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Bulk Reactions in Amphiphilic Acrylic Copolymers Studied by Time/Temperature-Resolved Pyrolysis–Field Ionization Mass Spectrometry

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ABSTRACT: Amphiphilic acrylate and methacrylate homo- and copolymers containing long side chains were investigated by time/temperature-resolved pyrolysis–field ionization mass spectrometry. Hydroxyl, ester, and amide groups are present in these side chains. In the first step, ethylene glycol and degradation products of the lipid side chain are thermally liberated by reactions between hydroxyl groups and these ester or amide groups, which involve cross-linking. Further heating above 350 °C leads to unselective thermal degradation of the char. The cleavages from the lipid side chains increase drastically with increasing hydrophilic content. In contrast, the lipid monomer is selectively formed by depolymerization of the polymers with high lipid content.

Introduction

Pyrolytic methods are widely used for the investigation of polymers.[1–4] Pyrolysis (Py) products of a large number of polymers have been successfully identified by means of mass spectrometry (MS).[5,6] Several ionization techniques available for MS of technical and biopolymers have been described.[7] For identification of the thermal products, soft ionization modes are preferred in order to minimize mass spectrometric fragmentation in the Py–MS studies. As the method of choice, field ionization[8,9] (FI) MS is used to produce spectra containing highly abundant mass signals due to molecular ions of the pyrolysis products. This technique has already been applied to a large number of polymers.[10,11] Improvements in instrumentation[12,13] have allowed the registration of highly abundant mass signals due to molecular ions of the pyrolysate > 1000 Da.[14–19]

In this paper a series of amphiphilic copolymers is investigated by time/temperature-resolved Py–FIMS. To aid in the interpretation of copolymer spectra, experiments have been performed with the lipid monomer (a methacrylate derivative containing a long side chain), 2-hydroxyethyl acrylate (HEA), the lipid homopolymer, and poly-HEA.

The amphiphilic copolymers were synthesized with different lengths of a hydrophilic spacer in the polymer backbone. This main-chain spacer is composed of hydrophilic repeating units of HEA.[20,21] The spacer groups decouple the polymer backbone from the amphiphilic side chains at the gas-water interface. This enables the polymer to organize itself into highly ordered monolayers. Furthermore, these monolayers can be condensed into a solid analogue phase and transferred by the Langmuir–Blodgett technique onto a solid support to build up multilayers.[22,23] Small-angle X-ray scattering experiments[24] and grazing-incidence reflection FT-IR spectroscopy[25] of Langmuir–Blodgett multilayers from amphiphilic copolymers show an enhanced thermal stability of the layer by increasing spacer length.

With an increase in the hydrophilic content of the polymer main chain and retention of the amphiphilic side groups, the thermal stability of the multilayer structures must be attributed to the enhanced hydrophilic spacer. One possible explanation of this stability is a microphase separation into the hydrophilic amorphous polymer region containing hydroxyl groups and the hydrophobic crystalline bilayers of long alkyl chains. At higher temperatures (above about 120 °C), this leads to cross-linking reactions in the hydrophilic region caused by the high concentration of free hydroxyl groups.

If side-chain reactions occur prior to the splitting of the polymer main chain, time/temperature-resolved Py–MS is an excellent method for detecting the species split off from the side chain. At higher temperatures, the pyrolysate of the polymer backbone is detected. Such behavior has also been found in Py–MS studies with poly(vinyl chloride) and poly(vinyl acetate), for example. The evolution of hydrochloric acid and acetic acid prior to the scission of the polymer main chain has been shown.[26] On the other hand, monomers and oligomers are well-known thermal degradation products of a large number of different polymers.[27] For example, the molecular ion of methyl methacrylate is nearly exclusively formed by Py–MS of poly(methyl methacrylate) by using either chemical ionization[28] or field ionization[4] under the experimental conditions described in this paper. Thus, monomer formation can also be expected with the polymers containing the lipid methacrylate subunit. In contrast to the poly(methyl methacrylate), pyrolysis of polyacrylates often yields monomer and oligomers.[29] In addition, further thermal fragmentation occurs. The degree of fragmentation increases with increasing length of the polymer side chain.[29] Hence, olgiomers and oligomer fragments can be expected from samples containing sequences of HEA subunits. As studies of polyesters[30] and polyamides[31] have shown that intermolecular ester and amide exchange reactions occur on a large scale, similar reactions may be expected to occur with the samples described here. In particular, free hydroxyl end groups

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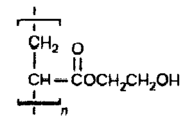
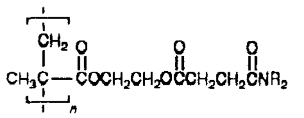
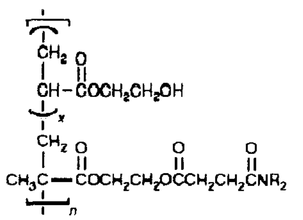
Table I
Structures of the Polymers Investigated

polymer	structure
A	 $-[CH_2-CH(COOCH_2CH_2OH)]_n-$
B	 $-[CH_2-C(CH_3)(COOCH_2CH_2OCCH_2CH_2CNR_2)]_n-$
C–E	 $-[CH_2-CH(COOCH_2CH_2OH)]_x-[CH_2-C(CH_3)(COOCH_2CH_2OCCH_2CH_2CNR_2)]_n-$

[a] Copolymer C: $x = 1$. Copolymer D: $x = 5$. Copolymer E: $x = 10$.

present in the HEA subunits may react with ester or amide groups in neighboring side chains. These reactions lead to a cross-linked residue accompanied by the formation of volatiles from the side chains. Hence, cross-linking is indicated by low molecular weight products released during this process.

The aim of the present study is to investigate the dependence of cross-linking reactions on the hydrophilic content. The possibility of detecting volatiles released during cross-linking allows one to distinguish between reactions of hydroxyl groups at amide groups and different types of ester groups. The comparison of the thermal behavior of the copolymers may also give some indication of different degradation pathways.

Experimental Section

The Py–FIMS experiments were performed by using the modified direct inlet system of a double-focusing Finnigan MAT 731 mass spectrometer. Experimental details of the equipment and methodology used have been reported.[12,13] Small pieces of the bulk samples were heated in the direct probe, without any pretreatment, from 50 to 700 °C in high vacuum at about 10^{-3} Pa with a heating rate of 1.2 °C s^{-1}. During the heating about 30 spectra were recorded in the mass range 50–1000 Da. The thermal degradation products were ionized at 8-kV emitter potential, and the counter electrode was at −3 kV. All mass spectra were recorded electrically and averaged with the Finnigan MAT SS 200 data system.

Results and Discussion

The structures of the polymers are given in Table I. Two homopolymers and three copolymers containing monomeric subunits of both homopolymer components were investigated. The ratio between the monomeric subunits of the homopolymers, i.e., 2-hydroxyethyl acrylate (HEA) and the methacrylic lipid monomer B, is either 1, 5, or 10 in these copolymers.

The thermal behavior of the five samples is compared in the thermograms in Figure 1, where the total ion count is plotted versus the probe temperature. It is clear that the degradation pathway depends dramatically on the HEA content. The appearance of two maxima in the total ion count indicates at least two different degradation pathways. Whereas two maxima are observed with the poly-HEA (sample A), only one maximum is present with the lipid homopolymer, sample B. The thermograms of the three copolymers C–E show an increase of the total ion count at the second maximum corresponding to the increase of the HEA content. Furthermore, the first maximum of the total ion count is slightly shifted to lower temperatures. Thus, it is clear that the thermal degradation mechanism is dependent on the copolymer composition.

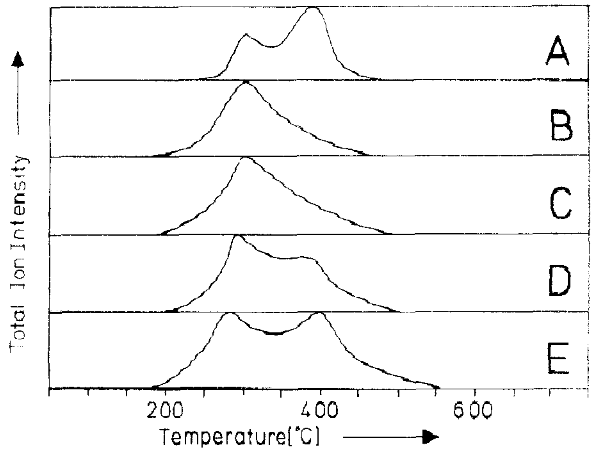


Figure 1. Temperature dependence of the total ion counts observed by Py–FIMS with the samples listed in Table I.

In order to gain more information, the spectra recorded at different temperatures were examined separately to allow investigation of the degradation pathway. Figure 2 shows a single-scan spectrum of the poly-HEA homopolymer A recorded at 300 °C (Figure 2a), the spectrum summed over the entire temperature range from 50 to 750 °C (Figure 2b), and the temperature dependence of the formation of selected ions (Figure 2c). The probable structures assigned to the mass signals observed are listed in Table II. In Figure 2a, the difference between the mass signals in each series is 116 Da, which corresponds to the molecular weight of the monomeric subunit. These signals are mostly due to carboxonium ions, which result from mass spectrometric fragmentation of thermally formed oligomers.

Surprisingly, although field ionization is a soft method, abundant signals of molecular ions of high-mass pyrolysates are missing in Figure 2a. On the other hand, fragmentation is known for polar substances such as low molecular weight aliphatic alcohols and esters[32] and with high-mass degradation products obtained from polyester pyrolysis.[30] The degree of fragmentation is especially high for molecules containing two or more polar functional groups containing oxygen. Similar behavior can be expected for the pyrolysates obtained from poly-HEA.

The single-ion profiles given in the thermograms in Figure 2c show that the significant signals observed in Figure 2a appear mostly in the temperature range of the first maximum of the total ion count. The representative ions *m/z* 159 and 287 are selected in the thermogram. Ethylene glycol (*m/z* 62) is released by reactions between hydroxyl and ester groups of HEA subunits and reaches a maximum at 330 °C. The total ion count decreases at this temperature. As reactions between reactive groups linked to different polymer main chains are probable, cross-linking is expected in addition to intramolecular transesterifications. This effect can be explained by a decrease of intact HEA sequences with an increasing number of cross-linkages. At temperatures above 350 °C, random thermal degradation of the cross-linked residue occurs, forming mass signals at each nominal mass between *m/z* 200 and 800. These signals are dominant in the spectrum summed over the entire temperature range from 50 to 750 °C, Figure 2b. The temperature profile

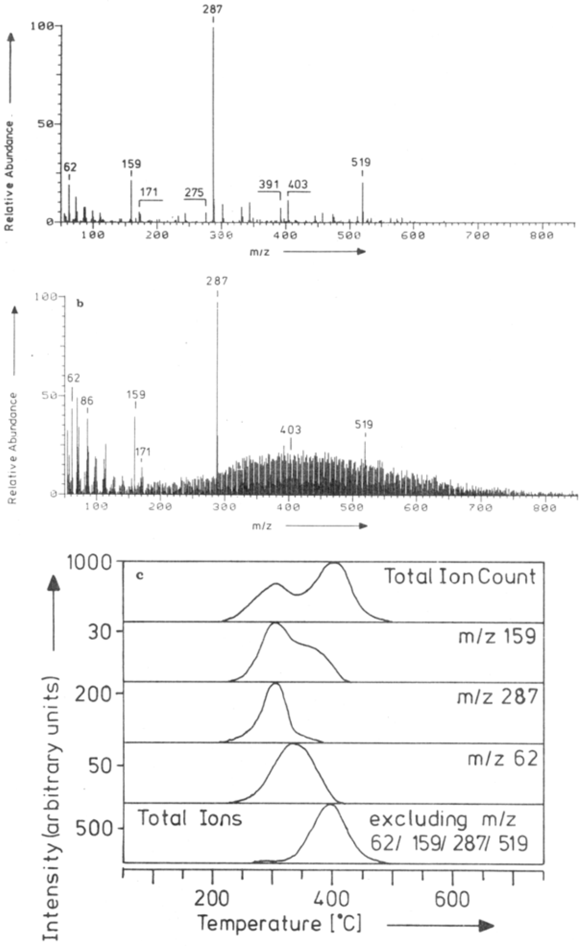
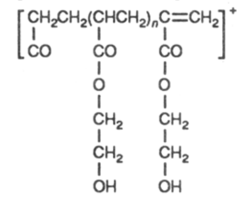
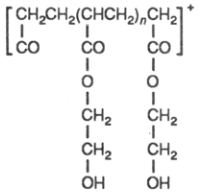


Figure 2. Py–FIMS of poly-HEA: (a) single-scan spectrum recorded at 300 °C, (b) spectrum summed over the entire temperature range from 50 to 750 °C, (c) temperature profiles of the total ion count, the signals *m/z* 159, 287, and 62, and the count of all ions excluding *m/z* 62, 159, 287, and 519.

Table II
Structures Assigned to Mass Signals Observed in the Py–FI Spectrum of Poly-HEA

m/z	*n*	structure
56		$[CH_2{=}CHCHO]^{\cdot+}$
62		$[HOCH_2CH_2OH]^{\cdot+}$
171	0	
287	1	
403	2	
519	3	
159	0	
275	1	
391	2	

of the total ion count excluding the most abundant signals observed in Figure 2a shows that these additional signals only appear in the temperature range of the second maximum between 350 and 450 °C and represent the pyrolysate of the polymer backbone.

The Py–FI spectra of the lipid monomer and the lipid homopolymer B shown in Figure 3 look very similar.

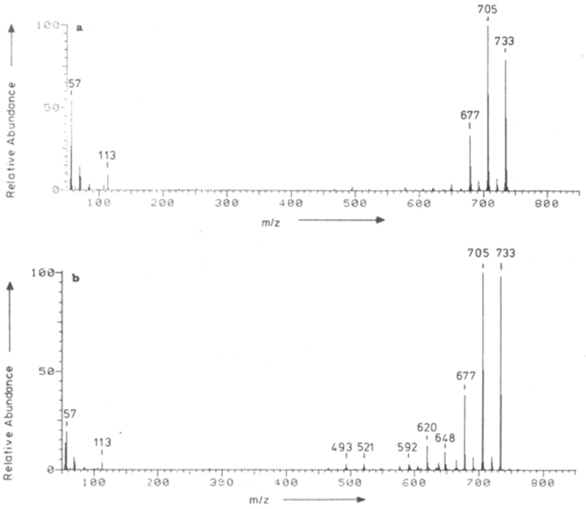
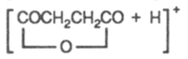


Figure 3. Py–FI spectra of (a) the lipid monomer and (b) the lipid homopolymer B.

Table III
Structures Assigned to Mass Signals Observed in the Py–FI Spectra of the Samples B–E[a]

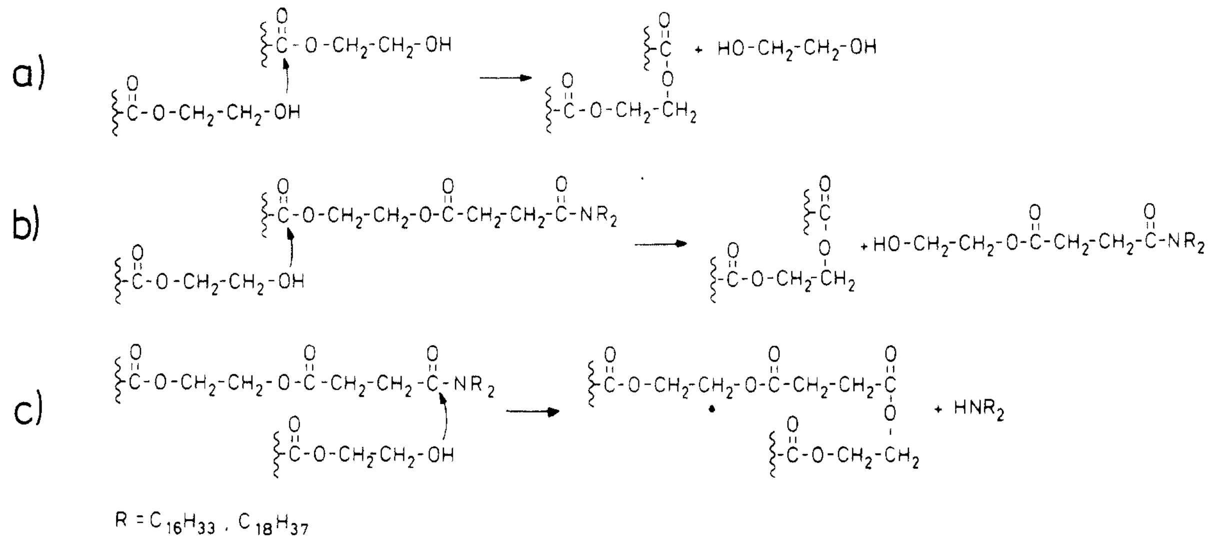
m/z		structure
57	F	$[C_4H_9]^+$
62	M	$[HOCH_2CH_2OH]^{\cdot+}$
101	F	
113	F	$[CH_2C(CH_3)COOCH{=}CH_2 + H]^+$
282	F	$[RNH{=}CH_2]^+$
254		
521	M	$[HNR_2]^{\cdot+}$
493		
465		
621	M	$[R_2NCOCH_2CH_2COOH]^{\cdot+}$
593		
565		
648	F	$[R_2NCOCH_2CH_2\text{-}COOCH{=}CH_2 + H]^+$
620		
592		
665	M	$[R_2NCOCH_2H_2COOCH_2CH_2OH]^{\cdot+}$
637		
609		
733	M	$[R_2NCOCH_2CH_2COOCH_2\text{-}CH_2OCOC(CH_3){=}CH_2]^{\cdot+}$
705		
677		

[a] M = molecular ion, F = fragment ion, and R = $C_{18}H_{37}$, $C_{16}H_{33}$.

Hence, depolymerization is the predominant degradation pathway. Structures assigned to mass signals observed are included in Table III. As the two long aliphatic side chains linked to the amide nitrogen belong to mixtures of C_{16} and C_{18} alkyl chains, three mass signals due to molecular ions result. There are no significant changes in the single-scan spectra recorded at temperatures between 200 and 400 °C.

The Py–FI spectra of the three copolymers C–E are shown in parts a–c of Figure 4. As the lipid monomer B content decreases, the relative intensities of the molecular ions of lipid monomer B decrease from copolymer C to copolymer E. The mass signals observed are predominantly due to products cleaved from the long side chains of the lipid subunit B; see Table III. These species can be formed by reactions of free hydroxyl end groups in the HEA subunits A with the side chains of the lipid subunits B. The connection between the cleavage of side chains and the formation of new ester bonds in the residue is shown in Scheme I. The hydroxyl groups can react with ester (a,b) as well as amide (c) groups. Only with copolymer C is the depolymerization to monomer B favored over the side-chain scission.

Scheme I
Reaction Scheme of Volatile Pyrolysate Formation during the Cross-Linking Process



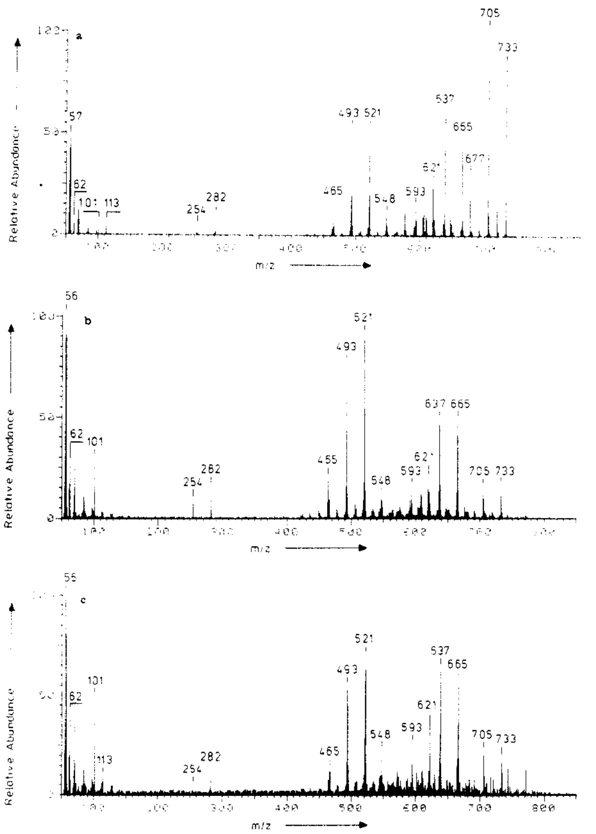


Figure 4. Py-FI spectra of the copolymers summed over the entire temperature range from 50 to 750 °C: (a) copolymer C, (b) copolymer D, (c) copolymer E.

Although sequences of HEA subunits are present in copolymers D and E, the corresponding series of mass signals separated by 116 Da (from the HEA homopolymer A) are missing in these spectra. Reactions between HEA subunits and the side chains of the lipid subunit seem to be preferred over the depolymerization to HEA or HEA oligomers. It is logical that the decrease of sequences of intact HEA subunits by cross-linking prevents the formation of HEA oligomers. With increasing cross-linking, the relative abundances of mass signals due to the pyrolysate of the cross-linked network increase from 2 to 20% for copolymer D, copolymer E, and poly-HEA, respectively.

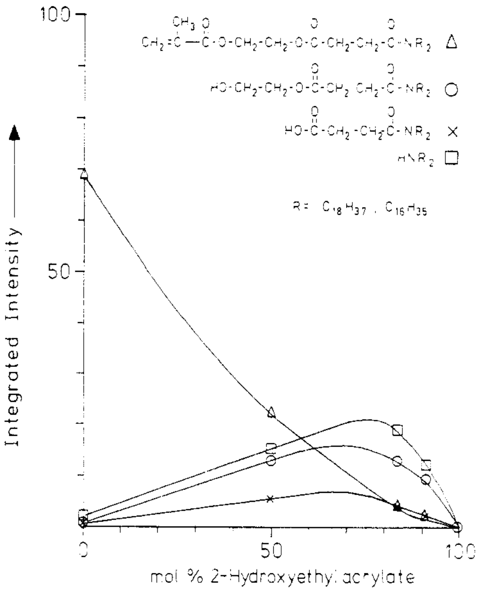


Figure 5. Integrated intensities (i.e., the sum of the intensities of all ions is 100%) of molecular ions due to the lipid monomer B and products formed by cleavage of the lipid monomer side chain plotted versus the HEA content.

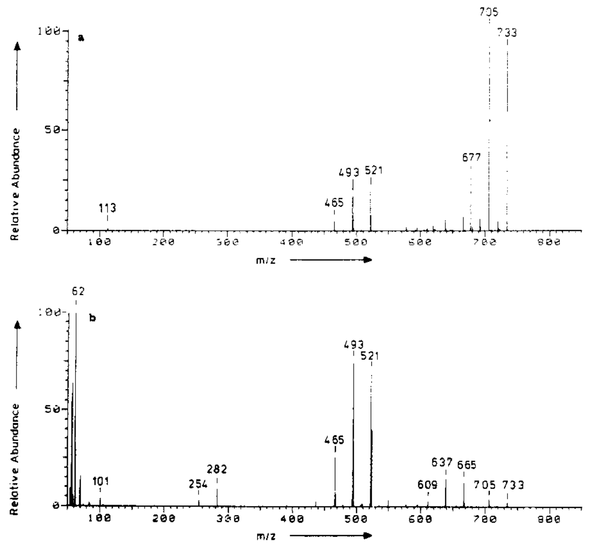


Figure 6. Py-FI single-scan spectrum of (a) copolymer C and (b) copolymer E recorded at approximately 250 °C.

In order to compare the degree of depolymerization with the degree of cleavage of the lipid side chains, the integrated intensities for the molecular ions of the lipid monomer and products formed by cleavage of the side chain are plotted versus the HEA content in Figure 5. Obviously, the relationship between the content of lipid subunit B and the formation of molecular ions due to this unit is not linear. Cleavage from the side chain becomes more favorable with increasing HEA subunit content. The mobility of sequences in these subunits seems to be important for side-chain reactions.

Single-scan spectra recorded at the beginning of thermal degradation provide additional indications of the importance of the side-chain mobility. Single-scan spectra of the copolymers C and E recorded at 250 °C are shown in parts a and b of Figure 6, respectively. This temperature represents the early part of degradation (see Figure 1). Whereas the degradation of copolymer C starts with depolymerization, the degradation of copolymer E starts with the transesterification reactions together with the formation of ethylene glycol and scissions of the side chain of the lipid subunit B. In contrast to the spectra summed over the entire temperature range (Figure 4), in the single-scan spectra (Figure 6) the dialkylamine formation is strongly preferred to the splitting of other products from the lipid side chain during the cross-linking process. Whereas ethylene glycol forms the base peak with copolymer E, this signal is completely missing in the single-scan spectrum of copolymer C. As both copolymers are made from the same monomeric subunits, steric effects can be assumed to cause the differences observed.

With an increase of the temperature from 250 to 300 °C, cross-linking also occurs with copolymer C, and depolymerization increases with copolymer E. Hence, the single-scan spectra at the beginning of degradation show more differences in the degradation pathways of the copolymers than observed in the spectra summed over the entire temperature range. With copolymer D, cross-link reactions and depolymerization start about the same time.

Additional information about the complex degradation mechanism is obtained by selected ion profiles of the different degradation products. Figure 7 shows the profiles of the main pyrolysates listed in Table III for the three copolymers C (Figure 7a), D (Figure 7b), and E (Figure 7c). The maximum of the monomer formation is shifted from 270 to 310 °C from copolymer C to copolymer E. The formations of the products formed from the lipid side chain by cross-link reactions reach their maxima between 290 and 300 °C with all three copolymer samples. These temperature profiles explain the large differences of the spectra of the copolymers C and E shown in Figure 6 in the early degradation stage.

The formation mechanism of ethylene glycol is more complex. Two maxima are obtained with copolymer E. The second maximum is observed at 330 °C, which is in good agreement with that of poly-HEA. Surprisingly, a further maximum is observed at about 220 °C. This maximum increases with increasing HEA content, although poly-HEA shows the maximum at 330 °C. With copolymer D, a shoulder is observed instead of the first maximum observed for copolymer E.

The two maxima in the temperature profiles due to the degradation products terminated by a carboxylic end group indicate at least two different pathways for their formation. The dependence of this maximum on the copolymer composition remains unclear.

The sum of the intensities of all ions in the mass ranges *m*/*z* 120–250 and 290–460 is used representatively for all of the numerous low abundant mass signals. The maximum is at about 400 °C as observed for the random degradation of poly-HEA. The intensity of these signals drastically increases with increasing HEA content. It should be noted that some signals in these mass ranges may also result from fragments of the lipid subunit. In the case of copolymer C the formation of products by random degradation at about 400 °C is negligible. The signals giving the maximum at 300 °C are due to fragments from the lipid components and not from random degradation of a cross-linked residue.

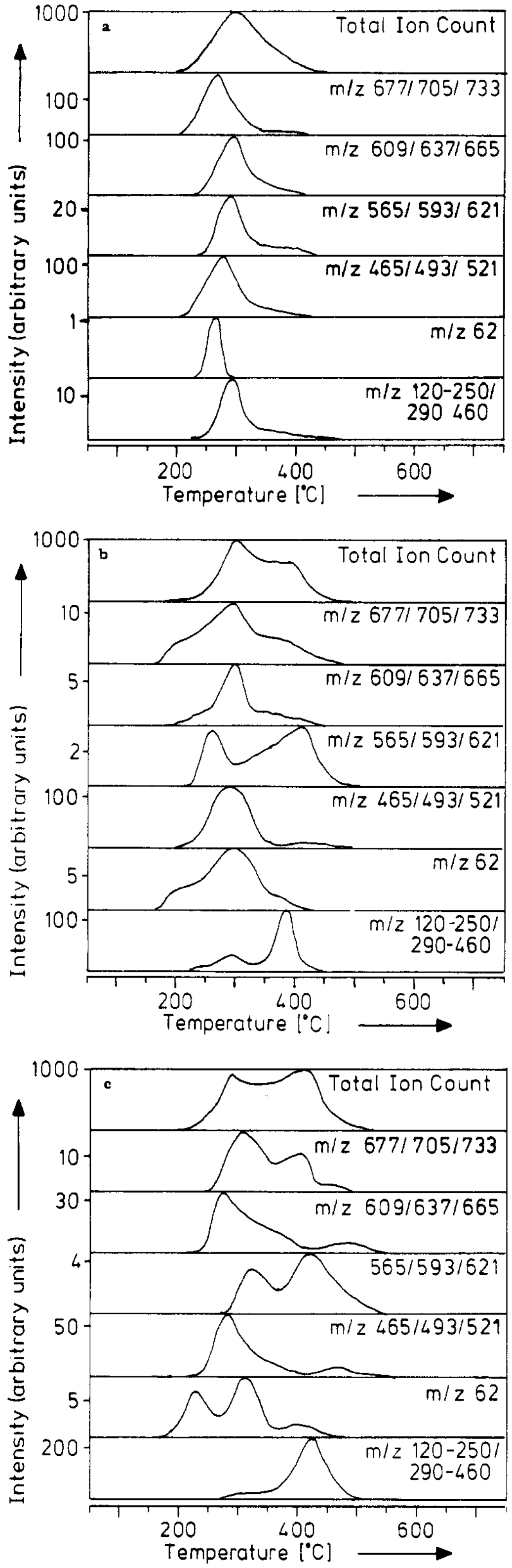


Figure 7. Temperature profiles of ions listed in Table III for (a) copolymer C, (b) copolymer D, and (c) copolymer E.

Conclusions

The thermal properties of the copolymers investigated strongly depend on the content of the HEA spacer subunits. With the copolymers containing long sequences of HEA subunits, the degree of cleavage in the lipid side chain is high. These polymers show high order in Langmuir–Blodgett multilayers. On the other hand, side-chain cleavage reactions are very poor with the 1:1 HEA–lipid copolymer, and the order of this polymer in Langmuir–Blodgett multilayers is also low. Hence, the mobility of the polymer subunits seems to be of particular importance for the different polymer properties. Well-organized Langmuir–Blodgett multilayers as well as thermal cleavage from the side chains is favored when the mobility is high. In the 1:1 copolymer, steric hindrance reduces the highly ordered Langmuir–Blodgett multilayers.[21,24] At the same time the decreased transesterification reactions and amide cleavage lead to a lower degree of cross-linking and less stable multilayers.

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