

Synthesis and characterization of polymers from β -propiolactone and poly(ethylene glycol)s

Piero Cerrai, Mario Tricoli and Fulvio Andruzzi*

Centro Studi Processi Ionici di Polimerizzazione e Proprietà Fisiche e Tecnologiche di Sistemi Macromolecolari, CNR, Via Diotisalvi 2, I-56100 Pisa, Italy

and Maurizio Paci

Dipartimento di Scienze Chimiche, Università di Roma, Tor Vergata, I-00133 Roma, Italy

and Massimo Paci

Dipartimento di Ingegneria Chimica, Università di Pisa, Via Diotisalvi 2, I-56100 Pisa, Italy

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Uncatalysed polymerizations of β -propiolactone with low-molecular-weight poly(ethylene glycol)s were carried out in bulk, at temperatures in the range of 70 to 120°C. ^1H nuclear magnetic resonance (n.m.r.) and differential scanning calorimetry (d.s.c.) measurements on the resulting products indicated a block copolymer structure. Gel permeation chromatography (g.p.c.) and d.s.c. analyses showed that in some cases the copolymerization is accompanied by homopolymerization of β -propiolactone, probably due to the presence of residual water in the poly(ethylene glycol). N.m.r. and infra-red (i.r.) spectra of copolymers revealed the presence of hydroxyl and carboxyl end groups. The copolymerization reaction may be visualized as a two-step process, in which the ring opening of β -propiolactone takes place on both the hydroxyl groups of poly(ethylene glycol), followed by repetitive monomer addition forming an ester-ether-ester triblock copolymer.

(Keywords: lactone; polyols; uncatalysed polymerization; block copolymer; end-group determination)

INTRODUCTION

It is known that lactones may undergo ring opening by active hydrogen compounds, either in the presence or in the absence of catalyst, to give polymers containing hydroxyl end groups^{1,2}.

Syntheses and application of polyester glycols obtained from different lactone monomers by such a polymerization process have been reported in the patent literature³⁻⁵ and in a previous review⁶. However, to our knowledge, no example either of catalysed or of non-catalysed polymerization of lactones with polymeric glycols has been reported so far.

The presence of functionality, based on active hydrogen, at the polymer chain ends may be the key step in forming block copolymers via polymerization with a lactone, when monomer addition takes place on the reactive terminal groups of the polymeric substrate.

The purpose of the present paper is to examine the possibility of preparing ether-ester block copolymers by reacting a highly strained lactone, such as β -propiolactone, with poly(ethylene glycol)s under uncatalysed reaction conditions.

EXPERIMENTAL

Materials

β -Propiolactone (PL), from Fluka, was purified by vacuum distillation with tolylene 2,4-diisocyanate (2% w/w), dried with calcium hydride overnight and then fractionally distilled (50°C at 10 mmHg). Purified monomer was further distilled *in vacuo* into glass ampoules equipped with break-seals which were sealed off and stored in a refrigerator.

Poly(ethylene glycol) standards, from Polysciences Inc., with number-average molecular weight of 600 (PEG 600), a viscous liquid, and 1470 (PEG 1470), a crystalline solid melting at 51–52°C, were used as received.

Poly(β -propiolactone) as reference polymer was prepared by cationic polymerization of PL with perchloric acid at 0°C in methylene chloride solution. The product, after purification by repeated precipitations into methanol from methylene chloride solution, was obtained as a crystalline powder melting at 85–87°C.

Procedure and apparatus

The polymerizations were carried out in glass phials sealed under vacuum. The measured volume of PL was dispensed from a precision burette into a phial

* To whom correspondence should be addressed

containing the preweighed amount of PEG, previously degassed at $\sim 80^\circ\text{C}$. After sealing off, the phial was maintained at one of the temperatures listed in Table 1. Once the reaction mixture apparently had reached the maximum viscosity (usually after 72 h), the phial was opened and the mixture dissolved in methylene chloride. The polymeric products were quantitatively recovered by precipitation in a 10-fold excess of methanol, washed several times with aqueous methanol and dried *in vacuo* at 50°C . The recovered products were proved by g.p.c. to be completely free from any unreacted PL and PEG.

When necessary for analytical purposes, polymer samples were subjected to acylation by acetyl chloride in methylene chloride solution containing pyridine, at room temperature. After separation of the pyridine hydrochloride by centrifugation, the products were purified by precipitation in excess methanol and dried under vacuum.

^1H nuclear magnetic resonance spectroscopy

Spectra were run on a Bruker WP-80-SY instrument with a 30° pulse ($1.1\ \mu\text{s}$) and a relaxation delay of 0.9 s. The number of scans was typically 32. Sample concentration was $20\ \text{mg ml}^{-1}$ in anhydrous chloroform- d_1 . The chemical shift (ppm) scale was referred to tetramethylsilane (TMS), assuming the signal of a trace amount of chloroform as resonating at 7.26 ppm. Probe temperature was 34°C .

Infra-red spectroscopy

I.r. spectra were recorded with a Perkin-Elmer 283B instrument, on solid film samples prepared by melting the polymers on KBr discs.

Differential scanning calorimetry

D.s.c. traces were obtained with a Perkin-Elmer DSC-4 instrument at scanning speed of $20^\circ\text{C min}^{-1}$.

Gel permeation chromatography

G.p.c. measurements were performed with a Millipore-Waters GPC-II chromatograph fitted with three ultrastayragel columns with pore size 100, 500 and $10^3\ \text{\AA}$,

for a total plate number of $\sim 50\ 000$. Tetrahydrofuran, as carrier solvent, was used at room temperature with $1\ \text{ml min}^{-1}$ flow rate, by admitting $30\ \mu\text{l}$ per column of 0.3% (w/v) polymer solution.

Vapour pressure osmometry

Number-average molecular weights (\bar{M}_n) were determined in ethylene dichloride at 30°C with a Wescan 233 osmometer. Sucrose octaacetate and polystyrene were used as calibration standards.

RESULTS AND DISCUSSION

Results and experimental conditions of various polymerization experiments are summarized in Table 1.

For the initial characterization of the polymerization products, we thought ^1H n.m.r. spectroscopy helpful for giving insight into the structure and chemical composition of the materials. A typical ^1H n.m.r. spectrum for a PEG 600-PL polymerization product is shown in Figure 1. The two triplets of equal intensity centred at 2.64 and 4.34 ppm and the singlet at 3.62 ppm have been assigned in that order to a and b methylene protons of homosequences of PL ester units and to the methylene protons of homosequences of PEG oxyethylene units. These assignments are based on comparison with the reference spectra of PEG and PL homopolymers.

One of the inherent difficulties encountered in the characterization of block copolymers is to obtain pure copolymers which do not contain homopolymeric contaminants. However, since the polymer sample was free from any residual PEG, the single resonance observed at 3.62 ppm in the spectrum of Figure 1 was considered to arise only from homosequences of PEG oxyethylene units linked together with segments of PL ester units to form a block copolymer. Similar consideration could not be made for the PL homosequences, since the presence in the sample of sizable amounts of PL homopolymer was suggested by gel permeation chromatography. The g.p.c. chromatograms of the sample R5 of Table 1 (sample A) and of the same sample after fractionation (sample B) are shown in

Table 1 Uncatalysed bulk polymerizations of β -propiolactone (PL) with poly(ethylene glycol) (PEG)

Exp. no.	Composition (mol%) ^a				Temp. (°C)	Yield ^c (wt %)	\bar{M}_n ($\times 10^{-3}$)
	Feed		Product				
	PEG ^b	PL	PEG ^b	PL			
R1	0	100.0	—	—	70	0	—
R2	7.0	93.0	9.1	80.9	70	67	3.1
R3	15.4 ^d	84.6	7.8	92.2	70	66	2.6
R4	30.9 ^d	69.1	16.4	83.6	70	72	3.3
R5	41.3 ^d	58.7	13.1	86.9	70	58	2.2
R6	60.5 ^d	39.5	22.3	77.7	70	48	2.1
R7	50.0 ^e	50.0	12.1	87.9	70	65	13.0
R8	50.0 ^e	50.0	15.5	84.5	95	63	12.4
R9	50.0 ^e	50.0	14.5	85.5	120	58 ^f	12.5 ^g

^a Determined from ^1H n.m.r. spectra

^b Expressed in mol % of oxyethylene base unit

^c Estimated as weight of recovered polymer/total weight of reagents

^d PEG 600

^e PEG 1470

^f Value inclusive of 20% crosslinked material

^g Determined on the non-crosslinked soluble polymer

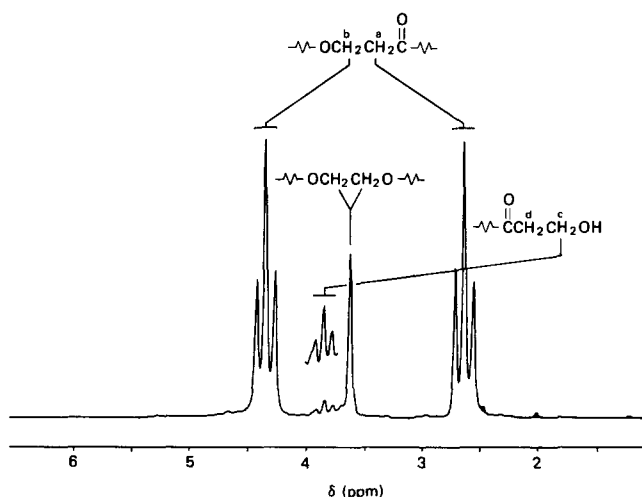


Figure 1 80 MHz ^1H n.m.r. spectrum of a PEG 600-PL polymerization product (sample R5 of Table 1), observed as 2% (w/v) solution in CDCl_3 . The small filled-in peaks on the right are due to unknown impurities or oligomers

Figure 2. As seen from this figure, the g.p.c. traces of samples A and B consist of two partially resolved peaks varying in magnitude. The possibility that these curves might represent different bimodal molecular-weight distributions (*MWD*) of the same polymer was considered unlikely. Indeed, it is difficult to attribute to this system properties like those of typical dielectric (cationic or anyway catalysed) polymerizations, which give rise to bimodal polymer *MWD*. Therefore, the two peaks of A and B were more realistically considered to belong to different polymeric species. In particular, supposing the PEG content in the two samples is proportional to the copolymer fraction, the peak with the higher retention volume (~ 21.2 ml), whose relative proportion decreases as the PEG content decreases, has been attributed to the block copolymer. Conversely, the peak at ~ 20.2 ml, whose proportion increases as PEG decreases, has been associated with the PL homopolymer.

The d.s.c. thermograms of the same samples of Figure 2 are shown in Figure 3. Trace A displays a melting endotherm with a temperature at peak maximum of 84°C and a prominent shoulder with tailing on the low-temperature side. Conversely, trace B exhibits appreciable reduction of the shoulder and endotherm

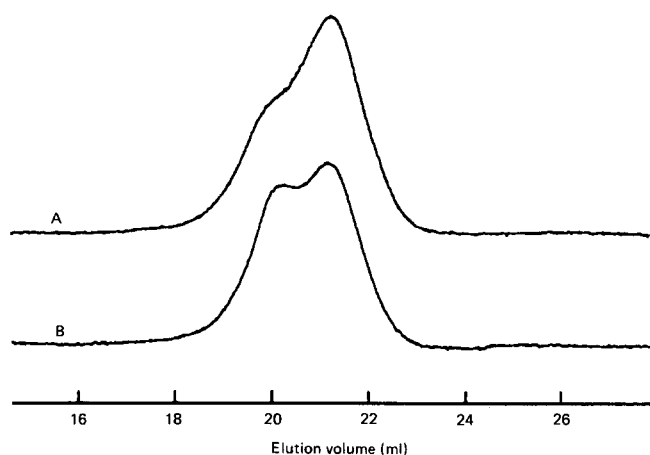


Figure 2 G.p.c. traces of PEG 600-PL polymerization product: trace A, sample R5 of Table I; trace B, same as A after reprecipitation from methylene chloride by methanol, with a 1:1 ratio of solvent to precipitant. PEG content (mol% of oxyethylene units): A, 13.1; B, 7.7

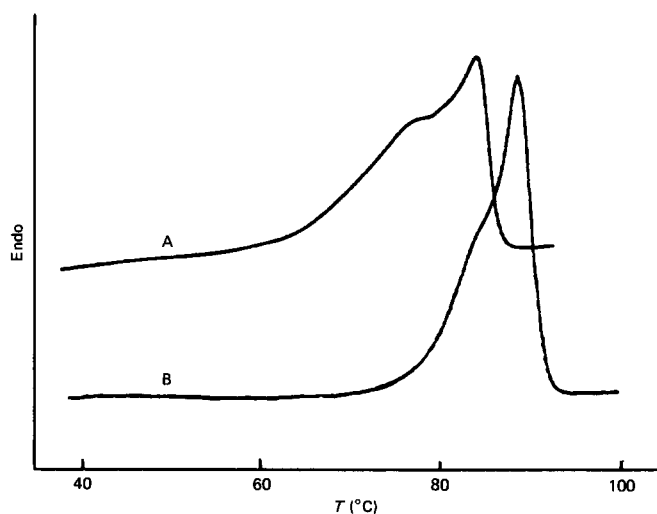


Figure 3 Second-run heating d.s.c. traces of PEG 600-PL polymerization product; curves A and B represent same samples as in Figure 2

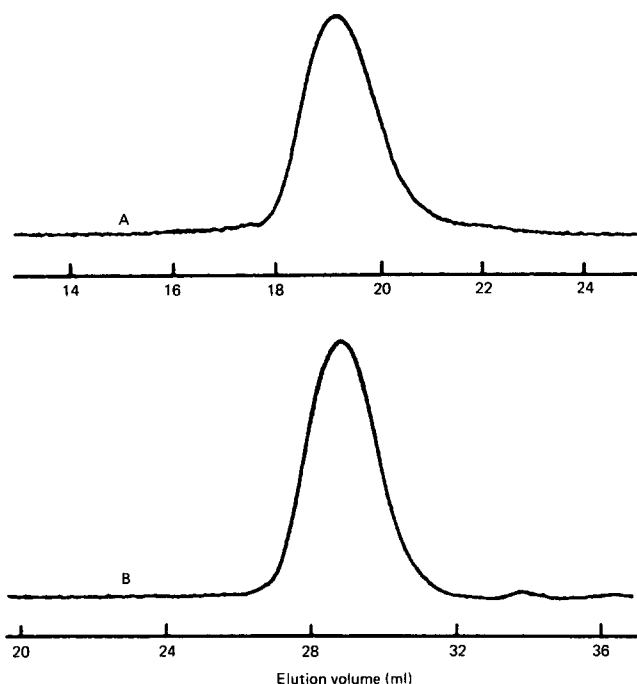


Figure 4 G.p.c. curves of PEG 1470-PL polymerization product (sample R7 of Table I): curves A and B, chromatograms obtained with three (100, 500 and 10^3 Å) and four (100, 500, 10^3 and 10^4 Å) ultrastaygel columns, respectively

sharpening. Furthermore, the temperature of the endotherm peak is shifted towards a value ($\sim 88^\circ\text{C}$) very close to the melting temperature of the PL homopolymer, as shown by comparison with d.s.c. traces of a reference sample of PL homopolymer. All these changes are consistent with different contents in both samples of a material with a melting temperature lower than that of the homopolymer. It is reasonable to identify the lower-melting material with the block copolymer, owing to the presence in its backbone of the flexible polyether (soft) segments, which are effective in reducing the melting temperature.

Attempts to obtain pure copolymer samples from the polymeric mixture were unsuccessful, although several fractionation procedures, based on different solvents and temperatures, were tried.

Copolymerization products apparently free from PL homopolymer were obtained when PEG 1470 was used. Typical g.p.c. curves of a copolymerization product containing PEG 1470 (R7 of Table I) are shown in Figure 4. Trace A consists of a single, virtually symmetric, peak, which exhibits a value of elution volume lower than those of the g.p.c. curves of Figure 2, due to its higher molecular weight. No change in the pattern of R7 trace was observed by repeating the g.p.c. measurement under improved resolution conditions, except for the presence of a small peak at higher elution volume, due to unknown low-molecular-weight material (trace B). These results indicate that the product examined consists substantially of pure copolymer.

The n.m.r. spectrum of this sample is very similar to the spectrum of Figure 1, thus suggesting a block structure for the copolymer. Further evidence in favour of this structure is provided by comparison of the copolymer d.s.c. trace with that of a PEG 1470-PL homopolymer blend reproducing the copolymer composition. These thermograms, designated respectively as A and B, are presented in Figure 5. Trace B shows two quite distinct

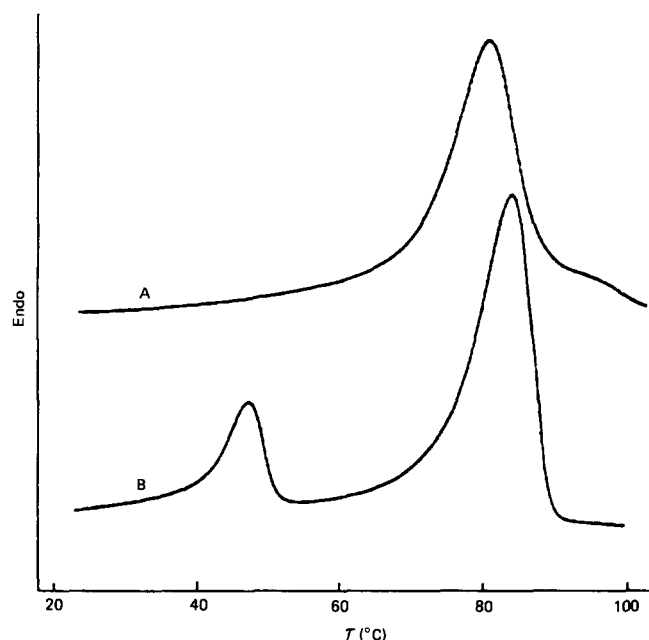


Figure 5 Second-run heating d.s.c. traces showing the melting behaviour of the PEG 1470-PL polymerization product (sample R7 of Table I) (curve A) and of PEG 1470-PL homopolymer mixture (curve B), having the same molar composition as sample R7

thermal transitions, at ~ 47 and $\sim 84^\circ\text{C}$, associated with the melting of PEG and PL homopolymer crystals, respectively. The temperatures of the two transitions are very close to those measured separately for each pure component. Furthermore, the relevant enthalpy changes are as expected on the basis of the blend composition.

These facts demonstrate the mutual immiscibility of the two polymeric species. It is worth, now, noting that the melting peak of PEG is no longer recognizable in the copolymer d.s.c. trace A, which shows only one melting endotherm at a temperature (81°C) slightly lower than that of the pure PL homopolymer. These results, and in particular the absence of a separate crystalline phase of PEG 1470 in the sample of copolymer, unambiguously prove that in this material the PEG soft segments are chemically linked to the PL polyester segments to give a block structure.

According to the copolymerization scheme that will be proposed later, this copolymer may be assumed to have a triblock (PPL-PEG-PPL) structure.

As a further step in polymer characterization, it was considered to be advantageous to monitor the polymer end groups, for the mechanistic information they can provide.

End-group assignments are presented in the previously examined spectrum of Figure 1. It is seen from this spectrum that the low-intensity triplet at 3.85 ppm has been attributed to the c methylene protons of a terminal ester unit carrying a primary hydroxyl group. No distinction could be made between terminal ester units of the copolymer and PL homopolymer. To confirm the above assignments, the polymer sample was acetylated (cf. 'Experimental') and the respective n.m.r. spectrum recorded (Figure 6). In this spectrum the triplet at 3.85 ppm is no longer discernible, whereas a new single resonance appears at 2.02 ppm, in the typical absorption region of aliphatic methyl esters. Its chemical shift is similar to that recently reported for the methyl ester end group in poly(β -propiolactone)⁷. Therefore, the new

singlet has been assigned to the methyl protons of the acetyl moiety incorporated into the copolymer and/or the PL homopolymer, as an ester end group resulting from the reaction of the acetyl chloride with the terminal hydroxyls.

The apparent lack in the spectrum of Figure 1 of the weak triplet expected for d methylene protons is explained by its overlap with the polymer triplet at 2.64 ppm. This was confirmed by the relevant spectrum at 300 MHz (not shown), which proved the presence of the expected triplet on the high-field side of the 2.64 ppm polymer triplet. Similarly, the lack in the spectrum of the acetylated polymer (Figure 6) of the triplet clearly observable at 3.85 ppm in the spectrum of the non-acetylated polymer (Figure 1) can be explained by its migration under the polymer triplet at 4.34 ppm, as a result of the deshielding effect exerted by the ester group on c methylene protons. Thus, it follows from the spectra of Figures 1 and 6 that the formation of hydroxyl end groups takes place in the copolymerization of PL with PEG 600.

The weak peak at 3.7 ppm in the spectrum of Figure 6 may be assigned to the methyl protons of ester groups, probably arising from methanolysis of anhydride linkages formed in the polymerization reaction and already present in the original sample (cf. Figure 1).

Quantitative estimates of hydroxyl end groups in acetylated polymers were made according to the peak area ratio of methyl protons to protons of the polymer units. From these measurements, values in the range 1.3–0.7 were obtained for the relevant hydroxyl content, expressed as moles of hydroxyl group per mole of product polymer. These values are considerably lower than the theoretical value, assumed to be equal to 2, and this fact prompted us to search for other different end groups.

The i.r. spectrum of the sample of Figure 1, in the 4000–2500 cm^{-1} region, is shown in Figure 7. In this spectrum, besides the C–H stretching band (ν_{CH_2} , 2925–2850 cm^{-1}) of the polymer units, a strong and broad band appears in the 3600–2700 cm^{-1} range, where absorption of hydroxyl and carboxyl groups generally occurs. The portions of this band on which the overtone at 3440 cm^{-1} falls (arising from the ester carbonyl absorption) has been attributed to the hydroxyl end groups, while the portion

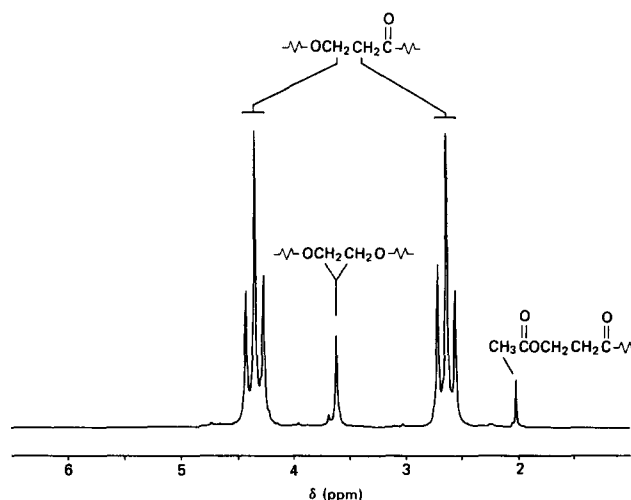


Figure 6 80 Hz ^1H n.m.r. spectrum of PEG 600-PL polymerization product (sample R5 of Table I) after acetylation (cf. 'Experimental'). Conditions as in Figure 1

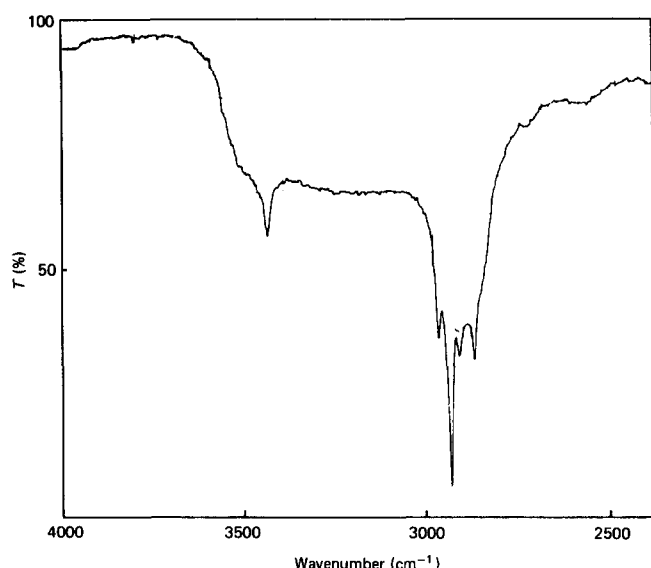
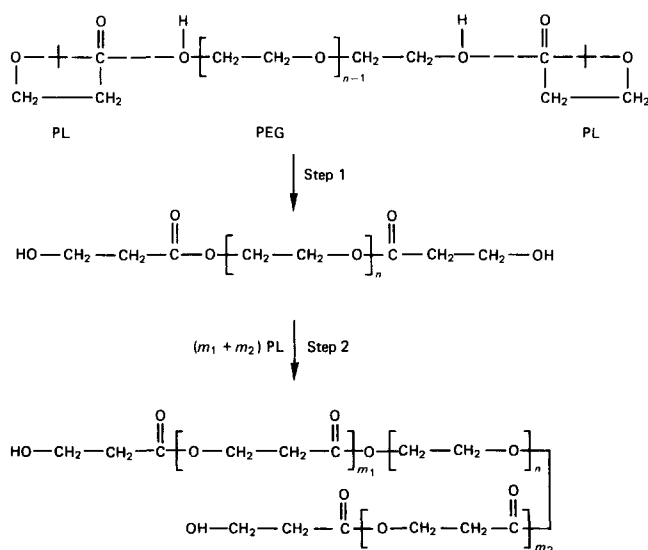


Figure 7 Partial i.r. spectrum of PEG 600-PL polymerization product (sample R5 of Table 1). Melting film between KBr discs

centred near 3200 cm^{-1} , and partially overlapped by the C-H absorption, is indicative of carboxylic groups. The presence of these groups was confirmed by subjecting the presumed carboxyl functions of the polymer to exchange reaction with excess acetyl chloride in methylene chloride solution. The i.r. spectrum of the reaction product, recovered by vacuum evaporation of all the volatile components, showed the disappearance of the hydroxyl band, a marked decrease of the carboxyl band and the appearance of the characteristic absorption of the linear aliphatic anhydride at 1820 cm^{-1} . After hydrolysis of the product in aqueous THF, the anhydride band disappeared completely, while the carboxyl band was restored to its original intensity. Terminal hydroxyl and carboxylic groups were detected also in the copolymers obtained from PL and PEG 1470. However, quantitative measurements of these groups were difficult, in this case, because of their lower concentration due to the higher copolymer molecular weights.

As far as the polymerization mechanism is concerned, a reasonable approach to this can be based on the assumption that the uncatalysed ring-opening reaction of PL with PEG is expected to be similar to that found for the hydrolysis reaction:



Step 1 is the nucleophilic attack of PEG hydroxyl on the PL carbonyl group to give bis- β -hydroxy poly(oxyethylene) diester. Similar bimolecular reaction has recently been postulated for the uncatalysed ring opening of cyclic acid anhydrides with aliphatic alcohols⁸. By repeating this step, the hydroxy diester reacts further to form a triblock PL-PEG-PL copolymer containing ether and ester segments (step 2).

Owing to the absence of any externally added catalyst, the copolymerization process is regarded as a uncatalysed reaction; however, step 1 may be considered as initiation by a proton-donor compound (PEG). According to the above scheme, the ring cleavage of PL is depicted as taking place at the acyl-oxygen bond. This mechanism is responsible for the formation of hydroxyl terminal groups; however, the well established presence of carboxyl end groups, in addition to the hydroxyl groups, indicates that an alkyl-oxygen bond-breaking mechanism is also operative. Anyway, it is difficult at present to establish if this second mechanism takes place in the initiation step or as an inversion of the acyl-oxygen cleavage during the growth reaction. On the other hand, more detailed considerations in this context are beyond the scope of this investigation.

The reaction of PL with PEG proceeds rather slowly and does not lead to quantitative conversion, possibly due to establishment of an equilibrium. Anyway, the data of Table 1 show rather scattered values of polymer yield, composition and M_n for the experiments R2-R6. The irregularity of the results of the copolymerizations of PEG with PL most notably depends on the simultaneous formation of the PL homopolymer, which certainly makes the whole copolymerization process more complex than would be expected on the basis of the reaction scheme in steps 1 and 2.

The concurrent homopolymerization of PL may be explained if one assumes initiation by the residual water contained in the liquid PEG 600. Pure and well dried PL does not polymerize under vacuum at 70°C ; however, in the presence of small quantities of intentionally added water, it slowly polymerizes. Most probably, the first step of this ring-opening polymerization is the hydrolysis of PL with subsequent formation of β -hydroxypropionic acid. Bimolecular hydrolysis of PL, under neutral conditions, has already been reported⁹. Presumably, this reaction is then followed by a slow propagation step involving addition and direct attachment of PL monomer to one or both the end groups of the acid. This type of polymerization of the PL monomer can be considered analogous to the already reported hydrolytic polymerization of ϵ -caprolactam¹⁰.

Conversely, regular and reproducible results are observed for the experiments R7-R9 of Table 1, where block copolymers free of PL homopolymer are formed. For these triblock copolymers a satisfactory agreement, within experimental uncertainty, is found between the measured M_n values and those calculated on the basis of the copolymer composition. The ratio of the average length of the polyester segment to the length of the polyether segment varies between 2.3 and 2.4.

Reaction temperatures outside the range 70 – 120°C were not used. Indeed, below 70°C the initially liquid reaction mixture tends to solidify before attaining the maximum copolymer yield, whereas above 120°C extensive intermolecular dehydration of the hydroxyl end groups of the copolymer takes place with formation of

double bonds, which in turn polymerize to give crosslinking. These side reactions were already observed, even if to a minor extent, at 120°C.

The polymerization results described above show that it is possible to prepare a block copolymer from β -propiolactone and poly(ethylene glycol), under appropriate conditions, in the absence of catalyst. However, the use of a highly strained monomer such as β -propiolactone gives rise in the same polymerization process to both acyl- and alkyl-oxygen cleavages of the ring. For this reason, it is difficult to control the structure of the polymer end groups.

Further work along these lines is in progress with the aim of extending the uncatalysed synthesis of block copolymers to other less strained lactones.

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