Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

α-Methacryloyl-ω-Hydroxyl-Poly(ε-Caprolactone) Macromonomer: Synthesis, Characterization, and Copolymerization

Y. Liu[a]; M. Schulze[a]; A. -C. Albertsson[a]
[a] Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden

To cite this Article Liu, Y. , Schulze, M. and Albertsson, A. -C.(1998) 'α-Methacryloyl-ω-Hydroxyl-Poly(ε-Caprolactone) Macromonomer: Synthesis, Characterization, and Copolymerization', Journal of Macromolecular Science, Part A, 35: 2, 207 — 232
To link to this Article: DOI: 10.1080/10601329808001974
URL: http://dx.doi.org/10.1080/10601329808001974

J.M.S.—PURE APPL. CHEM., A35(2), pp. 207–232 (1998)

α-METHACRYLOYL-ω-HYDROXYL-POLY(ε-CAPROLACTONE) MACROMONOMER: SYNTHESIS, CHARACTERIZATION, AND COPOLYMERIZATION

Yan Liu, Margit Schulze, and Ann-Christine Albertsson*
Department of Polymer Technology
The Royal Institute of Technology
S-10044 Stockholm, Sweden

ABSTRACT

α-Methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer was synthesized using stannous 2-ethyl hexanoate ($Sn(oct)_2$) as catalyst and 2-hydroxyethyl methacrylate (HEMA) as initiator. The macromonomer was characterized by SEC, IR and ^{1}H-NMR. The results confirmed the expected macromonomer structure, namely linear poly(ε-caprolactone) carrying a methacryloyl group and one hydroxyl end group. The polymerization kinetics and mechanism are discussed. The molecular weight and polydispersity of the macromonomer depended on the concentrations of $Sn(oct)_2$ and HEMA as well as the molar ratio of Sn/OH, respectively. The results imply that both $Sn(oct)_2$ and HEMA act as the initiator participating in the polymerization. The copolymers from macromonomer and HEMA or macromonomer and trimethylene carbonate were synthesized through solution free radical or bulk ring-opening polymerizations. The expected graft structure of poly(2-hydroxyethyl methacrylate-*g*-ε-caprolactone) copolymer and block structure of poly(ε-caprolactone-*b*-trimethylene carbonate) copolymer were confirmed by ^{1}H-NMR.

INTRODUCTION

Macromonomers, also referred to as *Macromers*, are linear macromolecules or oligomers carrying polymerizable functional groups at their chain end; the polym-

erizable functional groups can be placed at one chain end or both chain ends. The chain ends can comprise unsaturated groups, which can participate in radical or ionic polymerizations, heterocycles active in ring-opening polymerizations or functional groups that can participate in polycondensation reactions. Depending on the type of end-functionality, the polymerization of macromonomers results in graft copolymers or networks. A variety of macromonomers have been synthesized as precursors of graft copolymers and interpenetrating polymer networks, having great potential as coatings, adhesives, compatibilizers, emulsifiers, and biomaterials [1-5].

Macromonomer technology is a proven method to combine hydrophobic with hydrophilic components and a potential method to combine slow-degrading with fast-degrading components. In some applications, a precise balance of hydrophilicity and hydrophobicity is required. When a polymeric material is coated with a graft copolymer the backbone of which is of the same chemical nature as the substrate, the incompatible grafts accumulate on the surface, thereby modifying it. Such graft copolymers can be used as antistatic agents, surface humidifiers, dye binding intermediates, adhesives, lubricants, and so on. One can also change or control the degradation rate of materials by combining components with different degrading properties and adjusting the composition of the copolymers to suit various applications, such as drug release or microsphere preparation [6, 7].

The macromer technique has also been used to synthesize degradable polymers with heteroatomic chains [8] and to synthesize poly(dodecyl acrylate)-g-poly(caprolactone) using poly(ε-caprolactone) methacrylate macromonomer [9].

However, despite the considerable accumulation of experience in macromer-based synthesis, there are still controversies concerning the mechanism of the Sn-initiated or catalyzed polymerization. Most authors consider that stannous octanoate initiates a cationic polymerization. Kricheldorf and his co-workers proposed an 'insertion mechanism' [10]. According to this mechanism, the absence of an init-iation step is consistent with the independence of the molecular weight on mono-mer/initiator ratio. The results of the bulk polymerization of caprolactone in the presence of stannous octanoate have been interpreted as a coordination-chemical activation by complexation of the carbonyl group by the metal atom [11].

This paper deals with the synthesis and characterization of poly(ε-caprolactone)-HEMA macromonomers and its copolymerization with HEMA and trimethylene carbonate. The ring-opening polymerization of ε-caprolactone was investigated to understand how reaction conditions influence the structure and properties of the resulting polymers.

EXPERIMENTAL

Materials

ε-Caprolactone (6-hexanolactone, 2-oxepanone or oxepan-2-one), 2-hydroxyethyl methacrylate (HEMA) and stannous 2-ethyl hexanoate (stannous octanoate or $Sn(oct)_2$) were purchased from Aldrich Chemicals.

ε-Caprolactone was dried over molecular sieves (4Å) at room temperature for more than 24 hours, and distilled under reduced pressure (65°C/0.4mm Hg). HEMA was also dried over molecular sieves (4Å) at room temperature for more than 24 hours, and distilled under reduced pressure (60°C/0.35mm Hg). Trimethylene carbonate (1,3-Dioxan-2-one or TMC) was synthesized as described previously [12]. The monomer was reprecipitated from toluene to cold *n*-hexane before use. Toluene was dried over molecular sieves (4Å) and sodium wire at room temperature for more than 24 hours. DMF was dried over molecular sieves (4Å). Stannous 2-ethyl hexanoate was distilled under reduced pressure (170°C/0.4mm Hg) and used as a 0.4 M solution in toluene. Toluene was removed by the usual method under reduced pressure [13, 14]. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and dried for 24 hours at 25°C under reduced pressure before polymerization.

Synthesis of Macromers

The bulk melt polymerizations were carried out in 25 ml rubber septum vials, dried at 110°C and flushed with argon; the samples were stirred by means of Teflon-coated magnetic bars. Monomers and initiator were added to the dried vials. The vials were filled in a glove box. The vials with monomers and initiator were degassed *in vacuo* and flushed three times with dried argon. The vials were immersed in a thermostatic oil bath-stirrer and held at constant temperature (120°C) for the desired reaction time (24 hours). The initial mol% composition of HEMA was less than 20%. After the polymerization was complete, the crude products were dissolved in methylene dichloride 25-35% (w/v) and then precipitated into a tenfold excess (by volume) of stirred cold hexane/solid CO_2. The hexane was filtered or decanted, and the polymer was washed with hexane at least three times. The polymer was then transferred to a specimen jar and dried for 72 hours at room temperature *in vacuo*.

Copolymerization of Macromers and 2-Hydroxyethyl Methacrylate (HEMA)

The macromers, HEMA and AIBN were dissolved in DMF at different compositions on the basis of the weight of macromer and HEMA. AIBN at a con-

centration of 1% of total weight of monomers (macromonomer and HEMA) was used as the copolymerization initiator. AIBN was used as a solution in benzene (31 mg/ml). The vials with monomers and initiator were evacuated and flushed three times with dried argon. The vials were heated at 60 °C for 24 hours. The solute was then precipitated in tenfold excess of hexane and treated as described above. Copolymers were dried *in vacuo* at 60 °C for 6 hours.

Copolymerization of Macromers and Trimethylene Carbonate (TMC)

The macromers, TMC and Teflon-coated magnetic stirring bars were placed in dried reaction vials sealed with a rubber septum. A solution in toluene of stannous 2-ethyl hexanoate was introduced using a syringe. The vials with samples were degassed *in vacuo* and flushed three times with dried argon. The bulk melt polymerizations were carried out at constant temperature (90 °C) for the desired reaction time. After the polymerization was complete, the crude products were dissolved in chloroform and then precipitated into a tenfold excess (by volume) of stirred cold methanol/solid CO_2. The methanol was subsequently decanted, and the polymer was washed with methanol at least three times. The polymer was then transferred to a specimen jar and dried to a constant weight at room temperature *in vacuo*.

Characterization

Waters size exclusion chromatography (SEC) equipment was used to determine the molecular weight and molecular weight distribution. A Waters 6000A pump with five Ultrastyragel® columns (10^5, 10^4, 10^3, 500 and 100 Å pore sizes) and chloroform as the eluent (for copolymer THF was used as the eluent) with a flow rate of 1.0 ml/min were used at 25 °C with a Waters RI 401 refractive index detector. The SEC system was calibrated with polystyrene standards with narrow molecular weight distributions ($M_w/M_n<1.09$).

To determine the structure and conversion, ^{1}H-NMR spectra were recorded using a Bruker AC-400 Fourier Transform-Nuclear Magnetic Resonance spectrometer (FT-NMR). The macromonomer samples were dissolved in deuterochloroform and copolymer samples in deuterodimethylsulphone (Aldrich Chemicals) or deuterochloroform. Tetramethylsilane was used as internal standard (δ=0 ppm).

Infrared analyses were made on a Perkin-Elmer FT-IR 1725X spectrometer. The samples were analyzed as a cast chloroform solution on NaCl plates with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Metal carboxylates are generally considered to behave as catalysts rather than as initiators of the ring-opening polymerization of lactones. Indeed, metal carboxylates, such as stannous octanoate, are usually added with active hydrogen compounds, such as alcohols, as coinitiators. Rafler and Dahlmann argued that stannous octanoate does not act purely as an initiator, because the M_n values of poly(D,L-dilactide) did not decrease with increasing stannous octanoate concentration [15]. However, the range of stannous octanoate concentrations studied needs to be taken into consideration and a careful purification of starting components is essential to obtain detailed information on the polymerization mechanism.

Tin salts, in particular stannous 2-ethyl hexanoate, are known to be good catalysts of the polymerization of lactones. Up to now, only the tin(II) bis(2-ethyl-hexanoate) catalyst has been known to yield high molecular weight polylactones when a low catalyst concentration is used [13]. It is also a preferred initiator accepted by the FDA as a food additive [16, 17]. Most authors believe that these catalysts initiate a cationic polymerization, yet conclusive experimental evidence for such a mechanism has not been presented so far. The polymerization mechanisms of ε-caprolactone with most stannous compound catalysts are still not clear.

The water present in commercial unpurified $Sn(oct)_2$ participates in a hydrolysis equilibrium which causes the presence of free 2-ethyl hexanoic acid and stannous hydroxide. Therefore, a further purification of stannous 2-ethyl hexanoate is necessary because of its extreme hygroscopicity.

In order to obtain reliable and detailed information on the mechanism for ε-caprolactone ring opening polymerization using 2-hydroxyethyl methacrylate as initiator and stannous 2-ethyl hexanoate as catalyst or coinitiator, stannous 2-ethyl hexanoate was distilled under reduced pressure(170 °C/0.4Torr) before use and added as a 0.4 M solution in toluene.

$Sn(oct)_2$ catalyst dissolved readily in the monomer melt ensuring homogeneous catalysis, which is important in order to obtain good reproducibility of the polymerization.

Influence of the Concentration of Stannous Octanoate on the Macromonomer Molecular Weight and Polydispersity

To determine the influence of $Sn(oct)_2$ concentration on the molecular weight and polydispersity (PD) of macromonomer, polymerizations were carried

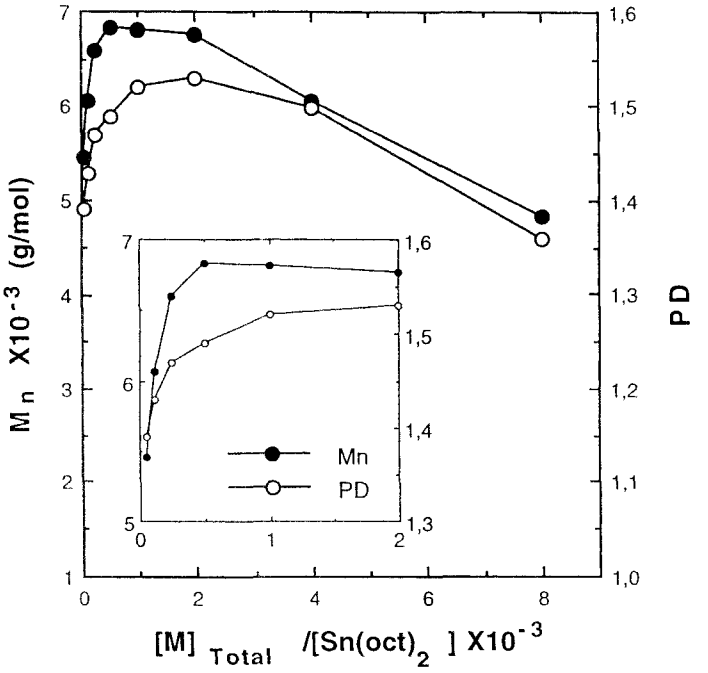


Figure 1. Molecular weight, M_n, and polydispersity as a function of the concentration of stannous 2-ethyl hexanoate.

out with a molar ratio (defined here as the ratio of the total number of moles of ε-CL and HEMA to the number of moles of $Sn(oct)_2$) in the range 57 to 8000; the molar ratio of ε-CL to HEMA was kept constant. The molecular weight and polydispersity of the macromonomer were calculated from SEC data. As Figure 1 and Table 1 show, the M_n and PD values increase with decreasing $Sn(oct)_2$ concentrations up to M_n=6800 at a $[M]_{total}/[Sn(oct)_2]$ molar ratio of circa 500 and PD=1.53 at a $[M]_{total}/[Sn(oct)_2]$ molar ratio of 2000. As the $Sn(oct)_2$ concentration is decreased further (above a molar ratio of ca. 500), the M_n value remains approximately constant then decreases again.

The increase in molecular weight with decreasing $Sn(oct)_2$ concentration shows that $Sn(oct)_2$ affects the formation and number of activated centers. The higher the $Sn(oct)_2$ concentration, the greater the number of activated centers, which results in lower molecular weight polymers when all monomers have been consumed. These results are consistent with a mechanism of Lewis acid-catalyzed transesterification between the lactone and hydroxyl groups [13, 18], as shown in

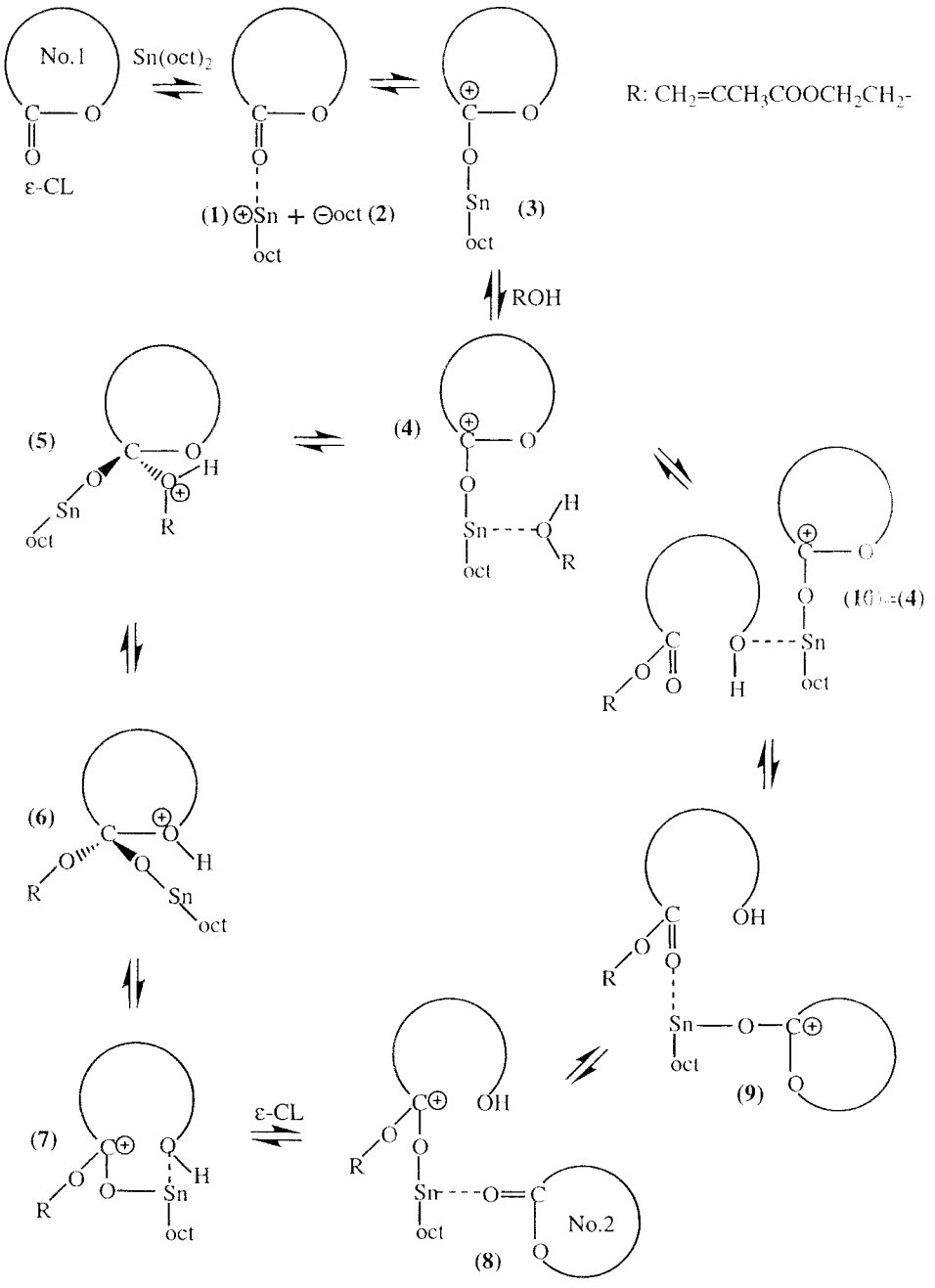
TABLE 1. Influence of the Stannous 2-Ethyl Hexanoate Concentration on the Bulk Ring-Opening Polymerization of ε-Caprolactone in Presence of 2-Hydroxyethyl Methacrylate[a]

Sample	$[M]_{Total}/[Sn(oct)_2]$	M_n	M_w	DP[b]	PD
7103	57	5400	7600	47	1.39
7102	113	6100	8700	52	1.43
7231	250	6600	9700	57	1.47
7232	500	6800	10200	59	1.49
7233	1000	6800	10400	59	1.52
7234	2000	6800	10400	58	1.53
7235	4000	6100	9100	52	1.50
7236	8000	4800	6600	41	1.36

[a] CL/HEMA (molar ratio)=15, reaction temperature is 120 °C, reaction time is 24 hours. [b] DP is the average polymerization degree based on M_n.

Scheme 1. Based on this mechanism, the dissolved $Sn(oct)_2$ first coordinates by its free 5p or 5d orbitals with the caprolactone carbonyl group to activate the monomer. Then the activated monomer or caprolactone/Sn^+(oct) complex reacts with a hydroxyl group of the alcohol. In the present case, the activated monomer reacts with HEMA. The caprolactone/Sn^+(oct) complex will have a cationic character as shown in the resonance structures depicted in Scheme 1. As a result of the resonance, the electron density at the carbon is decreased, making it more susceptible to a nucleophilic attack by hydroxyl-containing compounds which are likely to be the true initiators of the polymerization [13].

In the absence of HEMA, $Sn(oct)_2$ alone can initiate the caprolactone to polymerize. Under these conditions, poly(ε-caprolactone) is formed with a higher molecular weight, M_n= 35983, M_w=83668, PD=2.33 (Table 2). HEMA alone cannot initiate caprolactone to polymerize. After 24 hours of polymerization, some low molecular weight (M_n=570, M_w=788, PD=1.38) oligomers could be isolated but the yield was less than 2%. This result supports the idea that a caprolactone/Sn^+(oct) complex is formed before chain propagation begins. The formation of a caprolactone/Sn^+(oct) complex is a necessary condition for chain propagation initiated by a hydroxyl-containing initiator. Thus, caprolactone/Sn^+(oct) complex probably functions as the active species and polymerizes caprolactone. When both $Sn(oct)_2$ and HEMA were present, polycaprolactone M_n ranges from 532 to 15871, M_w from 652 to 48506, and PD from 1.14 to 3.06 (Table 2).



Scheme 1. Proposed Polymerization Mechanism of the Stannous 2-Ethyl Hexanoate-Catalyzed Bulk Ring-Opening Polymerization of ε-Caprolactone in Presence of 2-Hydroxyethyl Methacrylate

TABLE 2. Influence of Presence and Absence of Hydroxyl-Compound on Molecular Weight and Its Distribution of α-Methacryloyl-ω-Hydroxyl-Poly(ε-caprolactone)[a]

Composition in the feeding	M_n	M_w	PD	Yield (%)
CL+HEMA	600	800	1.38	< 2
CL+HEMA+Sn(oct)$_2$	500 - 15900	600 - 48500	1.14 - 3.06	12 - >95
CL+Sn(oct)$_2$	36000	83700	2.33	>95

[a] Reaction temperature is 120 °C.

Similarly, a tin-oxygen bond is formed by a complex of lactic acid or its dimer with a tin halogenide, which acts as the active species to initiate the polymerization of L,L-lactide with Sn(II) or Sn(IV) halogenides [10]. Rafler *et al*. observed that the commonly-used tin carboxylates and a series of other tin compounds accelerate the ring-opening polymerization catalytically via a coordination chemical activation [19].

The polymerization begins when the OH-containing compound reacts with the lactone/Sn$^+$(oct) complex **4** through a nucleophilic attack at the carbon **5** (Scheme 1). Another monomer coordinates to the Sn atom to form a new complex **8** (Scheme 1). This intermediate **8** may react with the hydroxyl group via both intramolecular attack or intermolecular attack to cause chain growth or chain-transfer growth. This process can continue until all the monomer is consumed.

In the proposed mechanism, the catalyst is not chemically bound to the growing chain end **10** (Scheme 1). This implies that one catalyst molecule can switch from one chain end to another and that the number of polymer chains able to polymerize can be larger than the number of catalyst molecules.

The proposed mechanism agrees with the increase of the molecular weight with conversion, as shown in Table 3. During polymerization, an initiation of new polymer chains will take place continuously. For this reason, the number average molecular weight will not continuously increase with conversion, but the PD increases during polymerization. Ester-ester interchange reactions are not expected to play a significant part in the increase of molecular weight.

The observed maximum value of molecular weight implies that an appreciable molar ratio of Sn atoms to OH groups is necessary for complex-formation (Figure 1). This is consistent with the data shown in Figure 2, which indicates that molecular weight decreases when the OH/Sn molar ratio increases.

TABLE 3. Conversion, Molecular Weight and Its Distribution of α-Methacryloyl-ω-Hydroxyl-Poly(ε-caprolactone) as a Function of Polymerization Time[a]

Sample	Time (h)	Conversion (%)	M_n	M_w	DP[b]	PD
7251	0.5	86.0	3600	4100	31	1.14
7252	1.0	96.5	4400	5500	37	1.25
7253	2.0	96.8	4800	6400	41	1.33
7254	5.0	97.4	5800	8500	50	1.46
7255	9.0	96.7	6500	9800	56	1.51
7256	20.0	95.8	6800	10400	59	1.52
7231	24.0	-	6600	9700	57	1.47
7257	48.0	94.3	6500	9400	56	1.46
7258	72.0	94.2	6400	9400	55	1.46

[a] CL/HEMA (molar ratio)=15, $[M]_{Total}/[Sn(oct)_2]=250$, reaction temperature is 120 °C. [b] DP is the average polymerization degree based on M_n.

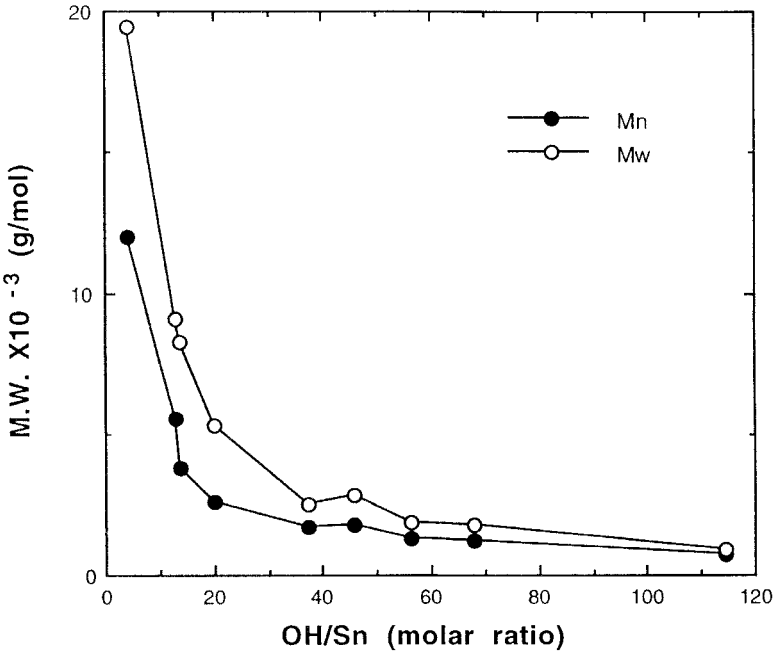


Figure 2. Molecular weight of α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer as a function of OH/Sn molar ratio

TABLE 4. Influence of Hydroxyl-Compound Concentration on the Bulk Ring-Opening Polymerization of ε-Caprolactone in Presence of Stannous 2-Ethyl Hexanoate[a]

Sample	CL/HEMA (molar ratio)	M_n	M_w	DP[b]	PD
8021	4.0	3600	4200	30	1.20
8022	5.0	3900	4900	33	1.27
8023	7.0	4400	5800	38	1.30
8024	10.0	5300	7500	46	1.41
8025	15.0	6600	9900	57	1.50
8026	18.1	7200	11200	63	1.54
8027	45.5	9300	14800	80	1.60

[a] [CL]/[Sn(oct)$_2$]=250, reaction temperature is 120 °C, reaction time is 24 hours.

[b] DP is the average polymerization degree based on M_n.

In most cases, the polydispersity of poly(ε-caprolactone) macromonomer is less than 1.5 (Table 1, 3 and 4). This indicates that polymerization proceeds with a rapid initiation, (in some cases instantaneous initiation), which narrows the molecular-weight distribution [20].

Influence of CL/HEMA Molar Ratio on the Macromonomer Molecular Weight and Polydispersity

To determine the influence of alcohol concentration on the molecular weight and polydispersity (PD) of macromonomer, polymerizations were carried out with a molar ratio of ε-CL to HEMA in a range 4 to 46, where the molar ratio of ε-CL to Sn(oct)$_2$ was kept constant. The effect of initial [CL]/[OH] on polycaprolactone molecular weight and molecular-weight distribution above 90% conversion is shown in Figure 3.

It was found that the molecular weight (M_n) was inversely proportional to the initial alcohol concentration within the molecular weight range (3600 to 9300 g/mol) studied (Table 4). With increasing CL/HEMA molar ratio, i.e. with decreasing HEMA concentration, the molecular weight of the macromonomer obtained increases. This observation shows that HEMA actually participates in the formation of the activated centers. This result was expected since HEMA acts as an initiator of the polymerization via the reaction of its hydroxyl group with the lactone/Sn$^+$(oct) complex (**4** and **5** in Scheme 1). Similar behavior was reported for the diol-initiated polymerization of δ-valerolactone [21] and ε-caprolactone [22].

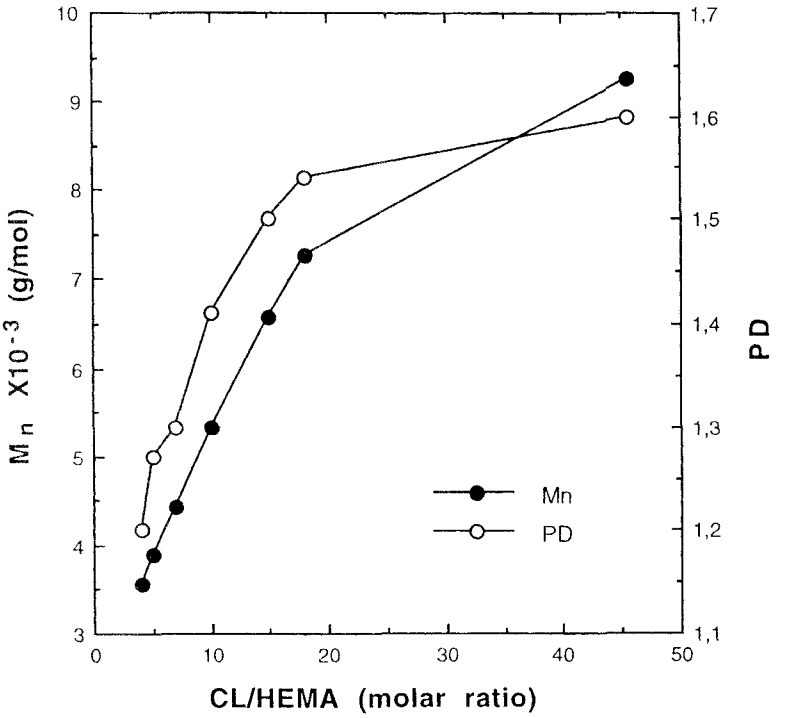


Figure 3. Molecular weight, M_n, and polydispersity of α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer as a function of ε-caprolactone/2-hydroxyethyl methacrylate molar ratio.

This supports the proposed mechanism in which HEMA acts as an initiator and $Sn(oct)_2$ as a coinitiator. In the CL/HEMA molar ratio range 4-20, the molecular weight of macromonomer is directly proportional to the ratio of monomer to initiator. The correlation coefficient is approximately equal to one, (see Figure 4). However, the line does not pass through the origin. It is possible to control the molecular weight of macromonomer by using different molar ratios of monomer to initiator. The polydispersity ranges between 1.2 and 1.54 (Table 4). Schindler and Pitt argued that the hydroxyl-initiated ring-opening polymerization of lactones catalyzed by stannous octanoate proceeds without termination reaction and involves only chain propagation and transesterification [23]. This simple mechanism results in monodisperse polymers for low degrees of transesterification.

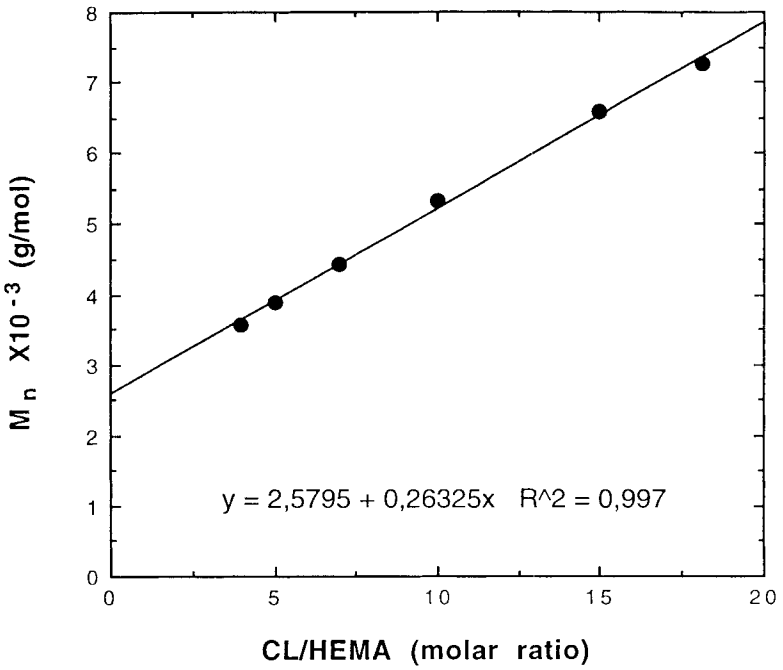


Figure 4. The linear correlation between molecular weight, M_n, of α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer and the molar ratio of ε-caprolactone/2-hydroxyethyl methacrylate.

Influence of the Molar Ratio of Hydroxyl Groups (HEMA) to Stannous Atoms (Stannous Octanoate), OH/SN, on the Molecular Weight of PCL-HEMA Macromonomer

In order to understand the influence of the hydroxyl groups, the polymerization was investigated as a function of the OH/Sn molar ratio. Different molar ratios of hydroxyl group (HEMA) to stannous atom substantially affect the molecular weight of the PCL-HEMA macromonomer, as shown in Figure 2. The lower the OH/Sn molar ratio, the higher the molecular weight of the PCL-HEMA macromonomer. Moreover, it seems that the highest molecular weight could be reached when the OH/Sn molar ratio approached unity. This observation fits with the observation of a maximum value of molecular weight with decreasing $Sn(oct)_2$ concentrations (Figure 1). These results indicate that an appreciable molar ratio of Sn atoms to OH groups is necessary for the complex-formation.

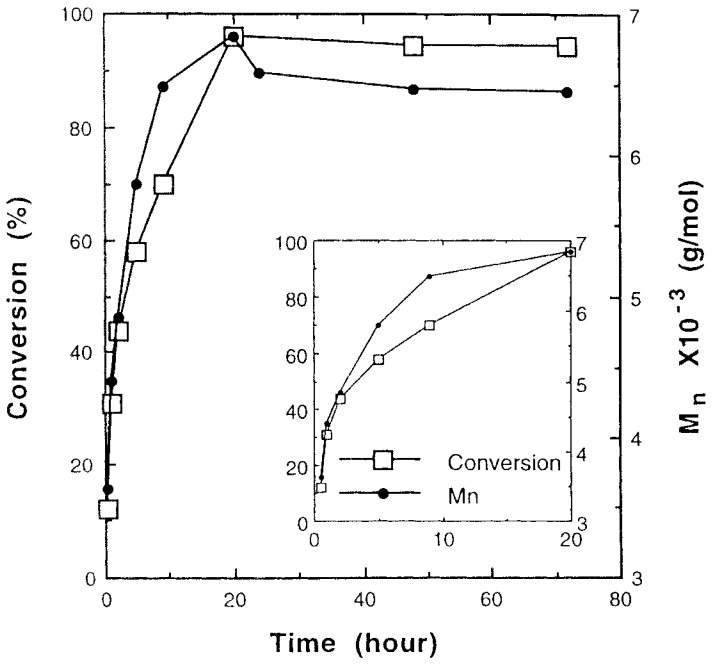


Figure 5. Monomer conversion and molecular weight, M_n, of α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer as a function of time

Polymerization Kinetics

The conversion of ε-caprolactone to poly(ε-caprolactone) was determined by ^{1}H-NMR spectroscopy. The signals at δ = 3.65 ppm (PCL) and δ = 4.18 (CL) have been used to calculate the conversion.

M_n increased gradually with the reaction time and the conversion increased quickly without any induction period (Figure 5 and Table 3) The results indicate a fast initiation and propagation process. When the monomer was completely consumed M_n remained approximately constant. No phase separation was observed throughout polymerization.

Plotting the conversion of ε-caprolactone alongside the change in polymer molecular weight with time, a linear part in the conversion curve could be observed (Figure 5) in spite of the quite rapid increase.

Failure to reach 100% conversion may reflect the reversible nature of the ε-caprolactone polymerization [24]. In any case, further heating causes transesterification and a possible formation of cyclic oligomers [25]. Previous studies showed that

stannous 2-ethylhexanoate might work as a depolymerization catalyst for the polymerization of oxepan-2,7-dione both in bulk melt and in CH_2Cl_2 solution [26, 27].

Due to the electrophilic nature of the coordination complex, degradation of the previously-formed polymer can occur, as shown in Figure 5 and in Table 3. If the degradation of the polymer occurred randomly, the molecular weight distribution of the polymer should increase. However, the molecular weight distributions of the polymer decrease after 20 hours (Table 3). The results show that the degradation proceed from the end of polymer chain. In addition, this effect will be enhanced by the diminished coordination of the hydroxyl compound by the lactone/Sn^+(oct) complex.

From the simultaneous increase of molecular weight and PD with conversion, it can be concluded that the number of polymer chains increases during polymerization (Table 3).

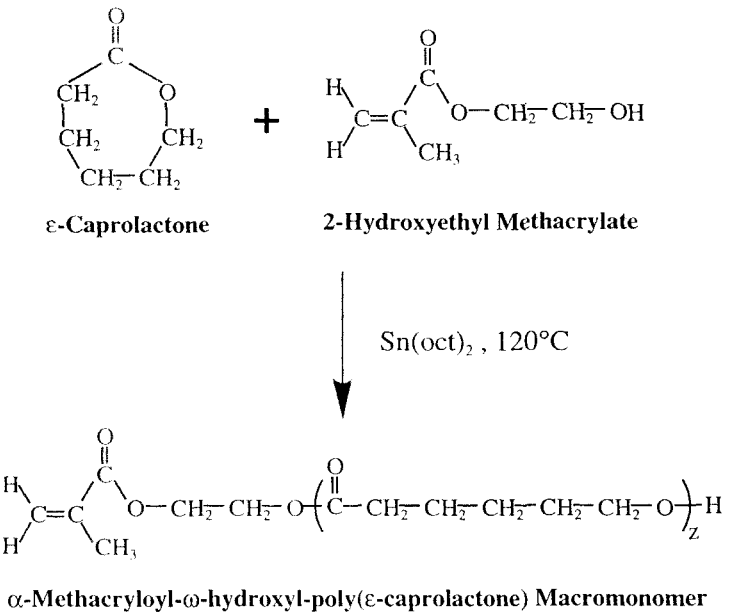
Polydispersity values of 1.14 (see Table 3) provide some indication that the polymerization has a partially 'living' character.

The molecular weight of the whole system increases slowly in a stepwise manner.

Characterization of the Macromonomer

The polymerization of macromonomer is illustrated in Scheme 2. Figure 6 shows the infrared spectrum of the macromonomer. The existence of hydroxyl groups at the end of the polymer chains was confirmed by the IR absorption band of the hydroxyl group. A small sharp band observed at 3583 cm^{-1}, is attributed to a free alcohol hydroxyl group and a characteristic, wide and strong band centered at 3401 cm^{-1}, is attributed to an associated alcohol. The strong complexation of hydroxyl groups was probably caused by strong hydrogen bonds between hydroxyl groups themselves or between the Sn atoms of stannous octanoate and hydroxyl groups. The band at 1728 cm^{-1} indicated the $\nu_{C=O}$ for chain ester groups in poly(ε-caprolactone) and the band at 1639 cm^{-1} showed $\nu_{C=C}$ for the carbon-carbon double bond in the HEMA unit.

According to the literature [28-32], a triplet signal around δ=3.63-3.65 ppm in the ^{1}H-NMR spectrum should be assigned to the HO-CH_2- end-groups of the PCL-HEMA macromonomers (Figure 7). This has been confirmed by esterification of the -C$\underline{H}_2$OH end groups of ω-hydroxypoly(ε-caprolactone) with $(CF_3CO)_2O$ leading to -C$\underline{H}_2$OC(O)CF_3 [27]. After esterification, a triplet at δ 3.65 disappeared and a new one at δ 4.28, arising from an ester end group, was formed. Assignment of the triplet at δ 3.64 has been additionally confirmed by reaction of



Scheme 2. Polymerization Scheme and Chemical Structure of Poly(ε-caprolactone) Macromonomer

the oligodiol, α,ω-dihydroxypoly(ε-caprolactone) with $(CF_3SO_2)_2O$ [30]. The spectrum of the resulting product showed a new triplet at δ 4.64, whereas a triplet at δ 3.64 completely disappeared, because of the formation of an ester end group. After the reaction of the terminal methylene protons with methacryloyl chloride, this peak completely disappeared, whereas new olefin proton signals at 5.53 and 6.07 were formed [28].

The remaining multiplets, centred at δ=1.4, 2.1 and 3.95 ppm, correspond to the main-chain protons of HO-poly(ε-caprolactone)-OH [9, 29 and 30].

The proton of the hydroxyl end group could not be detected by ^{1}H-NMR in chloroform, probably because of a coordination between the hydroxyl end group and Sn atoms of stannous octanoate or a strong hydrogen bond interaction amongst the hydroxyl end groups [33].

Storey and co-workers reported the polymerization of poly(ε-caprolactone) initiated with water, ethylene glycol, and 1,4-butanediol [33]. All polymerizations were carried out in bulk using stannous octanoate as catalyst. Using gated decoupling(decgate) ^{13}C-NMR spectroscopy, they confirmed that water-initiated poly(ε-

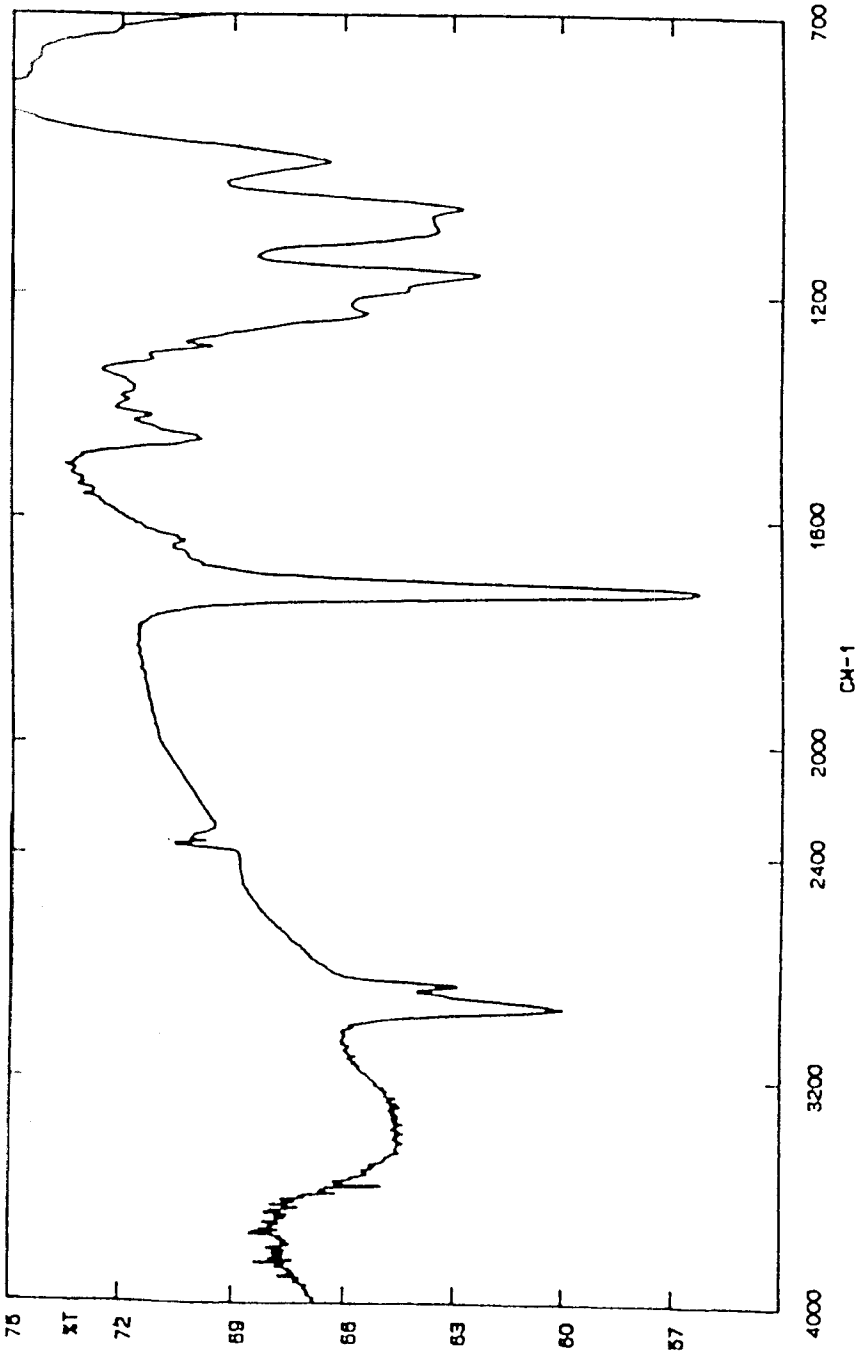
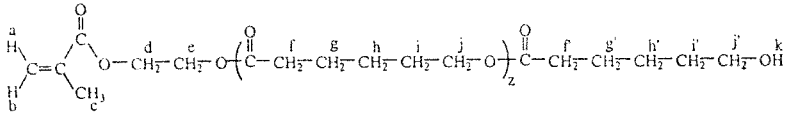


Figure 6. IR spectrum of the α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer



PCL-HEMA Macromonomer

Assignment	Chemical shift δ (ppm)	Integral intensity	Type of protons	Multiplicity
a	6.11	2.16	**H**-C=	s
b	5.58	2.07	**H**-C=	s
c	1.93	10.58	CH_3	s
d+e	4.33	12.13	CH_2	m
f+f'	2.29	53.36	CH_2	m
g+g',i+i'	1.63	118.92	CH_2	m
h+h'	1.37	53.24	CH_2	m
j	4.06	44.85	CH_2	t
j'	3.63	4.73	CH_2	t

$CDCl_3$, 400 MHz, 25 °C.

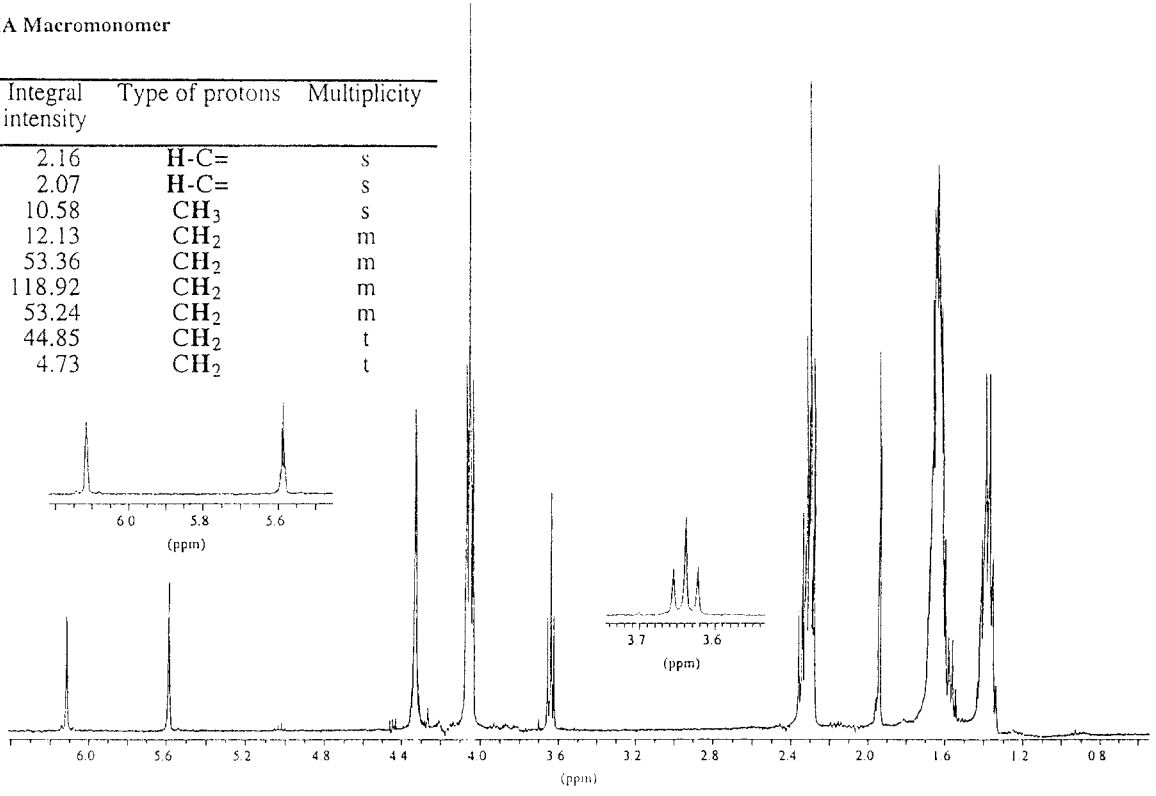


Figure 7. ^{1}H-NMR spectrum and data of the α-methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer

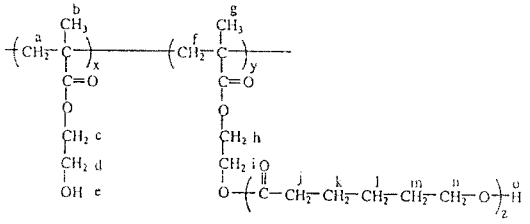
caprolactone) was a linear poly(ε-caprolactone) chain carrying one carboxylic acid group and one hydroxyl end group. In our ^{1}H-NMR spectra, there is no peak observed above δ=7.3, and therefore no carboxylic acid end groups. This indicates that the polymerization of poly(ε-caprolactone) was initiated by HEMA not by water. Spectra of diol-initiated poly(ε-caprolactone) were consistent with a linear poly(ε-caprolactone) chain containing the initiator residue and carrying two hydroxyl end groups. By comparison with the ^{1}H-NMR spectra of the macromonomer (Figure 7), chemical shifts at δ =6.11, 5.58, 1.93 and 4.33 could be assigned to HEMA initiator residue, indicating that a methacryloyl group was attached to the end of a linear poly(ε-caprolactone) chain.

We concluded that stannous octanoate acted as catalyst as well as coinitiator affecting the formation and number of activated centers because of the observed decrease of molecular weight with increasing stannous octanoate concentration while the ROH concentration was held constant (Figure 1 and Table 1). However, IR and ^{1}H-NMR analyses of the reaction mixture failed to show any trace of fragments of the stannous octanoate initiator incorporated in the polymer structure via lactone insertion into stannous octanoate either by alkyl-oxygen or acyl-oxygen cleavage. The reason probably is that stannous octanoate is not chemically bound to the growing chain end **10** (Scheme 1). It could be removed during purification.

The results confirmed the expected structure of poly(ε-caprolactone) with a ω-methacryloyl end-group and an OH end-group, representing a telechelic prepolymer or telechelic oligomer. When this oligomer reacts with the other monomers only by means of its end groups, it could be considered as a macromonomer or macromer.

Copolymerization of PCL-HEMA with HEMA and TMC

To test the reactivity of the ω-methacryloyl end-groups of poly(ε-caprolactone) macromonomer, solution copolymerization of poly(ε-caprolactone) macromonomer with HEMA using AIBN as a catalyst was carried out. At a reason-able unit ratio of HEMA/caprolactone, a graft copolymer was isolated, consisting of a poly(2-hydroxyethyl methacrylate) main chain and poly(ε-caprolactone) graft chains. The ^{1}H-NMR spectrum of the graft copolymer and the assignment of the structure are shown in Figure 8. The disappearance of shifts at δ 6.11 and 5.58 shows that the end double bond has been converted into a carbon-carbon single bond to form the polymer main chain during polymerization. The analysis confirms the expected graft copolymer structure (Scheme 3).



Poly(HEMA)-*g*-poly(ε-CL)

Assignment	Chemical shift δ (ppm)	Type of protons	Multiplicity
a+f	0.95	CH_2	s, wide
b+g	0.78	CH_3	s, wide
c	3.90	CH_2	s, wide
d	3.58	CH_2	s, wide
e	1.79	OH	s, wide
h	2.89	CH_2	s
i	2.73	CH_2	s
j	2.27	CH_2	t
k+m	1.53	CH_2	m
l	1.29	CH_2	m
n	3.98	CH_2	t

DMSO-d_6, 400 MHz, 25 °C

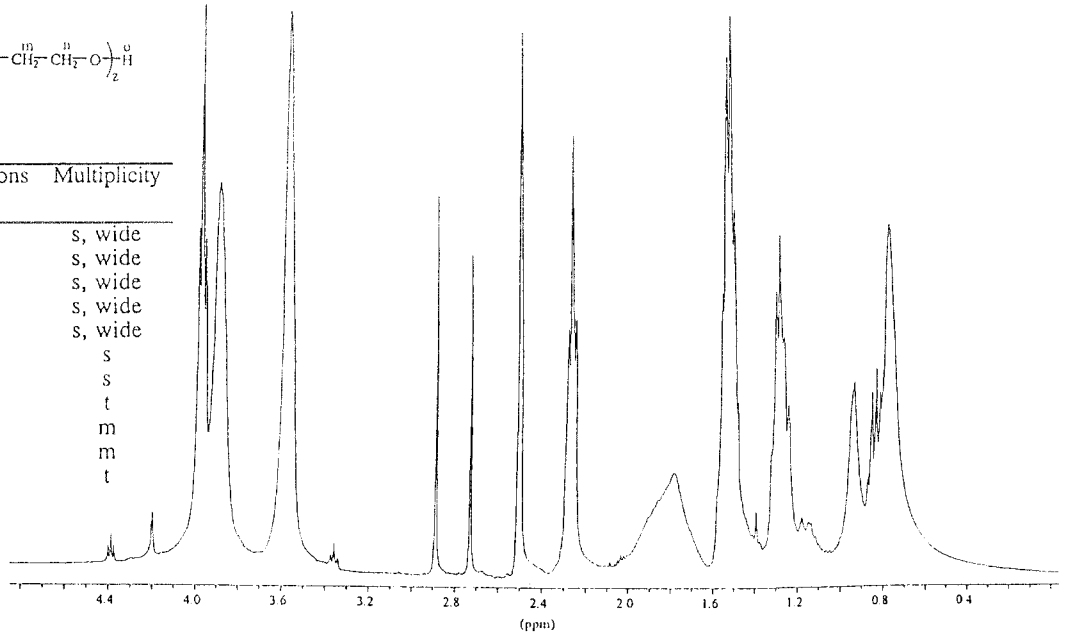
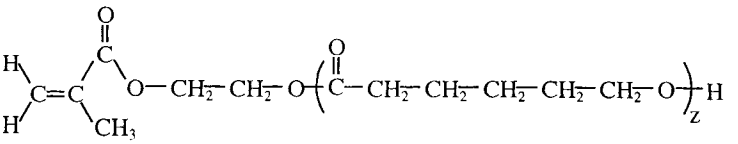
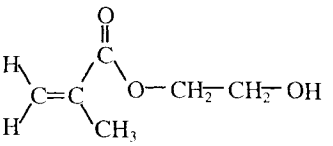


Figure 8. ^{1}H-NMR spectrum and data of poly(2-hydroxyethyl methacrylate-***g***-ε-caprolactone) copolymer

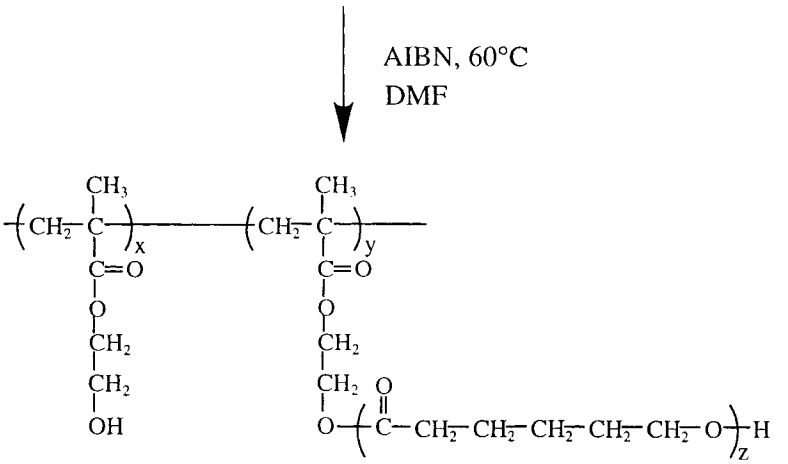


α-Methacryloyl-ω-hydroxyl-poly(ε-caprolactone) Macromonomer

+



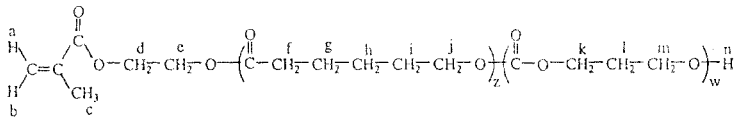
2-Hydroxyethyl Methacrylate



Poly(2-hydroxyethyl methacrylate-*g*-ε-caprolactone) Copolymer

Scheme 3. Graft Copolymerization of 2-Hydroxyethyl Methacrylate and Poly(ε–caprolactone) Macromonomer

In addition, block copolymers can be prepared using the terminal hydroxyl groups of polylactones. Copolymerization of PCL-HEMA with TMC using stannous octanoate as a catalyst was carried out. A copolymer (M_n 9536 and M_w 16818) of TMC with PCL-HEMA (M_n 5514 and M_w 9025) and a copolymer (M_n 14931 and M_w 25646) of TMC with PCL-HEMA (M_n 11978 and M_w 19345) were prepared.

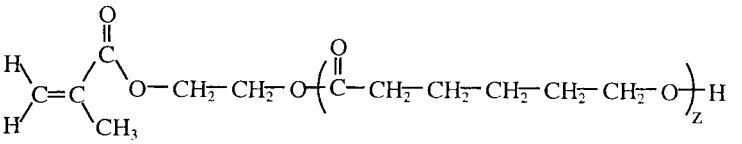


Poly(ε-CL)-*b*-poly(TMC)

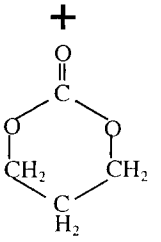
Assignment	Chemical shift δ (ppm)	Type of protons	Multiplicity
a	6.07	H-C=	s
b	5.53	H-C=	s
c	1.90	CH_3	m
d+e	4.40	CH_2	t
f	2.29	CH_2	t
g+i	1.63	CH_2	m
h	1.36	CH_2	m
j	4.04	CH_2	t
k+m	4.22	CH_2	t
l	2.03	CH_2	m
m'	3.72	CH_2	t

$CDCl_3$, 400 MHz, 25 °C.

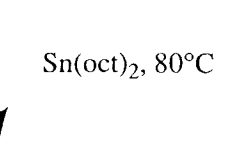
Figure 9. ^{1}H-NMR spectrum and data of poly(ε-caprolactone-***b***-trimethylene carbonate) copolymer

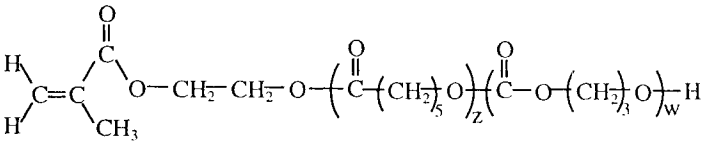


α-Methacryloyl-ω-hydroxyl-poly(ε-caprolactone) Macromonomer



Trimethylene Carbonate





Poly(ε-caprolactone-*b*-trimethylene carbonate) Copolymer

Scheme 4. Block Copolymerization of Trimethylene Carbonate and Poly(ε-caprolactone) Macromonomer

The ^{1}H-NMR spectrum of the graft copolymer and the assignment of the structure are shown in Figure 9.

The results show that OH end groups of PCL-HEMA macromonomer can react as initiators for the further copolymerization of ring carbonates.

CONCLUSION

α-Methacryloyl-ω-hydroxyl-poly(ε-caprolactone) macromonomer was synthesized using stannous 2-ethyl hexanoate as catalyst and 2-hydroxyethyl methacrylate as initiator. The macromonomer was characterized by SEC, IR and ^{1}H-NMR (Scheme 4).

Stannous octanoate was shown to act as an coinitiator as well as catalyst. Our results showed that the formation of a caprolactone/Sn^{+}(oct) complex is a necessary condition for chain propagation initiated by a hydroxyl-containing initiator. HEMA acts as an initiator of the polymerization via the reaction of its hydroxyl group with the lactone/Sn^{+}(oct) complex. The results indicated that a considerable molar ratio of Sn-atoms to OH-groups is necessary for complex-formation.

IR and ^{1}H-NMR showed the expected macromonomer structure, namely linear poly(e-caprolactone) chains, each carrying one methacryloyl and one hydroxyl end group.

We concluded that both of the end functional groups of PCL-HEMA, i.e. α-methacryloyl and ω-hydroxyl, have the reactivity required to participate in free radical copolymerizations in solution or bulk ring-opening copolymerizations.

ACKNOWLEDGEMENTS

We acknowledge Professor Sigbritt Karlsson for scientific discussions and suggestions. Dr. Ronnie Palmgren and Carina Eldsäter are thanked for their helpful technical assistance.

REFERENCES

[1] C. H. Bamford and E. F. T. White, *Trans. Faraday Soc.*, *54*, 268 (1958).

[2] R. Milkovich and M. T. Chiang, US Patent 3,786,116 (1974); R. Milkovich, *ACS Polym. Prepr., Div. Polym. Chem., 21(1)*, 40 (1980).

[3] Y. Yamashita, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, *36*, 193 (1981).

[4] P. Rempp, P. Masson, J. S. Vargas, and E. Franta, *Plaste-Kautschuk*, *28*, 365 (1981).

[5] a) H. Q. Xie and W. Sun, *ACS Polym. Prepr., Div. Polym. Chem.*, *25(2)*, 67 (1984); b) H. Q. Xie and Y. Liu, *Eur. Polym. J.*, *27(12)*, 1339 (1991).

[6] J. M. Onyari and S. J. Huang, *Polymeric Materials Science & Engineering*, *72*, Proceedings of ACS, Division of Polymeric Materials: Science & Engineering, Spring Meeting 1995, Anaheim, California, 137 (1995).

[7] J. M. Onyari and S. J. Huang, *J. Macromol. Sci.-Pure Appl. Chem.*, *A33(5)*, 571 (1996).

[8] Ph. Dubois, R. Jerome, and Ph. Teyssie, *Macromolecules*, *24*, 977 (1991).

[9] S. Sosnowski, M. Gadzinowski, S. Slomkowski, and S. Penczek, *J. Bioact. Compat. Polym.*, *9(4)*, 345 (1994).
[10] H. R. Kricheldorf and M. Sumbel, *Eur. Polym. J.*, *25(6)*, 585 (1989).
[11] G. Rafler and E. Bonatz, *Angew. Makromol. Chem.*, *229*, 199 (1995).
[12] A.-C. Albertsson and M. Sjöling, *J. Macromol. Sci.-Pure Appl. Chem.*, *A29(1),* 43 (1992).
[13] A. J. Nijenhuis, D. W. Grijpma, and A. J. Pennings, *Macromolecules*, *25,* 6419 (1992).
[14] P. J. A. in't Veld, W.-P. Ye, R. Kalp, P. J. Dijkstra, and J. Feijen, *Makromol. Chem.*, *193*, 1927 (1992).
[15] J. Dahlmann and G. Rafler, *Br. Polym. J.*, *23(3)*, 235 (1990).
[16] D. K. Gilding and A. M. Reed, *Polymer*, *20,* 1459 (1979).
[17] S. H. Kim, Y.-K. Han, Y. Ha Kim, and S. I. Hong, *Makromol. Chem.*, *193,* 1623 (1992).
[18] Y. J. Du, P. J. Lemstra, A. J. Nijenhuis, H. A. M. van Aert, and C. Bastiaansen, *Macromolecules*, *28(7)*, 2124 (1995).
[19] J. Dahlmann and G. Rafler, *Acta Polymer*, *44*, 103(1993).
[20] G. Odian, *Principles of Polymerization*, 3rd Ed., John Wiley & Sons, Inc., New York, (1991) p. 377 .
[21] K. Saotome and Y. Kodaira, *Makromol. Chem.*, *82,* 41 (1965).
[22] A. Schlinder, Y. M. Hibioada, and C. G. Pitt, *J. Polym. Sci. Polym. Chem. Ed.*, *20,* 319 (1982).
[23] A. Schindler and C. G. Pitt, *ACS Polym. Prepr., Div. Polym. Chem.*, *25(1)*, 257 (1984).
[24] R. F. Storey, K. R. Herring, and D. C. Hoffman, *J. Polym. Sci.: Part A: Polym. Chem.*, *29*, 1759 (1991).
[25] R. D. Lundberg and E. F. Cox, *Lactones*, in *Ring-Opening Polymerization*, Vol. 2, K. C. Frisch and S. L. Reegens, Eds., Dekker, New York, 1969.
[26] A.-C. Albertsson and S. Lundmark, *J. Macromol. Sci.-Chem.*, *27*, 397 (1990).
[27] S. Lundmark, M. Sjöling, and A.-C. Albertsson, *J. Macromol. Sci.-Chem.*, *A28(1)*, 15 (1991).
[28] R. Nomura and T. Endo, *Polym. Bull.*, *35(6)*, 683 (1995).
[29] A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski, and S. Penczek, *Macromolecules*, *23,* 1640 (1990).
[30] A. Duda, *Macromolecules*, *27*, 576 (1994).
[31] S. Sosnowski, M. Gadzinowski, and S. Slomkowski, *Macromolecules*, *29*,

4556 (1996).

[32] H. R. Kricheldorf, T. Mang, and J. M. Jonte, *Macromolecules*, *17*, 2173 (1984).

[33] R. F. Storey and A. E. Taylor, *J. Macromol. Sci.-Pure & Appl. Chem.*, *A33(1)*, 77 (1996).

Received July 15, 1997
Revision received September 16, 1997