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Primary Thermal Decomposition Processes in Aliphatic Polyesters Investigated by Chemical Ionization Mass Spectrometry

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ABSTRACT: The thermal decomposition mechanisms of several polyesters, derived from aliphatic diols and bicarboxylic acids, and polylactones were studied by direct pyrolysis–mass spectrometry, using both positive chemical ionization and negative chemical ionization. In fact, it was found that the thermally formed compounds are not stable under electron impact conditions. Instead, the results obtained by positive and negative chemical ionization indicate that intramolecular exchange reactions predominate in the primary thermal fragmentation processes, causing the formation of cyclic oligomers, which are particularly stable under chemical ionization conditions. The only exception is given by poly(β-propiolactone); in this case the thermal decomposition mechanism involves β-hydrogen transfer reactions.

Introduction

The characterization of polymers by direct pyrolysis–mass spectrometry (DP–MS) yields important structural information.[1-5]

Typical applications of this method include structural identification of homopolymers, differentiation of isomeric structures, copolymer composition and sequential analysis, identification of oligomers formed in the polymerization reactions, and identification of volatile additives contained in polymer samples.[5]

In the direct pyrolysis–mass spectrometry technique,[5] polymers are introduced via the direct insertion probe and the temperature is increased gradually up to a point at which thermal degradation reactions occur; the volatile oligomers formed are then ionized and detected.

The mass spectrum of a polymer obtained under these conditions is therefore that of the mixture of oligomers formed by pyrolysis.

A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal oligomers formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and fast detection, reduces to a great extent the occurrence of secondary reactions, so that almost exclusively primary fragments are detected. Consequently, the information thus obtained is of particular importance in order to assess the primary thermal decomposition mechanism of a polymer.

Furthermore, since pyrolysis is achieved very close to the ion source and no problem of transport exists, fragments of high mass, which are often essential for the structural characterization of the polymer, can be detected, whereas they are often lost with other techniques.

The main problem connected with this technique is, however, the identification of the products in the spectrum of the multicomponent mixture produced by thermal degradation. In fact, in the overall end spectrum of a polymer, the molecular ions of the thermal oligomers will appear mixed with the fragment ions formed in the ionizing step.

In some instances, identification of thermal degradation products can be achieved by using soft ionization methods and exact mass measurements and by matching spectra of authentic samples with those obtained from the polymer.[5]

This article describes the use of positive and negative chemical ionization in the investigation of the primary thermal fragmentation processes of some polylactones and polyesters derived from aliphatic diols and bicarboxylic acids (Table I).

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Table I
Structure, Thermal Stability, and Viscosity of the Polyesters Investigated

name	structure	PDT[a]/°C	η_{inh}[b]
poly(ε-caprolactone)	$-[CO(CH_2)_5O]_n-$	420	0.31[c]
poly(δ-valerolactone)	$-[CO(CH_2)_4O]_n-$	385	0.18[c]
poly(pivalolactone)	$-[COC(CH_3)_2CH_2O]_n-$	410	1.48[d]
poly(β-propiolactone)	$-[COCH_2CH_2O]_n-$	230	0.10[c]
poly(lactic acid)	$-[COCH(CH_3)O]_n-$	365	1.23[c]
poly(glycolic acid)	$-[COCH_2O]_n-$	340	0.51[d]
poly(ethylene succinate)	$-[CO(CH_2)_2COO(CH_2)_2O]_n-$	410	0.12[c]
poly(ethylene adipate)	$-[CO(CH_2)_4COO(CH_2)_2O]_n-$	380	0.16[c]

[a] Temperature of maximum decomposition rate of the polymer. [b] $\eta_{inh} = (\ln \eta_r)/c$, $c = 0.5$ g/dL. [c] In chloroform. [d] In phenol/tetrachloroethane 60/40.

Cyclic oligomers (mainly monomers) were originally reported as pyrolysis products by Carothers and Collaborators.[6-8] The electron impact (EI) mass spectral data available on aliphatic polyesters[9-14] do not allow one to draw conclusions about the primary thermal fragmentation mechanisms that operate in these polymers since several cyclic aliphatic esters and lactones do not exhibit significant molecular ions. This makes it difficult to establish if these compounds are generated as primary thermal fragments and moreover does not permit the determination of the distribution of cyclic oligomers generated in the pyrolysis.

Chemical ionization mass spectra show molecular ions characteristic of cyclic oligomers in poly(ethylene terephthalate) and poly(butylene terephthalate),[15,16] indicating that chemical ionization may be useful also in the case of aliphatic polyesters listed in Table I.

Experimental Section

Materials. β-propiolactone and δ-valerolactone were commercial products purified by distillation under vacuum.

Poly(ε-caprolactone), poly(ethylene adipate), and poly(ethylene succinate) were pure samples obtained from Aldrich.

Poly(pivalolactone), poly(lactic acid), and poly(glycolic acid) were pure samples obtained from Polysciences, Inc.

The model compound for poly(glycolic acid) (2,5-*p*-dioxanedione, glycolide) was synthesized according to a procedure described elsewhere.[17]

Other basic materials were commercial products appropriately purified before use.

Polymerization. Poly(δ-valerolactone) and poly(β-propiolactone) were synthesized by bulk polymerization.

In a typical procedure (poly(β-propiolactone)), into an ampule were introduced 3.96 g (0.055 mol) of β-propiolactone and a known amount of potassium carbonate as a catalyst (0.076 g, 1 wt %). A nitrogen stream was bubbled in the mixture; the ampule was then sealed and heated in an oil bath to about 100 °C over a period of 2 h. The reaction mixture, after cooling, was dissolved in chloroform, filtered, and precipitated in petroleum ether. The polymer was filtered, washed, and dried in vacuo at 40 °C for 24 h. Yield 80%.

Viscometry. Inherent viscosities [$\eta_{inh} = (\ln \eta_r)/c$; $c = 0.5$ g/dL] were measured in a Desreux–Bishoff suspended level viscometer that contained a coarse sintered glass filter attached just below the reservoir through which the solutions passed as they rose into the capillary. The temperature was maintained at 30 ± 0.01 °C.

Thermogravimetry. Thermal analyses were performed with a Perkin-Elmer TGS/2 apparatus in a nitrogen atmosphere (60 mL/min) at a heating rate of 10 °C/min. Polymer decomposition temperatures (PDT) of the investigated polyesters, as indicated by the maxima in their differential thermogravimetric curves, are listed in Table I.

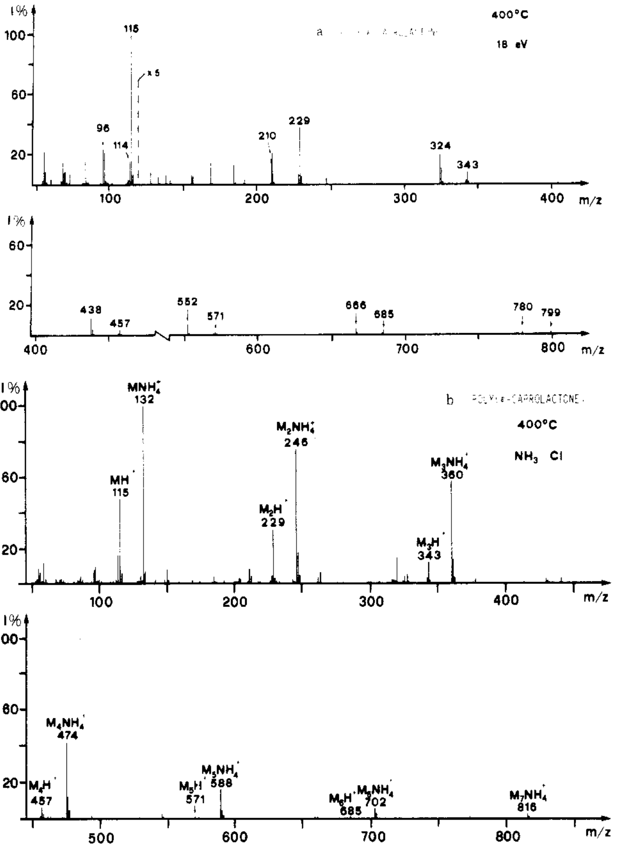


Figure 1. (a) EI mass spectrum (18 eV) and (b) ammonia CI mass spectrum of the products of the thermal degradation of poly(ε-caprolactone) at 400 °C.

Mass Spectrometry. A double-focusing Kratos MS 50 S equipped with the standard electron impact or chemical ionization sources and a DS 55 data system was used to obtain mass spectra.

The instrument was scanned from *m/z* 1000 to *m/z* 20, with a scan rate of 10 s/decade.

Perfluorokerosene (PFK) was used for computer calibration; the ion source was maintained at 200 °C.

Positive chemical ionization (CI) and negative chemical ionization (NCI) mass spectra were obtained with isobutane or ammonia as reagent gases.

Polymers were pyrolyzed directly in the ion source with standard Kratos probes, heated from 30 to 400 °C at a heating rate of 10 °C/min.

Reagent gases. Isobutane (99.5%) and ammonia (99.998%) were purchased from Matheson Gas Products.

Results

Thermal Stability. The thermal stabilities of the polyesters investigated, as indicated by the maxima in their differential thermogravimetric curves (polymer decomposition temperature, PDT), are reported in Table I.

Temperatures of maximum volatilization observed at the mass spectrometer by monitoring the total ion current (TIC) for polymers in Table I match pretty well with those recorded by thermogravimetry.

These data indicate that the polymers show comparable thermal stability; the only noticeable exception is constituted by poly(β-propiolactone), which shows a PDT of 230 °C. The difference of the PDT of this polymer from the PDTs of the other polyesters accounts for the difference in the mechanism of thermal degradation of this polymer.

Mass Spectra. Poly(ε-caprolactone). The EI mass spectrum of poly(oxycarbonylpentamethylene) (poly(ε-caprolactone)), recorded at a reduced electron energy of 18 eV, is shown in Figure 1a. The spectrum was obtained at a probe temperature of 400 °C.

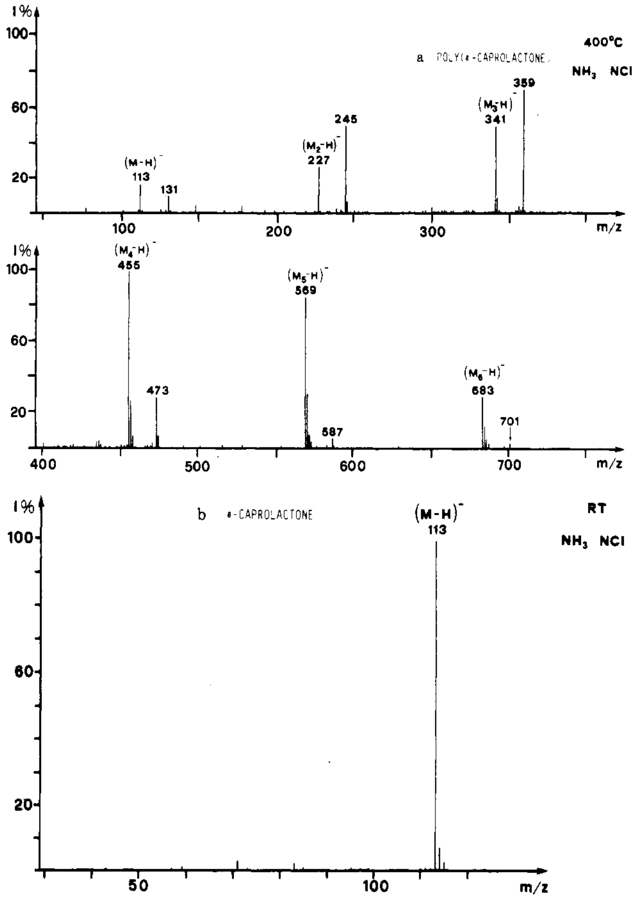


Figure 2. (a) Ammonia NCI mass spectrum of the products of the thermal degradation of poly(ε-caprolactone) at 400 °C. (b) Ammonia NCI mass spectrum of ε-caprolactone.

The mass spectrum shows only small amounts of monomeric caprolactone (m/z 114), while the most intense peaks are due to EI fragmentation, yielding two series of peaks with hydroxyl and carboxonium ions (m/z 115 + n114, n = 0–6) or ketene and olefin (m/z 96 + n114, n = 0–6) end groups.[10-12]

From this EI spectrum, very little can be therefore learned about thermal products originating in the pyrolysis of poly(ε-caprolactone).

The CI mass spectrum of this polymer recorded at a probe temperature of 400 °C, using ammonia as reagent gas, is shown in Figure 1b. This spectrum shows very intense peaks at m/z 132 + n114 (n = 0–6). These peaks are interpreted as the NH_4^+ adducts of the cyclic oligomers formed in the thermal decomposition process. Together with these, other peaks corresponding to $(M + H)^+$ cyclic oligomers at m/z 115 + n114 (n = 0–5) are also present in the spectrum. They are formed by ammonia loss from the NH_4^+ adducts, as confirmed by a series of metastable peaks: m/z 213.2 (transition 246 → 229), 326.8 (transition 360 → 343), 440.6 (transition 474 → 457).

In Figure 2a is reported the negative CI (NCI) mass spectrum of poly(ε-caprolactone), recorded using ammonia as reagent gas at a probe temperature of 400 °C. This spectrum shows intense peaks at m/z 113 + n114 (n = 0–5); these peaks derive from the loss of a proton from cyclic oligomers $(M - H)^-$. This process, common in NCI, is supported by the NCI mass spectrum, recorded with ammonia as reagent gas, of the monomeric pure caprolactone, reported in Figure 2b.

Another series of peaks, which are very stable under the NCI conditions, is present in the mass spectrum in Figure 2a at m/z 131 + n114 (n = 0–6). These peaks correspond to carboxylate anions, originated from the cyclic oligomers by NCI.

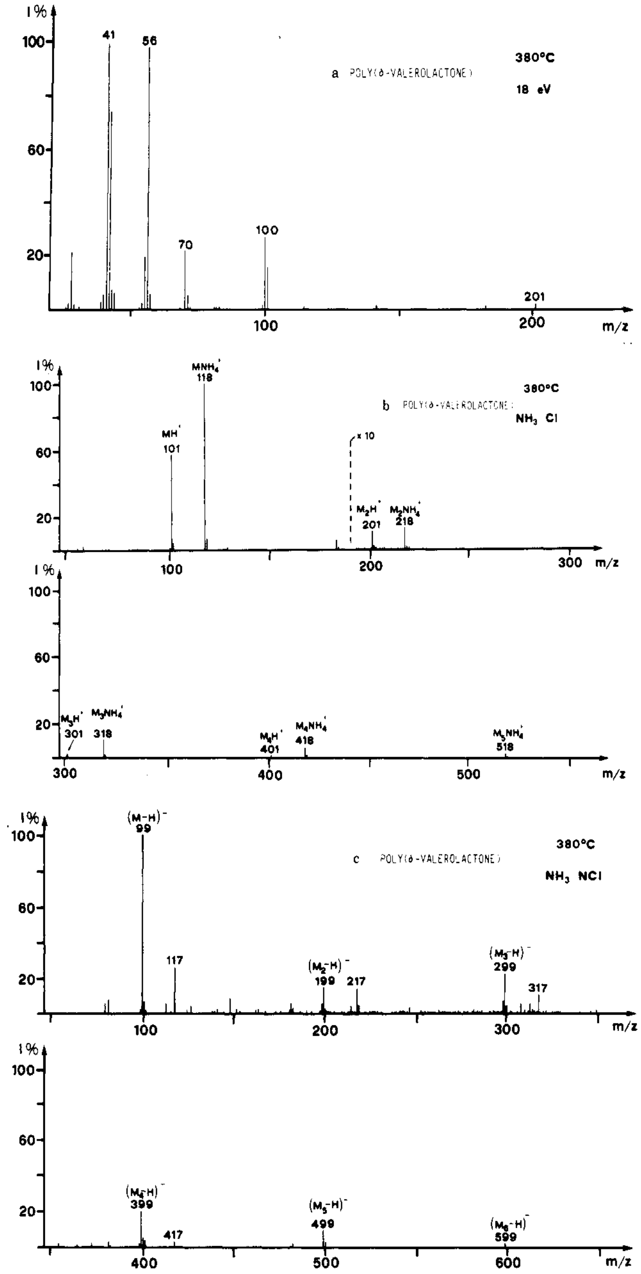


Figure 3. (a) EI mass spectrum (18 eV), (b) ammonia CI mass spectrum, and (c) ammonia NCI mass spectrum of the products of the thermal degradation of poly(δ-valerolactone) at 380 °C.

From these results one can infer that the pyrolytic breakdown of poly(ε-caprolactone) leads to the formation of cyclic oligomers. The latter are not stable under EI conditions and cannot be seen in the mass spectrum, whereas, with a softer ionization technique as CI, they produce intense peaks.

Poly(δ-valerolactone). The EI mass spectrum of poly(oxycarbonyltetramethylene) (poly(δ-valerolactone)), recorded at 18 eV and at a probe temperature of 380 °C, is reported in Figure 3a. The spectrum exhibits a small-intensity peak corresponding to the cyclic monomer (m/z 100), whereas other peaks present in the mass spectrum are due to EI fragmentation.

The ammonia CI mass spectrum reported in Figure 3b shows instead peaks corresponding to NH_4^+ adducts (m/z 118 + n100, n = 0–4) and to $(M + H)^+$ quasi-molecular ions (m/z 101 + n100, n = 0–3) of cyclic oligomers at higher masses.

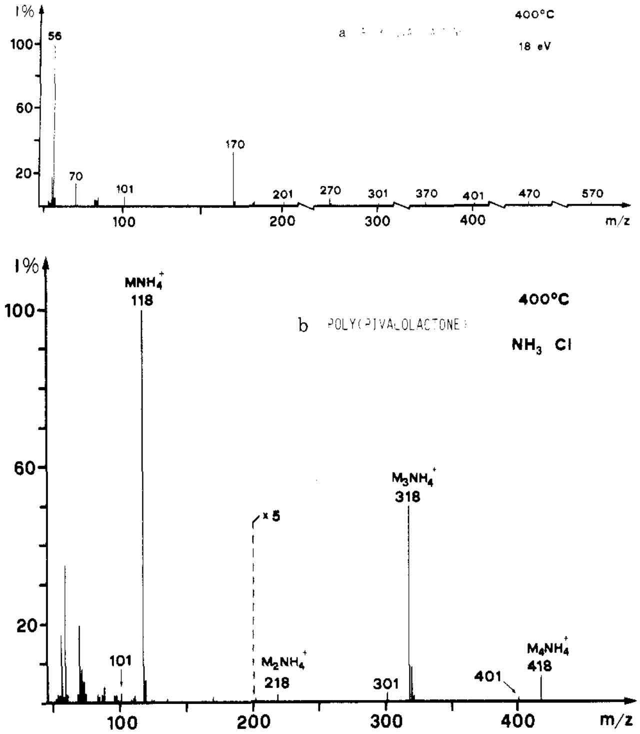


Figure 4. (a) EI mass spectrum (18 eV) and (b) ammonia CI mass spectrum of the products of the thermal degradation of poly(pivalolactone) at 400 °C.

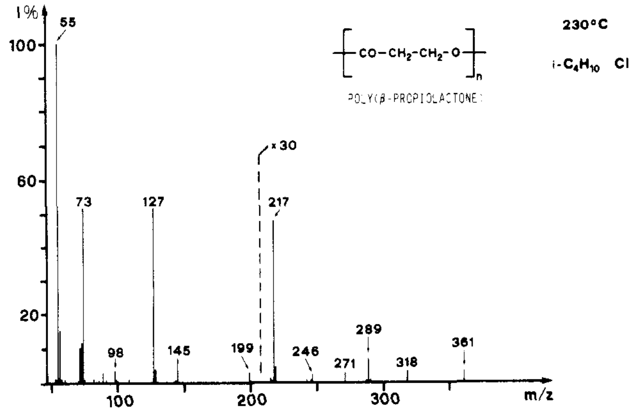


Figure 5. Isobutane CI mass spectrum of the products of the thermal degradation of poly(β-propiolactone) at 230 °C.

These oligomers are also detectable in the NCI mass spectrum, recorded with ammonia as reagent gas at a probe temperature of 380 °C, reported in Figure 3c. In this spectrum peaks corresponding to $(M - H)^-$ ions of cyclic oligomers are present with high intensity (m/z 99 + n100, n = 0–5). The remaining peaks present in the NCI mass spectrum, together with these quasi-molecular ions, are the respective carboxylate anions (m/z 117 + n100, n = 0–3).

Poly(pivalolactone). The EI (18 eV) and ammonia CI mass spectra of poly(oxycarbonyl-1,1-dimethylethylene) (poly(pivalolactone)), obtained at a probe temperature of 400 °C, are reported in Figure 4, parts a and b, respectively.

The comparison between the two spectra shows that peaks corresponding to molecular ions of cyclic oligomers (m/z = n100) are absent in the EI mass spectrum, while a peak at m/z 118 corresponding to the NH_4^+ adduct of the cyclic monomer is the base peak of the spectrum in Figure 4b, and peaks of higher cyclic oligomers are also present (m/z 218, 318, and 418).

Furthermore, the CI mass spectrum shows that the intramolecular exchange process leading to the cyclic oligomers is the preponderant thermal process occurring when the polymer is slowly pyrolyzed (10 °C/min).

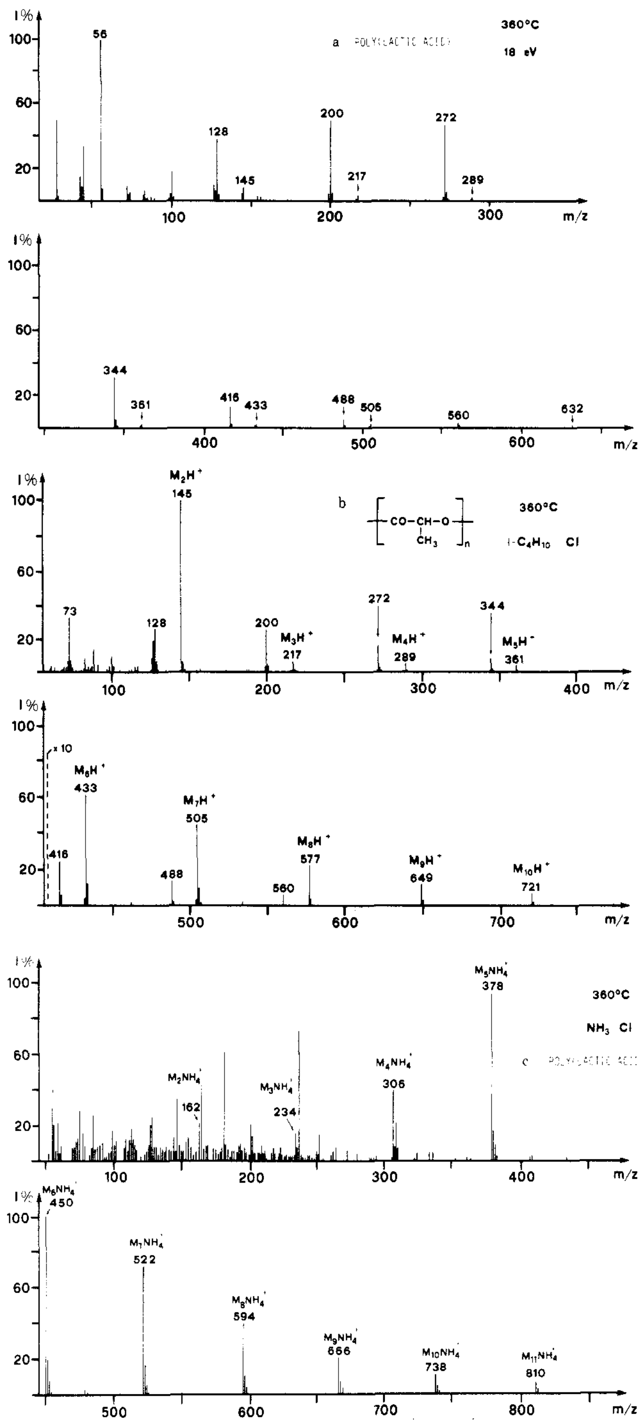


Figure 6. (a) EI mass spectrum (18 eV), (b) isobutane CI mass spectrum, and (c) ammonia CI mass spectrum of the products of the thermal degradation of poly(lactic acid) at 360 °C.

Poly(β-propiolactone). As it can be noted from Table I, the PDT of this polylactone is considerably lower than the other polymers. This is a strong indication that the thermal decomposition process of poly(β-propiolactone) is different from the other polylactones investigated. In fact, it is known[18] that the poly(β-propiolactone) thermally decomposes via cis-elimination process, with the formation of fragments with olefin and carboxylic end groups.

The isobutane CI mass spectrum of poly(oxycarbonylethylene) (poly(β-propiolactone)), obtained at a probe temperature of 230 °C, is shown in Figure 5. This spectrum shows peaks at m/z 73, 145, 217, 289, and 361, corresponding to the quasi-molecular ions of the open-chain

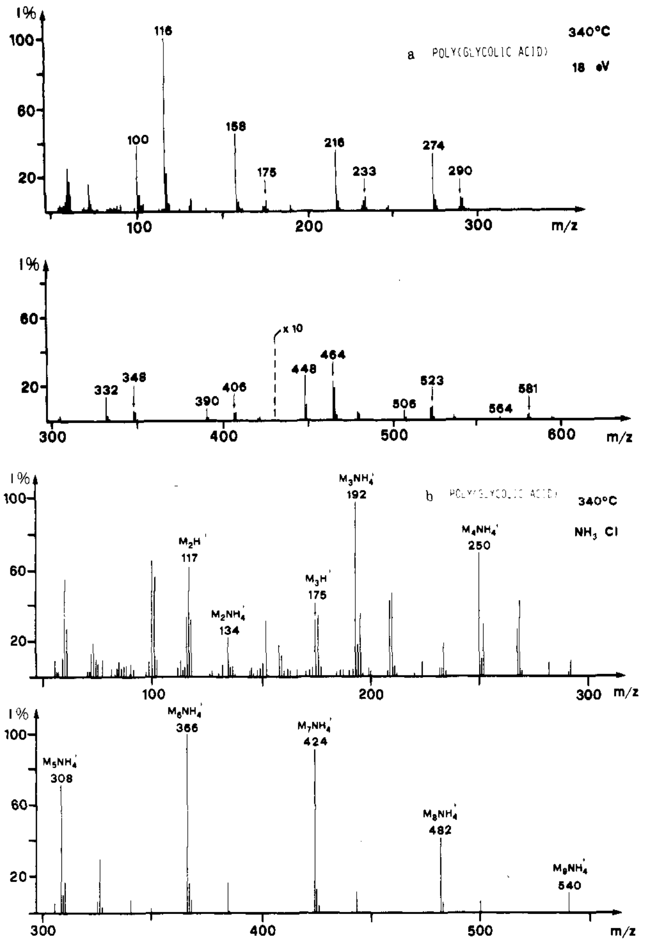


Figure 7. (a) EI mass spectrum (18 eV) and (b) ammonia CI mass spectrum of the products of the thermal degradation of poly(glycolic acid) at 340 °C.

primary thermal fragmentation products, and other peaks at m/z 55, 127, 199, and 271, which correspond to hydroxyl group loss from the above compounds

$$CH_2{=}CH\text{-}[COOCH_2CH_2]_n\text{-}COOH$$

The hydroxyl loss is characteristic for the carboxylic group.

Poly(lactic acid). The detection of cyclic oligomers, originating from pyrolysis, by soft ionization techniques, is well represented in Figure 6, parts a–c, where EI (18 eV), isobutane CI, and ammonia CI mass spectra of poly(lactic acid) are reported. The spectra were obtained at a probe temperature of 360 °C.

In the EI mass spectrum (Figure 6a) molecular ions corresponding to cyclic oligomers are nearly absent, while in the CI mass spectra peaks corresponding to $(M + H)^+$ ions or NH_4^+ adducts of cyclic oligomers are the only peaks present (m/z 145 + n72, n = 0–8; m/z 162 + n72, n = 0–9).

Poly(glycolic acid). The same considerations can be made for poly(oxycarbonylmethylene) (poly(glycolic acid)). The EI (18 eV) and the ammonia CI mass spectra, recorded at a probe temperature of 340 °C, are reported in Figure 7, parts a and b, respectively.

Whereas in Figure 7a the peaks corresponding to thermal fragments are nearly absent or very weak (except for glycolide, m/z 116), the CI mass spectrum in Figure 7b shows intense peaks corresponding to NH_4^+ adducts of cyclic oligomers (from dimer to heptamer) (m/z 134 + n58, n = 0–7). This interpretation is supported by the isobutane CI mass spectrum, shown in Figure 8a, where peaks corresponding to $(M + H)^+$ quasi-molecular ions of cyclic oligomers are present (m/z 117 + n58, n = 0–9).

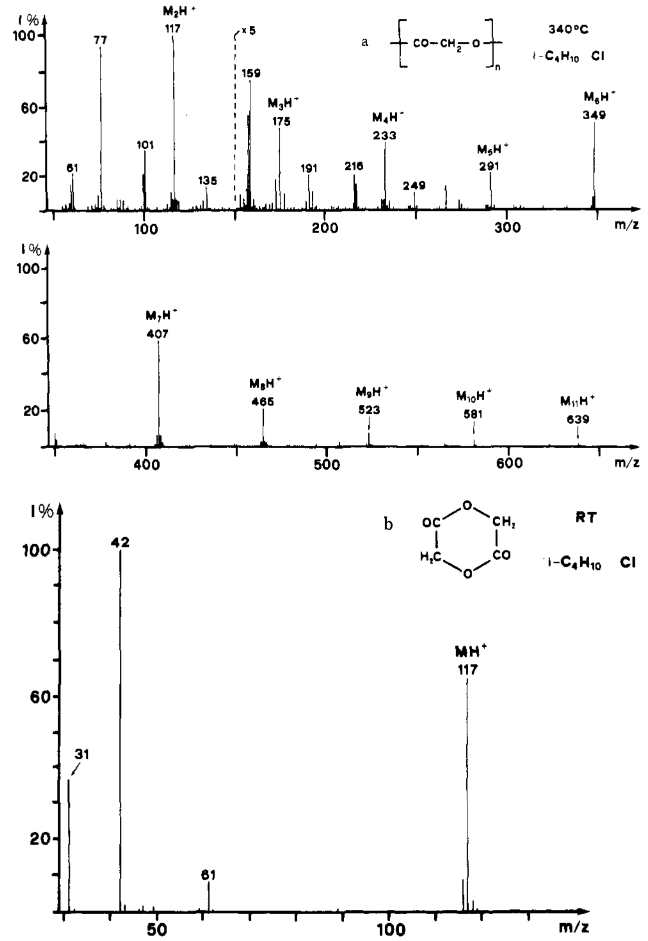


Figure 8. (a) Isobutane CI mass spectrum of the products of the thermal degradation of poly(glycolic acid) at 340 °C. (b) Isobutane CI mass spectrum of glycolide.

In Figure 8b the isobutane CI mass spectrum of an authentic sample of glycolide (cyclic dimer) is reported. When comparing the mass spectra in Figure 8, it appears that actually the cyclic dimer is the primary thermal fragmentation product, originating from the pyrolysis of poly(glycolic acid).

Poly(ethylene succinate). The pyrolysis EI mass spectrum of poly(ethylene succinate), obtained at a probe temperature of 400 °C and 18 eV, is reported in Figure 9a. In this spectrum molecular ions corresponding to cyclic oligomers are absent and all peaks correspond to EI fragmentation.

The ammonia CI mass spectrum is reported in Figure 9b. Peaks corresponding to adducts of the cyclic oligomers with NH_4^+ (m/z 162 + n144, n = 0–3) are very intense. The protonated cyclic oligomers (m/z 145 + n144, n = 0–3) are also present and they derive from the NH_4^+ adducts by metastable transitions (m/z 129.8, transition m/z 162 → 145; m/z 272.9, transition m/z 306 → 289; m/z 416.6, transition m/z 450 → 433).

Poly(ethylene adipate). The pyrolysis EI mass spectrum of poly(ethylene adipate), obtained at a probe temperature of 380 °C and 18 eV, is reported in Figure 10a.

In Figure 10, parts b and c, the isobutane and ammonia CI mass spectra are reported.

The mass spectrum in Figure 10b is characterized by peaks corresponding to $(M + H)^+$ cyclic oligomers up to tetramer (m/z 173 + n172, n = 0–3). Unfortunately, these peaks have the same masses of peaks present in the EI mass spectrum, and they could at least in part originate from the same fragmentation pathways as those observed in EI spectra.

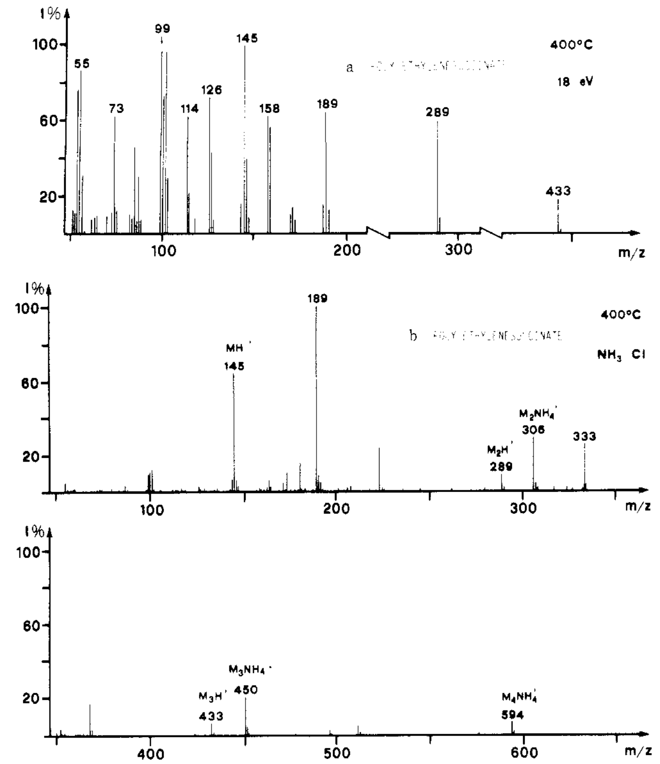


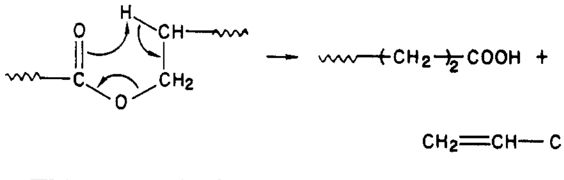
Figure 9. (a) EI mass spectrum (18 eV) and (b) ammonia CI mass spectrum of the products of the thermal degradation of poly(ethylene succinate) at 400 °C.

To meet this objection, the ammonia CI mass spectrum, obtained at the same temperature, is reported in Figure 10c. The mass spectrum shows peaks corresponding to NH_4^+ adducts of the cyclic oligomers from monomer to tetramer (m/z 190 + n172; n = 0–3). The peaks corresponding to $(M + H)^+$ cyclic oligomers are also present; they derive from the adducts by metastable loss of ammonia (m/z 328.8, transition m/z 362 → 345; m/z 500.5, transition m/z 534 → 517; m/z 672.4, transition m/z 706 → 689).

Thermal Fragmentation Mechanisms. The CI mass spectral data relative to the polyesters in Table I indicate that intramolecular exchange reactions predominate in the primary thermal fragmentation processes of these polymers, causing the formation of cyclic oligomers. Because these products are not stable under EI conditions, they are not seen in the EI mass spectra while they are predominant in the pyrolysis CI mass spectra.

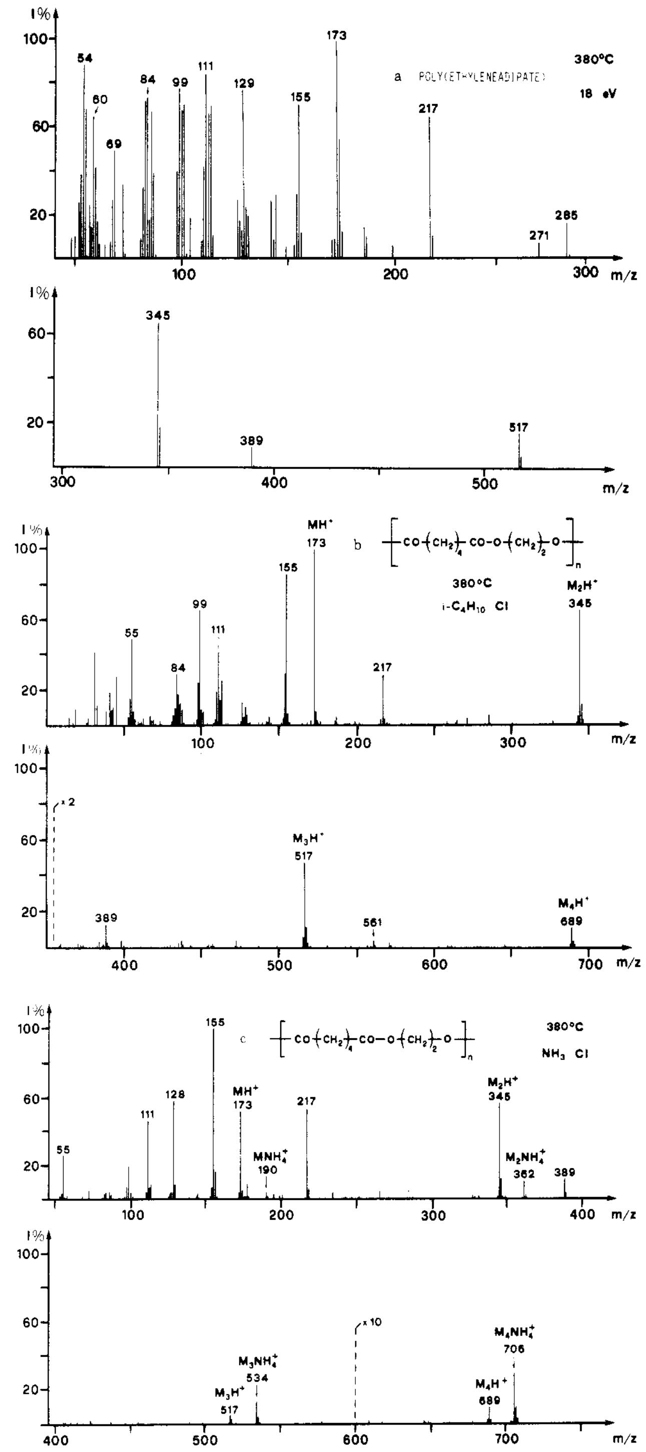
These results are in agreement with those obtained by Carothers[6-8] and by Semlyen[21,22] on aliphatic polyesters and also with other data on other polycondensation polymers, as we have previously reported. Among carbonyl-containing polymers, polycarbonates[19] and polyurethanes[20] yield cyclic oligomers as primary thermal fragmentation products, and it has been observed that these processes are remarkably selective.

CI data confirm also that poly(β-propiolactone) decomposes thermally via an intramolecular hydrogen transfer process, favored by a six-membered ring transition state.[9,18]



$$\rightarrow \sim\!\!\sim\!\!\sim\!(CH_2)_2COOH + CH_2{=}CH{-}CO\!\sim\!\!\sim\!\!\sim$$

This process is also common in aromatic–aliphatic polyesters,[14] and it is competing here with the intramolecular cyclization mechanism seen above.



$$\left[CO(CH_2)_4CO{-}O(CH_2)_2O\right]_n$$

Figure 10. (a) EI mass spectrum (18 eV), (b) isobutane CI mass spectrum and (c) ammonia CI mass spectrum of the products of the thermal degradation of poly(ethylene adipate) at 380 °C.

Dimethyl substitution in poly(pivalolactone) is sufficient to divert the reaction pathway toward cyclization.[9]

For the other polyesters listed in Table I, the intramolecular exchange process is favored over the hydrogen transfer.

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Registry No. ε-Caprolactone (homopolymer), 24980-41-4; poly(ε-caprolactone) (SRU), 25248-42-4; δ-valerolactone (homopolymer), 26354-94-9; poly(valerolactone) (SRU), 26499-05-8;

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pivalolactone (homopolymer), 24969-13-9; poly(pivalolactone) (SRU), 26497-98-3; β-propiolactone (homopolymer), 25037-58-5; poly(β-propiolactone) (SRU), 24938-43-0; lactic acid (homopolymer), 26100-51-6; poly(lactic acid) (SRU), 26023-30-3; glycolic acid (homopolymer), 26124-68-5; poly(glycolic acid) (SRU), 26009-03-0; ethylene succinate (copolymer), 25569-53-3; poly(ethylene succinate) (SRU), 25667-11-2; ethylene adipate (copolymer), 24938-37-2; poly(ethylene adipate) (SRU), 24937-05-1; glycolide, 502-97-6.

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Kinetics of the Copolycondensation by Aminolysis, Alcoholysis, and Interchange Reactions in the Synthesis of Poly(ester amide)

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ABSTRACT: Amino- and/or hydroxyl-terminated poly(ester amides) of low molecular weight were synthesized via aminolysis, alcoholysis, and interchange reactions of diamine amide and diol ester of dibasic acids. The kinetics of polycondensation with amide (or ester) interchange reaction and copolycondensation were investigated by using *N,N'*-bis(2-aminoethyl)sebacamide and bis(2-hydroxyethyl) sebacate as monomers. The rate constants of aminolysis and alcoholysis reactions in the copolycondensation and the ratios of diamine and diol components incorporated into the copolymer were determined from the equations derived previously. It was found that the rate constants of the four reactions had the following sequences under the same reaction conditions: aminolysis > ester interchange > amide interchange > alcoholysis reactions. The reactivity ratios of the copolycondensation ($r_1 = 10.03$, $r_2 = 0.19$) were calculated on the basis of the rate constants. The composition diagram of the copolycondensation was constructed, which was similar to the composition diagram of radical copolymerization in the case $r_1 > 1$ and $r_2 < 1$.

Introduction

Hydroxyl-terminated polyesters with low molecular weight were synthesized in many laboratories for use as the soft blocks in polyurethane.[1-4] The kinetics of the polyesterification between dibasic acids and diols and of the copolyesterification between different diol esters of dibasic acids by ester interchange reactions were also intensively investigated.[5-10]

By changing the soft blocks in the polyurethane molecules with hydroxyl- and/or amino-terminated poly(ester amide) instead of hydroxyl-terminated polyester, the physical properties of the polyurethane would be changed significantly. The amide groups in the poly(ester amide) had hence the capability of forming hydrogen bonds, contrary to the ester groups in the polyester. Recently several poly(ester amides) were synthesized.[11-17]

The synthesis of hydroxyl- and/or amino-terminated poly(ester amides) can be accomplished by the reaction of dibasic acid and diol together with diamine. Another way to obtain the poly(ester amide) is aminolysis, alcoholysis, and interchange reactions between diol ester and diamine amide of dibasic acids.

In the previous paper we reported the kinetics of copolyesterification of diol esters of dibasic acids[9] and of copolyamidation of diamine amides of dibasic acids.[10]

In this paper we report the synthesis of hydroxyl- and/or amino-terminated poly(ester amides) and the kinetics of copolycondensation of diol ester and diamine amide of dibasic acids by aminolysis, alcoholysis, and interchange reactions.

Kinetics

Polycondensation. It was found that the kinetics of polyesterification of diol ester of dibasic acid was second order with respect to the concentration of ester and hydroxyl groups as follows:[9]

$$2\ \mathrm{HOROOCR'COOROH} \xrightarrow{k_e} \mathrm{HOROOCR'COOROOCR'COOROH} + \mathrm{HOROH} \quad (1)$$

$$-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t = k_e[\mathrm{OH}][\mathrm{COO}] \quad (2)$$

At the initial stage of the polycondensation the concentrations of hydroxyl and ester groups are equal; we obtain therefore second-order kinetics

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