Thermal Degradation and Mass Spectrometric Fragmentation Processes of Polyesters Studied by Time-/Temperature-Resolved Pyrolysis–Field Ionization Mass Spectrometry

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ABSTRACT: Linear polyesters of the lactone and the diol–dicarboxylic acid types have been pyrolyzed in the ion source of a mass spectrometer. The gaseous degradation products were softly ionized by means of field ionization. Oligomers were the dominant products observed as protonated species. In contrast to the general experience with soft ionization mass spectrometry, with polyesters distinct mass spectrometric fragmentation occurs forming singly charged and doubly charged carboxonium and hydroxonium ions, respectively. Single fragments are formed with high intensity when the simultaneous formation of several double bonds is possible with the structural subunits present. In addition, cyclic six-membered transition states and the possibility of the formation of stable cyclic fragments increase the degree of fragmentation. Finally, a fundamental interpretation of the processes of polyesters in pyrolysis–field ionization mass spectrometry is given.

Introduction

Open-chain[1,2] as well as cyclic[3,4] oligomers have been reported as dominant thermal degradation products of several polyesters. As shown by the investigations of sequential copolyesters,[5] transesterification reactions occur prior to the formation of volatiles. Recently, similar results were obtained by direct pyrolysis–field ionization mass spectrometry (Py–FIMS) of mixtures of poly(ethylene succinate), poly(butylene adipate), and poly(neopentyl succinate).[6] In this case, only *intermolecular* transesterification enables the formation of the mixed oligomers found. The main mass signals observed were due to protonated cyclic oligomers and doubly charged ions. With lower abundances, species terminated by olefinic, hydroxyl, or carboxonium end groups were observed.

In the present study, additional polyesters were investigated in order to evaluate whether general degradation mechanisms operate with all of the samples. The aim of these soft ionization investigations was to obtain basic information on the correlation between the structural units present in the original polymer and the observed mass signals in FIMS. The main question is, how can the pyrolysis products be used to elucidate the structure of the polymeric starting material. Knowledge of the fundamental degradation processes is necessary not only for the investigation of technical polymers but even more so for that of complex specimens such as biological and geochemical materials.[7-10]

Experimental Section

Field ionization is a soft ionization mode yielding high amounts or molecular ions.[11] The Py–FIMS experiments were performed using the modified direct introduction system of a double-focusing Finnigan MAT 731 mass spectrometer. The thermal degradation products were ionized at 8-kV emitter potential; the counter electrode was at −3 kV. All mass spectra were recorded electrically and averaged with the Finnigan MAT SS 200 data system. Experimental details of the equipment and methodology used have been published.[12,13] The samples were heated without any pretreatment from 50 °C to 700 °C in high vacuum at about 10^{-3} Pa with a heating rate of 1.2 °C s^{-1}. In order to investigate whether low mass signals are formed some samples are additionally recorded in the mass range 15–500 Da (Da = dalton). The spectrum shown for poly(hexamethylene sebacate) was composed from two measurements.

The butanediol diacetate model compound was prepared by Dr. C. Puglisi and Prof. G. Montaudo, University of Catania, Italy. All other samples are technical products obtained from the companies Aldrich, Polysciences, and Janssen.

Results and Discussion

The structures and molecular weights of the repeating units in the investigated polyesters are listed in Table I. Both types of polyesters, i.e., diol–dicarboxylic acid type polymers and polylactones, are included.

Adsorption on the FI emitter, preferably of polar compounds, enables protonation and formation of multiply charged ions. Thus, generally protonated oligomers are observed in the Py–FI spectra, accompanied by series of singly and doubly charged species. At nominal mass resolution, doubly charged species are easily distinguished from singly charged products by $[M + 1]^{2+}$ ions appearing approximately half a mass unit above the main signals. One possibility of the formation of protonated species could be mass spectrometric fragmentation of higher oligomers as observed with electron impact.[2] The second, more likely possibility is a proton-transfer reaction to oligomers, which can easily occur if polar oligomers are adsorbed on the FI emitter. The formation of protonated species was confirmed by the measurements of low molecular weight substances such as the caprolactone monomer and butanediol diacetate. Furthermore, diols (for example, $HO-(CH_2CH_2)_n-OH$) and dicarboxylic acids appear as protonated species.

Diol–Dicarboxylic Acid Type Polyesters. Relative abundances and structures assigned to mass signals observed in the Py–FI spectra of the samples I–VI are listed in Table II. Carboxonium ions and fragments terminated by olefinic or hydroxyl end groups are obtained. Such species have also been found with EI[2,14] and FI[6] spectra of poly(ethylene succinate), poly(neopentyl succinate), and poly(butylene adipate). The fragment *m/z* 31 due to hydroxymethylene is common to all samples investigated.

In comparison of the relative abundances of the mass signals listed in Table II, some general trends in the dependence of dominant thermal degradation and mass spectrometric fragmentation mechanisms on the different monomeric subunits can be seen. As described below in

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Table I
Polyesters Investigated

	M^a	structure of the monomeric unit	name
I	158	$OCH_2CH_2CH_2OCOCH_2CH_2CO$	poly(trimethylene succinate)
II	172	$OCH_2CH_2OCOCH_2CH_2CH_2CH_2CO$	poly(ethylene adipate)
III	186	$OCH_2CH_2CH_2OCOCH_2CH_2CH_2CH_2CO$	poly(trimethylene adipate)
IV	284	$O{-}(CH_2)_6{-}OCO{-}(CH_2)_8{-}CO$	poly(hexamethylene sebacate)
V	192	$OCH_2CH_2OCO{-}p{-}C_6H_4CO$	poly(ethylene terephthalate)
VI	220	$OCH_2CH_2CH_2CH_2OCO{-}p{-}C_6H_4CO$	poly(butylene terephthalate)
VII	270	$OCH_2{-}C(CH_3)_2{-}CH_2OCO{-}(CH_2)_8{-}CO$	poly(neopentyl sebacate)
VIII	72	$OCH(CH_3)CO$	poly(lactic acid)
IX	86	$OCH(CH_3)CH_2CO$	poly(3-hydroxybutyric acid)
X	114	$OCH_2CH_2CH_2CH_2CH_2CO$	poly(caprolactone)
XI	120	$O{-}p{-}C_6H_4CO$	poly(*p*-hydroxybenzoic acid)

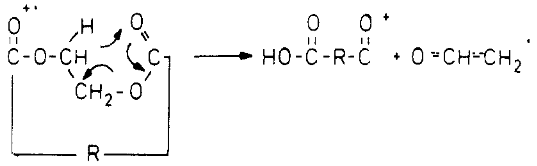
[a] Molecular weight of the monomeric subunit.

Table II
Mass Signals Observed with the Diol–Dicarboxylic Acid Type Polyesters

series	*n*	polymer[a] I	II	III	IV	V	VI
$[oligomers + H]^+$							
A	0	159 (44)	173 (25)	187 (72)	285 (24)	193 (5)	220* (1)
	1	317 (25)	345 (44)	373 (90)	569 (40)	385 (7)	440* (6)
	2	475 (32)	517 (70)	559 (94)	853 (24)	577 (2)	660* (1)
	3	633 (60)	689 (36)	745 (36)			
	4	791 (19)	861 (28)	931 (13)			
	5	949 (8)					
$[HO(M_n)CO\mathit{X}CO]^+$							
B	0	101 (51)	129 (5)	129 (21)	185 (77)	149 (29)	149 (5)
	1	259 (5)	301 (1)	315 (1)	469 (22)	341 (79)	369 (2)
	2		473 (45)	501 (1)	753 (21)	533 (100)	589 (1)
	3		645 (50)			725 (7)	
	4		817 (16)				
	5		989 (1)				
$[CH_2{=}CH{-}(CH_2)_x{-}O(M_n)CO\mathit{X}CO]^+$							
C	0	141 (19)	155 (39)	169 (7)	267 (14)	175 (3)	203 (1)
	1				551 (17)	367 (9)	
	2		499 (1)	541 (4)	835 (10)	559 (17)	
	3					751 (9)	
$[HOCH_2CH_2{-}(CH_2)_x{-}O(M_n)CO\mathit{X}COOH + H]^+$							
D	0			205 (3)	303 (7)		
	1	335 (2)		391 (12)	587 (3)		
	2	493 (4)		577 (13)			
$[CH_2{=}CH{-}(CH_2)_x{-}O(M_n)CO\mathit{X}COO{-}(CH_2)_x{-}CH{=}CH_2 + H]^+$							
E	0	199 (19)		227 (5)	367 (12)		274* (1)
	1	357 (21)		413 (4)	651 (27)		494* (1)
	2	515 (10)					714* (1)
	3	673 (11)					
	4	831 (5)					
$[HOCH_2CH_2{-}(CH_2)x{-}O(M_n)CO\mathit{X}COO{-}(CH_2)_x{-}CH{=}CH_2 + H]^+$							
F	0	217 (33)	217 (4)	245 (54)	385 (8)		
	1	375 (26)	389 (3)	431 (32)	669 (7)		
	2	533 (19)	561 (3)	617 (21)			
	3	691 (10)	733 (1)	803 (1)			
	4	849 (8)					
Doubly Charged Ions $[CO\mathit{X}CO]^{2+}$							
G	0				84 (25)	66 (1)	
	1	121 (22)	142 (2)	149 (7)	226 (9)	162 (6)	176 (1)
	2	200 (2)				258 (8)	
$[CO\mathit{X}COO(M_n){-}(CH_2)_x{-}CH{=}CH_2 + H]^{2+}$							
H	0	71 (14)	78 (12)	85 (100)	134 (17)	88 (1)	
	1	150 (9)	164 (3)	178 (18)	276 (11)		
$[CH_2{=}CH{-}(CH_2)_x{-}OCO(M_n)\mathit{X}COO{-}(CH_2)_x{-}CH{=}CH_2 + 2\,H]^{2+}$							
1	0	100 (18)	100 (8)	114 (60)			
	1	179 (25)	186 (5)	207 (33)			
	2	258 (19)	272 (2)	300 (9)			
	3	337 (5)		393 (3)			
	4	416 (3)					

[a] m/z (relative abundance); * unprotonated ion species; X = dicarboxylic acid subunits (for structures see Table I).

Scheme I
Mass Spectrometric Fragmentation of Ester Oligomers Containing Ethylene Subunits



detail, the main degradation pathway is highly dependent on the chain length of the diol subunit, whereas the influence of the dicarboxylic acid subunit is less important. As the formation of protonated cyclic oligomers is common to most polyester samples, only differences in this behavior are mentioned in the following.

Polyesters Containing Ethylene Subunits. A common attribute to the polyesters containing ethylene subunits is the mass spectrometric fragmentation forming the ion series $[M_n - 43]^+$, which is due to species terminated by a carboxylic end group at the one end and a carboxonium ion at the other (see series B in Table II). Beside samples II and V, this series was also found in the Py–FI spectrum of poly(ethylene succinate).[6] These results show that mass spectrometric fragmentation is favorable, splitting the resonance-stabilized radical $\cdot CH_2CH{=}O$ from the ethylene glycol subunits. A stable six-membered transition state in the hydrogen-transfer process is involved, as illustrated in Scheme I.

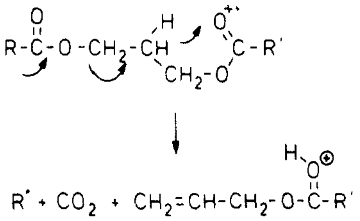
In earlier EIMS studies,[15] cyclic trimers have been identified in poly(ethylene terephthalate). Using time-/temperature-resolved Py–FIMS, volatile oligomers are liberated prior to the formation of oligomers from the polymer backbone.[6] Below the temperature of the polymer backbone degradation, the signal *m/z* 533 is exclusively formed in the FI spectrum of sample V. As with EIMS,[14,15] the cyclic trimer is unstable under Py–FIMS conditions. With field desorption (FD) MS (e.h.c. 12 mA) both the molecular ion due to the monomer and the fragment at 533 were observed.[15] With chemical ionization the dominant signal is formed by the protonated molecular ion.[16] As protonated oligomers, including the trimer, are observed in the Py–FI spectra in the temperature range of the polymer backbone degradation, but the trimer is known to be unstable, these oligomers can only be formed as mass spectrometric fragments of higher oligomers or further high-mass degradation products.

Further species common to all polyesters containing ethylene subunits are doubly charged fragments terminated by either carboxonium ion and/or olefinic end groups in combination with protonation at the neighboring ester group. These species form series G, H, and I in Table II.

As significant doubly charged ions are absent with EI,[3] CI,[3] and fast atom bombardment (FAB)[17,18] MS, their formation must be due to field-induced processes. This presumption is supported by the field desorption spectrum of poly(ethylene adipate) in which the doubly charged series I in Table II forms the ion series with the highest relative abundance and is observed up to *m/z* 702.[17]

Polyesters Containing Trimethylene Subunits. The samples containing trimethylene subunits yield high-abundance species due to series F in Table II. This fragment series formed from cyclic oligomers is complementary to series B observed in the spectra of polyesters with other diol subunits. In addition to the species listed in Table II, a minor series due to protonated diols is observed. The corresponding species are absent in the spectra of polyesters II and IV–VI.

Scheme II
Mass Spectrometric Fragmentation of Ester Oligomers Containing Trimethylene Subunits



With polyesters I and III containing trimethylene subunits, the relative abundances of doubly charged ions are much higher compared with those of all polyesters containing other diol subunits. Whereas the possibility of the formation of carboxonium ions is little dependent on the dicarboxylic acid subunits, the formation of olefinic end groups in combination with protonation at the neighboring ester group is highly dependent on the chain length of the diol subunit. With samples I and III, the 2-fold event of this fragmentation pathway yields the high-abundance signals in series I. To a much lower degree, the corresponding series are also formed with samples containing ethylene or butylene subunits. Adsorption on the FI emitter allows the ionization of two ester groups independent from each other. The preference of the formation from polyesters containing the trimethylene subunit can be explained by a favorable six-membered transition state, as shown in Scheme II. In addition, the possibility of simultaneous CO_2 elimination may also favor this fragmentation pathway. With the ethylene and butylene samples, less favorable five- and seven-membered structures are necessary.

Polyesters Containing Butylene Subunits. The signal *m/z* 54 due to butadiene forms the base peak in the spectra of poly(butylene adipate) (sample II) and poly(butylene terephthalate).[6] With sample II, the butadiene signal represents 70% of the total ion intensity. All further mass signals appear with relative abundances below 6%. Obviously, cis elimination occurs, forming butadiene and degradation products terminated by carboxylic acid end groups. If one olefinic end group is already formed, butadiene formation via cis elimination at the neighboring ester group is highly preferred to random cleavages of further ester groups.

In order to check whether butadiene may result as a mass spectrometric fragment, an experiment was performed with butanediol diacetate as a model compound. Fragments terminated by a carboxonium ion and fragments terminated by an olefinic end group with and without protonation of the neighboring ester group are seen. The relative abundance of the butadiene signal was only 3%. Hence, the butadiene formed from the polymer can be assigned to a thermally formed product, whereas species terminated by an olefinic end group may result as well from thermal reactions as from mass spectrometric fragmentation.

Polyesters Containing Succinic Subunits. The spectra of poly(ethylene succinate)[6] and sample I show a high-abundance signal at *m/z* 56, which can be assigned to propionaldehyde formed from the diacid subunit. As the species of series B in Table II appears with high abundance with $n = 0$, but not with higher values of n, this signal is assigned to the protonated cyclic succinic anhydride. Random formation of corresponding open-chain products terminated by one carboxylic and one carbox-

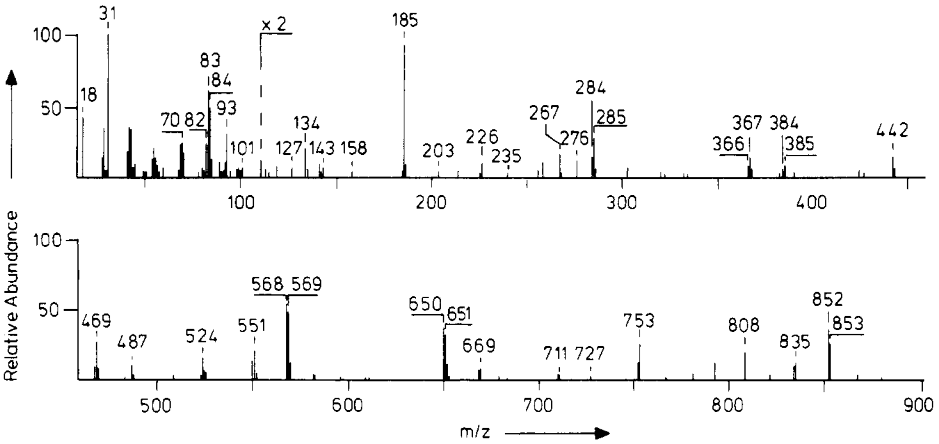


Figure 1. Py-FI mass spectrum of poly(hexamethylene sebacate).

onium group is of minor importance.

Polyesters Containing Adipic Subunits. A diagnostic signal for these polyesters appears at *m/z* 110 and is assigned to butyrodiketene. As corresponding products containing additional polymer repeating units are missing and diketenes are not formed with other dicarboxylic acid subunits, this effect is due to the chain length. Butyrodiketene has also been found with EI[2,3] and FD[17] and the corresponding protonated species with CI[3] and FAB.[17,18] Hence, the formation of butyrodiketene is a thermal process.

A further diagnostic signal at *m/z* 84 also observed by CI[3] and FAB[17,18] is due to cyclopentanone. The formation is independent of the diol subunit. Furthermore, FI spectra of polyamides containing this adipic subunits also show this signal.[19,20] Cyclopentanone was found as the main thermal degradation product in Py-GC studies of polyamides with adipic subunits.[21] These results show that the adipic acid subunit alone is responsible for cyclopentanone formation, and substitution at both carbonyl groups of this subunit is unimportant.

Similar to the succinic polyesters, series B in Table II is mostly due to the protonated cyclic anhydride, which forms a stable seven-membered ring.

Polyesters Containing Terephthalate Subunits. Characteristic signals are seen at *m/z* 166 and *m/z* 149. These signals are due to the molecular ion of terephthalic acid and the corresponding carboxonium fragment $[M - OH]^+$ formed by the loss of a hydroxyl radical from the molecular ion.

Poly(hexamethylene sebacate). Some differences are observed between the spectrum of poly(hexamethylene sebacate) shown in Figure 1 and other samples listed in Table II. Abundant series of oligomers appear as well as $[M_n]^{+\bullet}$ and $[M_n + H]^+$ ions. Fragmentation leads to carboxonium end groups on a large scale, as indicated in Table II. As with poly(butylene adipate),[6] thermal cis elimination forming one olefinic and one carboxylic end group is favorable. Whereas butadiene is the predominantly formed product with poly(butylene adipate), random cis elimination takes place with poly(hexamethylene sebacate) forming high-mass products terminated with olefinic or carboxylic acid end groups. The series of diolefines at *m/z* 366 and 650 is formed with similar abundances as the fragment series at *m/z* 367 and 551. Protonated dicarboxylic acids are observed at *m/z* 203 and 487. One of the carboxylic acid end groups is thermally formed, the other by mass spectrometric fragmentation. Protonated carboxylic acid end groups are known as mass spectrometric fragments of aliphatic polyesters[6] and low molecular weight esters.[22] Furthermore, with the butandiol diacetate model compound the low-abundance signal due to protonated acetic acid indicates the formation of protonated carboxylic acids by mass spectrometric fragmentation of esters.

Field-induced splitting of ester bonds yields mass spectrometric fragments terminated by a carboxonium end group. As the thermally formed open-chain products are terminated by olefinic or carboxylic acid end groups, the corresponding fragments with a carboxonium group at the one end and an olefinic (series C) or carboxylic (series B) end group at the other form a high-abundance ion series. Several doubly charged ions are observed, which are terminated by at least one carboxonium group. In contrast to the polyesters containing short-chain diols, doubly charged ions terminated by olefinic end groups combined with protonation at the neighbored ester group are less favorable. As pointed out with the trimethylene samples, such species are unfavorable with long-chain diol subunits.

In addition to the series B and C, series of mass signals appear one mass unit below. Probably, ketene end groups are formed instead of carboxonium end groups. Such species have been observed in EI spectra.[2]

Cleavages also occur in the sebacate subunit. Nonanic acid appears at *m/z* 158, accompanied by the species *m/z* 442, which contains one additional polymer repeating unit. Furthermore, the series $[M_n - 44]^+$ observed at *m/z* 524 and 808 is formed by fragmentation of the sebacate subunit combined with the loss of CO_2. Indeed, a minor mass signal at *m/z* 44 due to CO_2 is observed in the temperature range of polymer degradation.

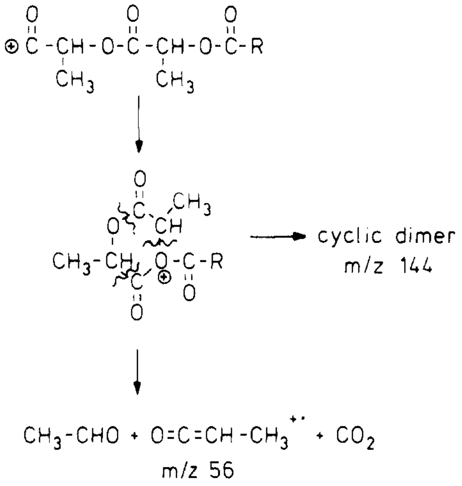
Poly(neopentyl sebacate). The spectrum contains only two series of abundant mass signals due to protonated oligomers and fragments terminated by one carboxylic and one carboxonium end group; see Table III. Further end groups are hydroxyl and protonated carboxylic acid. The formation of olefines via cis elimination is impossible with the neopentyl subunit. Hence, signals due to olefins are missing. As with poly(neopentyl succinate),[6] the signal at *m/z* 56 is due to isobutene formed from the diol subunit.

Doubly charged species are terminated by a carboxonium group at one end. The alkyl cations present in the doubly charge species *m/z* 120 and 127 have been described as end groups of singly charged fragments in EI spectra.[24] Doubly charged fragments containing such end groups were also found in the Py-FI spectrum of poly(neopentyl succinate).[6]

Table III
Structures Assigned to Mass Signals Observed with Poly(neopentyl sebacate)

n	*m/z* (rel abund)	structures assigned
	56 (100)	isobutene
1	271 (13)	$[M_n + H]^+$
2	541 (41)	
3	811 (19)	
0	185 (19)	$[CO-(CH_2)_8-CO(M_n)OH]^+$
1	455 (22)	
2	725 (9)	
3	995 (1)	
0		$[H-(CH_2)_8-CO(M_n)OH]^{+\bullet}$
1	428 (9)	
2	698 (1)	
0	289 (1)	$[HO-(CH_2)_6-OCO-(CH_2)_8-CO(M_n)OH + H]^+$
1	559 (10)	
2	829 (1)	
0		$[HOCO-(CH_2)_8-CO(M_n)OH + H]^+$
1	473 (16)	
2	743 (3)	
	Doubly Charged Ions	
	84 (36)	$[CO-(CH_2)_8-(M_n)CO]^{2+}$
	93 (25)	$[CO-(CH_2)_8-CO(M_n)OH + H]^{2+}$
	120 (29)	$[CO-(CH_2)_8-CO(M_n)OCH_2C(CH_3)_2]^{2+}$
	127 (21)	$[CO-(CH_2)_8-CO(M_n)O-CH_2C(CH_3)CH_2CH_3]^{2+}$

Scheme III
Mass Spectrometric Fragmentation of Lactic Acid Oligomers



Polylactones

Poly(lactic acid). The summed Py–FI mass spectrum of poly(lactic acid) shows two predominant mass signals at *m/z* 56 (base peak) and 144 (dimer, 40% relative abundance). Surprisingly, higher oligomers up to 900 Da only appear with relative abundances below 1%. In contrast, these oligomers have been observed with high abundances using EI,[3,23-25] CI,[3,24,25] and negative CI[24,25] MS.

The fragmentation pathway is suggested in Scheme III. As known from the diol–dicarboxylic acid type polyesters listed in Table II, carboxonium ions are formed on a large scale. With poly(lactic acid), the carboxonium ion primarily formed may immediately rearrange to a very favorable six-membered cyclic structure due to the dimeric lactid. Three cleavages of single bonds are involved in further fragmentation, but at the same time three double bonds are formed and very stable products result. An alternative mechanism is the direct splitting of methyl ketene from the carboxonium fragment. This pathway is also combined with the formation of the stable byproducts CO_2 and acetic aldehyde. Obviously, the possibility of the simultaneous formation of several highly stable species enables the extensive fragmentation in FIMS.

Surprisingly, the mechanism given in Scheme III is dominant with FI but not with CI and EI. Probably, polarization effects in the adsorbed molecules in the high electric field may promote this fragmentation pathway.

Poly(3-hydroxybutyric acid). Protonated oligomers up to *m/z* 1000 are observed in the FI spectrum shown in Figure 2. The thermal degradation yields open-chain oligomers terminated by one carboxylic and one olefinic end group.[1] As shown in Scheme IV, the monomer formed via two cis eliminations is crotonic acid. The base peak at *m/z* 69 is due to the carboxonium ion of crotonic acid. Further species terminated by a carboxonium end group are seen with low abundances. If a carboxonium ion is formed by random ionization of an ester group in an oligomer, this species may undergo further fragmentation forming the favorable α,β-unsaturated carbonyl compound *m/z* 69. As with poly(lactic acid), the formation of highly stable fragments containing double bond systemes favors extensive fragmentation.

Poly(caprolactone). The ion series $[M_n + H]^+$ and $[M_n - 18]^+$ give the predominant signals in the Py–FI spectrum, Figure 3. These series are due to protonated oligomers and to fragments terminated by an olefinic end group at the one end and one ketene end group at the other. The base peak at *m/z* 114 is assigned to the cyclic monomer that is formed thermally. The formation of a cyclic monomer by a zipper mechanism is known as the much preferred thermal degradation mechanism.[26] The appearance of the ion at *m/z* 115 with 50% relative abundance indicates protonation of the monomer, similar as observed for the oligomers. In addition, protonation is also observed with the caprolactone monomer.

Surprisingly, fragments terminated by carboxonium ions are missing. As such species are formed with other samples, their formation is probable and further fragmentation of such species primary formed can be expected. In the case of poly(caprolactone), the formation of the seven-membered cyclic monomer is very favorable.

As with the open-chain pyrolyzates from poly(hexamethylene sebacate), fragments terminated by ketene end groups are produced. Such fragments are also observed with EI[3,27] and, to a lower degree, in the CI[3] spectrum. The complementary end group formed during this fragmentation is hydroxyl. Fragments terminated by one hydroxyl and one protonated carboxylic end group are seen at *m/z* 133, 247, 361, 475, 589, and 703.

Specific doubly charged fragments only observed in the FI mode are seen at *m/z* 99 and 106. The corresponding structures are given in Scheme V. The fragment *m/z* 106 is formed via a seven-membered transition state. As seen with the diol–dicarboxylic acid type polyesters, the ring size is combined with the possibility of splitting the methylene–oxygen bond. In contrast to those polymers, the fragmentation of caprolactone oligomers also occurs via the most favorable six-membered transition state forming the fragment *m/z* 99. Indeed, this reaction may be promoted by the simultaneous formation of formaldehyde, but cleavages of methylene–methylene bonds are not observed with all other samples investigated.

Poly(*p*-hydroxybenzoic acid). Because of the absence of aliphatic groups, ester cleavage via a six-membered transition state is not possible. The only possible degradation pathways are either hydrolysis, ester exchange

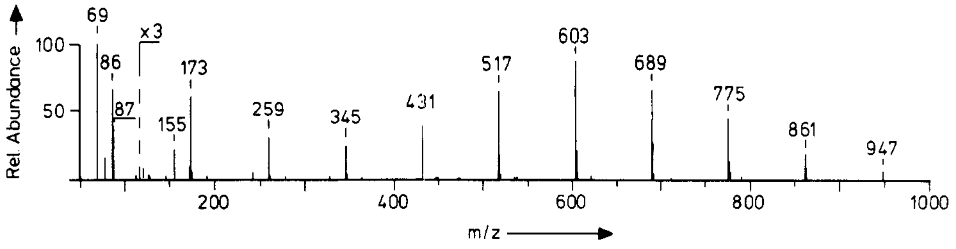


Figure 2. Py-FI mass spectrum of poly(3-hydroxybutyric acid).

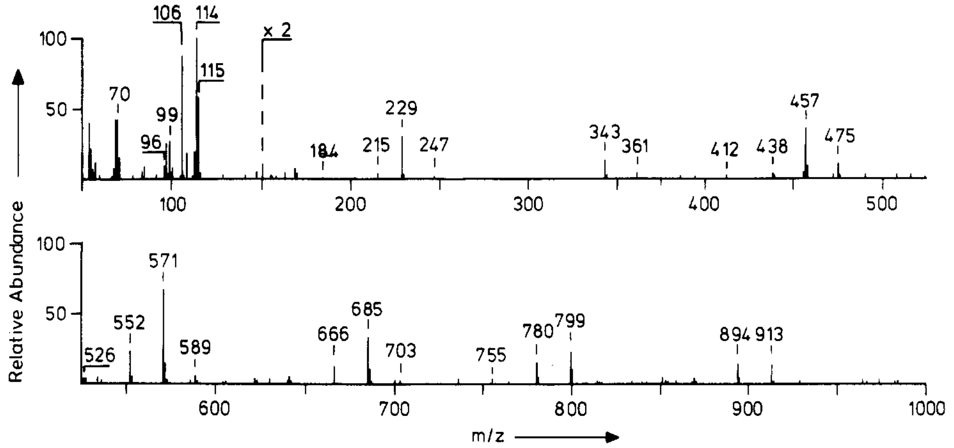
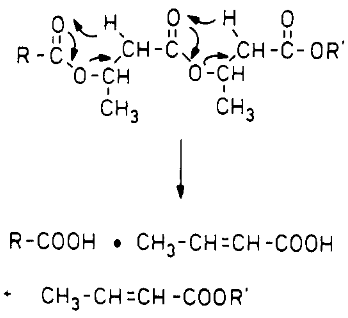
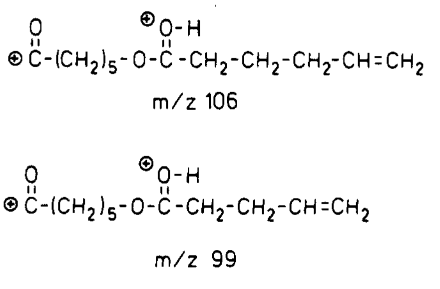


Figure 3. Py-FI mass spectrum of poly(caprolactone).

Scheme IV
Thermal Formation of Crotonic Acid from Poly(3-hydroxybutyric acid) via Two Cis Eliminations



Scheme V
Structures Assigned to Doubly Charged Species Observed in the Py-FI Spectrum of Poly(caprolactone)



$$\oplus\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_5\text{-}O\text{-}\overset{\oplus O\text{-}H}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$$

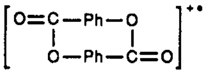
m/z 106

$$\oplus\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_5\text{-}O\text{-}\overset{\oplus O\text{-}H}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$$

m/z 99

reactions, or the formation of radicals by chain scission. Radical formation leads to a large number of secondary reaction products containing bisphenyl subunits. Structures assigned to the mass signals observed are listed in Table IV. Under the experimental conditions employed, the total ion count reaches its maximum at about 500 °C. At this high temperature, ester exchange reactions are not preferred over free radical formation with this polymer. On the other hand, predominantly oligomers have been obtained with low energy EIMS at 330 °C, using a much slower heating rate of only 10 °C/min.[28]

Table IV
Mass Signals Observed in the FI Spectrum of Poly(*p*-hydroxybenzoic acid) and Their Tentatively Assigned Structures

m/z (rel abund)	structure[a]
120 (100)	$[O{=}Ph{=}CO]^{+\bullet}$
121 (53), 241 (11), 361 (5), 481 (1), 601 (1)	$[HOPh\text{-}(COOPh)_n\text{-}CO]^+$
94 (18), 214 (5), 334 (12), 454 (2), 574 (1)	$[HPhO\text{-}(COPhO)_n\text{-}H]^{+\bullet}$
138 (30), 258 (6), 378 (2)	$[HOPh\text{-}(COOPh)_n\text{-}COOH]^{+\bullet}$
170 (3), 290 (3), 410 (6), 530 (1), 650 (1)	$[HPhPh\text{-}(OCOPh)_n\text{-}OH]^{+\bullet}$
186 (3), 306 (4), 426 (2), 546 (1)	$[HOPhPh\text{-}(OPhCO)_n\text{-}OH]^{+\bullet}$
197 (5), 317 (11), 437 (7), 557 (3), 677 (2)	$[HOPhPh\text{-}(COOPh)_n\text{-}CO]^+$
240 (5)	

[a] Ph = C_6H_4.

Conclusions

Pyrolysis–field ionization mass spectrometry is well suited for the investigation of polyesters. In contrast to the majority of other chemical structures, significant mass spectrometric fragmentation occurs with FIMS of molecules containing two or more ester groups. Adsorption of the polar ester groups on the FI emitter leads to the unusually high amounts of doubly charged fragments. Mass spectrometric fragmentation is lower than with low-energy EI but more intense than with chemical ionization. In spite of the fact that more fragmentation is observed with FI than with CI, in many cases more abundant high-mass signals are seen in the FI spectra. Cyclic species and the possibility of simultaneous formation of several double bonds and conjugated double bond systems drastically favor fragmentation. Hence, the fragmentation pathway is promoted with selected chain lengths between the ester groups. The degree of mass spectrometric fragmentation strongly depends on the diol subunit, whereas the influence of the dicarboxylic acid subunit is low.

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Registry No. I (copolymer), 28158-21-6; I (SRU), 28725-67-9; II (copolymer), 24938-37-2; II (SRU), 24937-05-1; III (copolymer), 36568-42-0; III (SRU), 36221-42-8; IV (copolymer), 26745-88-0; IV (SRU), 26762-10-7; V (SRU), 25038-59-9; VI (copolymer), 26062-94-2; VI (SRU), 24968-12-5; VII (copolymer), 28158-15-8; VII (SRU), 28759-54-8; VIII (homopolymer), 26100-51-6; VIII (SRU), 26023-30-3; IX (homopolymer), 26063-00-3; IX (SRU), 126296-86-4; X (homopolymer), 24980-41-4; X (SRU), 25248-42-4; XI (homopolymer), 30729-36-3; XI (SRU), 26099-71-8.

Surface Modification of Poly(tetrafluoroethylene-*co*-hexafluoropropylene). Introduction of Alcohol Functionality[1]

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ABSTRACT: The reduction of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) was studied with regard to the kinetics of reaction and the product structure. The thickness of the resulting modified surface layer (depth of reaction) can be controlled by using reaction time and temperature. At −78 °C the thickness can be controlled in the range of 45–90 Å using reaction time; at 0 °C the thickness can be controlled in the range of 250–800 Å. The air-sensitive reduction product contains carbon–carbon double and triple bonds, aliphatic C–H bonds, alcohols, carbonyls, and very little fluorine. The sources of the oxygen and C–H functionality were studied. Hydroboration followed by oxidation introduces alcohol functionality to the surfaces. The alcohols exhibit low reactivity in esterification reactions, but yields can be improved by using acylation catalysts; their reactivity is analogous to hindered alcohols in solution. Base-catalyzed addition of ethylene oxide renders surface-bound primary alcohols, increasing the reactivity of the surface toward esterification. Lower yields of primary alcohols can be directly introduced to the surface by reaction of the reduced layer with 9-BBN, followed by carbonylation and reduction.

Introduction

Our study of the surface chemistry of fluorinated polymers[2-6] has been with the objective of preparing model substrates from which surface structure-property and structure-reactivity correlations can be drawn. Chemically resistant polymer film samples were chosen[7] to prepare substrates with reactive surfaces and inert interiors so that

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