Study of Poly-ε-caprolactone Bulk Degradation

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Synopsis

The thermal stability of poly-ε-caprolactone samples obtained by ring-opening polymerization in the presence of different metal alkoxides has been investigated. A significant degradation of the polyesters is observed under isothermal conditions at 120°C. The degradation is related to the nature of the endgroup, the presence of catalyst residues, and the presence of molecular oxygen. The hydroxyl endgroups play a determinant role in the process. They probably give rise, under the influence of catalyst residues, to hydroperoxides which are responsible for the polymer degradation by a radical reaction. It is shown that this is clearly different from the change in molecular weights distribution due to the well-known ester interchange reaction (transesterification equilibrium). Resulting methods for the polymers stabilization are indicated.

INTRODUCTION

The availability of ε-caprolactone from petrochemical processes and the possibility of polymerizing it to high molecular weight polyesters by highly active organometallic catalysts[1] has recently promoted a very active research in this field. This interest has been further corroborated by the appealing properties of these polymer, such as their high biodegradability and their unusual compatibility.[2] In particular, we have demonstrated the very high efficiency of initiators such as some aluminum alkoxides[3] and a new family of soluble bimetallics[4,5] in promoting a "living" polymerization of this monomer. These latter compounds allow a perfect control of the molecular weight and of the nature of the endgroups.

The degradation of polymers has always had a key importance from both practical and mechanistic points of view. Knowledge of the resistance of commercially available materials during use is essential. In addition, a detailed structural approach of the main degradation mechanism may be most helpful in predicting the behavior of polymers exposed to particular environmental factors and ultimately in preventing the degradation processes. The thermal stability of poly-ε-caprolactone (PCL) has already been the subject of several studies;[2,6] however, to our knowledge, there is no detailed investigation relative to the intimate mechanism of the thermal and oxidative degradation processes. Our aim is to analyze the parameters influencing the stability of the polymers prepared by the above-mentioned catalysts and, as far as possible, to determine the degradation mechanisms and the methods to circumvent the degradation.

EXPERIMENTAL

Reagents. ϵ-Caprolactone: commercial reagent (pure grade, Fluka) dried over CaH_2 at room temperature, and then distilled under reduced pressure (10^{-2} mm Hg). Toluene: practical grade, dried by refluxing over $LiAlH_4$, and then distilled under argon atmosphere. Antioxidant: commercial Anox NS reagent (Bozetto Ind., Italy).

Catalysts. Aluminum isopropoxide: commercial reagent (practical grade), purified by distillation under reduced pressure (10^{-2} mm Hg). Aluminum-zinc oxoalkoxides: the preparation of these catalysts is described in detail elsewhere.[4]

Polymerization Procedure. The polymerizations were carried out by stirring the reactant in toluene solution in a flask previously dried and flushed with argon and maintained at a constant temperature ($\pm 1°C$) in a thermostated bath for the necessary period of time. The reaction was stopped by adding about 50 ml of a $2N$ HCl solution. The catalyst residues were extracted repeatedly (four times) with a $2N$ aqueous HCl solution, and the toluene solution of polymer was washed with water up to neutral pH. The polymeric product was precipitated in heptane (after elimination of about $\frac{2}{3}$ of the toluene under reduced pressure) and dried for 24 hr at room temperature under vacuum.

Treatment of Polymers with the Disodium Salt of EDTA. The polymers isolated following the above procedure were redissolved in toluene (5% in weight). These solutions were treated for 24 hr at room temperature with 100 ml of an aqueous Na_2·EDTA solution (0.05 mole/l). After extraction of the metallic residues, the polymers were again isolated as described above.

Thermal Treatment of the Polymers. The thermal treatments of poly-ϵ-caprolactone samples in the presence of oxygen were carried out in a ventilated oven maintained at 120°C for the necessary period of time. The treatments performed in an inert atmosphere were carried out in a flask previously flushed with argon and maintained at the suitable temperature in a thermostated bath.

Polymer Characterization. The number-average molecular weights were determined on m-cresol solution at 80°C (with an accuracy of about 5%), using a Hewlett-Packard membrane osmometer (H.S.M.O. Model 502). The intrinsic viscosities were measured in benzene at 30°C with a Desreux-Bischoff dilution viscometer. The gel permeation chromatograms were ob-
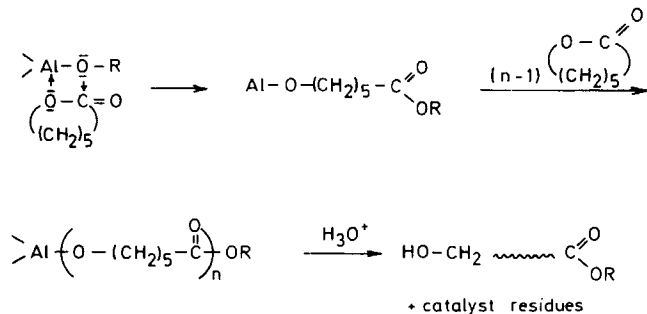

Fig. 1. ϵ-Caprolactone polymerization by metal alkoxides.

tained at 30°C with a Waters Model 200 apparatus, using 0.3% polymeric solutions in tetrahydrofuran.

Acetylation of Hydroxylic Endgroups. The isolated polymer (3 g) was dissolved in a mixture of toluene (50 ml) and acetyl chloride (15 ml) under argon atmosphere. This solution was stirred at room temperature for 24 hr. The acetylated polymer was isolated following the method previously mentioned. Viscometric measurements prove the absence of any significant degradation when this procedure is employed.

RESULTS AND DISCUSSION

Preparation and Properties of the Polyesters

Aluminum isopropoxide and aluminum-zinc oxoalkoxides $(RO)_2AlOZnO-Al(OR)_2$ rank among the best initiators for ring-opening lactone polymerization, and a detailed study has demonstrated the perfectly "living" character of the polymerization[3,4] they initiate. Thus, these catalysts allow an excellent control of molecular weight and MW distribution (M_w/M_n less than 1.2) of the polyesters produced.

On the other hand, it has been shown[3,4] that these polymerizations proceed through a simple insertion of the lactone molecules into an Al—OR bond of the catalyst, i.e., a selective acyl-oxygen cleavage of the lactone ring takes place in a way which maintains the chain bound to the catalyst through an alkoxide link. Therefore, the nature of the endgroup of the polymeric chains obtained after hydrolysis is also closely controlled. On the one end of the chain, an ester function corresponding to the alkoxide group of catalyst is present, and, on the other end of the molecule, a hydroxyl group resulting from the hydrolysis of the Al—OP bond is present. This is illustrated in Figure 1.

It has been interestingly observed that PCL chains terminated by a hydroxyl group are much more stable than the ones terminated by a carboxylic acid group.[2] This probably is due to the catalytic action of the latter group in ester bond cleavage. Our PCL samples, with one hydroxyl and one ester endgroup, confirm that behavior. Indeed, once that catalyst residues are extracted with a dilute HCl solution, no changes are observed in the intrinsic viscosity of the samples after *a year exposure to air* at room temperature, even in the absence of any stabilizing agent (Table I).

TABLE I
Stability of PCL at Room Temperature

Time of exposure to air at room temperature, months	$[\eta]$, dl/g[a]
1	0.451
2	0.452
3	0.454
9	0.455
12	0.451

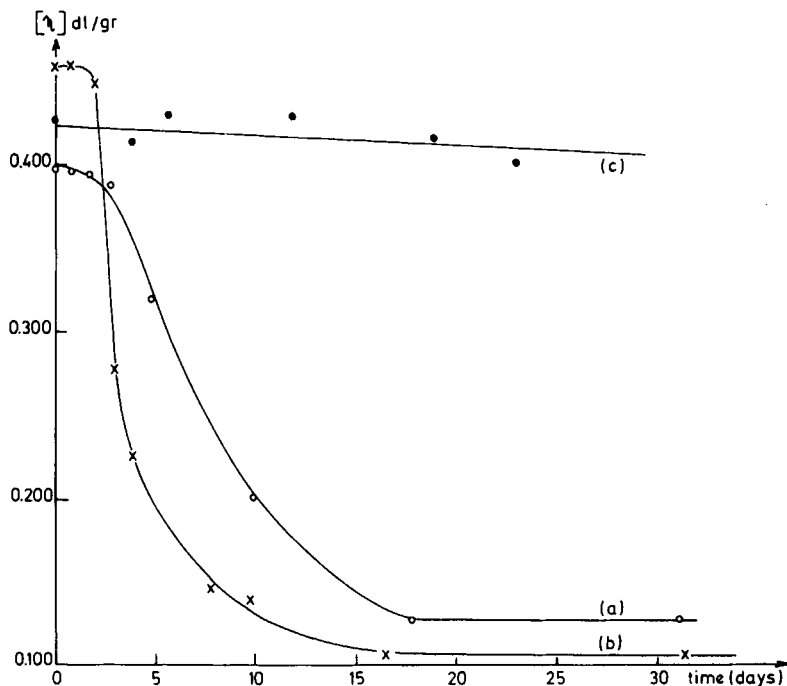[a] Measured in benzene at 30°C ($\overline{M}_n$ 25,000).

Fig. 2. Influence of thermal treatment in air at 120°C on intrinsic viscosity of a poly-ε-capro-lactone sample prepared with (a) aluminum isopropoxide (O); (b) $(nC_4H_9O)_2AlOZnOAl(OnC_4H_9)_2$ (×) and (c) further acetylated (●).

The Thermooxidative Degradation

However, when PCL is heated in air at 120°C, the intrinsic viscosity of the same polyester sample decreases significantly after a short induction period (Fig. 2). It is interesting to point out that, whatever the nature of the initiator, aluminum isopropoxide (2a) or aluminum-zinc oxoalkoxide (2b), the intrinsic viscosity curve levels off without any major further change after reaching a constant value of about 0.1 dl/g ($\bar{M}_n \simeq 5400$). The same phenomenon has been observed by other authors,[6] and it was explained on the basis of an ester interchange reaction between the polyester chains. Our experiments, however, clearly indicate that a simple ester interchange reaction cannot be responsible for the rapid decrease observed in the intrinsic viscosity. Actually, after acetylation of the hydroxyl endgroup, the intrinsic viscosity of the polyester remains practically constant, as illustrated in Figure 2c. These results stress the important role played by hydroxyl endgroups in the degradation reaction of these polyesters.

In order to elucidate the mechanisms of this degradation process due to the presence of the hydroxyl endgroups, we have studied *the influence of the catalyst residues and the role of the oxygen* on the course of the reaction.

Generally, a complete removal of catalyst residues from a polymeric material is very difficult to perform by a simple extraction with aqueous acid solution. For this reason, some PCL samples have been extracted, in a second purification step, with a dilute aqueous solution of the disodium salt of ethylenediaminetetraacetic acid (Na_2·EDTA). Because of this more efficient
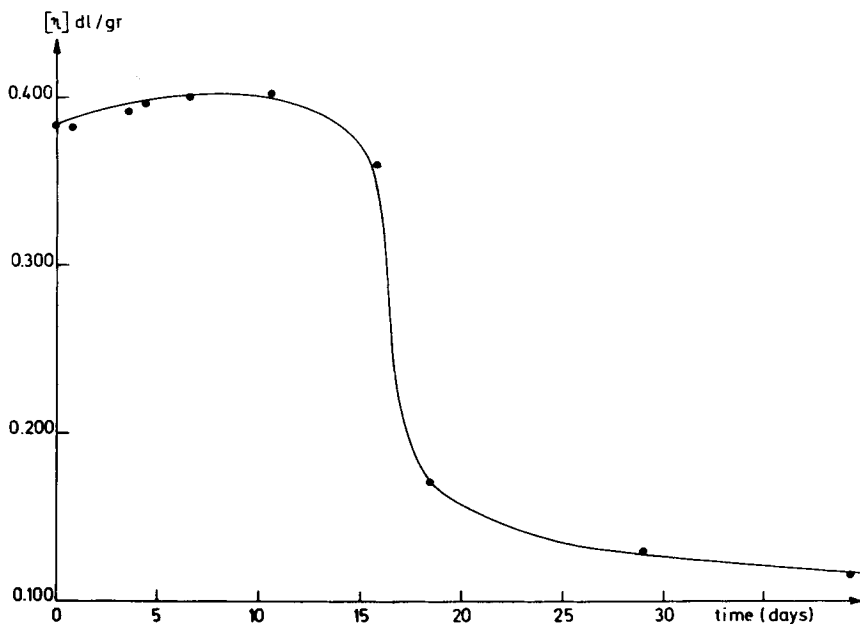
Fig. 3. Influence of thermal treatment in air at 120°C on intrinsic viscosity of a poly-ε-capro-lactone sample extracted by Na$_2$·EDTA.
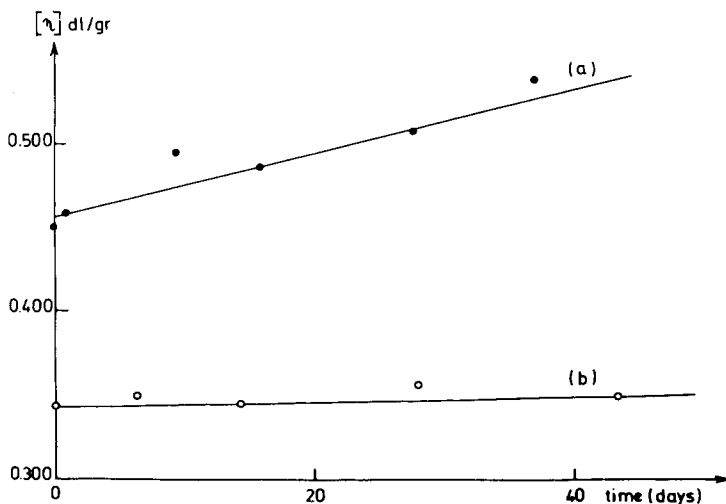

Fig. 4. Influence of thermal treatment in air at 120°C. on the intrinsic viscosity of a poly-ε-ca-prolactone sample non extracted by Na$_2$·EDTA: (a) in an argon atmosphere (●); (b) in air and in the presence of an antioxydant (AnOX NS) (○).

technique, the degradation reaction of polyester (at 120°C in air) is characterized by a much longer induction period, as shown in Figure 3.

On the other hand, the essential influence of the oxygen on the degradation is apparent when the hydroxyl-terminated polyester is heated (extracted only with HCl solutions) at 120°C under an argon atmosphere. As shown in Figure 4a, with this treatment no decrease (in fact, a slight increase, see following section) of the intrinsic viscosity is observed under these conditions.
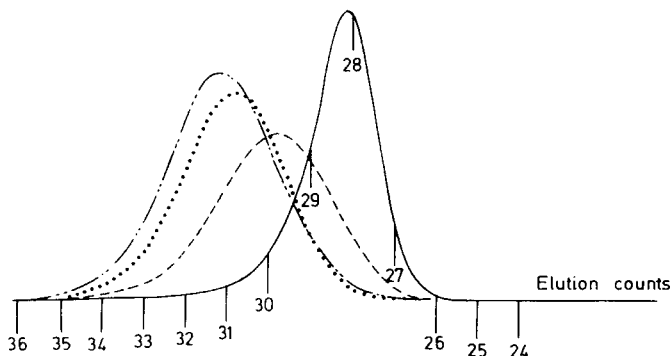
Fig. 5. Gel permeation chromatograms of a poly-ε-caprolactone sample: as such (——), or after 91 hr (– –), 233 hr (· · · ·), and 739 hr (– · · –), at 120°C in air.

These experimental results lead to the conclusion that, in air at 120°C, the thermal degradation of poly-ε-caprolactone is due essentially to an oxidative process. In a first step, the hydroxyl endgroups are probably converted to hydroperoxide by an autoxidation reaction in the presence of oxygen. The reaction is promoted by the catalyst residues present in the sample. At 120°C, these groups undergo a decomposition into free radicals (i.e., POOH → PO· + ·OH), which may in turn initiate the degradation reaction of the polyester following a radical-type process. This leads to a random scission of the polymer chains as shown in the Figure 5. The degradation process is characterized by a significant broadening of the molecular weight distributions ($\bar{M}_w/\bar{M}_n \simeq 3.4$, from an initial value 1.3) together with an important decrease of the number-average molecular weights ($\bar{M}_n$).

The hypothesis of a radical-type degradation is also strongly supported by the absence of any MW decrease when a free-radical inhibitor (5%) is added to a hydroxyl-terminated polyester not extracted with Na_2·EDTA. Figure 4b illustrates the excellent thermal stability of such a PCL sample heated in air at 120°C.

The induction period characteristic of the degradation curves (Fig. 2) probably corresponds to the period of time required for the transformation of the hydroxylic endgroups into hydroperoxide functions. The increasing of this induction period observed when PCL has been extracted by Na_2·EDTA (Fig. 3) might be related to the corresponding decrease in the concentration of the metallic residues which probably catalyze the hydroxyl endgroup oxidation.

Modifications of the Molecular Weight Distributions by Transesterification Reactions

Polyesters are known to generally undergo ester interchange reactions. Also, polyesters generated by condensation reactions between glycols and dibasic acids display the most probable molecular weight distribution.[7] Therefore, if ester interchange reactions are taking place during thermal treatment of condensation polyesters, their observation is difficult since no significant modification of the molecular weight distributions is to be expected.[6]
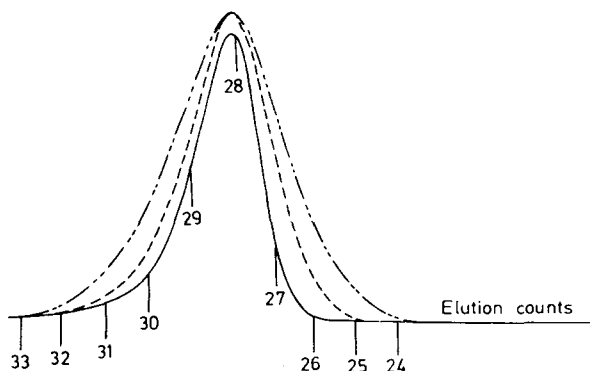
Fig. 6. Gel permeation chromatograms of a poly-ε-caprolactone sample: as such (———), or after 49 hr (– –), and 712 hr (– · · –), at 120°C in an argon atmosphere.

In that respect, the polyesters derived from ring-opening lactone polymerization are ideal model materials, since the molecular weight distribution in PCL samples obtained with the catalysts used for this study is very narrow. Therefore, as a result of the ester interchange reactions, the ratio $\bar{M}_w/\bar{M}_n$ has to approach a value of 2 following the increase in $\bar{M}_w$ (and related properties such as bulk and solution viscosities), with the colligative properties such as $\bar{M}_n$ remaining constant. Obviously, these hypotheses are based on the assumption that no simultaneous degradation phenomenon occurs.

The data shown in Figure 6 demonstrate that the molecular weight distribution in these PCL samples ($\bar{M}_w/\bar{M}_n = 1.3$) is definitely broadened without any significant variation of $\bar{M}_n$ when they are heated in an argon atmosphere. The final $\bar{M}_w/\bar{M}_n$ value obtained is 1.95 (after correction for diffusion), and this corresponds very well to the theoretical value expected for such a reaction (2.00). In addition, the results gathered in Table II show that when heated at 190°C in an inert atmosphere, the intrinsic viscosity of PCL is also increasing, in agreement with the presence of these ester interchange reactions.

CONCLUSIONS

These results demonstrate clearly the existence of two simultaneous processes taking place during the thermal treatment of poly-ε-caprolactone: a radical initiated thermooxidative degradation and a statistical ester interchange reaction. They also suggest different straightforward techniques for

TABLE II
Effect of Ester Interchange Reactions on the Intrinsic Viscosity of a PCL Sample

Time of heating at 190°C, hr	$[\eta]$, dl/g[a]
0	0.535
100	0.546
164	0.586
360	0.610

[a] Measured in benzene at 30°C ($\bar{M}_n$ 25,000).

avoiding the degradation of polyesters under the conditions used in this investigation.

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