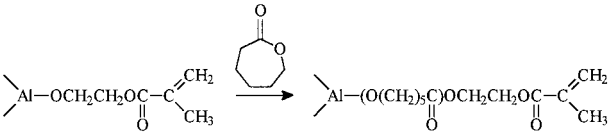
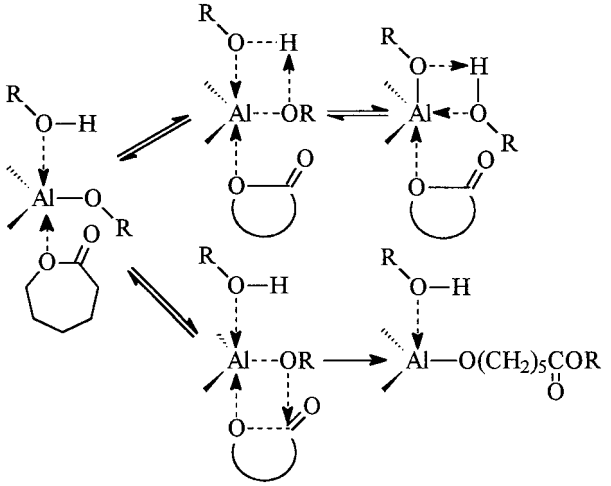


Figure 1 Heterogeneous polymerization of ε-caprolactone in toluene with HEMA as starting alcohol, such as [CL]/[HEMA] = 11.3. The experimental conditions are:
(a) [CL] = 1.45*M*, [HEMA] = 0.128*M*, [Al] = 5.21 10^{-3}*M*.
(b) [CL] = 1.55*M*, [HEMA] = 0.137*M*, [Al] = 1.22 10^{-2}*M*.
(c) [CL] = 1.25*M*, [HEMA] = 0.111*M*, [Al] = 7.49 10^{-3}*M*.

Coordinated anionic ring-opening polymeriza-



Scheme 2 The first insertion will hardly change the chemical structure of the active center.



Scheme 3 Competition between the coordination-insertion mechanism of the ε-caprolactone polymerization and the exchange reaction between the complexed alcohol and the alkoxides groups.

tion is usually described by an coordination-insertion mechanism, the monomer being first coordinated to the Lewis acid before insertion into the metal–oxygen bond. Due to the lone electrons pairs, the alcohol molecules are another Lewis base that may also compete for the coordination of the Lewis acid. The kinetic investigations on ethylene oxide polymerization have clearly shown their drastic influence on the catalytic activity.[26] In addition to the basic character of the oxygen atom due to the lone pairs, the alcohol function allows the formation of hydrogen bonds with the oxygen atom of the alkoxide group, which increase the strength of the coordination complex. Furthermore, the establishement of these hydrogen bonds allows one to propose a structure for the transition step that could simply explain the exchange process through an exchange of the hydrogen bonds as depicted in Scheme 3.

It must be stressed that the free alcohol molecules include both starting alcohol molecules in excess and any polymer chain having undergone the transfer reaction and, hence, end-capped by the hydroxyl group allowing an additional linkage through the hydrogen bonds. This hydrogen bond is, therefore, the essential chemical characteristic for the reaction because it allows both a stronger coordination and the exchange reaction.

Another evidence for the exchange reaction may be illustrated by the development of a novel continuous polymerization process[33]: a column filled with a catalytic bed made of grafted aluminium benzylate is fed continuously by a solution of another alcohol in toluene. The analysis of the products evolved shows the elution of the benzylic alcohol. We observed the same behavior by replacing the alcohol by an oligomer. It may also be underlined that the feasibility of such a continuous process clearly shows that the Si—O—Al bond is not affected by the exchange reaction and that no insertion occurs in this bond.

Although the composition of this system appears rather simple, the overall catalytic behavior is complex: actually, the activity does not simply depend on the monomer concentration, which suggests a competition of coordination on the active centers of the various Lewis bases present in the reactional medium.[26] This fact implies that the monomer molecule is able to compete with alcohol on a coordination center. All the coordinations are expected to be reversible. The alcohol displacement by the monomer could be due to both a concentration effect and stronger interactions with the active center. (It must be recalled that the experimental procedure implies firstly the addition of the alcohol molecules in excess so that all the vacancies are supposed to be occupied by an alcohol molecule.) This complexation of the metal atom by one alcohol enhances the nucleophily of the oxygen atom of the alkoxide. Thus, the reactivity towards the ring opening of the monomer increases, as well as the catalytic activity. When increasing the alcohol concentration, the reactivity increases until the monomer cannot approach the metal atom, which leads to a decrease of the catalytic activity. On the other hand, an active center can also be surrounded by two CL units. In that case, one CL unit enhances the nucleophily of the oxygen atom and activates the insertion of the second one. The coordination energies are around −20.5 kcal/mol.[34]

The kinetic behavior dependence on the aluminium concentration may be interpreted in the same way. It was then of interest to investigate how the catalytic activity depends on the concentration of the active centers to choose an optimum between the activity and the amount of silica to be used. As shown in Figure 2, the activity increases slowly and then tends to level off, so that an amount of around 500 mg of silica previoulsy heated at 450°C under vacuum (i.e., 0.6 mmol Al for 10 g of monomers) was retained for further investigations.

Figure 3 displays the ^{1}H-NMR spectrum of a polycaprolactone macromonomer obtained with 2-hydroxyethyl methacrylate as transfer agent. The peaks assignments have been done according to

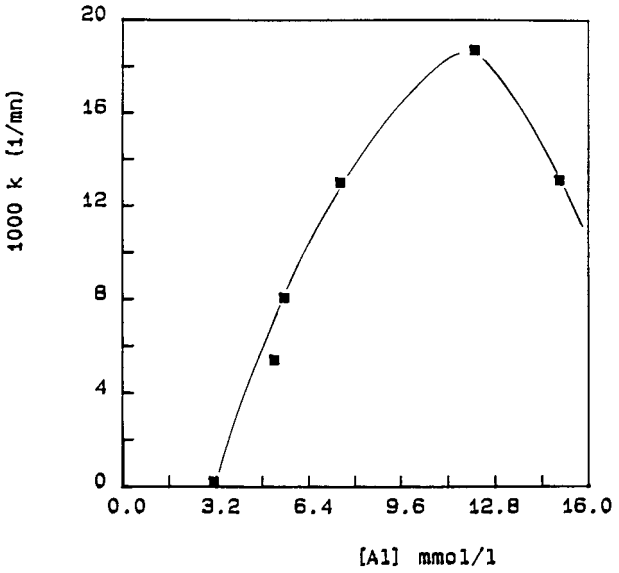


Figure 2 Heterogeneous polymerization of ε-caprolactone with HEMA as starting alcohol: catalytic activity as a function of the amount of grafted active centers.

Kricheldorf.[35] The intensity related to the peak assigned to the protons belonging to the last methylene of the end unit of the chain (Hi′, δ = 3.64 ppm instead of 4.06 ppm for all Hi) is the same as that of the vinylic protons located at the polymerizable α-end-group of the polymer chain (Ha and Hb at 5.61 and 6.13 ppm, respectively), indicating there is actually one hydroxyl end group per initiator residue. In other words, polycaprolactone oligomers are effectively end-capped by the methacryloyl group.

^{1}H-NMR can also be used to estimate the average molecular weight M_n from the relative intensities of protons belonging to the polymer chain and those coming from the grafted radical. The degrees of polymerization are increasing with the monomer conversion Q, according to

$$DP_n = \frac{[\mathrm{CL}]_0}{[\mathrm{HEMA}]} Q$$

indicating the polymerization displays a "living-like" character.

Figure 4 displays the SEC traces of the macromonomers obtained with 2-hydroxyethyl methacrylate as transfer agent. No signal due to residual 2-hydroxyethyl methacrylate is observed. This point indicates the complete consumption of the transfer agent and has already been clearly evidenced by ^{1}H-NMR and gas chromatography.[26] The molecular weight distributions are narrow, although a little broader than those expected from the Poisson distribution. This may be due to an unsuited SEC calibration based on polystyrenes standards and corrected with Mark–Houwink parameters for polycaprolactones, but also to the influence of the end groups, which cannot be quite neglected in case of too low molecular weights. A broadening of the molecular weight distribution is observed that was attributed to some residual very fine silica particles.[28]

Some other attempts have been made with methacrylic acid as the protic reagent. Although we observed that some gas evolved due to the formation of the aluminium carboxylate, polymerizations failed, probably because the oxygen atom of the aluminium carboxylate is not nucleophilic enough to open the ε-caprolactone ring (Scheme 4). This feature was already noticed by Jérôme as well as by Inoue, who reported that ε-caprolactone cannot be polymerized by the tetraphenylporphinatoaluminium carboxylates in contrast to alkoxides.[36]

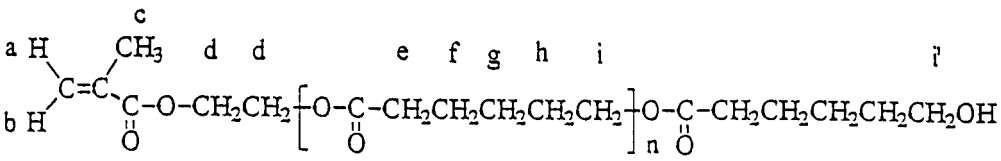
Polymerization in Homogeneous Medium

Because of the residual silica particles that impede a clear SEC analysis, some polymerizations have been carried out in homogeneous medium using tetraisobutylaluminoxane (Tibalox) as the initiator. The determination of MWD is of importance not only in a macromolecular engineering viewpoint but also in order to ascertain some assumptions on the exchange processes: narrow MWD can be observed providing that the exchange processes are to be faster than the propagation steps. For instance, Inoue reported a chain transfer reaction 8–10 times faster than the propagation step.[24]

Polymerizations have been carried out with hydroxyethylmethacrylate and hydroxymethylstyrene as starting agents. The monomer consumption has been followed by GC and SEC. As in the heterogeneous mode, a first induction period is observed, followed by a first-order kinetic. Additional mass spectrometry characterizations have also been made using soft ionization technique (LSIMS) to shed some light on the eventual formation of macrocyclics that cannot be separated by SEC owing to the too low molecular weights.

Size Exclusion Chromatography

SEC allows us to follow both the kinetics of polymerization and the molecular weight distribution



Proton	δ (ppm)	Intensity
a	5.61	1.01
b	6.13	1.00
c	1.95	3.14
d	4.35	3.94
e	2.31	18.32
f + h	1.61 - 1.68	41.41
g	1.36 - 1.41	18.32
i	4.04 - 4.08	16.26
i'	3.65	1.85

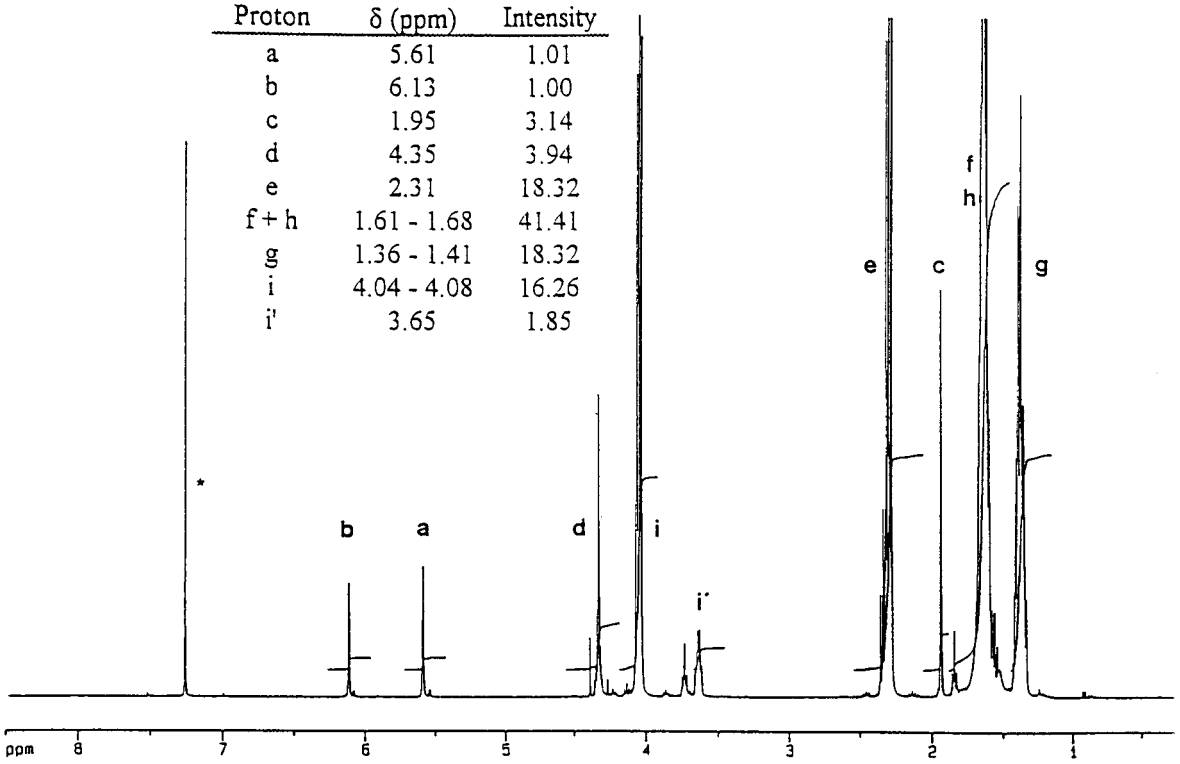


Figure 3 ^{1}H-NMR polycaprolactone macromonomer obtained with 2-hydroxyethyl methacrylate as transfer agent in $CDCl_3$ (*).

as function of time (Fig. 5). This method was developed 15 years ago to investigate the copolymerization of low molecular weight styrenic macromonomers of PEO with various vinylic monomers.[3,37,38] The pertinent parameter to be considered is the ratio $S_1/(S_1 + S_2)$, where S_1 is the area related to the macromonomer (which is oligocaprolactone end-capped with the alcohol radical). $S_1(0)$ is the area related to the starting alcohol and S_2 that related to solvent and ε-caprolactone. The solvent was used as an internal standard to allow the comparison for various conversions.

In one insert is depicted the enlargement of the elution zone of the macromonomer and shows the evolution of the molecular weights. The average degree of polymerization of the first macromonomer (t = 115 mn; DPn = 4.6) is low enough so that the individual oligomers are eluted as separated peaks.

The second insert displays the dependence of the $S_1/(S_1 + S_2)$ ratio on the conversion. The area S_i is proportional to the molar refraction difference $\Delta R_i = n_i - n_{THF}$ and the weight concentration of the solute:

$$S_i = kC_i\Delta R_i .$$

As developed in the Appendix, the variation of ΔR_i with the conversion will be neglected. The ratio can be expressed as

$$\frac{S_1}{S_1 + S_2} = \frac{\text{PCL + ROH}}{\text{PCL + ROH + S + CL}} = \frac{\text{PCL + ROH}}{\text{S + ROH + CL}_0}$$

where CL_0 denotes the initial monomer concentration and CL_0 = PCL + CL.

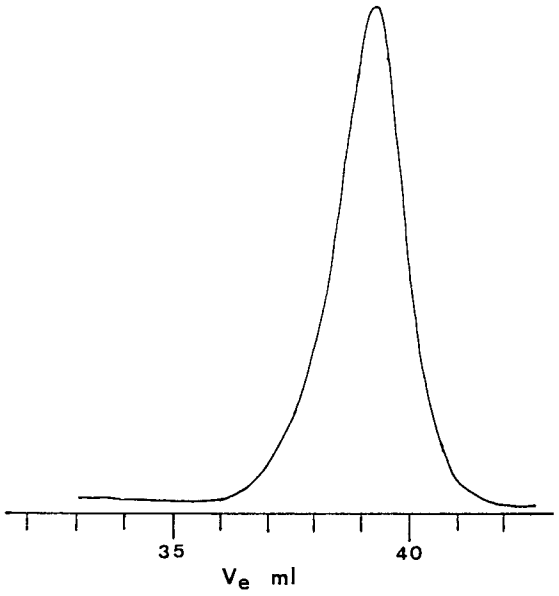


Figure 4 GPC trace of the ω-hydroxy polycaprolactone macromonomer obtained with HEMA as transfer agent. M_n = 1730, M_w = 2240 (PS standards). M_n = 1200 (PCL correction). According to the experimental procedure, the expected degree of polymerization is 10.

Because PCL = $Q \cdot CL_0$, where Q is the conversion, this ratio can be written as:

$$\frac{S_1}{S_1 + S_2} = \frac{\text{ROH}}{\text{S} + \text{ROH} + \text{CL}_0} + \frac{Q \cdot \text{CL}_0}{\text{S} + \text{ROH} + \text{CL}_0} = \text{A} + \text{B} \cdot Q$$

and must be a linear function of the conversion. Using the SEC data obtained for a 100% conversion as references allowed us to check that conversions measured by SEC are in a quite good agreement with those obtained by gas chromatography and NMR (Fig. 6), that validates the above treatment.

Table I reports the dependence of the molecular weight distribution on the conversion as deduced from the SEC results (Fig. 7). The results deserve some comments: (a) as shown in figure 7, the degree of polymerization increases linearly with the conversion while the polydispersity index decreases according to that expected from a Poisson distribution:

$$I = 1 + \frac{n}{(n + 1)^2}$$

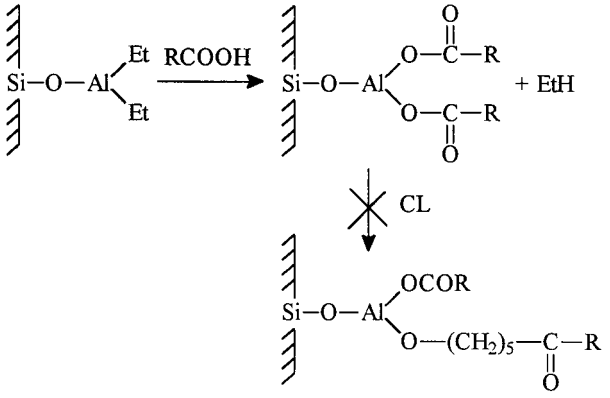
where n is the measured DP_n.

The exchange process is then fast enough with respect to the propagation steps so that all the oligomers spend the same fraction of time on the active centers and have the same probability to insert a new caprolactone unit in their chain. (b) The DP_n/Q ratio keeps a constant value, equal to the DP expected from the [Monomer]/[Alcohol] ratio.

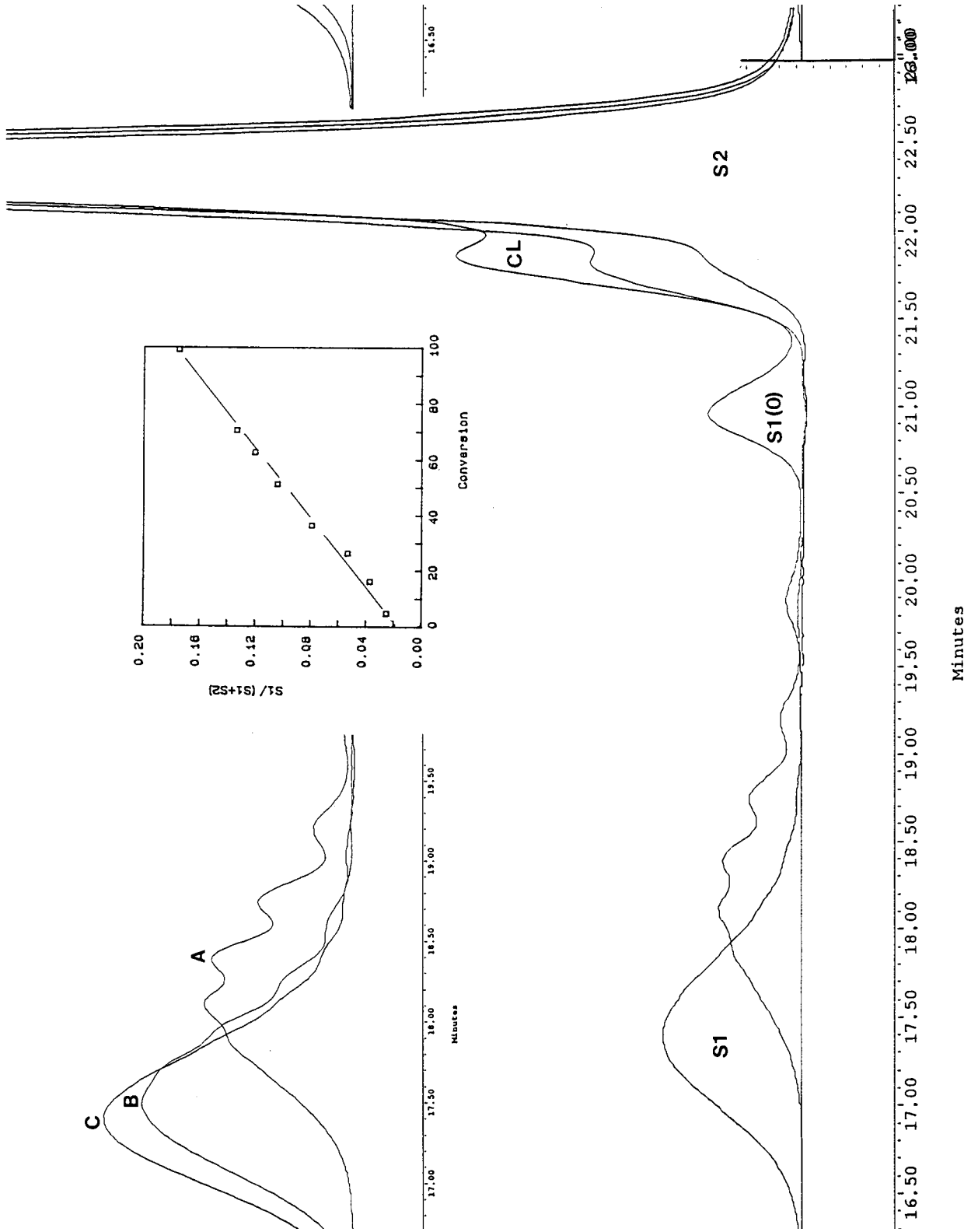
As a conclusion, this system displays some characteristics of a living polymerization. Because of the chain transfer, the criteria for ideal living polymerization are not totally fulfilled so that this polymerization may be rather classified as quasiliving polymerization.[39] However, in the macromolecular engineering framework, the important point is to be able to control the degrees of polymerization by the [monomer]/[alcohol] ratio. The equilibrium between chains grafted on the active centers and the dormant chains (i.e., the hydroxyl end-capped oligomers) does not alter the MWD, which can be described by a Poisson distribution.

Mass Spectrometry

Mass spectrometry is a method of choice for investigating the composition of the oligomer samples, provided soft ionization techniques are used, so that the molecular species are not broken and the molecular peaks are available. For that aim, we made use of liquid secondary ion mass spectroscopy (LSIMS). The question is, however, to be sure of the molecular weight distribution as deduced from this technique. Some articles have reported the determination of molecular weight distributions of poly(ethylene glycols) and their derivatives by fast atom bombardement (FAB-MS), which is a technique quite close to LSIMS.



Scheme 4 The aluminium carboxylate are unable to open the ε-caprolactone ring.


S2
CL
S1(0)
S1
A
B
C
Minutes
Conversion
S1/ (S1+S2)
0.20
0.16
0.12
0.08
0.04
0.00
0
20
40
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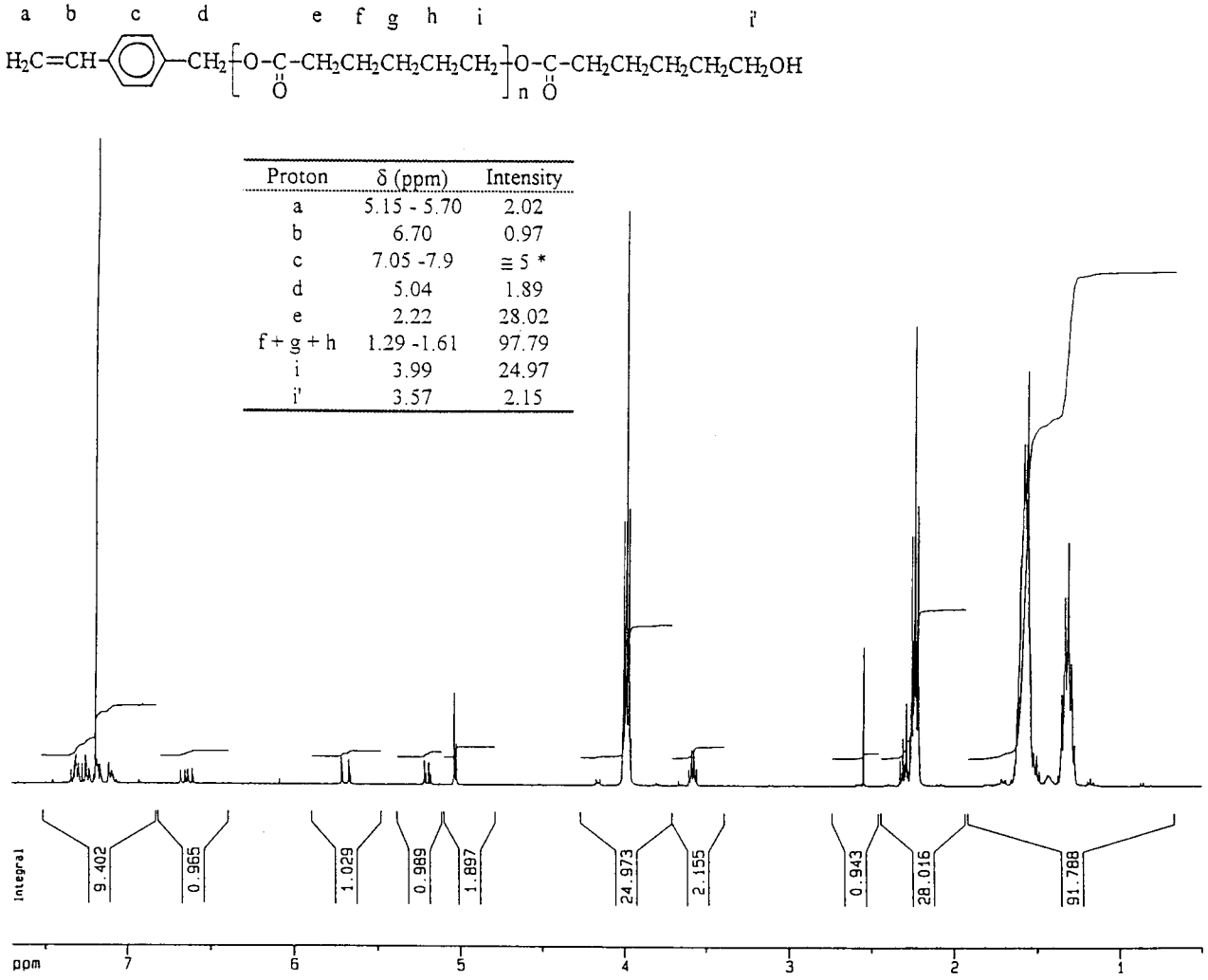


Figure 6 ^{1}H-NMR polycaprolactone macromonomer obtained with hydroxymethyl styrene (HMS) as transfer agent in $CDCl_3$. Expected degree of polymerization: 13.

It seems the fragmentation of $(M + Na)^+$ species of the highest molecular weight cannot be avoided[40] while the distribution of the protonated $(M + H)^+$ molecular ions is in a good agreement with that achieved by SEC.[41]

Figure 8 displays the evolution of the mass spectra of a macromonomer with the conversion. Hydroxymethylstyrene (M = 134) has been used as the α-end group. Protonated molecular species $(M + H)^+$ are detected at $m/z = 134 + 114n + 1$. Assuming that the abundances are directly related to the concentration of the corresponding oligomers in the sample, the number average molecular weight can easily be calculated. Such results are reported in Table II, which show some discrepancies when compared with those achieved by SEC: MS results are lower than those obtained by SEC, particularly in the higher molecular weights range.

Other protonated molecular species at m/z

Figure 5 Evolution of the SEC chromatograms (Tibalox as initiator and HMS as alcohol). S_1: area related to the macromonomer. S1(0) corresponds to the starting alcohol ($t = 0$). S2: area related to the solvent and ε-caprolactone. In the inserts are displayed the dependence of the S1/(S1 + S2) ratio on the conversion and the enlargement of the elution zone of the macromonomer. The polymerization times are 115 mn (A), 170 mn (B), 230 mn (C).

Table I SEC Results for Caprolactone Oligomerization with HMS as Starting Alcohol. $[\varepsilon - CL]_0/[HMS]_0 = 13$

Q GC 100%	M_n (PS)[a]	M_w[a]	*I*	M_n (PCL)[b]	*DPn*	*DPn/Q*
36.3	1045	1180	1.13	745	5.37	14.8
51.1	1295	1430	1.10	915	6.84	13.4
62.5	1565	1705	1.08	1095	8.44	13.5
70.3	1800	1945	1.08	1250	9.81	13.95
99.2	2315	2490	1.07	1590	12.75	12.85

Solvent: toluene. The experimental degree of polymerization *DPn* measured by ^{1}H-NMR was found to be around 14.
[a] Polystyrene standards.
[b] M_n of the oligopolycaprolactone after correction for PCL according to Mark–Houwink coefficients and subtraction of the HMS molecular weight (see the Experimental).

$= 114n + 1$ may be related to macrocycles, but their relative abundance deserves some comments.

They might originate from the polymerization process itself because lactones ring-opening polymerizations are known to give macrocyclics, the amount of which depends on the initiator.

It must be noticed that these macrocyclics do not induce additional NMR resonance peaks so that they cannot be easily detected. In addition, their presence does not affect the determination of the degree of polymerization. Nevertheless, they would alter the molecular weights distribution, particularly if taking into account the high relative abundance. SEC results clearly show that the polydispersity keeps low values, decreasing as the molecular weight increases.

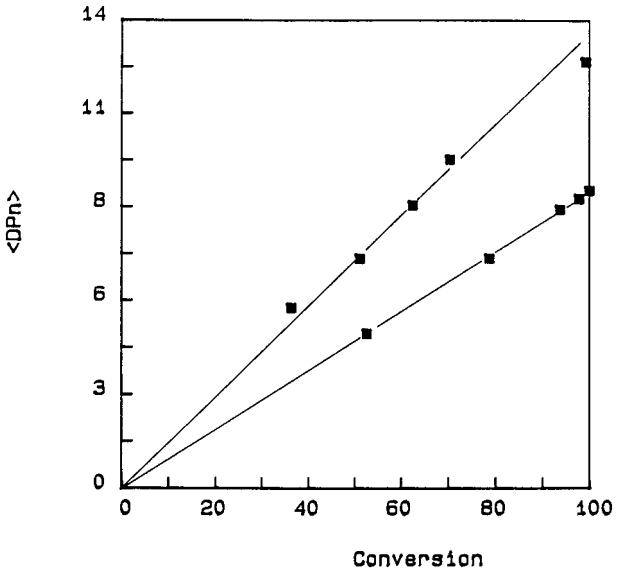


Figure 7 Evolution of the degree of polymerization with the conversion. The values obtained for 100% conversion is in a good agreement with the [Caprolactone]$_0$/[Alcohol] ratio.

Another explanation would be side reactions taking place during ion formation and desorption during the MS procedure. Each particle coming from the source strikes the liquid sample and generates a collision cascade. Molecular ions of the sample molecules can be desorbed intact and analyzed, but lower fragments can also be produced, particularly if considering that transesterification reactions are acid catalyzed (Scheme 5). A simple Monte Carlo simulation allows one to build polymer chains according to a living process and to proceed at random to backbiting reactions.[42] The results evidence a bimodal distribution corresonding to the linear and cyclic oligomers. In addition, as expected, the molecular weights of the linear oligomers are decreasing while the broadening of their MWD is noticed.

Copolymerization

This paragraph reports some preliminary results concerning the copolymerization of the ω-hydroxypolycaprolactones with styrene that will be developed in a next article. The reactions have been monitored by SEC to follow the disapperance of the macromonomer as well as the evolution of the copolymer molecular weight according to procedures we developed 15 years ago.[43] SEC can be used to measure the amount of copolymer and the amount of residual macromonomer (Fig. 9). The solvent was used as an internal standard to allow the comparison for various conversions. The copolymers have been characterized by NMR.

The average molecular weights remains at a constant value instead of an expected continuous

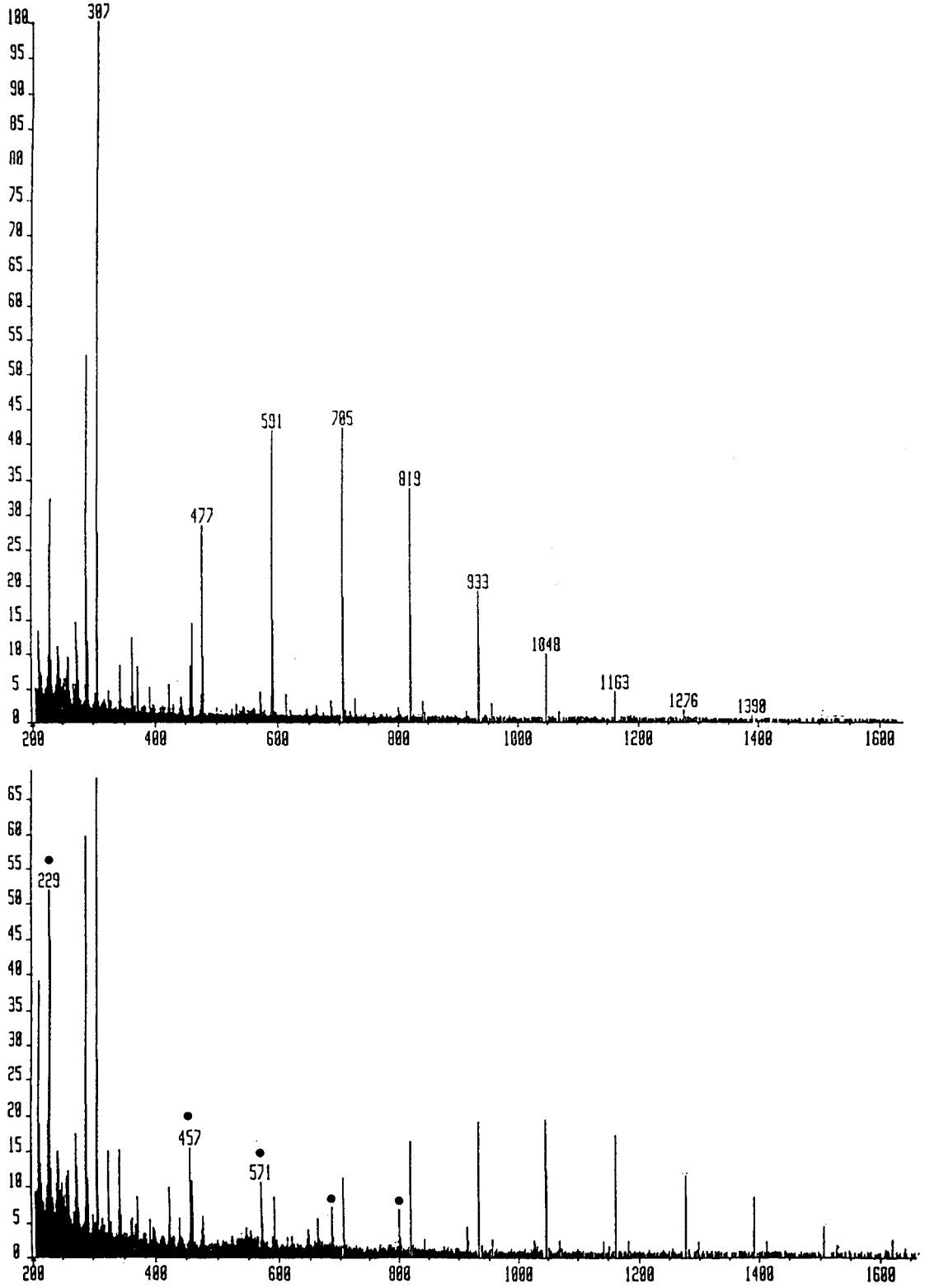


Figure 8 Evolution of mass spectrum of ω-hydroxypolycaprolactone with conversion Q (HMS as α-end group). (a) $Q = 52.6\%$; (b) $Q = 98\%$. The black points denote the macrocyclics. The peaks at $m/z = 289$ and 307 are due to the m-NBA ($M = 153$): $289 = (2M + 1) - H_2O$; $307 = 2M + 1$.

Table II Comparison of the Degrees of Polymerization of Oligocaprolactones Determined from SEC and MS

Q	52.6	78.7	93.7	97.8
DP_n SEC	4.6	6.8	8.3	8.6
DP_n MS	5.8	6.3	7.0	7.0

decrease. The increase of molecular weights was already observed during the radical copolymerization of styrenic macromonomers of polyoxyethylene of low DP. This behavior was interpreted in terms of radical transfer promoted by the benzylic hydrogen atoms[44] and the value of the transfer constant was estimated around 0.021. In the present case, the tendency for the molecular weights to keep a constant value may be explained by either the smaller value of the transfer constant or a lower probability of chain transfer.

Additional ^{1}H-NMR experiments have been performed in C_6D_6 in order to follow the kinetics *in situ* and trying to classify this reaction among the copolymerizations of styrene with alkyl methacrylates without falling into the tedious procedures for determining the reactivity ratios. To do that, we simply compare the kinetics results to those computed from reactivity ratios reported in the literature.[45]

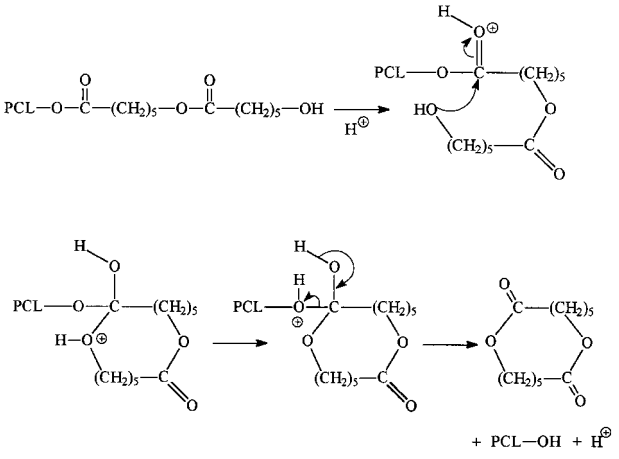
The polycaprolactone macromonomer was previously synthesized in C_6D_6, and styrene was directly added in the solution. This procedure was chosen because crystallization of the samples occurs in the solid state, which makes the redissolution in apolar solvents such as benzene or toluene rather difficult. It can be dissolved in chloroform, but this solvent is a strong transfer agent in radical polymerization. Some ^{1}H-NMR spectra of the reactional medium are displayed in Figure 10. The spectra may become complicated due to the resonance peaks of caprolactone monomer, but the chemical shifts domain of the protons belonging to the polymerizable double bonds is quite clear.

The hydrogen resonances of the methylene groups (4.35 ppm; refered as **d** in Fig. 3) as well as those of the methyl groups (1.95 ppm; refered as **c**) in the HEMA moiety are shifted towards high field when polymerizing and cannot be used as internal standard. We then took the resonance peak of the methylene group refered as **e** at 2.3 ppm to quantify the amount of residual monomers. Preliminary results are displayed in the inset in Figure 10. The experimental data are to be compared with the computed curves from the following reactivity ratios $r_{MMA} = 0.45$; $r_S = 0.47$.[45] The first two points are in quite good agreement with the computed curve. The confidence of the last point is questionable due to the very low values of the Ha and Hb resonance peak intensities of the methacrylate group.

More in-depth investigations of the reactivity of the macromonomers and further characterizations of the copolymers will be reported in another article.

CONCLUSION

Coordinated anionic ring opening polymerization of ε-caprolactone in protic conditions allows one to synthesize easily functionalized oligomers in mild conditions. The active centers are aluminium alkoxides that can be used either in homogeneous phase or grafted on a inert porous support. Using hydroxyethyl methacrylate and hydroxymethylstyrene as starting alcohols affords the corresponding macromonomers with the corresponding polymerizable end groups. Their syntheses have been monitored by NMR and SEC. The degree of polymerization is controled by the Monomer/Alcohol ratio. The exchange reaction between aluminium alkoxides and free alcohols does not affect the molecular weight distribution, which keeps a low polydispersity as expected from a Poisson distribution. This narrow MWD suggests that macrocycles observed by mass spectroscopy originate from side reactions taking place during ion



Scheme 5 Formation of macrocycles by acid-catalyzed transesterification.

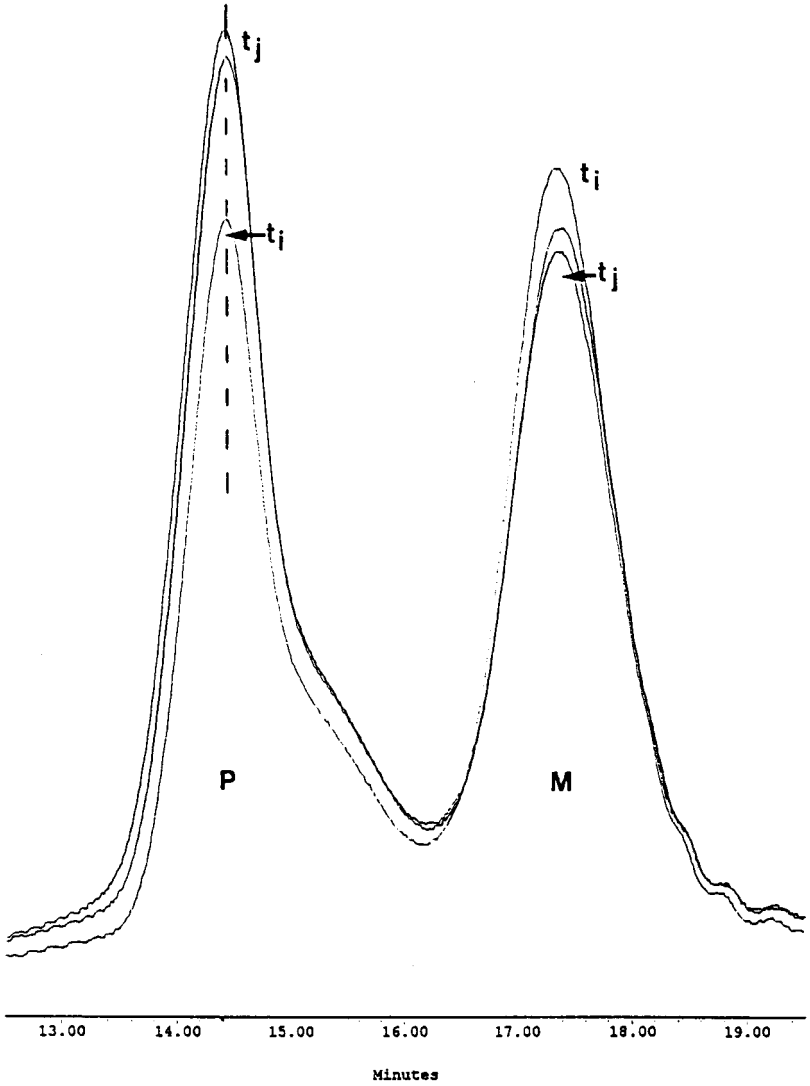


Figure 9 Evolution of SEC chromatograms of copolymer and macromonomer with conversion. Note that, although copolymerization occurs, there is no change in the elution volume of the copolymer.

formation rather that from the polymerization process itself. PCL macromonomers and styrene have been copolymerized. A first analysis *in situ* of the reactional medium shows that the PCL oligomer chain does not change noticeably the reactivity ratios.

Experimental Part

Reagents

ε-Caprolactone, toluene, dichloroethane, and the different alcohols are kept under argon on molecular sieves 3 Å. Alkyl aluminiums (TEA, TiBA, and Tibalox) are diluted with heptane to a 1*M* concentration. All the reactions are carried out in Schlenck-type glassware with greaseless fittings under pure dry argon. Hydroxymethylstyrene has been synthesized according to Bamford et al.[46] by hydrolysis of vinylbenzylchloride via acetylbenzylchloride.

Preparation of the Catalytic System

Silica (Grace 432; pore volume: 1.2 mL/g; surface area: 320 m^2/g; mean particle size ranging from 70 μm to 1 mm) is dehydrated at 450°C for 2 h. The content of silanol groups, determined by titration with triethylaluminium, is equal to 1.2 mmol/g. Alkyl aluminium (2 mL, 1*M* in heptane) is re-

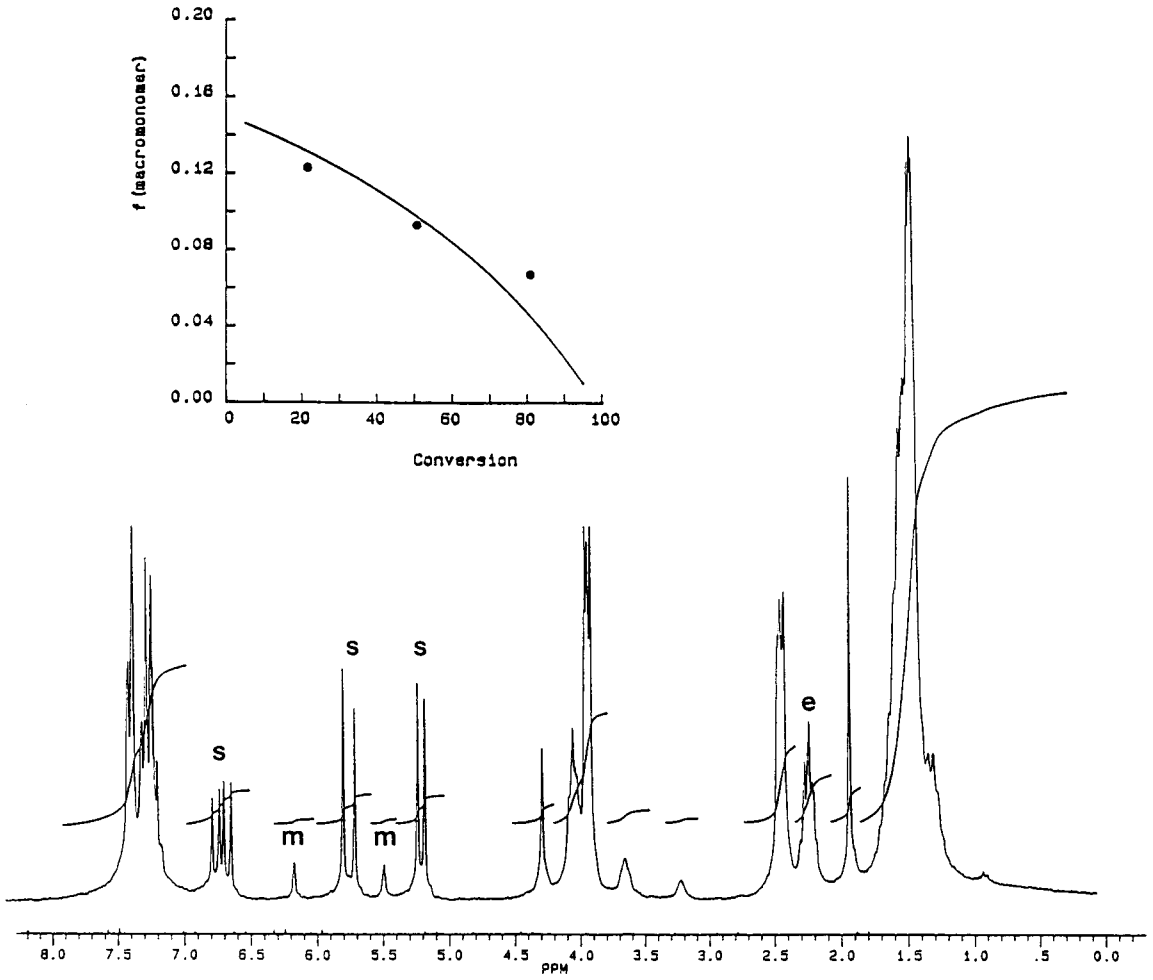


Figure 10 Following the copolymerization of styrene and ω-hydroxy polycaprolactone macromonomer by ^{1}H-NMR in C_6D_6. The peaks **m** and **s** are assigned to the olefinic protons of the macromonomer and the styrene respectively. The peak **e** was used as internal standard. In the insert is reported the simulation of the monomer feed variation with the conversion ($r_{MMA} = 0.45$; $r_S = 0.47$). The experimental data are reported as black points.

acted at room temperature on a suspension of 500 mg silica in 50 mL toluene. After 15 min, the excess of alkyl aluminium is removed by washing three times with toluene. The starting alcohol is then added to the medium and allowed to react at 45°C for 2 h.

Polymers Synthesis

The polymerizations are carried out in toluene in a 250 mL round-bottom flask. The catalytic system is transferred under argon in the flask. The reaction mixture is stirred at 50°C and the kinetic is monitored by gas chromatography and size exclusion chromatography. After the appropriate time, silica is allowed to decant, the solvent is removed by rotary evaporation, and the recovered polymers carefully dried (under vacuum at 50°C) and weighted to determine the conversion degree.

Copolymerizations

The solutions of ω-hydroxy polycaprolactone macromonomer, styrene, and AIBN (1% molar) in toluene are stirred at 60°C. The polymerization medium was analyzed by GC and SEC. In the latter case, toluene was used as internal standard. A copolymerization was carried out in C_6D_6 to follw the monomer consumption by NMR.

Gas Chromatography

The analysis were carried out using an Intersmat IGC 112F with a FID detector. Column: SE30 on

Table III Dependence of the Refractive Index Increment on the Degree of Polymerization ($\Delta n = n - n_{THF}$ with $n_{THF} = 1.4070$)

m	0	1	3	4	5	10
n	1.554	1.515	1.493	1.488	1.484	1.477
Δn	0.147	0.108	0.086	0.081	0.077	0.070

Chromosorb W-HP at 150°C. Injector and detector at 180°C. N_2 as carrier gas.

Size Exclusion Chromatography

Size exclusion chromatography was performed in THF by using a Waters chromatograph equipped with a Styragel HT6E column and a refractometer. Molecular weights were calculated by using polystyrene standards with a correction for polycaprolactone according to the Mark–Houwink coefficients proposed by Schindler et al.[47]: K = 1.395 10^{-4} dL/g; a = 0.786. Another calibration curve was recently proposed by Pasch et al.[48] from which the following coefficients can be deduced: K = 2.38 10^{-4} dL/g; a = 0.757 (with K = 1.4 10^{-4} dL/g; a = 0.72 for polystyrene). This latter calibration gives molecular weights slightly lower (around one monomer unit less for it) than those obtained from the first one. However it may be the contribution of the functional end group in the hydrodynamic radius is difficult to handle in the case of these very low molecular weights. So, we prefered to use the Schindler's calibration because the resulting degrees of polymerization are more in agreement with those obtained from the NMR spectra.

Mass Spectrometry Measurements

The MS measurements were made by using a VG ZAB 2SEQ instrument operating under LSIMS conditions. The compounds were dissolved in $CHCl_3$ and put on a m-nitrobenzyl alcohol matrix. The probe target was bombarded by 35 keV cesium ions. The ion source acceleration voltage was kept at 8 kV.

APPENDIX

The refractive index can be calculated from the Vogel's formula:

$$n = \frac{R_v}{M}$$

where M is the molar weight of the solute. The molar refraction R_v is estimated from group contributions

For oligocaprolactone with HMS as α-end group, n can be expressed as

$$n = \frac{208.33 + 167.40m}{134 + 114m}$$

where m is the degree of polymerization. Table III reports the dependence of the molar refraction difference on the degree of polymerization. For oligopolycaprolactone, the degree of polymerization of which is equal to 10 after complete conversion, it is clear that the variation of n can be neglegted for conversions higher than 30%.

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