Polyether–polyester block copolymers by non-catalysed polymerization of ε-caprolactone with poly(ethylene glycol)

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The polymerization of ε-caprolactone (CL) with poly(ethylene glycol) (PEG) of low molecular mass was carried out in bulk at 185°C. Gel permeation chromatographic analysis of polymerization mixtures indicated quantitative incorporation of CL monomer into PEG without formation of CL homopolymer. Characterization by infra-red and ^{1}H nuclear magnetic resonance spectroscopy of the resulting polymeric products, with respect to their structure, end-groups and composition, showed that these are best described as ether–ester block copolymers, whose polycaprolactone chain can be regulated by changing the amount of reacted CL. All the copolymers examined were crystalline, as confirmed by differential scanning calorimetric analysis, and showed different thermal behaviours depending on their composition.

(Keywords: ε-caprolactone; poly(ethylene glycol); uncatalysed polymerization; block copolymers)

INTRODUCTION

It is well established (see a recent literature review[1]) that block copolymers, because of their actual and potential applications, have gained an increasing level of importance over the last 10 years. As to the particular area of tailored ether–ester block copolymers, based on recurring ε-caprolactone and oxirane structural units, relatively few studies[2,3] and patents[4–6] concerning their synthesis and characterization have so far been published.

In a recent paper[7] we have reported a simple route to obtain hydroxy-terminated ether–ester block copolymers from the binary system β-propiolactone/poly(ethylene glycol) without any catalyst, but taking advantage of the well known lactone reactivity towards active hydrogen compounds. However, the undesirable occurrence of variable amounts of β-propiolactone homopolymer and carboxyl end-groups was observed, probably due to the high strain of the lactone ring. In keeping with this trend, we considered it to be worth while to extend our studies to a less strained cyclic ester, such as ε-caprolactone, in order to find more suitable conditions for obtaining pure hydroxy-functionalized block copolymers with well defined structure. The polymerization of ε-caprolactone anionically initiated by sodium poly(ethylene glycol) to produce ether–ester block copolymers was reported some time ago[2]; however, in that case the copolymers formed were contaminated by substantial amounts of lactone homopolymer.

In this paper we report results which provide direct evidence for the quantitative formation of a hydroxy-terminated ether–ester block copolymer when ε-caprolactone (CL) is polymerized with chemically unmodified poly(ethylene glycol) (PEG) as prepolymer, under heating and in the absence of any catalyst or initiator.

EXPERIMENTAL

Materials

ε-Caprolactone (*CL*). CL (from Janssen Chimica) was purified by vacuum distillation in the presence of 2% 2,4-diisocyanato-1-methylbenzene. After drying over calcium hydride, it was redistilled. The fraction collected at 96–98°C (5 mbar) was used in the polymerization experiments. This product does not homopolymerize when heated alone for several days at 185°C under vacuum.

Poly(*ethylene glycol*) (*PEG*). PEG of well defined physicochemical characteristics was obtained through extraction and recrystallization, with boiling anhydrous ethyl ether, of the commercial product supplied by EGA-Chemie, Steinheim. The waxy crystalline solid, with melting point 41°C, molecular mass ($\bar{M}_n$) 950, dispersity index ($\bar{M}_w/\bar{M}_n$) 1.10 and hydroxy terminal functionality 2, was denoted PEG-950 and used in this study.

Poly(*oxyethylene*) (*POE*) *and poly*(*ε-caprolactone*) (*PCL*). POE as reference homopolymer with molecular

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mass 1000 (m.p. 40°C) was obtained by repeated fractionation of a Polysciences Inc. commercial product.

PCL homopolymers of different molecular masses (1000–3000) were prepared by bulk anionic polymerization of PL with sodium at room temperature. The product of molecular mass 1000 was purified by repeated precipitation into methanol from methylene chloride solution (m.p. 60°C).

Procedure

Polymerization mixtures were prepared by introducing with a precision syringe, under nitrogen atmosphere, a predetermined volume of CL monomer into a Pyrex phial containing the preweighed amount of degassed PEG-950. The phial was then connected to the vacuum line and, after cooling at liquid-nitrogen temperature, it was evacuated, sealed off and placed in a thermostat at 185°C. A slow and progressive viscosity increase of the bulk homogeneous mixture was always observed during the polymerization and quantitative conversion of the initial CL–PEG mixture to copolymer was achieved over a 30–80 h period. After cooling at room temperature, the phial was opened and the polymerization product recovered in the form of a more or less friable crystalline solid.

Polymer characterization

Gel permeation chromatography (*g.p.c.*). Polymer g.p.c. analyses were performed using a Millipore–Waters GPC-II apparatus with tetrahydrofuran (THF) as eluant at a flow rate of 1.0 cm^3 min^{-1}. Sample concentrations were 0.20–0.30% (m/v). Two sets of three Ultrastyragel columns of 500, 500, 10^3 Å and 500, 10^3, 10^4 Å pore size respectively were employed, according to whether PEG prepolymer or polymerization products were to be analysed. Measurements of the relevant dispersity indices ($\bar{M}_w/\bar{M}_n$) were made on the basis of calibration curves obtained either from PEG standards (Polysciences Inc.) having $\bar{M}_w/\bar{M}_n$ values between 1.05 and 1.10, or from suitable reference samples obtained from copolymer fractionation. This was accomplished by taking advantage of the different solubility behaviour of the copolymers depending on their chemical composition. For example, when the major component of the copolymer was the oxyethylene unit homosequence, fractions with an acceptably narrow g.p.c. peak could be obtained by fractionally precipitating the copolymer from warm methanol or methanol–ethyl ether solutions. The polymerization products, examined by g.p.c. just as they were obtained, were shown to be free from any unwanted CL homopolymer (PCL) and unreacted PEG, and to have $\bar{M}_w/\bar{M}_n$ values ranging from 1.15 to 1.20.

Vapour pressure osmometry (*v.p.o.*). Number-average molecular masses ($\bar{M}_n$) of the polymers produced were measured in 1,2-dichloroethane solution, using a Wescan 233 osmometer operating at 30°C. Sucrose octaacetate was used as calibration standard.

Infra-red spectroscopy (*i.r.*). The i.r. analyses of the copolymers, as solid films obtained by melting the samples on KBr discs, were carried out with a Perkin–Elmer 283-B instrument.

^1H nuclear magnetic resonance spectroscopy (*n.m.r.*). Spectra of polymers in $CDCl_3$ solution were recorded on a Bruker WP-80-SY instrument, with a 30° pulse (1.1 μs) and a relaxation delay of 0.9 s. The number of scans was typically 32 and sample concentrations were in the range 20–30 mg cm^{-3}. Chemical shifts were obtained relative to tetramethylsilane, assuming the signal of a trace amount of $CHCl_3$ as resonating at 7.26 ppm. Probe temperature was 24°C.

Differential scanning calorimetry (*d.s.c.*). D.s.c. measurements were carried out on a Perkin–Elmer DSC-4 instrument equipped with an Intracooler-I apparatus. Samples were cooled from the melt at a rate of 0.1°C min^{-1}. The subsequent heating traces were recorded at 20°C min^{-1}.

RESULTS AND DISCUSSION

The bulk polymerization of CL with PEG-950 as prepolymer in the absence of any catalyst at 185°C is a relatively slow process. Preliminary experiments have shown that at temperatures higher than 185°C (i.e. 220°C) the process speeds up slightly, while at lower temperatures the polymerization slows down. In particular at 130°C the system requires a reaction cycle of several days to obtain acceptable monomer conversion. The time–conversion curve of a CL–PEG mixture at 185°C is reported in *Figure 1*. The plot clearly shows that CL monomer conversion quantitatively occurs within 30 h from the beginning of the reaction. Analogous values of reaction time and conversion were already observed by other authors for the polymerization of CL initiated by active hydrogen compounds, such as ethylene glycol, under similar experimental conditions[8,9]. No indication of CL homopolymer formation, of side reactions and of possible thermodynamic equilibrium was obtained under the adopted experimental conditions.

G.p.c. traces of the same CL–PEG polymerization mixture at different reaction times are shown in *Figure 2*. Comparison of trace B with trace A clearly indicates, after 6 h from the beginning of the reaction, the disappearance of the PEG peak (V_e = 24.7 ml), a substantial decrease of the CL monomer peak (V_e = 32 ml) and the appearance of a new rather narrow and symmetrical peak at lower V_e values (22.3 ml).

This latter peak has been reasonably attributed to the formation of a new polymeric species, namely a presumed PEG–CL copolymer, as a result of the incorporation of CL into the PEG macromolecule. Indeed, for a greater reaction extent (trace C) the copolymer peak area increases, while the relative peak position shifts towards lower elution volumes (21.3 ml) from that of PEG prepolymer, thus reflecting an increase of molecular mass

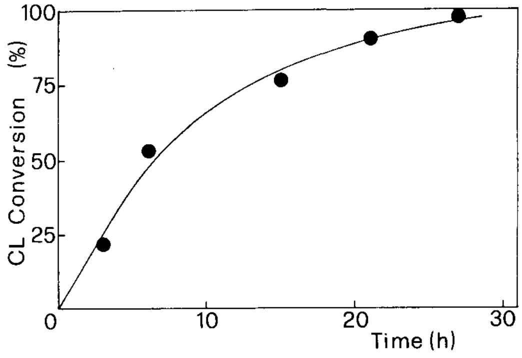


Figure 1 Time–conversion curve for the bulk polymerization of ε-caprolactone (CL) with poly(ethylene glycol) (PEG-950) at 185°C (run R3, *Table 1*)

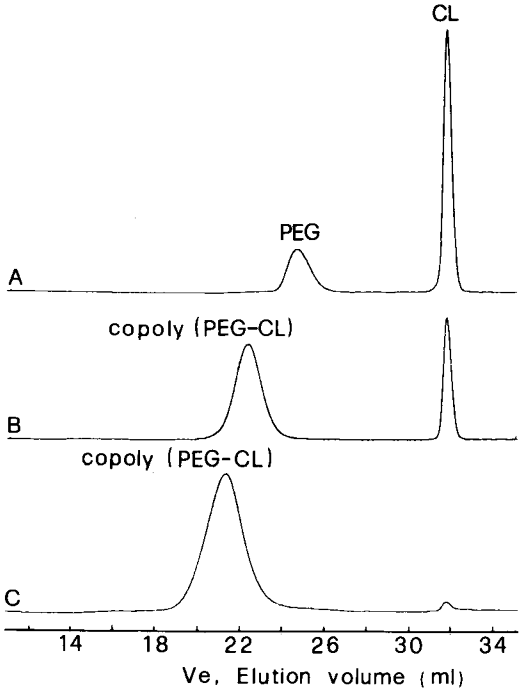


Figure 2 Polymerization of ε-caprolactone (CL) with poly(ethylene glycol) (PEG-950) (run R3, *Table 1*): (A) g.p.c. trace of the unreacted starting mixture; (B) and (C) g.p.c. traces of the same mixture after 6 and 27 h at 185°C, respectively

certainly arising from further incorporation of CL into the copolymer. There were no peaks other than those shown. Furthermore, no change in the pattern of trace C was revealed by varying the chromatographic conditions and the column efficiency. It was therefore concluded that the examined polymerization product is a true copolymer not contaminated by free PCL and residual PEG.

From trace C of *Figure 2* a $\bar{M}_w/\bar{M}_n$ ratio of 1.18 was calculated. However, some broadening of the g.p.c. peak was observed when the polymerization product was kept for longer time at 185°C, once quantitative consumption of CL monomer was reached. Indeed, after an additional 24 h at 185°C the $\bar{M}_w/\bar{M}_n$ ratio of the resulting polymer changed from 1.18 to 1.35, whereas both the symmetry and position of the corresponding g.p.c. peaks were substantially retained. This fact has been taken to indicate the occurrence of possible intermolecular ester interchange at 185°C, and it is to be expected that such reaction continues with time until the establishment of the most probable molecular mass distribution.

In order to gain insight into the chemical structure of the various PEG–CL polymerization products, they were subjected to n.m.r. measurements. A typical spectrum is reported in *Figure 3* (trace A). The spectrum exhibits a sharp singlet centred at 3.7 ppm, two equally intense triplets at 4.1 and 2.3 ppm, and a multiplet at about 1.5 ppm. The singlet resonance at 3.7 ppm has been attributed to the methylene protons of the oxyethylene units of PEG, while the other three groups of signals have been assigned in that order to the a, b and c methylene protons of the oxycarbonyl-1,5-pentamethylene unit homosequence derived from CL ring opening.

These assignments were made by comparison with literature spectra[2] as well as with spectra of binary mixtures based on POE (or PEG) and PCL. Since the sample proved to be free from contaminants, such as PCL and any residual PEG prepolymer, its structure was considered to consist of segments of CL and oxyethylene units chemically joined end-to-end to form a true ether–ester block copolymer. The mole fraction of each component unit in the copolymer is readily determined from the integral peak area ratio of the methylene protons a, b, c or d to the total protons.

The ether–ester nature of the copolymer was demonstrated also by its i.r. spectrum, which displayed the characteristic absorption bands at 1730, 1160 and 1100 cm^{-1} due to the stretching mode of C=O, C–O and C–O–C groups, respectively. Moreover, the spectrum showed in the 3500–3200 cm^{-1} range the characteristic band of hydrogen-bonded hydroxyl, strongly suggesting the presence of terminal hydroxyl functions in the copolymer. To corroborate this attribution, the sample was treated with acetyl chloride and subjected to further spectroscopic observation. While the hydroxyl absorption was no longer discernible in the i.r. spectrum of the acylated sample (not shown here), a new distinct resonance is observable in the respective n.m.r. spectrum (resonance e of *Figure 3* (trace B)). The new signal appears as a singlet at 2.04 ppm in the resonance region of the methyl group of acetic esters. Its position is indicative of a methyl coupled with a weak electron-withdrawing group. In particular, its chemical shift is very close to that recently reported for the methyl protons of the acetate end-group in the polymerization product of β-propiolactone with PEG[7] and in β-propiolactone homopolymer[10]. Therefore, the assignment of the above

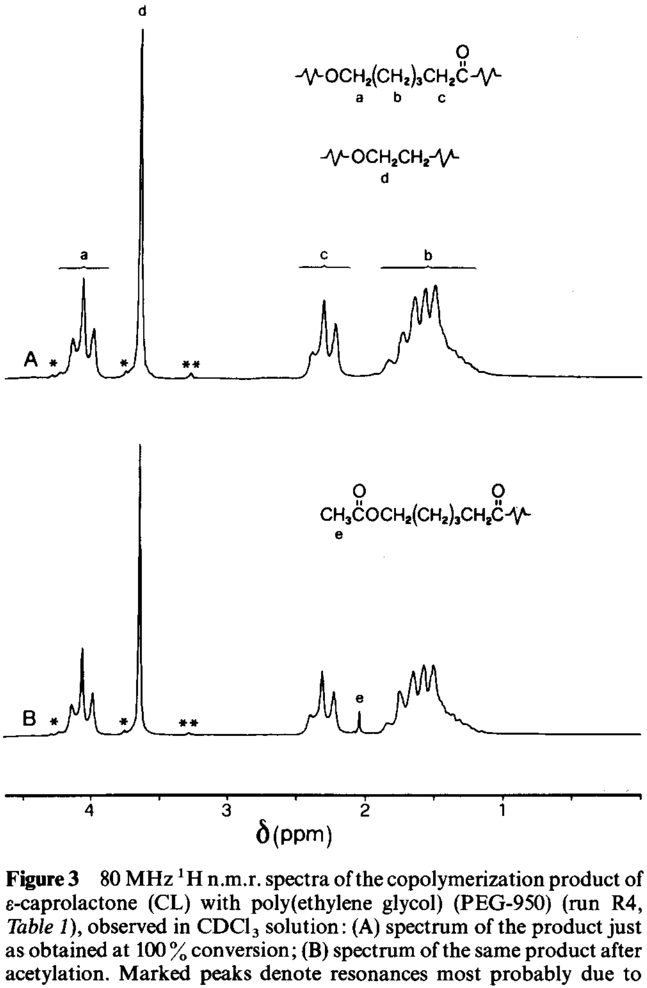


Figure 3 80 MHz ^{1}H n.m.r. spectra of the copolymerization product of ε-caprolactone (CL) with poly(ethylene glycol) (PEG-950) (run R4, *Table 1*), observed in CDCl$_3$ solution: (A) spectrum of the product just as obtained at 100% conversion; (B) spectrum of the same product after acetylation. Marked peaks denote resonances most probably due to block junctions (*) and unknown impurity (**)

Table 1 Compositional and molecular mass data of polymerization products from ε-caprolactone (CL) and poly(ethylene glycol) (PEG-950) in bulk at 185°C

		Copolymer[a]						
			Composition[c] (mol %)		Total $\bar{M}_n \times 10^{-3}$		Block $\bar{M}_n \times 10^{-3}$	
Exp. no.	Feed mole ratio, CL/PEG	Structure[b]	OE[d]	CL	Expt.[e]	Calcd.[f]	POE[g]	2 × PCL[h]
R1	4.00	PCL–POE–PCL	84.83	15.17	1.42	1.39	0.97	2 × 0.225
R2	9.00	PCL–POE–PCL	67.92	32.08	2.00	2.11	0.90	2 × 0.550
R3	19.00	PCL–POE–PCL	50.98	49.02	3.00	3.32	0.86	2 × 1.070
R4	39.00	PCL–POE–PCL	33.39	66.61	5.60	5.85	0.91	2 × 2.345
R5	79.00	PCL–POE–PCL	21.20	78.80	9.50	10.13	0.89	2 × 4.305

[a] Obtained at 100% conversion

[b] Homosequences of ε-caprolactone and oxyethylene units are labelled PCL and POE, respectively

[c] Determined from ^{1}H n.m.r. spectra

[d] OE denotes oxyethylene base unit

[e] Measured by v.p.o.

[f] Derived from copolymer composition considering one PEG residue per copolymer molecule

[g] Calculated from the experimental $\bar{M}_n$ values and percentage mass of oxyethylene unit in copolymer

[h] Estimated as difference between the experimental total $\bar{M}_n$ of the copolymer and the $\bar{M}_n$ of the POE block

resonance peak is appropriate for the acetyl protons of the ester group arising from nucleophilic replacement of the chlorine atom in the acylating agent by the hydroxy end-group of the copolymer. Values of the degree of terminal hydroxyl functionality, as estimated from the peak area ratio of the acetyl protons to the protons of the copolymer units, ranged from 1.8 to 2.0.

Results concerned with the characterization of the copolymers obtained from different polymerization experiments are listed in *Table 1*.

It is seen from the compositional data that the molar fraction of CL units in the copolymer, as determined by n.m.r., increases as the content of CL monomer in the feed becomes higher. A linear relationship was found between the initial mole ratio of CL monomer to PEG and the ratio of CL structural units to OE units in the copolymer obtained at 100% conversion (*Figure 4*). Another relationship is also shown in the same figure, where the $\bar{M}_n$ values of the copolymer increase linearly with the CL/PEG ratio in the initial mixture. Extrapolation to zero content of CL monomer gives a $\bar{M}_n$ value which approximates to that of the starting PEG. Thus, it is possible to control the copolymer molecular mass and composition simply by changing the ratio of monomer to PEG. In this connection it is worth noting in *Table 1* the satisfactory agreement between the $\bar{M}_n$ values measured by v.p.o. and those calculated from compositional data, assuming one PEG unit per molecule of block copolymer formed. Again, the comparison between the $\bar{M}_n$ values of POE and PCL sequences, calculated according to a triblock copolymer structure, shows that the length of the terminal PCL block is proportional to the copolymer composition, while the length of the central POE block appears to be constant, as expected, within experimental errors. Conversion of each individual $\bar{M}_n$ value of POE block into that of the parent PEG molecule, together with the estimate of the corresponding mean value and one standard deviation, led to a $\bar{M}_n$ reliability interval of 924 ± 35.6. This figure is consistent with the molecular mass value of the starting PEG and corresponds to a percentage error of 7.8, which is quite reasonable if one considers that errors as high as 10% may be committed in v.p.o. and n.m.r. measurements.

All the copolymers examined were crystalline, as expected for block copolymers composed of crystallizable POE and PCL segments. Dilatometric and diffractometric results, indicating a lamellar structure for block copolymers based on POE and PCL sequences longer than those present in our samples, were previously reported by Skoulios *et al.*[11].

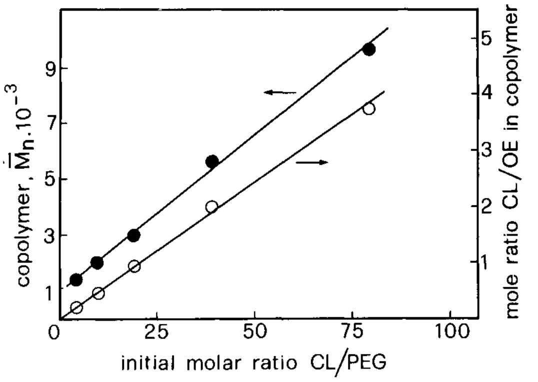


Figure 4 Polymerization of ε-caprolactone (CL) with poly(ethylene glycol) (PEG-950). Dependence of $\bar{M}_n$ (●) and of CL/OE unit ratio in copolymer (○) on the CL/PEG ratio in the feed. OE denotes oxyethylene repeat unit

In order to check the dependence of the thermal behaviour of the copolymers on their composition, d.s.c. measurements were carried out. Thermograms of copolymers with increasing content of CL units together with a reference mixture of POE and PCL homopolymers are shown in *Figure 5*. Trace A, concerning the copolymer most rich in POE, displays a single endotherm at 41°C very close to the melting temperature of crystalline POE homopolymer of comparable molecular mass. Therefore, this endotherm can be attributed to the melting of the copolymer POE block, whose ability to crystallize seems to remain substantially unaffected by the introduction of a few CL units into the copolymer. On increasing the content of CL units, a new endotherm associated with the melting of PCL segments appears at 46°C (trace B), whereas the melting of POE sequence is observed at lower temperature (36°C), thus indicating a melting-point depression. These two endotherms appear more separated in traces C and D. Actually, while the POE melting endotherm shows up substantially unchanged at 36°C in both traces, the PCL endotherm peak is shifted to

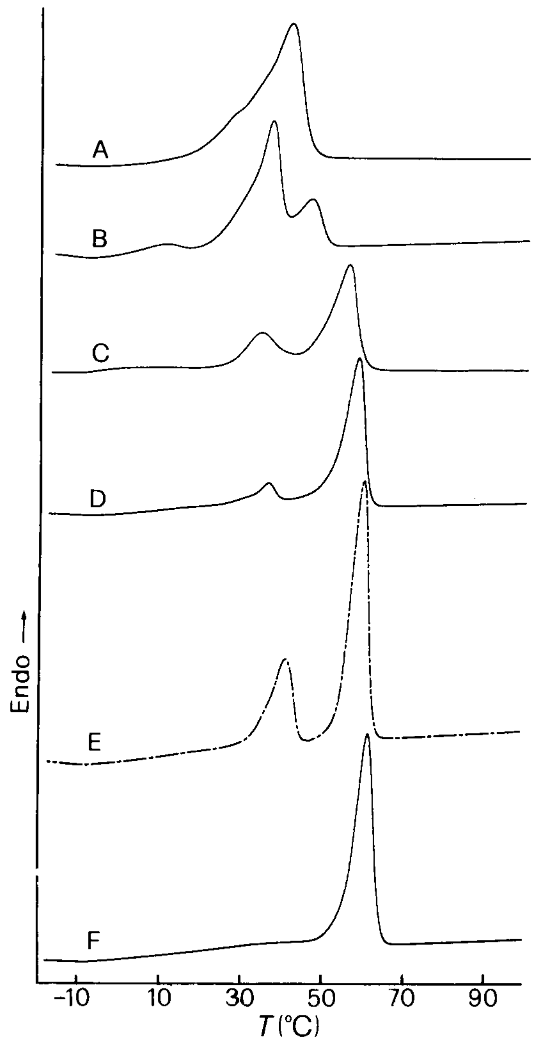


Figure 5 D.s.c. normalized thermograms of the copolymers of *Table 1* and a POE–PCL blend: (A) sample R1; (B) sample R2; (C) sample R3; (D) sample R4; (E) POE–PCL homopolymer mixture 50/50 mol%; (F) sample R5

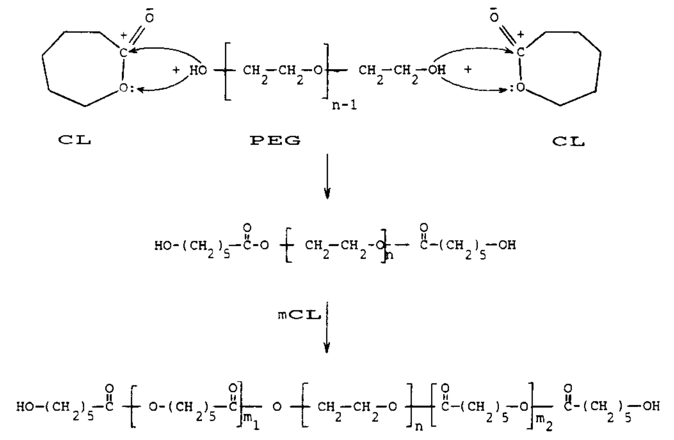
higer temperatures, 56°C (trace C) and 58°C (trace D), this latter being slightly below the melting point of pure PCL homopolymer. Furthermore, the relevant POE and PCL enthalpy changes are as expected on the basis of the copolymer composition. The observed melting depression of POE block may be explained in the following way. The sequence which crystallizes first, namely PCL, has a tendency to freeze the whole structure, thus imposing either imperfect crystallization or smaller crystallites onto the POE block. The latter factor can be excluded because the POE endotherm does not shift on varying the cooling rate.

The distortion of the basic lamellar structure of POE segment with subsequent lowering of the melting point has already been reported for other kinds of block copolymers, when the length of the second component block was increasing[12].

Trace E in *Figure 5* illustrates the thermal behaviour of a POE–PCL physical blend having the same composition as the copolymer of trace C and molecular masses of the homopolymeric components comparable with those of the copolymer blocks. It exhibits two distinct endotherms at 40 and 60°C corresponding to the melting of each pure POE and PCL homopolymer. The observed lack of mutual influence between POE and PCL suggests that the polymeric component phase separates into domains of sufficient size to preserve the individual properties of both homopolymers. A similar macrophase separation cannot take place in the copolymer sample, since the two homopolymeric components are covalently bonded. Finally, it is interesting to observe that the thermogram of the copolymer most rich in CL units (trace F) shows only one rather narrow endotherm peak at 61°C, due to the melting of PCL blocks. The lack of POE thermal transition in trace F proved to be independent of the instrumental detection limit, and therefore it may be explained by assuming that the terminal PCL blocks in the examined copolymer sample are sufficiently long to hinder crystallization of the central POE sequence. No evidence of glass transition temperatures has been obtained. Anyhow, no search for possible transitions of this type, below the examined temperature range, was made.

These results, coupled with the information obtained from other characterization measurements, allow one to conclude that the uncatalysed polymerization of CL with PEG produces a linear ether–ester copolymer of the type poly(CL)-*block*-poly(OE)-*block*-poly(CL).

As regards the polymerization mechanism, an exhaustive investigation in this respect is lacking at present. However, in order to account for the copolymer formation, a simple polymerization scheme may be formalized as follows:



The first step of this reaction scheme involves the addition of two CL molecules onto the PEG hydroxy groups to yield the corresponding bis-ε-hydroxy diester, through selective acyl-oxygen cleavage of the lactone ring. Then, the diester formed reacts further with CL according to the same ring-opening mechanism. Therefore, the copolymer formation proceeds, step by step, with the reaction between the hydroxyl function of the regenerated ε-hydroxycaproyl end unit and excess of CL monomer.

Such a polymerization mechanism is similar to those previously reported for the active-hydrogen-initiated polymerization of other lactones[7–9]. The abovementioned scheme is certainly hypothetical; however, it is consistent with observed experimental facts, such as quantitative copolymer yield, lack of side reactions, control of molecular mass by the CL/PEG ratio and presence of two alcoholic end-groups per copolymer macromolecule.

Further work on the polymerization of CL with PEG is in progress, with special reference to the synthesis of high-molecular-mass block copolymers and to the study of their structure–properties relationships.

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