Synthesis, Characterization, and Miscibility of Caprolactone Random Copolymers

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ABSTRACT: The ring-opening polymerization and copolymerization of ϵ-caprolactone, ϵ-methyl-ϵ-caprolactone, β,δ-methyl-ϵ-caprolactone (mixed isomers), and L-lactide using aluminum isopropoxide as initiator were investigated. The chain propagation proceeds through a living anionic type coordinated insertion mechanism. The kinetic features of this process are reported. The experimental monomer reactivity ratios indicate that ϵ-caprolactone and its methyl derivatives yield random copolyesters. However, the ϵ-caprolactone/L-lactide pair exhibits a departure from randomness with the preferred incorporation of L-lactide units. The thermal properties of the copolymers were investigated by differential scanning calorimetry. It was found that the crystallization of ϵ-caprolactone units is limited, in all cases, to copolymers which are rich in this sort of unit. At the same time, the crystallization of L-lactide units was observed in copolymers with high concentrations of this comonomer. Analysis of the melting point depression data of the copolymers indicates that the L-lactide units are almost completely rejected from the caprolactone crystals, whereas about 50% of the ϵ-methyl-ϵ-caprolactone and δ,δ-methyl-ϵ-caprolactone comonomer units are incorporated into the ϵ-caprolactone crystals due to an obvious structural similarity. Finally, poly(ϵ-caprolactone-*co*-ϵ-methyl-ϵ-caprolactone) samples are miscible with poly(vinyl chloride) (PVC) whatever the composition of the copolymer and the composition of the blend, whereas poly(ϵ-caprolactone-*co*-L-lactide) samples are miscible with PVC uniquely for copolymer L-lactide contents equal to or smaller than 40 wt %. In all cases where miscibility was found, a negative thermodynamic interaction parameter was computed.

Introduction

In the family of polyesters, poly(ϵ-caprolactone) (PCL) occupies a unique position since it is at the same time biodegradable[1,2] and miscible with a variety of polymers, including poly(vinyl chloride) (PVC), poly(styrene-*co*-acrylonitrile), nitrocellulose, cellulose propionate and butyrate, poly(epichlorohydrin), and bisphenol A polycarbonate.[3] In addition, PCL crystallizes very readily and cannot be quenched to a glass.[4]

The biodegradability and lack of toxicity of PCL is of great interest for the controlled release of drugs from subdermally implanted polymer devices. In this environment, PCL has a useful lifespan approaching 1 year.[2] However, other homopolymers and copolymers can be used for this purpose. For example, poly(DL-lactide) is an amorphous polyester that displays a greater rate of ester hydrolysis than PCL. Moreover, when used in the form of a copolymer, the reduction of the melting point of PCL below body temperature enhances its degradation rate.[5] Therefore, the random copolymerization of ϵ-caprolactone with substituted ϵ-caprolactones and lactide could be an attractive means to control simultaneously the crystalline properties and the biodegradation rate, or the useful lifetime, of PCL.

Blended with thermoplastics like PVC, PCL is miscible despite its pronounced semicrystalline character.[6] Unfortunately, PCL is able to crystallize in PVC/PCL blends at a rate and to an extent increasing with the polyester content. It is only at concentrations lower than about 40 wt % that the PCL crystallization is impeded over long periods of time. The progressive PCL crystallization into otherwise homogeneous polymer blends may prevent their technological development because of undesirable modifications in the material properties as a function of time. A solution to this problem would be to reduce, as extensively as possible, the ability of PCL to crystallize, if not in the pure state, at least in blends with miscible components. In that respect, it is of prime importance that the PCL miscibility remains unaffected by whatever structural modifications are required by the control of crystallinity.

It is expected that the introduction of alkyl side groups into the structure of the PCL backbone will depress the crystallinity of the polymer. This assumption is confirmed by the amorphous character of poly(γ-(*tert*-butyl)-ϵ-caprolactone) and of the copolymers of ϵ-caprolactone containing at least 25 mol % (33 wt %) γ-substituted ϵ-caprolactone units.[7] In addition, the use of other sorts of comonomers, like lactides, with ester repeat units of a different structure is also attractive.

The analysis of block copolymers has demonstrated that the crystallization of a specific block is hardly affected by its linking to an amorphous one.[8] However, the randomness of the copolymers is expected to have a marked effect on the control of the crystallizability of PCL. The random copolymerization of ϵ-caprolactone can only be achieved with comonomers obeying the same polymerization mechanism. Generally, cyclic compounds having the same chemical structure, differing from one another only in the number of units in the ring or by the presence of various substituents, could be copolymerized in the expected random fashion. For example, the copolymers of ϵ-caprolactone with ϵ-decalactone, δ-valerolactone, and γ-(*tert*-butyl)-ϵ-caprolactone behaved as single-phase systems[5,7] despite the absence of any direct evidence (i.e., reactivity ratios) of the formation of a really random structure.

The case of poly(ϵ-caprolactone-*co*-DL-lactide), synthesized in the presence of tin salts as catalysts, appears more complex: the calculated reactivity ratios suggest a block structure that might, however, be randomized by transesterification reactions.[2] Depending upon the temperature and the nature of the initiator, ϵ-caprolactone and glycolide yield copolyesters with a broad variety of molar

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compositions and sequence distributions. Complexing catalysts, such as aluminum isopropoxide, favor the incorporation of glycolide, do not cause intermolecular transesterification, and form copolyesters with a high degree of chemical heterogeneity of first order. Anionic catalysts initiate the homopolymerization of glycolide, whereas cationic initiators yield copolyesters richer in ε-caprolactone and catalyze intermolecular transesterification.[9]

Of course, heterocyclic compounds of different chemical structures can also be copolymerized with ε-caprolactone, but they usually lead to alternating or sequenced comonomer distributions. In that respect, we can mention the copolymerization of ε-caprolactone with tetrahydrofuran[9-11] and lactams.[12-16] It seems that these copolymers have an initial block structure which is more or less modified by a subsequent randomization. Copolymerizations of dibasic acid anhydride and epoxides[17] or N-substituted aziridines[18] are examples of an alternating mechanism.

In order to efficiently control the crystallization of the PCL backbone while keeping unmodified its other main characteristics such as its miscibility and ability to biodegrade, we have studied the copolymerization of ε-caprolactone with methyl-substituted ε-caprolactones and L-lactide. The copolymerization of these monomers, catalyzed by metal alkoxides such as aluminum isopropoxide and aluminum- or zinc-μ-oxoalkoxides, is of interest because these compounds promote a "living" polymerization of ε-caprolactone.[19-23] It is noted that poly(L-lactide) is a semicrystalline polyester with a melting point of 180 °C,[2] but the crystallization of L-lactide units in copolymers can be avoided if they are randomly distributed into the PCL backbone. It is also interesting to compare the structure of poly(ε-caprolactone-*co*-lactides) prepared with tin salts by Schindler et al.[2] with those prepared with aluminum isopropoxide in this work.

This paper aims at reporting the main mechanistic and kinetic features of the copolymerization of ε-caprolactone (CL) with ε-methyl-ε-caprolactone (MCL), β,δ-methyl-ε-caprolactone (XCL) (mixed isomers), and L-lactide (LA) using aluminum isopropoxide as catalyst. The reactivity ratios of the CL/MCL, CL/XCL, and CL/LA pairs will be reported as well as the melting behavior of the copolymers in the whole composition range and their miscibility with PVC.

Experimental Section

Monomers. The ε-caprolactone (Fluka) and L-lactide (CCA Biochem. B.V., Holland) used were commercial reagents. The ε-methyl-ε-caprolactone and β,δ-methyl-ε-caprolactone (mixed isomers) were kindly supplied by Interox (Brussels, Belgium). Each lactone was dried over CaH_2 under nitrogen at 25 °C and distilled under reduced pressure (10^{-2} mbar) just before use. L-lactide was dissolved in dry tetrahydrofuran (THF) in a flask connected to a second one containing oligo(styryllithium) (PSLi). Under reduced pressure, THF was distilled over PSLi, which reacted immediately with any protic compound. The THF distillation was then reversed, and this cycle was repeated two or three times, providing a dried solution of L-lactide.

Catalyst. Aluminum isopropoxide (Fluka) was distilled under vacuum (10^{-4} mbar) and dissolved into dry toluene. The concentration of the resulting solution was determined by complexometric titration of Al by EDTA.

Solvents. Toluene and THF were dried by refluxing over $LiAlH_4$ and a benzophenone–Na complex, respectively, and distilled under nitrogen atmosphere.

Polymerization Procedure. Polymerization was carried out, under stirring, in a toluene solution in a flask previously dried and purged with nitrogen. Solvent, monomers, and catalyst were added successively through rubber septums with syringes and stainless steel capillaries. L-lactide was handled as a dried solution in THF, but the solvent was distilled off and replaced by dry toluene before adding the other components (comonomer and catalyst). The reaction was stopped by adding an excess (relative to catalyst) of 2 N HCl solution, and the catalytic residues were extracted four times with a dilute acid solution. After the reaction mixture was washed with water up to a neutral pH, the polymeric product was precipitated into an excess of heptane (polylactone) or methanol (poly(L-lactide)) and dried under vacuum up to constant weight.

NMR Measurements. Solutions of copolyester in CCl_4 (or $CDCl_3$ for L-lactide-rich copolymers) were measured on a Varian T60 NMR spectrometer at 25 °C. Me_4Si was used as a shift reference.

Molecular Weight Determination. Molecular weights and molecular weight distributions were determined with a gel permeation chromatograph (Waters 200) operating at 25 °C in THF. The universal calibration method could be applied for poly(ε-caprolactone) by using poly(styrene) standards since the necessary viscosimetric relationships, in THF and at 25 °C, are known:[23]

$$[\eta] = 1.25 \times 10^{-4} M^{0.717} \quad \text{(for poly(styrene))}$$

$$[\eta] = 1.09 \times 10^{-3} M^{0.60} \quad \text{(for poly(ε-caprolactone))}$$

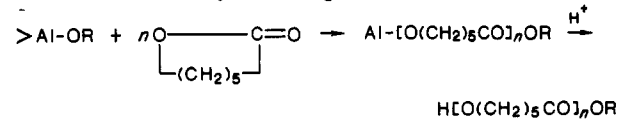
Calorimetry. Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer. The DSC was calibrated with ultrapure indium. The glass transition temperatures reported in this paper were recorded at the half-height of the corresponding heat capacity jump. The melting temperature values were recorded at the end of the melting curve.

After their insertion in the DSC apparatus, all samples were first cooled at 173 K and maintained at that temperature for 5 min. In some instances, the heat capacity–temperature curve of the nascent sample was then recorded at a heating rate of 20 K/min. In others, a first scan was made at a heating rate of 50 K/min, up to 403 K, in order to removal all traces of solvent. The sample was maintained 3 min at that temperature and quenched at 173 K. It was again left 10 min at this temperature before recording the heat capacity–temperature curve at a heating rate of 20 K/min.

Preparation of Blends. Blends were prepared by slowly casting films from (about 1%) THF solutions. The resulting films were dried under vacuum until they reached constant weight.

Results and Discussion

1. Kinetics and Mechanism of Methyl-ε-caprolactones and L-Lactide Polymerization. The ring-opening polymerization of ε-caprolactone (CL) is well documented, especially with alkoxide and bimetallic μ-oxoalkoxide catalysts.[19-21] Kinetic and structural data indicate a typical anionic type coordinated insertion mechanism. The perfectly living nature of the polymerization reaction has been ascertained and provides a useful route to obtain high molecular weight products with a narrow molecular weight distribution (polydispersity ≈ 1.05–1.10). The use of this type of catalyst led us to synthesize new block copolymers, i.e., poly(ε-caprolactone-*b*-β-propiolactone)[22] and poly(ε-caprolactone-*b*-vinylhydrocarbon).[23] The structural analysis of the first products of the chain propagation clearly shows that the reaction proceeds through insertion of the lactone units in the metal–alkoxide bonds, with a specific cleavage of the acyl–oxygen bond, resulting in the binding of the growing chain to the catalyst through an active alkoxide link:



$$H[O(CH_2)_5CO]_nOR \quad (1)$$

Before undertaking the copolymerization of CL with the comonomers selected in this study in the presence of aluminum isopropoxide as catalyst, we studied the polymerization mechanisms of these comonomers and, more

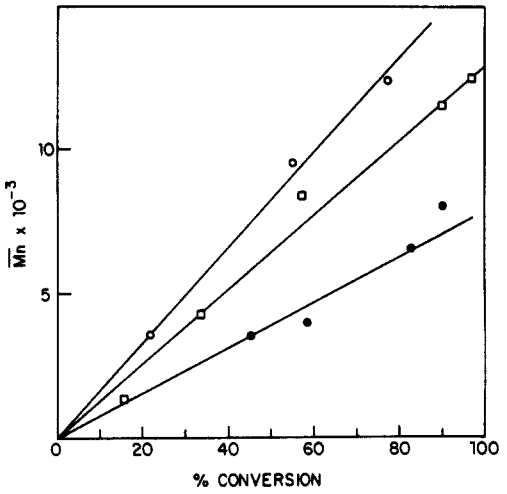


Figure 1. Dependence of M_n on the degree of conversion for the polymerization of (□) XCL (M/C = 200, 0 °C), (○) MCL (M/C = 200, 25 °C), and (●) LA (M/C = 50, 70 °C) by aluminum isopropoxide in toluene.

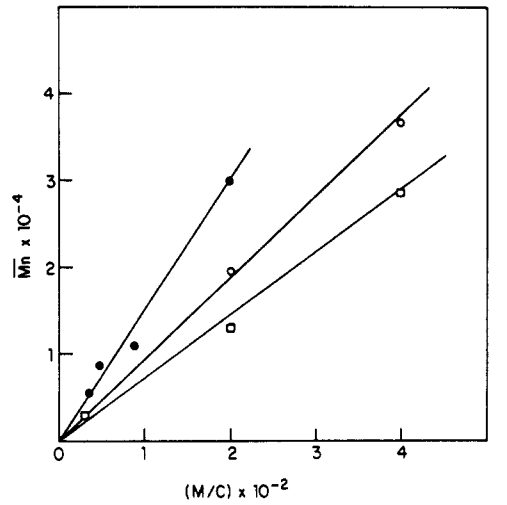


Figure 2. Dependence of M_n on the [monomer]/[catalyst] (M/C) ratio for the polymerization of (□) XCL at 0 °C, (○) MCL at 25 °C, and (●) LA at 70 °C by aluminum isopropoxide in toluene. [Monomer] = 1 mol L^{-1}.

specifically, we determined their relative intrinsic reactivity from the homopolymerization rates. By this method, the kinetic contribution to the control of the overall rate of the copolymerization process will be revealed. However, it is worth noting that in contrast with other types of catalyses the apparent reactivity ratios are also controlled by the thermodynamics through the relative formation constants of the different competing complexes formed between the catalyst and the monomers.[24]

Quite interestingly, the polymerization of ϵ-methyl-ϵ-caprolactone (MCL), β,δ-methyl-ϵ-caprolactone (mixed isomers) (XCL), and L-lactide (LA), catalyzed in toluene by aluminum isopropoxide, is practically quantitative. This observation means that the polymerization equilibrium is shifted toward open chains to the extent of more than 99%. These ring-opening polymerizations proceed without any secondary reactions, such as chain transfer or chain termination. This point is illustrated by the linear increase of the number-average molecular weight (M_n) of the polyesters formed with the degree of conversion of the reaction (Figure 1). An excellent correlation between M_n and the monomer-over-catalyst molar ratio (M/C) is also observed for reactions at complete conversion (Figure 2). The living character of these reactions is finally demonstrated by experiments of polymerization resumption involving the addition of a new amount of monomer to a completely polymerized system. The molecular weight of the polymer then increases proportionally to the weight percentage of added monomer. Provided the polymerization is stopped as soon as it comes to completion, the polydispersity of polymers prepared at 0 (XCL) and 25 °C (CL, MCL) remains narrow (≈1.1), while that of PLA prepared at 75 °C is slightly higher (≈1.2).

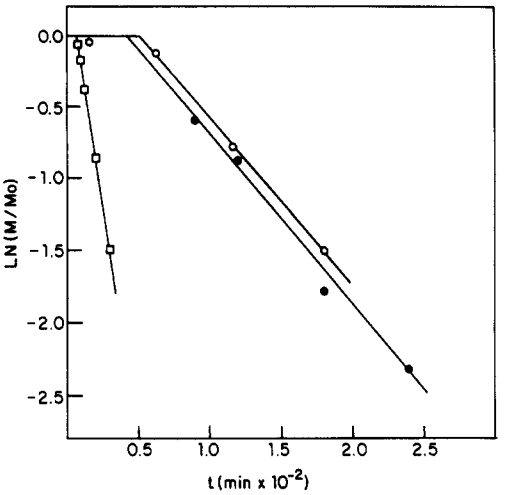


Figure 3. Monomer consumption as a function of time for the polymerization of (□) XCL (M/C = 200, 0 °C), (○) MCL (M/C = 200, 25 °C), and (●) LA (M/C = 50, 70 °C) by aluminum isopropoxide in toluene.

It is now worthwhile to investigate the kinetic features of the polymerization of MCL, XCL, and LA, as it proceeds in a well-controlled fashion in the presence of aluminum isopropoxide in comparison with the CL polymerization. The kinetics of the ring-opening polymerization of MCL, XCL, LA, and CL has been analyzed at the same conditions of solvent (toluene) and monomer concentration (1 mol L^{-1}), but at the temperature where the apparent reactivity of each monomer is optimum.

The polymerization of each monomer begins after a more or less important induction period. This may be indicative of a rearrangement of the catalytic coordination aggregates upon the addition of the polar cyclic monomer. It is well-known that in nonpolar solvents aluminum alkoxides associate due to the formation of intra- and intermolecular oxygen–metal coordinative bonds. The mean degree of association decreases significantly upon the increase of the dielectric constant of the medium or upon addition of suitable ligands such as alcohols.[19-21] This phenomenon is quite general, as illustrated by a further rearrangement of the catalytic aggregates that occurs upon the addition of a second lactone (β-propiolactone) into the polymerization medium resulting from the initial and complete conversion of CL.[22] The induction period can be completely suppressed if the catalyst is reacted with a small amount of monomer for a few hours; i.e., 10^{-2} mol of $Al(OR)_3$ is added to 3×10^{-2} mol of monomer for 6 h in toluene.

When this solution is used as catalyst, the polymerization proceeds regularly from the very beginning. In each case, the overall kinetics of polymerization follows a first current order in monomer, as illustrated by the linear dependence of the monomer consumption (ln (M/M_0)) as a function of reaction time t (Figure 3). M_0 is the initial monomer concentration and M the concentration of the unreacted monomer at time t. If the polymerization reaction is first order in catalyst, a straight-line relationship holds between (ln $(M/M_0)/t$) and the catalyst concentra-

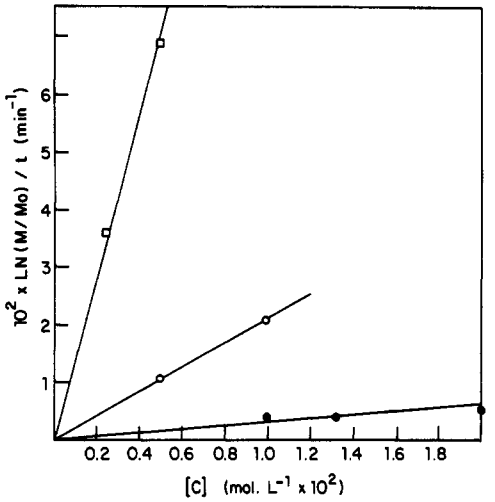


Figure 4. Determination of the order in catalyst for the polymerization of (□) XCL at 0 °C, (○) MCL at 25 °C, and (●) LA at 70 °C promoted by aluminum isopropoxide in toluene. [Monomer] = 1 mol L^{-1}.

Table I
Rate Constants of CL, MCL, XCL, and LA Ring-Opening Polymerization[a]

monomer	rate constant, min^{-1} mol^{-1} L
CL	243
MCL	2.12
XCL	13.8
LA	0.6

[a] Experimental conditions: [aluminum isopropoxide] = 5×10^{-3} mol L^{-1}; [monomer] = 1 mol L^{-1}; solvent, toluene; temperature, 25 °C, except for LA (70 °C) and XCL (0 °C).

tion c. Figure 4 shows that the experimental results support this suggestion regardless of the monomer considered in this work.

The polymerization of LA results in a semicrystalline material with a melting point of 173 °C, in agreement with the value reported elsewhere for poly(L-lactide).[2] This result means that the ring-opening polymerization promoted by the aluminum isopropoxide occurs without inversion of the configuration of the asymmetric carbon atoms of the monomer.

In conclusion, the polymerization of CL, MCL, XCL, and LA proceeds similarly. It follows a simple overall kinetics of the form $R_p = k[M][C]$, in agreement with a coordination type mechanism. Therefore, by reference to the thoroughly studied mechanism of CL polymerization, it is proposed that the polymerization of MCL, XCL, and LA operates on a catalytic coordination aggregate through the selective acyl–oxygen cleavage of the ring monomers with insertion into the Al–oxygen bond, as schematized by eq 1. This mechanism is supported by the apparent retention of the optical configuration of both asymmetric carbons of LA, which should be impossible if the ring opening took place at either the oxygen–carbon (sp^3) or the carbonyl–carbon (sp^3) bond. It is also meaningful that, in agreement with eq 1, the presence of hydroxy end groups has been recently identified by ^1H NMR in the case of poly(L-lactide).[25]

Finally, the rate constants of the ring-opening polymerization have been calculated from Figure 3 and are reported in Table I. It is obvious that the methyl substitution of CL is responsible for a very important decrease in the monomer polymerizability, probably due to steric effects from the substituent on the monomer–catalyst coordination site. An even more important decrease in reactivity is observed with LA. It can be explained by a

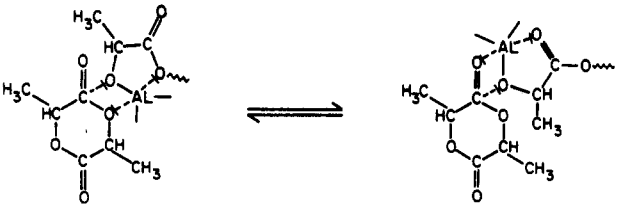


Figure 5. Competitive coordination to the Al atom between L-lactide and the penultimate unit of the growing PLA chain.

competition for the coordination site to the Al atom between the monomer and the oxygen atom of the penultimate unit of the growing chain, as tentatively schematized in Figure 5.

2. Copolymerization of ε-Caprolactone (CL) with Methyl-ε-caprolactones (MCL and XCL) and L-Lactide (LA). Since aluminum isopropoxide is an efficient catalyst for the polymerization of lactones and lactide, the copolymerization of CL with MCL, XCL, and LA may be considered and the monomer reactivity ratios determined in order to evaluate the sequence distribution of the monomer units in the copolymers. The copolymerization equation for mixtures of two monomers is well-known:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (2)$$

r_1 and r_2 are the monomer reactivity ratios, and $d[M_1]/d[M_2]$ represents the ratio of the two monomers in the increment of copolymer formed when the ratio of unreacted monomers is $[M_1]/[M_2]$.

The procedures available for the determination of r_1 and r_2 depend upon a careful analysis of the copolymers formed from a series of monomer mixtures of different compositions. As the composition of the copolymer changes continually with conversion, it is recommended that the copolymerization be limited to low degrees of conversion. A widely used method for this purpose involves the drawing of r_2 as a function of r_1,[26] corresponding to a simple rearrangement of eq 2, where the point of intersection of all the experimental lines represents the best experimental pair of r_1 and r_2 values. An alternative method, originally derived by Fineman and Ross,[27] consists in plotting Y vs. X according to

$$Y = r_1X + r_2 \quad (3)$$

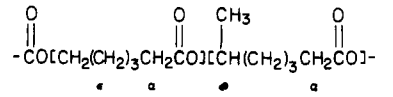
with

$$Y = f_1(1 - 2F_1)/(1 - f_1)F_1 \quad (3a)$$

$$X = f_1^2(F_1 - 1)/(1 - f_1)^2F_1 \quad (3b)$$

where f_i and F_i are the mole fraction of comonomer i in the monomer feed and in the copolymer, respectively. The intercept and slope of the plot of Y vs. X are equal to r_2 and r_1, respectively. r_i values obtained from each of the two methods are in agreement.

Copolymerization of CL (M_1) and MCL (M_2). This copolymerization was carried out in toluene at 25 °C at a total concentration of monomers of 1 mol L^{-1}, the monomer-over-catalyst molar ratio being 1000. The mole fraction composition of the copolymers formed at conversions of a few percents was determined by ^1H NMR spectroscopy. The molecular structure of this type of copolymer may be expressed as



where the methylene groups in α position are equivalent

Table II
Copolymerization of CL (M_1) with MCL and XCL (M_2)

comonomer M_2	wt % M_2	$[M_1]/[M_2]$	convn, %	$d[M_1]/d[M_2]$
MCL	10	10.11	0.90	15.67
	30	2.57	3.45	4.00
	50	1.13	0.80	1.78
XCL	10	10.11	0.97	10.11
	30	2.57	0.97	3.15
	50	1.13	2.87	1.22

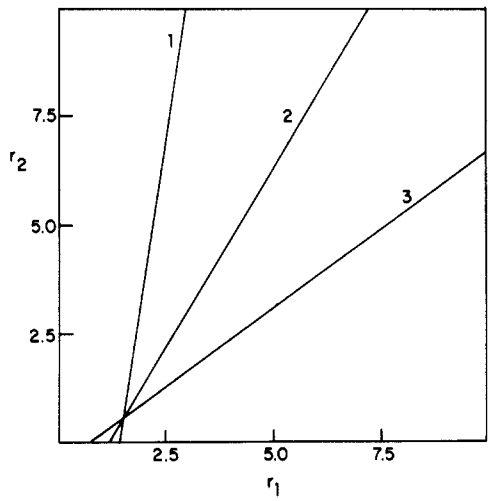


Figure 6. Plot of r_2 against r_1 for the copolymerization of CL and MCL by aluminum isopropoxide in toluene at 25 °C. M_1/M_2 = 10.11 (curve 1), 2.57 (curve 2), and 1.13 (curve 3).

in the two monomer units and their resonance is observed at 2.2 ppm. The protons in ϵ position are observed at a chemical shift of 3.9 ppm for the CL unit and 4.8 ppm for the MCL unit. Therefore, the copolymer composition data can be calculated from the relative areas of the ^1H resonance peaks at either 4.8 and 2.2 ppm or at 3.9 and 2.2 ppm.

Table II summarizes the experimental results corresponding to three series of copolymerization between CL and MCL. Figure 6 shows that the three lines intersect at the same point, which represents the proper values of r_1 and r_2, i.e., 1.5 and 0.6, respectively. Since $r_1r_2 = 0.9$, the CL/MCL copolymerization closely approaches the ideal copolymerization ($r_1r_2 = 1$), i.e., a random sequence distribution of monomer units. More precisely, CL is 1.5 times as reactive as MCL toward the CL insertion sites ($-CH_2OAl<$), while the MCL type of growing centers ($-CH(CH_3)O-Al<$) prefer to add the CL monomer by a factor of about 1.67 ($1/r_2$) as compared with the addition of MCL. This conclusion is of course valid only for copolymers formed at low degrees of conversion; the total product consists, in fact, of increments formed at progressively changing monomer ratios.

The behavior of the copolymerization reaction of CL with MCL is further illustrated by the dependence of the incremental copolymer composition F_2 as a function of the monomer composition f_2 (curve 2 of Figure 7). In addition, Figure 8 illustrates the behavior of an equimolar mixture of the two monomers (curve 2). The copolymer contains initially more CL than the monomer feed, but as the copolymerization progresses, the incremental composition is regularly enriched in MCL; this trend accelerates greatly at degrees of conversion greater than 80%. This behavior is in agreement with the polymerization rate constants of CL and MCL reported in Table I.

From the experimental values of k_{11}, k_{22}, r_1, and r_2, the k_{12} and k_{21} cross propagation rate constants can be calculated at 25 °C and compared: $k_{11} = 243$, $k_{12} = 162$, $k_{21} = 2.65$, and $k_{22} = 2.12$ min^{-1} mol^{-1} L. The substitution of the carbon atom in α position of the insertion site is responsible for a substantial decrease in the insertion rate as assessed by the comparison of k_{11} [CH_2OAl + CL] and k_{21} [$CH(CH_3)OAl$ + CL]. On the contrary, k_{11} and k_{12} (or k_{21} and k_{22}) values seem to indicate a relatively small effect of the methyl substitution of CL on the propagation rates.

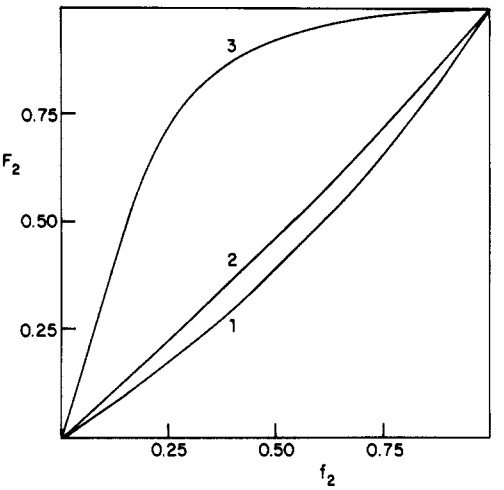


Figure 7. Incremental polymer composition F_2 (mole fraction) plotted against the monomer composition f_2 (mole fraction) for the copolymerization of CL/XCL at 0 °C (curve 1), CL/MCL at 25 °C (curve 2), and CL/LA at 70 °C (curve 3) by aluminum isopropoxide in toluene.

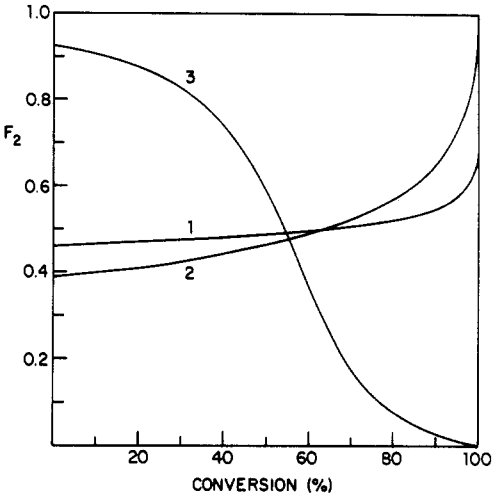


Figure 8. Incremental polymer composition F_2 against the degree of conversion for the copolymerization of CL/XCL at 0 °C (curve 1), CL/MCL at 25 °C (curve 2), and CL/LA at 70 °C (curve 3) by aluminum isopropoxide in toluene.

Copolymerization of CL (M_1) and XCL (M_2). Although the synthesis of ϵ-methyl-ϵ-caprolactone is well-controlled, that of β- or δ-methyl-substituted ϵ-caprolactone gives rise to a mixture of two isomers whose separation is not feasible by the usual analytical techniques. The available monomer mixture contains 44 mol % of the β isomer as determined by ^1H NMR spectroscopy, but it behaves as a "pure" monomer as assessed by the previously reported investigation of its polymerization kinetics.

^1H NMR analysis of poly(CL-*co*-XCL) is straightforward since the resonance of the methylene group in α position of the carbonyl group is again observed at 2.2 ppm for the two monomer units, whereas the resonance of the methyl group ($>CH-CH_3$) is found at 0.94 ppm regardless the isomer (β or δ) of the substituted monomer unit. The results obtained for three series of copolymerization are

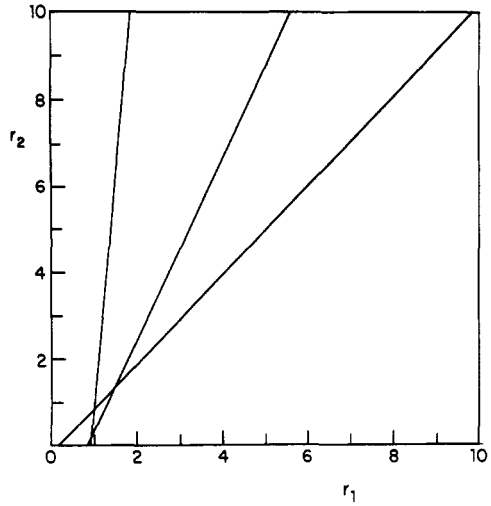


Figure 9. Plot of r_2 against r_1 for the copolymerization of CL and XCL by aluminum isopropoxide in toluene at 0 °C.

Table III
Copolymerization of CL (M_1) with LA (M_2)

f_2	convn, %	F_2	X	Y
0.081	5	0.26	-44.7	-7.44
0.123	1	0.38	-31.0	-2.80
0.165	1	0.57	-30.1	0.88
0.253	5	0.73	-23.6	5.10
0.345	2	0.85	-20.3	8.80
0.442	13	0.89	-12.9	8.95

reported in Table II. From Figure 9, an average point of intersection is found at $r_1 = 1.1$ and $r_2 = 0.8$. From curve 1 of Figures 7 and 8 it is obvious that the CL/XCL copolymerization is still closer to the ideal process than is the CL/MCL copolymerization. For instance, the composition of poly(CL-*co*-XCL) at an equimolar monomer feed is weakly dependent upon the degree of conversion up to about 95% (Figure 8).

Copolymerization of CL (M_1) and LA (M_2). This copolymerization was carried out at 70 °C and at a monomer-over-catalyst molar ratio of 200, all the other experimental conditions being kept unchanged. The copolymer composition could be calculated from the relative areas of the ^{1}H NMR resonance peaks of the methyne group in LA at 4.9 ppm and the methylene group in ϵ position in CL at 3.9 ppm. The experimental results are summarized in Table III and plotted according to eq 3 in Figure 10. The values of r_1 and r_2 thus obtained are 0.58 and 17.9, respectively. They are not very different from those reported by Schindler et al. for other conditions of temperature, solvent, and catalyst.[2]

When LA is used as a comonomer (as compared to MCL or XCL), the CL copolymerization does not lead anymore to a random sequence distribution of the monomer units. It is obvious that aluminum isopropoxide favors the incorporation of LA as compared to CL (curve 3 of Figures 7 and 8). The same behavior was reported for the glycolide/CL pair wherein blocky sequences of polyglycolide are formed.[9] Despite its departure from randomness, the CL/LA copolymerization has the advantage to favor the formation of blocks of LA rather than blocks of CL. In such conditions, LA may be considered as a potential agent for reducing the crystallinity of PCL.

It is amazing in that particular case that r_2 is larger that r_1, although the rate constant of LA polymerization is much smaller than that of CL (Table I). From the individual values of k_{ij} calculated at 70 °C, it is found that k_{11} (3645 min^{-1} mol^{-1} L) largely exceeds k_{22} (0.6 min^{-1} mol^{-1} L), whereas k_{22} is greater than k_{21} (0.033 min^{-1} mol^{-1} L).

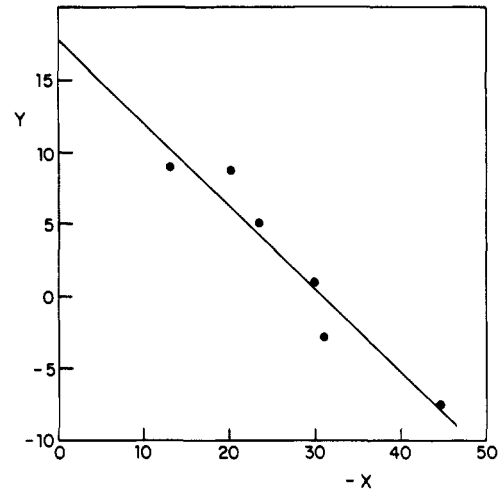


Figure 10. Analysis of the CL/LA copolymerization data according to the method of Fineman and Ross. $Y = f_1(1 - 2F_1)/(1 - f_1)F_1$ and $X = f_1^2(F_1 - 1)/(1 - f_1)^2F_1$. Catalyst, aluminum isopropoxide; solvent, toluene; temperature, 70 °C.

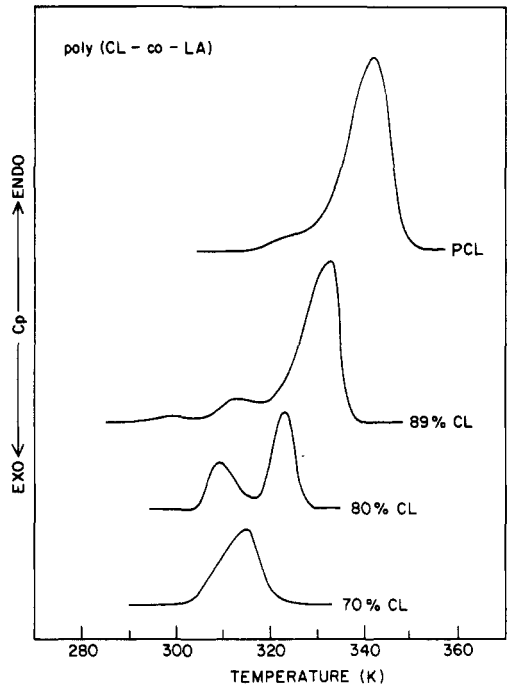


Figure 11. Melting endotherms of poly(CL-*co*-LA) samples of different compositions at a heating rate of 20 °C/min.

The relative values of k_{11} and k_{22} have already been accounted for in terms of steric effects and competitive coordination onto the Al atom between the monomer and the oxygen of the penultimate repeat unit (Figure 5). As CL is more basic than LA, it should behave as a better ligand for the catalyst ($Al(OR)_3$), resulting in a k_{21} value higher than the value of k_{22}. The discrepancy between that prediction and the experimental observation means that the rate-controlling step is likely to be the insertion of the coordinated monomer into the Al–OR bond rather than the monomer coordination itself.

3. Thermal Analysis of Copolymers. The three series of copolymers prepared in this study were analyzed by differential scanning calorimetry (DSC). Prepared at 25 °C, the poly(Cl-*co*-MCL) and poly(CL-*co*-XCL) exhibit a narrow polydispersity (≈1.2) compared to poly(CL-*co*-LA) synthesized at 70 °C (≈1.55). An example of this analysis is shown in Figure 11 for the poly(CL-*co*-LA) samples rich in CL. These samples were analyzed in their nascent form, i.e., as crystallized during the polymerization. They all

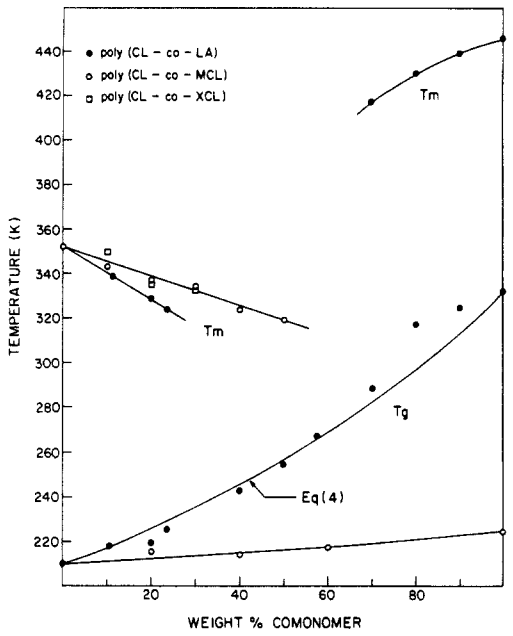


Figure 12. Phase diagram of poly(CL-*co*-LA), poly(CL-*co*-MCL), and poly(CL-*co*-XCL) copolymers.

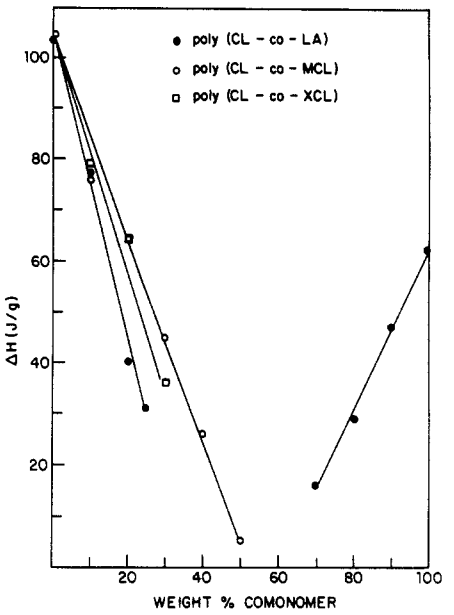


Figure 13. Enthalpy of fusion of PCL and PLA crystals in poly(CL-*co*-LA), poly(CL-*co*-MCL), and poly(CL-*co*-XCL) copolymers.

show a broad melting peak, with a well-defined maximum for PCL and the copolymer containing 70% CL and two maxima for the two other copolymers.

Figure 11 shows that the melting temperature of the PCL crystals, determined at the end of the melting curve, decreases with decreasing amounts of CL in the copolymer. At the same time, the enthalpy of fusion of the PCL crystals decreases as shown by the decrease of the area under the peak (the four curves of Figure 11 were obtained with samples of roughly equal weights). The copolymer containing 60% CL is amorphous since it does not show a PCL melting peak.

The double peak seen for the two copolymers containing 90 and 80% CL is a common feature of the melting of copolymers and homopolymers.[28] For these two copolymers, experiments were carried out at different heating rates, between 5 and 20 °C/min, and no significant change in the relative intensity of these two peaks could be detected, indicating that the high-temperature peak is not due to the annealing of the PCL crystals during the DSC run. These curves indicate a double-peak distribution of crystal sizes or the presence of two different types of morphology in the samples. This latter explanation is, however, not supported by microscopic and small-angle light scattering analyses.

The poly(CL-*co*-MCL) and poly(CL-*co*-XCL) samples give calorimetric results similar to those shown in Figure 11, but without any double peak. These results are summarized in Figures 12 and 13, which exhibit respectively the melting temperature T_m and the enthalpy of fusion ΔH of the PCL and PLA crystals. In the three cases, the crystallization of PCL (in the copolymer) is limited to copolymer compositions that are rich in CL, the disappearance of crystallinity being observed at LA and XCL compositions of 40%, and at a MCL composition of 50%. In this concentration range, the enthalpy of fusion decreases almost linearly (Figure 13).

Figures 12 and 13 also show that the homopolymers of MCL (PMCL) and XCL (PXCL) do not crystallize, but that PLA does. The crystallization of PLA is possible since it was prepared from L-lactide and since it is an isotactic active polymer. A melting point of 446 K (173 °C) was found for PLA, in fair agreement with the value given in ref 2. The addition of small amounts of CL comonomer to PLA also leads to decreases of T_m and ΔH, with the disappearance of PLA crystallinity at a CL concentration of 40%.

Figure 12 finally shows the glass transition temperature T_g of the poly(CL-*co*-LA) copolymers. It exhibits a regular increase of T_g with the copolymer composition, as expected for single-phase systems. Moreover, the T_g value of 332 K found for PLA is very close to the value of 330 K reported by Schindler et al.[2] for poly(DL-lactide). This general behavior is in all cases satisfactorily expressed by the Fox equation[29]

$$(1/T_g) = (w_1/T_{g1}) + (w_2/T_{g2}) \qquad (4)$$

where T_g is the glass transition temperature, T_{g1} and T_{g2} are those of components 1 and 2, and w_1 and w_2 are the corresponding weight fractions.

Similar T_g composition curves were found with the poly(CL-*co*-MCL) and poly(CL-*co*-XCL) copolymers except that the T_g variation is then very small, the T_gs of PCL, PMCL, and PXCL being found at 210, 224, and 216 K, respectively. The T_gs given above for PMCL and PXCL are slightly smaller than those reported by Seefried and Koleske[30] because these authors used a dynamic method of measurement whereas we used DSC.

The general melting behavior of the poly(CL-*co*-MCL) and poly(CL-*co*-XCL) copolymers is typical of that of random copolymers in which only one comonomer can crystallize. The poly(CL-*co*-LA) copolymers display a general melting behavior similar to that of random copolymers in which both comonomers can crystallize (although it has been shown in the preceding paragraphs that the copolymers do not have a completely random structure). In both cases, numerous similar examples can be found in the literature.[28]

However, only a few examples have been reported where one of the comonomers is CL. Goodman and Vachon reported the T_ms of copolymers of CL and ε-caprolactam.[17] They observed crystallization over the complete range of composition with a eutectic minimum at a CL composition of 20%. They generally found crystals of only one type, except at compositions close to the eutectic where both crystals were present simultaneously, without any indi-

Table IV
Morphology of Copolymers

comonomer content,[a] wt %	spherulitic radii, μm		
	poly(CL-*co*-LA)	poly(CL-*co*-MCL)	poly(CL-*co*-XCL)
0	250	250	250
10	40	75	60
20	10	25	25
30	*b*	20	10
70	500		
80	400		
90	600		
100	2500		

[a] The exact values may differ slightly from those indicated from one copolymer to the other. [b] A spherulitic morphology was not observed.

cation of isomorphism.[17] A similar result was found by Goodman and Valavanidis[16] for the assumed random copolymers of CL and ω-laurolactam with the coexistence of two types of crystals in a narrow composition range (75–80% of CL).

The crystallization of these two CL copolymers over the full range of concentration and the simultaneous presence of crystals of both comonomers at certain concentrations may be due to their noncompletely random structure. The occurrence of short blocks would favor these two phenomena. In contrast, the CL copolymers investigated in this work have an almost ideal random structure (except that with LA), and their crystallization was not possible at intermediate concentrations.

As mentioned above, the melting properties reported in Figures 11–13 are characteristic of samples analyzed in the nascent form, where the crystallization occurred during the polymerization. After crystallization under various isothermal or nonisothermal conditions, the same general features were observed, but with lower values of T_m and ΔH.

The copolymers that crystallize were also investigated by polarization microscopy. The samples used for these measurements were prepared by cooling the copolymers from 10 °C above their melting temperature to room temperature, at a cooling rate of 0.2 °C/min. Table IV shows that most samples exhibit a spherulitic morphology. The spherulites are large for the PCL and PLA homopolymers. In all cases, the spherulite radii of the copolymers are smaller than those of the corresponding homopolymers, and they decrease with increasing comonomer contents. In the copolymers, the added comonomer, which is not or only slightly incorporated into the PCL or PLA crystal (see the following), tends presumably to act as an impurity that forms a primary nucleus around which the spherulite can grow. The larger the number of nuclei, the smaller the average size of the spherulites which are volume filling in all cases. In addition, the larger the concentration of comonomer, the larger the number of nuclei formed, and the smaller the spherulite radii.

Table IV also shows that the LA comonomer seems to be slightly more active in creating nuclei than the MCL and XCL comonomers. This observation can be at least partially related to the fact that the LA comonomer is completely rejected from the PCL crystal, contrary to the MCL and XCL comonomers which are partially incorporated, as we will see in the next paragraphs. Furthermore, the spherulites in the poly(CL-*co*-LA) series tend to be more disordered than the spherulites in the poly(CL-*co*-MCL) and the poly(CL-*co*-XCL) series. This internal disorder of the spherulites increases, in the three series, with increasing comonomer concentrations.

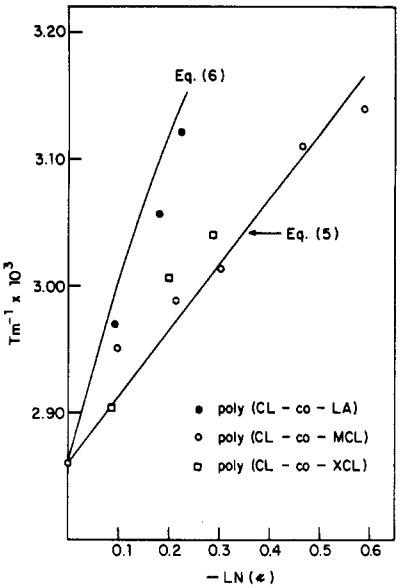


Figure 14. Analysis of the melting point (T_m) data of poly(CL-*co*-LA), poly(CL-*co*-MCL), and poly(CL-*co*-XCL) copolymers. Equation 6 was plotted by taking $r_1 = r_2 = 1$. For both eq 5 and 6, ΔH was taken equal to 16.1 kJ mol^{-1}.[34]

It has already been mentioned (Figure 12) that the addition of a comonomer to PCL decreases the value of T_m. It has also been seen that the poly(CL-*co*-MCL) and poly(CL-*co*-XCL) copolymers behave similarly in that respect but that the poly(CL-*co*-LA) copolymers give lower T_ms at similar compositions. This decrease of T_m for random copolymers can be expressed in first approximation by the Flory equation[28,31,32]

$$(1/T_m) - (1/T_m^0) = -(R/\Delta H) \ln x \qquad (5)$$

where T_m is the melting temperature of a random copolymer of mole fraction x, T_m^0 is the melting temperature of the corresponding homopolymer, R is the gas constant, and ΔH is the enthalpy of fusion of the homopolymer crystal. Equation 5 assumes that the copolymer is made of a comonomer A which is able to crystallize and a second comonomer B which does not crystallize under the chosen experimental conditions and which is rejected from the crystal.

Equation 5 is known to predict depressions in melting point that are too low.[28,31,32] A more satisfactory equation has been derived by Baur,[33] assuming again rejection of B from the crystal,

$$(1/T_m) - (1/T_m^0) = -(R/\Delta H)[\ln x - 1/L] \qquad (6)$$

where L is the average sequence length of the A and B comonomers. If L is large, eq 6 is reduced to eq 5. In practice, L has finite values that lead to a decrease in melting point which is more important than that predicted by eq 5. For copolymers in which the dissimilarity between the two comonomers units is large enough to warrant the exclusion of comonomer B from A crystals, eq 6 has been found to give satisfactory results.[28,33]

Figure 14 shows that the poly(Cl-*co*-LA) results follow closely eq 6 if L is taken equal to $1/2x(1 - x)$ [this substitution is strictly valid when $r_1 = r_2 = 1$]. This result suggests that the LA comonomers are rejected by the PCL crystals. This conclusion is certainly in agreement with the dissimilarity in structure between the CL and LA units and, therefore, it is not expected that the lactide units could be easily incorporated into PCL crystals. The same conclusion is reached when a more exact expression for L, which takes into account the r_1 and r_2 values determined previously for the CL/LA pair, is used.

Table V
Poly(CL-*co*-MCL) and Poly(CL-*co*-XCL): Analysis of Comonomer Insertion

comonomer compsn, wt %	caprolactone mol fractn	crystallizable units, mol fractn		comonomer inserted in crystal, %
		Poly(CL-*co*-MCL)		
10.5	0.905	0.928		24
21.4	0.805	0.896		47
28.3	0.740	0.874		52
39.9	0.628	0.795		45
47.4	0.555	0.771		49
			av	43
		Poly(CL-*co*-XCL)		
9.2	0.917	0.975		70
20.0	0.818	0.882		35
27.5	0.747	0.876		51
			av	52

In contrast, Figure 14 shows that the poly(CL-*co*-MCL) and poly(CL-*co*-XCL) data fall below those predicted by eq 6. This result can be interpreted as meaning that some B comonomer units are incorporated into the PCL crystals. This suggestion appears reasonable in view of the similarity between the MCL and XCL comonomers and the CL comonomers. If this assumption is made, eq 6 can be used to calculate the molar fraction of crystallizable comonomer that would be required to account for the experimental T_m. This analysis gives the values reported in Table V. It is seen that it requires 43% MCL and 52% XCL be incorporated into the PCL crystals.

4. Miscibility of Caprolactone Copolymers with PVC. It is well-known that PCL is miscible with a large number of polymers.[35] It is then expected that copolymers containing CL units could show some degree of miscibility with the polymers which are miscible with PCL. In this section, this idea will be investigated with poly(vinyl chloride) (PVC).

Two typical series of thermogram are shown in Figures 15 and 16. Figure 15 exhibits the heat capacity curves of PVC; poly(CL-*co*-LA) containing 80 wt % CL; and PVC/poly(CL-*co*-LA) blends containing 25, 50, and 75 wt % PVC. It is seen that the blends have a T_g which is at intermediate temperature relative to those of PVC and the copolymer. Therefore, these blends are miscible owing to the observation of a single T_g at any composition. This indicates extensive mixing between the two polymers but not necessarily molecular homogeneity due to the scale of observation of this experiment. It is interesting to note that the poly(CL-*co*-LA) containing 80 wt % CL does crystallize but that it suffices to add 25% PVC to the copolymer to hinder the crystallization, at least under the thermal conditions used in this figure (quenching at 320 °C/min down to 183 K). A slow cooling of the sample, or its crystallization at appropriate temperatures, leads to the crystallization of the copolymer in this blend, as we will see shortly.

In contrast, Figure 16 shows that the PVC/poly(CL-*co*-LA) blends, with a copolymer containing 43 wt % CL, exhibit two T_gs, one close to that of pure PVC and a second

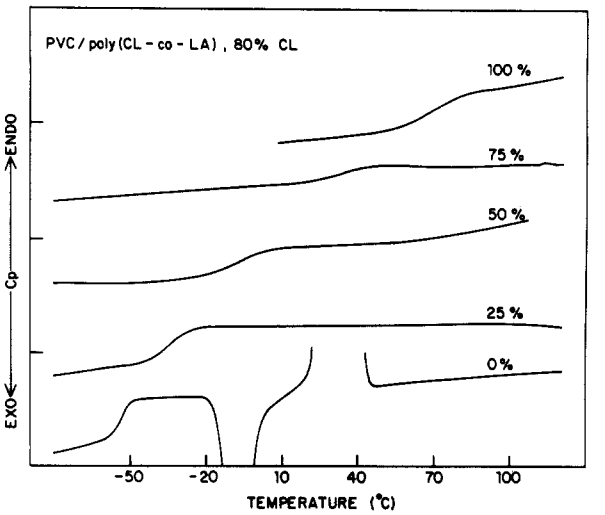


Figure 15. DSC thermograms for PVC/poly(CL-*co*-LA) blends containing 0, 25, 50, 75, and 100% PVC. The copolymer contains 80 wt % CL.

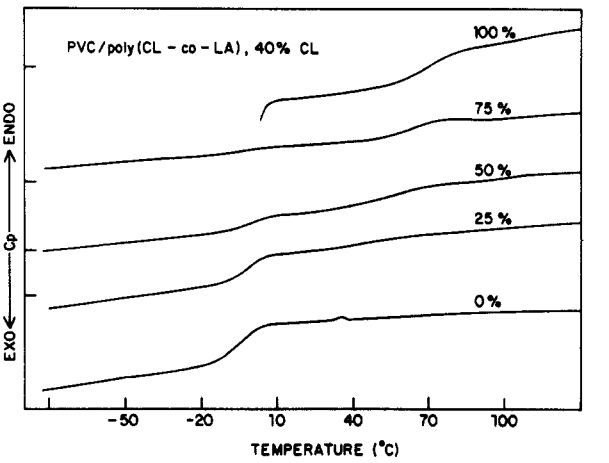


Figure 16. DSC thermograms for PVC/poly(CL-*co*-LA) blends containing 0, 25, 50, 75, and 100% PVC. The copolymer contains 40 wt % CL.

one close to that of the pure copolymer. This blend is therefore immiscible, whatever its composition.

Blends prepared by using poly(CL-*co*-LA) copolymers containing 50 and 60 wt % CL, poly(CL-*co*-MCL) copolymers containing 79, 60, and 39 wt % CL, and the PMCL homopolymer were analyzed in the same fashion. The result of this analysis is summarized in Table VI. It is seen that the poly(CL-*co*-MCL) copolymers, and pure PMCL, are fully miscible with PVC. The MCL comonomer has a chemical structure which is very similar to that of CL and similar degrees of miscibility are therefore observed.

Copolymers poly(CL-*co*-LA) containing 60 and 79 wt % CL are also fully miscible with PVC since all the blends investigated exhibit a single T_g. However, copolymers poly(CL-*co*-LA) containing 43 and 50 wt % CL show two T_gs when added to PVC. Therefore, poly(CL-*co*-LA) copolymers are miscible with PVC when their CL concen-

Table VI
Glass Transition Temperatures (in Kelvin) of PVC/Caprolactone Copolymer Blends

	wt % CL in poly(CL-*co*-LA)					wt % CL in poly(CL-*co*-MCL)				
wt % PVC in blend	100	79.9	60.4	50.3	46.6	100	78.6	60.1	39.2	0
0	210	219	242	255	267	210	215	214	217	224
25	257	239	259		274, 316	257	230	237	238	244
50	254	265	285	268, 341	273, 328	254	260	261	263	273
75	302	308	318	255, 341	269, 335	302	303	305	302	304
100	341	341	341	341	341	341	341	341	341	341

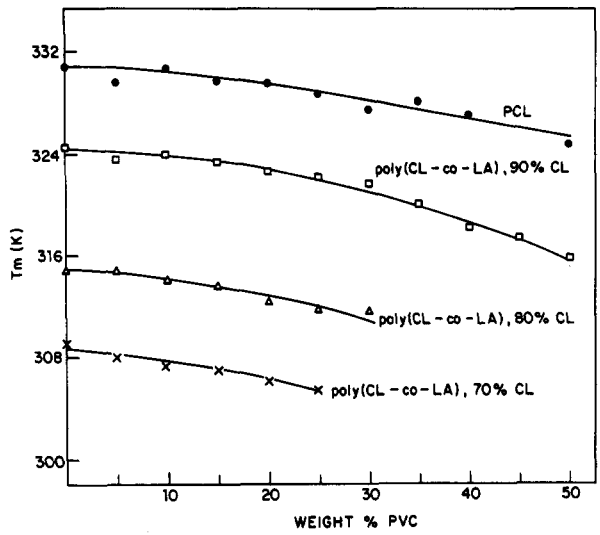


Figure 17. Melting temperatures of PCL/PVC and copolymer/PVC blends as a function of the PVC content.

tration is high. They become immiscible with PVC at high LA concentrations. It has not been possible to check the miscibility behavior of the PLA homopolymer with PVC because it is insoluble in most organic solvents, but it is suspected, from the data of Table VI, that it is immiscible.

The miscibility of poly(CL-*co*-MCL) copolymers, and of several poly(CL-*co*-LA) copolymers, with PVC is probably due to a specific interaction occurring between the carbonyl groups of CL and/or MCL with the α-hydrogens of PVC, as it has been suggested for PVC/PCL blends.[3] However, other types of interactions can occur simultaneously and contribute to the miscibility.[36]

In the poly(CL-*co*-LA) series, the same sort of interaction occurs between CL and PVC, but not between the LA comonomer and PVC despite the presence of a carbonyl group on this unit. It has been reported that miscibility is found between PVC and linear polyesters only if the ratio of the concentration of methylene groups to the concentration of carbonyl groups on each repeat unit, (the so-called CH_2/CO ratio) is optimum.[36,37] At high CH_2/CO ratios, the concentration of carbonyl groups is too low and the number of interactions too small to counteract the dispersive forces between the polymers. At low CH_2/CO ratios, it is believed that the polyester becomes too rigid and the polyester/polyester interactions become too strong to allow PVC/polyester interactions. The CH_2/CO ratio of PLA is 2, and polyesters, such as poly(β-propiolactone)[38] and others,[36,37] with such a ratio are known to be immiscible with PVC. On the other hand, PCL has a CH_2/CO ratio of 5 and is miscible with PVC. Therefore, miscibility can only occur at low LA concentrations in poly(CL-*co*-LA) copolymers. It is interesting to note that immiscibility occurs at a weight concentration of 50% in LA. This value corresponds roughly to an average CH_2/CO ratio of 3.1 for the copolymer. It is known that miscibility occurs between linear polyesters having a CH_2/CO ratio of 4 and PVC, but immiscibility is found between linear polyesters having a CH_2/CO ratio of 3 and PVC.[36,37]

The crystallization of PCL is observed in PVC/PCL blends and in PVC/caprolactone copolymer blends when the PVC content is not too high. Isothermal crystallization of PVC/poly(CL-*co*-LA) and PVC/poly(CL-*co*-MCL) blends was carried out at 263 and 281.5 K for more than 100 h. It was checked that the values of T_m do not change with longer crystallization times.

The corresponding T_ms are given in Figure 17. It is seen that a decrease occurs with increasing PVC content. This

Table VII
Thermodynamic Interaction Parameter

comonomer compsn, wt %	χ		
	crystzn temp, K		
	263	281.5	av value
	Poly(CL-*co*-LA)		
0	−0.20 ± 0.06	0.20 ± 0.05	−0.20
10	−0.25 ± 0.05	−0.28 ± 0.04	−0.26
20	−0.19 ± 0.04	−0.22 ± 0.07	−0.20
30	−0.19 ± 0.04	−0.27 ± 0.11	−0.33
	Poly(CL-co-MCL)		
0	−0.20 ± 0.06	−0.20 ± 0.05	−0.20
10	−0.33 ± 0.12	−0.27 ± 0.07	−0.30
20	−0.25 ± 0.07	−0.22 ± 0.12	−0.23
30	−0.30 ± 0.09	−0.25 ± 0.07	−0.27
40	−0.27 ± 0.11	−0.25 ± 0.13	−0.26

depression in melting point can be analyzed by the equation[39]

$$(1/T_m) - (1/T_m^0) = -RV_2\chi\phi_1^2/\Delta HV_1 \qquad (7)$$

where T_m is the melting temperature of the crystallizable polymer (polymer 2) in the blend; T_m^0 is its melting temperature before the addition of PVC; ΔH is the enthalpy of fusion of polymer 2 (16.1 kJ/mol for PCL[34]); V_2 and V_1 are the molar volumes of polymer 2 and polymer 1 (the diluent) repeat units (99.6 cm^3/mol for CL[34] and 44.3 cm^3/mol for PVC[40]); ϕ_1 is the diluent volume fraction, which is the sum of the volume fraction of PVC and the volume fraction of comonomer B when a copolymer is used;[41] and χ is the thermodynamic interaction parameter between the two polymers.

Using eq 7, we calculated the χ values shown in Table VII. All values are negative, indicating a favorable interaction between the CL units and PVC. χ is, within experimental error, independent of the copolymer composition. This result indicates that very favorable interactions can be found between the CL units of the copolymers and PVC. Moreover, this interaction is not significantly perturbed by the composition of the copolymer, at least within the composition range investigated. This indicates that the strength of interaction is not changed by the diluent effect brought about by the comonomer B. However, the number of interactions is certainly reduced since poly(CL-*co*-LA)/PVC blends become immiscible at LA concentrations of 50%.

In the above analysis, it was assumed that the major contributor to the melting point depression of PCL is its dilution with PVC. It is recognized that other factors, such as a change of lamellar thickness with composition[42] and the nature of the matrix,[43,44] can contribute to variations of T_m. However, these factors will likely oppose the depression in melting point brought by the specific interaction between the two polymers, leading to an underestimation of the values calculated in the above fashion. It is also recognized that thermodynamic melting temperatures should be used in this analysis,[45] but it is believed that the T_m determined at a given crystallization temperature, as reported in Table VII, suffices in first approximation to indicate the major trends as a function of copolymer composition. In fact, the χ value of −0.20 found at two temperatures for PCL/PVC blends is in excellent agreement with the value of −0.19 recently reported by Woo et al.[46] using thermodynamic melting temperatures.

Conclusions

Catalyzed by aluminum isopropoxide, the polymerization of CL, MCL, XCL, and LA obeys the same living anionic type coordinated insertion mechanism. The

methyl substitution of MCL and XCL is responsible for a decrease in the polymerization rate, as compared to that of CL, and this effect is much more pronounced for LA, probably due to a competitive coordination of the penultimate unit of the growing chain to the propagation site. The copolymerization of CL, MCL, and XCL closely approaches a random sequence distribution of monomer units. When CL is copolymerized with LA, a departure from randomness is observed, which results in the preferred incorporation of LA units.

Poly(CL-*co*-MCL) and poly(CL-*co*-XCL) samples crystallize only at high CL contents. On the other hand, poly(CL-*co*-LA) crystallizes both at high CL concentrations (PCL crystals) and at high LA concentrations (PLA crystals). From melting point depression data, it is concluded that upon crystallization the LA comonomer units of poly(CL-*co*-LA) are almost completely excluded from PCL crystals because of the significant difference of structure between the CL and LA comonomers. In contrast, due to a striking structural similarity between the CL, MCL, and XCL comonomer units, about 50% of the MCL and XCL comonomers of poly(CL-*co*-MCL) and poly(CL-*co*-XCL) are incorporated into the corresponding PCL crystals.

The miscibility of these copolymers with PVC was also investigated since the PCL homopolymer is well-known to be fully miscible with PVC (in the amorphous phase of the mixture). It was found that poly(CL-*co*-MCL) and poly(CL-*co*-XCL) are miscible with PVC regardless of the compositions of the copolymer and the blend, whereas poly(CL-*co*-LA) samples are miscible with PVC uniquely for copolymer LA contents equal to or less than 40 wt %. In all cases where miscibility was found, a negative thermodynamic interaction parameter was computed due to a specific interaction existing between the carbonyl group of the caprolactone units and the α-hydrogens of PVC.

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Registry No. β-XCL, 2549-60-2; MCL, 2549-59-9; LA, 4511-42-6; CL, 502-44-3; (CL)·(LA) (copolymer), 65408-67-5; (CL)·(MCL) (copolymer), 32681-10-0; (CL)·(β-XCL) (copolymer), 50586-46-4; PVC, 9002-86-2; triisopropoxyaluminum, 555-31-7; δ-XCL, 2549-58-8; (CL)·(δ-XCL) (copolymer), 102072-06-0.

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