Determination of Additives in Biomer and Lycra Spandex by Pyrolysis Tandem Mass Spectrometry and Time Temperature Resolved Pyrolysis Mass Spectrometry

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Synopsis

Pyrolysis mass spectrometry (Py-MS), time/temperature resolved Py-MS (TTR-Py-MS), and pyrolysis tandem mass spectrometry (Py-MS/MS) were used to determine the structure of an additive present in Biomer and Lycra Spandex. The additive was found to form a second phase in the polymer matrix which was insoluble in *N,N'*-dimethylacetamide. This insoluble portion (7% by weight) was separated by centrifugation. The structure of this additive is proposed to be poly(2-diisopropyl amino ethyl methacrylate) (DPA–EMA). The additive is present as a stabilizer for UV radiation and chloride and hypochlorite ion attack. A chloride containing compound of similar structure (2-diisopropyl amino ethyl chloride) (CAS No. 96-79-7) is also detected. This chloride-containing compound may be formed by reaction of the polymeric additive with chloride ions during storage or pyrolysis.

INTRODUCTION

As the Utah artificial heart program enters the clinical phase, and the materials in use become more sophisticated, the need for advanced analytical capabilities increases. The effects of polymer surface treatments, sterilization, implantation, and material processing need to be monitored. In the past the materials have been analyzed using infrared spectroscopy (IR),[1] gel permeation chromatography (GPC),[2] thermogravimetry (TG),[3] and pyrolysis mass spectrometry (Py-MS).[3-5] Among these techniques, Py-MS has been demonstrated to be effective in the identification of the components used in the manufacture of polyurethanes.[3-15]

A previous study of Biomer and Lycra Spandex identified these materials as poly(ether urethane urea)s (PEUU)s of identical composition. Both polymers are composed of a poly(tetramethylene glycol) (PTMG) soft segment capped with 4,4'-methylenebis (phenyl isocyanate) (MDI), and extended with ethylene diamine (EDA) (see Fig. 1). Also, additives were detected in these materials.[4] These additives were identified as an antioxidant and (possibly) an amine antistatic agent. In order to determine the structure of the antistatic agent and the way in which it is incorporated into the polymer, more advanced mass spectrometric techniques are required. By adding another

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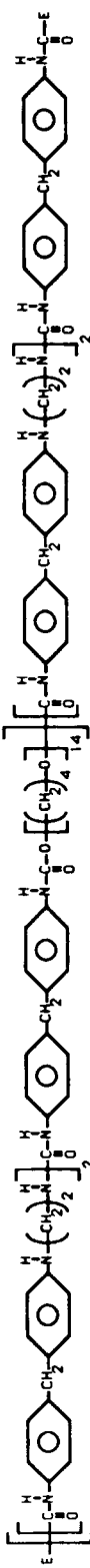

Fig. 1. Structure of Biomer and Lycra Spandex as determined in previous analyses of these materials. The *E* represents endgroups which have not been identified. Both Biomer and Lycra Spandex contain an antioxidant (4,4'-butylidene-bis(6-*tert*-butyl-*m*-cresol)). Lycra Spandex also contains a low molecular weight polydimethylsilicone oil.

dimension to the MS data (e.g., fragmentation patterns or temperature behavior) much more detailed information can be obtained. Tandem mass spectrometry utilizing collisionally activated dissociation (MS/MS and CAD, respectively) can be used to obtain fragmentation information from selected mass peaks.[16,17] The fragmentation is caused by kinetic collisions of the selected ions with a neutral reagent gas such as helium or argon. The energy of these collisions is of the same order as the energy transferred during electron impact ionization. Thus the "fragmentogram" can be used to identify the structure of the parent ion by applying the principles from EI fragmentation to the MS/MS spectrum.

The use of time/temperature resolved Py-MS (TTR-Py-MS) for polymer analysis is very useful in determining the degradation and/or volatilization sequence of the polymer.[18] Montaudo et al.,[6-11] in their studies of polymer degradation, used direct probe Py-MS to follow the degradation processes over minutes or even hours. Using the TTR-Py-MS information they were able to determine sequences of the polymers analyzed.

The use of TTR-Py-MS with flash pyrolysis methods (i.e., Curie-point or galvanically heated filament methods) with heating rates on the order of 100°C/s requires the use of factor analysis to deconvolute the overlapping degradation and pyrolysis processes. The use of factor analysis combined with TTR-Py-MS has been demonstrated by Windig et al.[19,20] for a bipolymer mixture, a wood sample, and an uncured rubber compound. In each of these examples, the factor analysis technique was able to deconvolute the pyrolysis curves into the mixture components without prior information on peak shapes and locations. Thus, by resolving "pure" component curves it is possible to monitor the degradation mechanisms and to elucidate how additives are linked into the polymer matrix.

In this study, Py-MS, TTR-Py-MS, and Py-MS/MS methods were used to identify the structure of the antistatic agent and determine how this additive is linked into the polymer.

EXPERIMENTAL

Samples of Biomer were taken from the liquid solution/suspension (30% solids in *N,N'*-dimethylacetamide) of one lot as received from the manufacturer (lot BSQXX9). Samples of Lycra Spandex were taken from fibers as received from the manufacturer. The samples for Py-MS and TTR-Py-MS were dissolved/suspended in *N,N'*-dimethylacetamide (DMAC) to form 1 mg/mL solutions.

The insoluble portions of Biomer and Lycra Spandex were isolated by making 10% (w/v) solutions of the polymers in a 1 : 1 mixture of acetone and DMAC. These solutions were then centrifuged at 38 g for 48 h. The solids which settled out were washed with DMAC, acetone, and pentane and vacuum-dried. The resulting material was weighed, and 1 mg/mL solution/suspensions were prepared in hexafluoroisopropanol. These solutions were used for Py-MS and TTR-Py-MS analyses. The mother liquor from these separations was reprecipitated in methanol and vacuum dried. The "clean" polymers were then dissolved in DMAC (1 mg/mL) for Py-MS analysis.

The model compound for the additive (2-diisopropylaminoethyl chloride hydrochloride) was dissolved in HPLC grade methanol to form a 1 mg/mL solution.

Five microliters of the prepared solutions (5 μg sample, dry weight) were coated onto continuously rotating ferromagnetic filaments (Curie-point temperature 610°C). The solvent was evaporated from the filament in a heated, filtered airstream. Subsequently, the filaments were drawn back into borosilicate reaction tubes for analysis by Py-MS or TTR-Py-MS.

Pyrolysis Mass Spectrometry

The Py-MS analyses of the polymers and the isolates from the polymers were carried out on an Extranuclear 5000-1 Curie-point Py-MS system interfaced to an IBM system 9000 microcomputer. The samples were analyzed under the following conditions: T_{eq} (Curie-point) of the filament 610°C, temperature rise time 5–5.5 s, total heating time 10 s, electron energy 12 eV, mass range scanned 20–260 amu, scan speed 100 amu/s, and total number of scans 100. The 100 scans were summed (signal averaging) by the data system, and the resulting average spectrum was stored on disk. Each sample was analyzed in triplicate.

Time-Resolved Pyrolysis MS

The TTR-Py-MS analyses of Biomer, Lycra Spandex, and their insoluble portions were carried out on an Extranuclear 5000-1 Curie-point Py-MS system interfaced with an IBM system 9000 microcomputer. The analysis conditions were as follows: T_{eq} of the filament 610°C, temperature rise time 5–5.5 s, total heating time 10 s, inlet temperature 200°C, electron energy 12 eV, (set value), mass range scanned 70–230 amu, and scan speed 1020 amu/s (6.33 scans/s). There was a 1-s delay between the start of the pyrolysis sequence and the start of scanning the mass spectrometer for all the samples. The resulting 38 scans were stored on a disk of an IBM system 9000 computer.

Tandem Mass Spectrometry

The MS/MS experiments were carried out on a system similar to the Extranuclear 5000-1 system which was designed and assembled in our lab. The system is composed of an electron impact ion source and lens assembly mounted on a quadrupole. A 0.5 cm ID $\times$ 2 cm long ferrite collision cell is attached to the end of this first quadrupole. The second quadrupole is attached to the exit of the ferrite collision cell. A continuous dynode electron multiplier was positioned at the exit of the second quadrupole for ion detection.

Small pieces of the insoluble fraction of Biomer (ca. 10 mg) were placed in a glass reaction tube and radiatively heated by the inlet heater. The following conditions were used to analyze the pyrolyzate: EI source energy 14 eV and CID ion energy approximately 40 eV with argon target gas. The argon was metered through a 25 μm i.d.$\times$ 3 mm long fused silica capillary into the collision cell. Overall system pressure was 6–7 $\times$ 10^{-6} torr (9 $\times$ 10^{-4} Pa). The total pumping speed of the system has greater than 1100 L/s using a Balzers

TPH110 turbomolecular pump in the ion source region and a Varian VK12C cryopump below the CID zone. The time-averaged spectra were acquired by an IBM system 9000 microcomputer interfaced to the instrument. The mass range scanned and the total scan times varied, depending on the particular experiment being performed.

RESULTS AND DISCUSSION

The pyrolysis mass spectra of Biomer and Lycra Spandex are shown in Figure 2. These spectra contain peaks which are characteristic of the diisocyanate (MDI), chain extender (ethylenediamine), and the polyol (PTMG). Also present in the spectra of Biomer and Lycra Spandex are peaks which were previously attributed[4] to a quaternary amine antistatic agent (*m/z* 213, 198, 163/165, 148/150, 140, and 114). The pyrolysis mass spectrum of the insoluble portion of Biomer [Fig. 3(a)] also exhibits these peaks. A spectrum of the clean (DMAC insoluble fraction removed) Biomer is shown in Figure 3(b). This spectrum shows a substantially lower intensity of the ions assigned to the antistatic agent (relative to the rest of the spectrum). Similar results were achieved for the Lycra Spandex extractions.

The results of the tandem MS analysis of Biomer are shown in Figure 4. The main MS/MS spectrum shows the fragmentation behavior of *m/z* 213. The presence of *m/z* 127 and 114 indicates that these fragments all have a common source. The fragmentation behavior of the prominent fragments of *m/z* 213 is summarized in Table I.

A common fragment in these spectra (either as a daughter ion or a loss) is 85/86 amu. From previous high resolution MS analysis of Biomer and Lycra Spandex,[4] it is known that the loss of 86 amu from *m/z* 213 is due to the loss

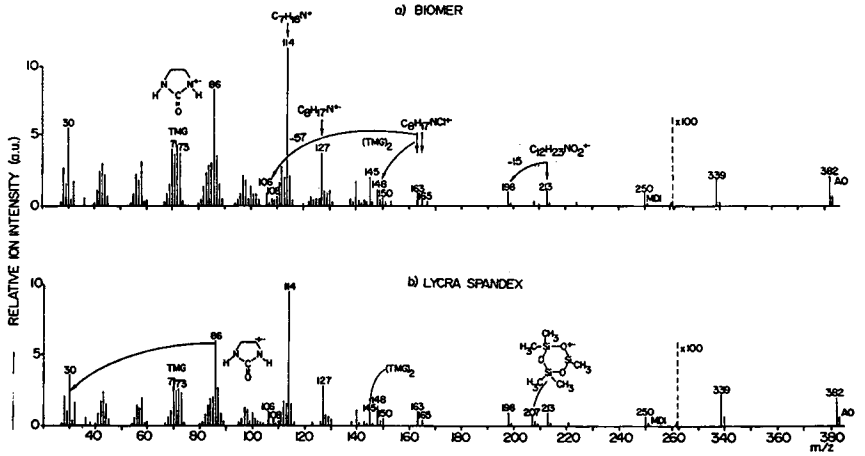

Fig. 2. Py-MS spectra of (A) Biomer (lot BSQXX9) and (B) Lycra Spandex. Note that similarity between the spectra. Peaks characteristic of the diisocyanate (MDI, *m/z* 208, 224, and 250), chain extender (ethylenediamine, *m/z* 30 and 86), polyol (PTMG, *m/z* 71, 73, 143, and 145), antioxidant (4,4′-butylidene-bis(6-*tert*-butyl-*m*-cresol), *m/z* 339 and 382), and the additive of interest (*m/z* 106/108, 114, 127, 140, 148/150, 163/165, 198, and 213) are present in both spectra. Formulae of the additive peaks are from high resolution MS measurements.[4] Lycra Spandex also contains a poly(dimethylsilicone) oil (*m/z* 207).

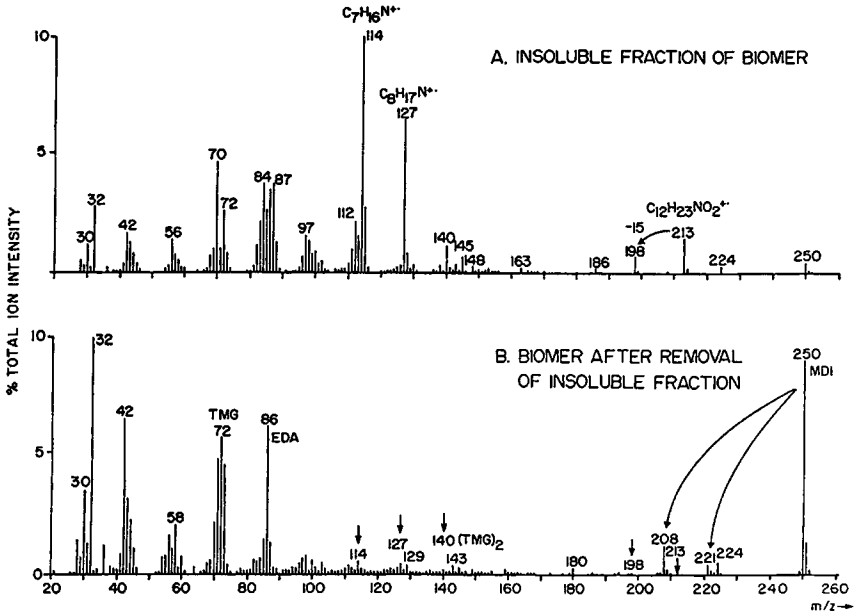

Fig. 3. Py-MS spectra of (A) the insoluble fraction of Biomer and (B) Biomer after removal of the insoluble fraction. The spectrum of the insoluble fraction is dominated by peaks due to the additive (m/z 114, 127, 140, 148/150, 163/165, 198, and 213). Some peaks due to the poly(urethane) components are present at m/z 86, 143, 145, 224, and 250. The spectrum of the clean Biomer shows a marked decrease in the intensity of the additive peaks.

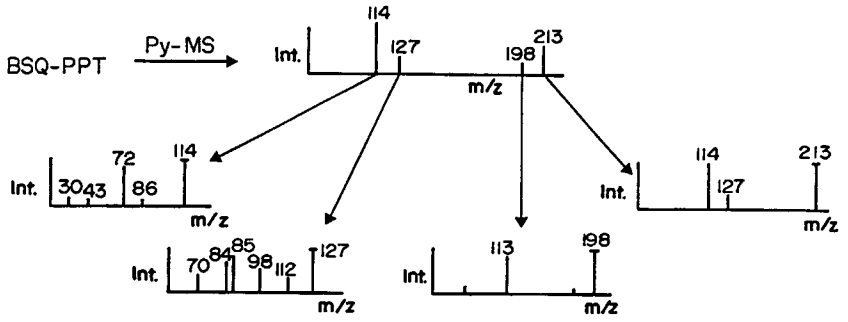

Fig. 4. MS/MS spectra from the analysis of the insoluble fraction of Biomer.

TABLE I
Summary of MS/MS Experiments from Biomer Lot BSQXX9

Py-MS parent ion	MS/MS fragments, listed in order of decreasing intensity.
114 amu	72, 30, 43, 86 amu
127 amu	70, 84, 85, 98, 112 amu
198 amu	113, 70, 156, 180 amu
213 amu	114, 127 amu

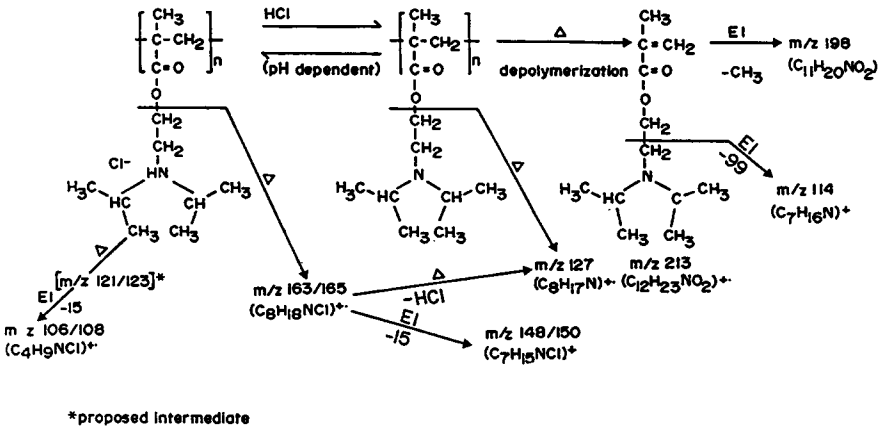

Fig. 5. Proposed fragmentation scheme for the chloride/hypochlorite ion stabilizer found in Biomer and Lycra Spandex. Molecular formulae come from high resolution mass measurements.[4]

of a $C_4H_6O_2$ moiety. Also, there is a loss of 99 amu (213–114) which is likely the loss of 85 or 86 amu and a methyl or methylene group. The combination of these facts suggests that the loss of 85 or 86 amu is due to the loss of a methacrylate group. Also, the loss of 99 amu is suggestive of a methyl methacrylate moiety. Alternatively, the 99 amu loss may be due to sequential loss of a methylene group and the methacrylate group.

The losses of 15 amu (213–198 and 127–112) is likely due to the loss of primary methyl groups. The presence of primary methyl groups is indicative of branching in the aliphatic portion of the additive molecule. This fragmentation information confirms previous high resolution MS measurements. Also, the high resolution MS measurements give the stoichiometry of *m/z* 213 and 198 as $C_{12}H_{23}NO_2$ and $C_{11}H_{20}NO_2$, respectively.[4] Based on both the MS/MS and high resolution MS data the following structure is proposed for *m/z* 213: 2-diisopropyl amino ethyl methacrylate. A fragmentation scheme for this compound and the other additive peaks is proposed in Figure 5.

To confirm this, a model compound which is similar to the proposed structure was analyzed (the methacrylate material was not readily available). The pyrolysis mass spectrum of 2-diisopropyl amino ethyl chloride hydrochloride is seen in Figure 6. This spectrum contains several of the peaks which were attributed to the antistatic agent and its chlorinated derivative in the Biomer and Lycra Spandex spectra. Primary among these peaks is *m/z* 114.

Fig. 6. Pyrolysis mass spectrum of 2-diisopropylaminoethyl chloride hydrochloride. Note the presence of peaks which are also present in the spectrum of the insoluble fraction of Biomer [Fig. 3(B), *m/z* 106/108, 114, 127, 148/150, and 163/165].

In the spectrum of the model compound, it is present as the product of the loss during pyrolysis and ionization of HCl, a chloride moiety and a methylene group. This fragment can also be easily formed from the proposed structure via the loss of the methacrylate group and a methylene group or loss of a methylmethacrylate group. Also present in the spectrum of the model compound are the peaks present in the Lycra Spandex and Biomer spectra which were found to contain chlorine. These peaks at m/z 106/108, 143/145, and 163/165 are formed by the loss of HCl and C_4H_9, HCl and CH_3, and HCl, respectively. This similarity in the mass spectral data suggests that the model compound is structurally similar to a portion of the additive.

The proposed structure of this additive is also supported by the literature. A patent issued to duPont covers the use of polymeric acrylates with amine side groups to give PEUU's resistance to chloride and hypochlorite ion attack and UV degradation.[21] Among the listed materials considered for use is poly(2-diisopropyl amino ethyl methacrylate) (DPA–EMA). For the examples given in the patent, the additives were present at the 5 w % level. The results of the extraction of the insoluble portion from Biomer and Lycra Spandex corresponds well with the patent information. For both the Biomer and Lycra Spandex the insoluble material which was isolated accounted for 7% of the weight of the polymer. The slightly higher percentage found experimentally may be accounted for by incomplete removal of polymer from the isolated additive. The incomplete separation of the additive from the polymer can be seen in the spectrum of the insoluble fraction [Fig. 3(a)], which contains some peaks due to the components of the PEUU (e.g., MDI, EDA, and PTMG).

The total ion current (TIC) curve from the TTR-Py-MS analysis of Biomer lot BSQXX9 is seen in Figure 7(a). This curve has a small shoulder followed by two maxima (labeled A, B, and C, respectively). The chemical processes (pyrolysis and volatilization of components in the polymer) which cause the maxima in the Biomer TIC were deconvolved using factor analysis techniques.[19,20] The TIC from the analysis of the insoluble fraction of Biomer contains an early maximum which is followed by a small shoulder and a large

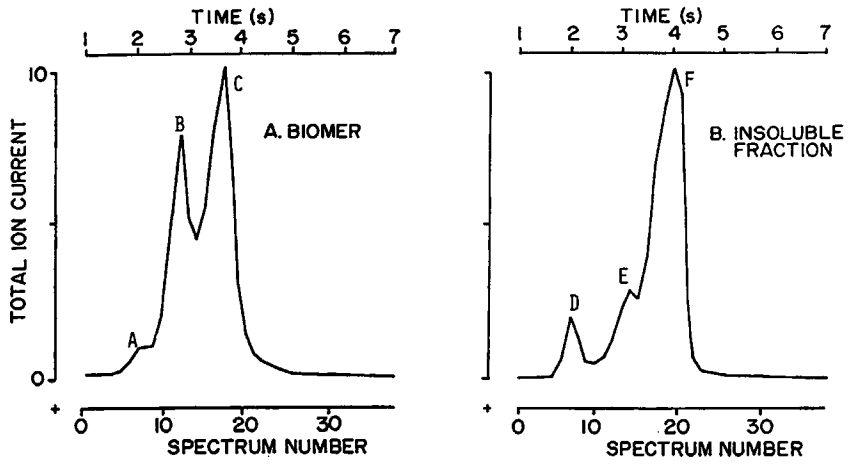

Fig. 7. Total ion current curves from the TTR-Py-MS analysis of (A) Biomer (lot BSQXX9) and (B) the insoluble fraction from Biomer.

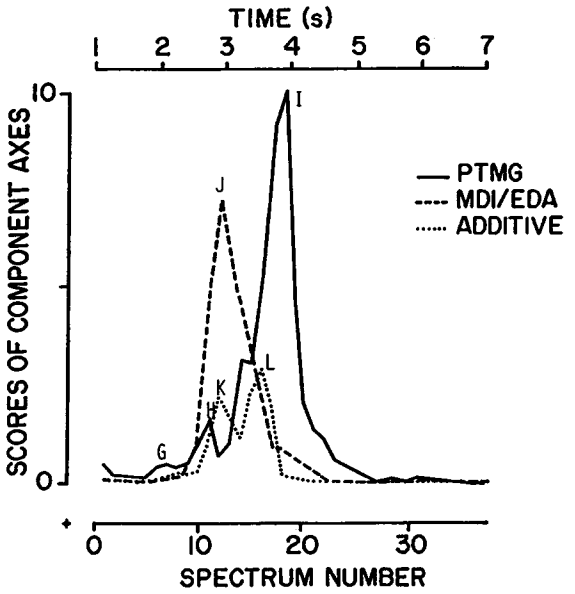

Fig. 8. Deconvoluted curves from the analysis of Biomer. Three components were isolated (i) MDI/EDA, (- - -) (ii) the chloride/hypochlorite ion stabilizer (· · ·), and (iii) PTMG (—).

maximum [see Fig. 7(b), labeled D, E, and F, respectively). The early maximum [peak D, Fig. 7(b)] is due to the volatilization and pyrolysis of a low molecular weight fraction of the insoluble fraction. The peak which follows [peak F, Fig. 7(b)] is due to the primary pyrolysis of the additive.

The TIC from the analysis of Biomer lot BSQXX9 was deconvoluted into the three component curves shown in Figure 8. Examination of the corresponding component spectra shows that these curves represent the volatilization and/or pyrolysis of the hard segment (MDI/EDA), the soft segment (PTMG), and the hindered amine additive. The maximum in the MDI/EDA component curve is closely aligned with the first maximum in the TIC of Biomer [Fig. 7(a)]. This indicates that the first process is the pyrolysis of the MDI/EDA segment in the PEUU. The MDI/EDA component spectrum contains peaks due to the additive and chlorinated additive fragments (m/z 114, 127, 106/108, 148/150, and 163/165). The single ion curves of these components indicate that the additive peaks (m/z 114 and 127) are present due to an overlap in the deconvolution. The chlorinated peaks are, however, produced at the same time/temperature as the MDI/EDA fragments.

Two possible scenarios for the presence of the chlorinated fragments with the MDI/EDA fragments are: (i) The chlorine-containing additive molecules (e.g., quaternary form of the polymeric additive) are formed before pyrolysis and bond (ionic or hydrogen bonds) to the relatively polar sites of the hard segment and are subsequently pyrolyzed when the hard segment pyrolyzes; (ii) chloride ions and additive molecules cluster near the hard segment, and upon pyrolysis chloride ions react with additive which is in the vicinity. The relatively low intensity of the chlorinated ions in the spectrum of the insoluble fraction [Fig. 3(a)] indicates that most of the chlorinated compounds are

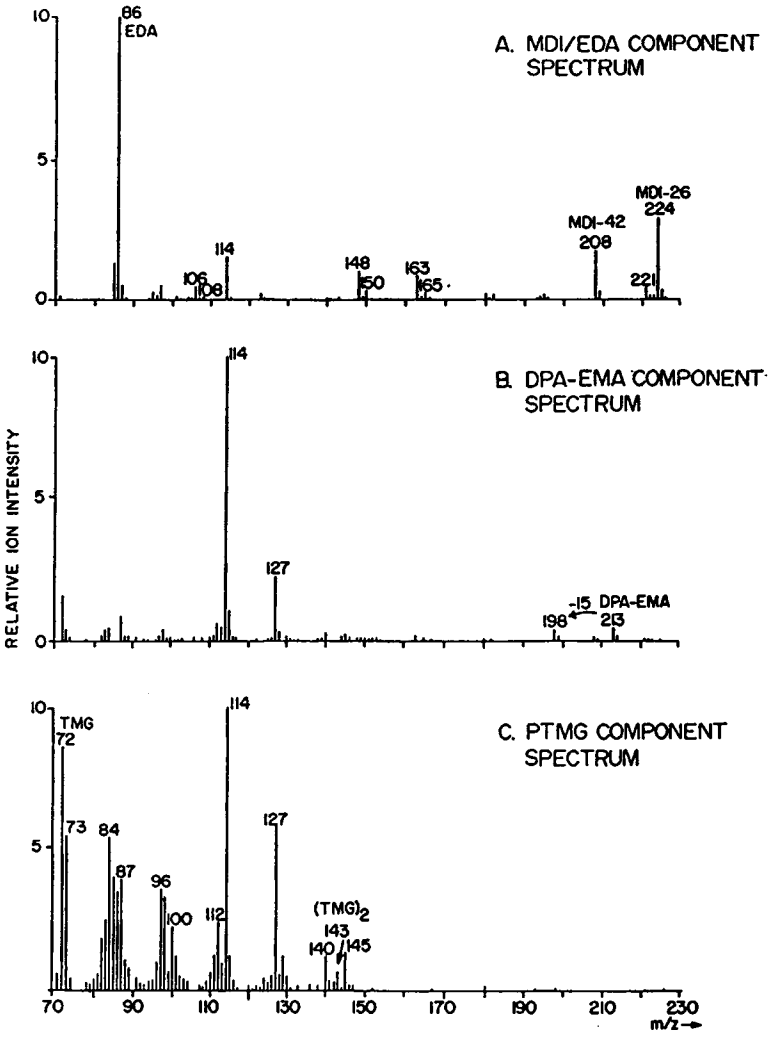

Fig. 9. Mathematically extracted spectra corresponding to the deconvoluted curves in Fig. 8. (A) MDI/EDA component spectrum. Note also the presence of chlorinated peaks from the additive (m/z 106/108, 148/150, and 163/165). (B) chloride/hypochlorite ion stabilizer component. (C) PTMG component spectrum. There is significant overlap with the m/z 114 and 127 peaks from the additive due to difficulty in deconvoluting the PTMG component.

produced during pyrolysis in the presence of the MDI/EDA segments in the polymer.

The mass spectral pattern characteristic of the additive (DPA-EMA) (m/z 114, 127, 198, and 213) is seen in the spectrum corresponding to the second deconvoluted curve [Fig. 9(b)]. Note that this component spectrum does not contain any of the mass peaks attributed to the chlorinated additive. The additive component curve has a small shoulder followed by two maxima (peaks K and L, Fig. 8). The small shoulder in the additive component curve corresponds with the first peak in the TIC of the extracted additive. This is apparently due to a low molecular weight fraction of the additive. The first

maximum of the additive component curve (peak K, Fig. 8) occurs at a substantially earlier time (lower temperature) than the pyrolysis of the additives as indicated by the TIC of the extracted additive [Fig. 7(b)]. Also, this first peak (peak K, Fig. 8) corresponds with the MDI/EDA component curve maximum (peak J, Fig. 8). This overlap suggests that the presence of the chloride ions near the hard segment or the binding of the chlorinated additive to the hard segments decreases the degradation temperature of the additive. It is not clear what is causing a portion of the additive to pyrolyze at a lower temperature. However, experiments involving different heating profiles or varying the pH of the polymer may indicate the mechanism of this pyrolysis reaction.

The second maximum in the additive component curve lies between the maxima of the hard and soft segment component curves (MDI/EDA and PTMG, respectively) but at a lower temperature than the primary pyrolysis of the extracted additive. This indicates that the second pyrolysis process of the additive in the polymer is due to additive molecules which are not associated with either the hard or soft segment of the PEUU. However, the decrease in the pyrolysis temperature relative to the extracted additive shows that the polymer matrix interacts with the additive to reduce its pyrolysis temperature. This behavior indicates that DPA–EMA is present in the polymer in three possible forms: (i) as a low molecular weight residual (small shoulder preceding the first maximum), (ii) associated (or bound to) with the hard segment of the PEUU and chloride ions, and (iii) in an unbound state, with no links to the hard segments in the PEUU.

The spectrum of the final deconvoluted curve contains typical PTMG fragments (m/z 72, 73, 100, 101, 129, 143, and 145). Also present are fragments from the additive at m/z 114 and 127 (due to difficulty in the deconvolution process). This curve also shows a small shoulder preceding two maxima. The shoulder indicates that some low molecular weight oligomers may be present. Examination of SICs of typical PTMG fragment ions (not shown) indicates that this shoulder is composed mainly of monomer fragment ions (m/z 71–74). The first maximum which follows this shoulder, however, is due to overlap in the deconvolution process. Further refinements of the deconvolution using target rotation or "pure mass" methods may eliminate this overlap. The second maximum is due to the pyrolysis and degradation of the PTMG soft segment.

The results of the TTR-Py-MS indicate that a portion of the additive is chemically linked into the structure on the polymer. The products of the primary pyrolysis of the additive can be deconvoluted from the pyrolysis products from the hard and soft segment. However, the component curve for the additive has two maxima, one of which coincides with the maximum of the hard segment. This, and the production of the chlorinated additive fragments simultaneously with the hard segment pyrolysis, suggest that a portion of the additive is bound to the hard segment as a quaternary ammonium chloride salt. This is not conclusive in determining linkage of the chlorinated moieties to the hard segment, it may only indicate where chloride ions are found (in the vicinity of the hard segment) which on pyrolysis react with DPA–EMA to form the chlorinated fragments seen in the mass spectra (m/z 106/108, 148/150, and 163/165).

CONCLUSIONS

The results of this study have identified the additive found in Biomer and Lycra Spandex as poly(2-diisopropyl amino ethyl methacrylate) (DPA–EMA). This additive forms a second phase in the polymer. This second phase is insoluble in *N,N'*-dimethylacetamide and accounts for 7% (by weight) of the total polymer. TTR-Py-MS results indicated that most of the additive is not linked into the polymer matrix, but a portion of the additive and a chlorinated quaternary form of the additive may be linked to the hard segment.

Furthermore, these results show the power of a combined mass spectrometric approach to the analysis of polymers. Separately, none of these techniques provided complete information on the structure or composition of the additive.

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