Determination of the Structure and Composition of Clinically Important Polyurethanes by Mass Spectrometric Techniques

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Synopsis

Curie-point pyrolysis mass spectrometry (Py-MS) and direct probe pyrolysis high resolution mass spectrometry (Py-HRMS) were used to identify the components and additives used in the synthesis and compounding of Biomer, Lycra Spandex, Tecoflex, and Pellethane. Two types of Biomer were identified (P and Q, our notation) which are composed of poly(tetramethylene glycol) (PTMG) capped with 4,4′-methylenebis(phenylisocyanate) (MDI) and chain-extended with ethylenediamine (EDA). Both forms contain 4,4′-butylidene-bis-(6-*t*-butyl-*m*-cresol) antioxidant, and Biomer Q also contains an additive which appears to be a quaternary ammonium chloride salt. Lycra Spandex was found to be identical to Biomer Q, with the exception that a low molecular weight polydimethylsiloxane oil is also present. This silicone oil can be removed by solvent extraction. Tecoflex (type SG80A) is composed of PTMG capped with 4,4′-diisocyanatodicyclohexylmethane and extended with 1,4-butanediol (BD). An industrial grade and a medical grade of Pellethane were analyzed. Both were composed of PTMG capped with MDI and extended with 1,4-butanediol. The industrial grade also contains an antioxidant, possibly butylated diphenylamine.

INTRODUCTION

Since the inception of the artificial heart program at the University of Utah, a major effort has focussed on the materials used in the construction of the artificial heart. Recently, a portion of this effort has been devoted to the determination of the chemical structure of the poly(ether urethane urea) (PEUU) which composes a large part of the artificial heart. The objectives of this effort are twofold: (1) to develop a baseline against which post-implant materials can be compared and (2) to monitor the quality of the PEUU as it is received from the manufacturer. Presently, at the University of Utah, Division of Artificial Organs, two commercial PEUUs are being used to make artificial hearts, Biomer and Pellethane, and two PEUUs, Lycra Spandex and Tecoflex, are being investigated for possible use. This study deals with the preimplant structural analysis of these four PEUUs.

The structural analysis of polymers has traditionally depended mostly on infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy

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(NMR). However, recent work by several groups has shown the efficiency of pyrolysis mass spectrometry (Py-MS) in identifying the components used in the manufacture of PEUUs. Montaudo et al.[1-7] have shown that decomposition products from the pyrolysis of polyurethanes and polyureas can be identified in the mass spectrometer. Furthermore, they have shown that the identity of these products is indicative of the structure of the PEUU pyrolyzed. A number of other workers, including Grassie and Zulfigar[8] and Voorhees et al.,[9-11] have studied the pyrolysis mechanisms of model PEUUs in detail. The initial decomposition is generally of two types: (1) dissociation (depolycondensation) to isocyanate and alcohol (polyol) and (2) concerted dissociation to amine, carbon dioxide, and olefin involving a six-membered ring intermediate. As a result of these processes, one normally expects to see reasonable yields of diisocyanate and chain extenders as volatile pyrolyzates. The polyol starting material decomposes in secondary reactions to yield characteristic low molecular weight fragments which can also be identified by mass spectrometry. Dussel et al.[12] have shown that Pyro-Field ion MS can rapidly identify the polyol, diisocyanate, and aromatic diamine chain extender components in PEUUs. Marshall[13] has demonstrated how direct probe Py-EI-MS can be used to identify commercial PEUU formulations. Richards et al.[14] and Coleman et al.[15] have reported in previous studies of Biomer that Py-MS can reliably identify the polyether, diisocyanate, and aliphatic diamine chain extender components.

Identification of the components used in the manufacture of PEUUs is aided by the availability of model PEUUs and literature data against which the Py-MS data can be compared. The identification of additives or impurities is, however, much more difficult, owing to the lack of reference compounds and literature data. It is possible to partially compensate for this lack of data by making high resolution mass measurements. Precise molecular formulae can be determined from the high resolution mass measurements (ppm accuracy). Often, the molecular formula, in addition to the Py-MS data and a knowledge of PEUU chemistry, is sufficient to identify additives or impurities present in the PEUU samples.

The results of the component analyses of Biomer, Lycra Spandex, Tecoflex, and Pellethane are reported here. For each polymer, the initial analysis was made via Py-MS. High resolution mass measurements were employed to confirm peak assignments and to aid in the identification of additives or impurities.

EXPERIMENTAL

Sample Preparation

Samples of Biomer were taken from artificial heart ventricles before implantation. Samples of Lycra Spandex, Tecoflex, and Pellethane were taken from bulk material as received from the manufacturers. A Lycra Spandex sample was extracted with acetone in a Soxhlet extractor. Milligram amounts of each of these samples (Biomer P, Biomer Q, Lycra Spandex, extracted Lycra Spandex, Tecoflex, Medical grade Pellethane, and Industrial grade Pellethane) were dissolved in *N,N'*-dimethylacetamide (DMAC) to form 0.1% (w/v)

solutions. Dissolution was aided by ultrasonic and vortex mixing. These solutions were stored in sealed glass vials at 4°C until analysis. Five microliters of the solutions (5 μg of sample) were applied to the ferromagnetic pyrolysis filaments (Curie-point temperature 610°C) and dried in a heated, filtered air stream as the filaments were continuously rotated. When the filaments were dry, they were drawn back into borosilicate glass reaction tubes. A detailed description of the sample preparation procedure for Curie-point Py-MS analysis has been presented previously.[16]

Py-MS Analysis

Py-MS analyses were performed with an Extranuclear 5000-1 Curie-point Py-MS system (the University of Utah). The samples were heated to the equilibrium temperature of the filament (610°C) in approximately 5 s, with a total heating time of 10 s and with the inlet at ambient temperature. During this heating process, volatiles were vaporized from the thin film of polymer into the ion source during and prior to the polymer decomposition. The products were ionized by electron impact with an electron energy of 12 eV (set value). The quadrupole mass filter was scanned from 20 to 260 amu or 160 to 400 amu at 1000 amu/s. One hundred scans were stored and summed (signal averaging) on an HP 5933A minicomputer system. Signal averaging thus included signals from both volatile and polymeric components of the total sample in a single spectrum.

Other Py-MS analyses were performed with a Finnigan MAT 311A/Incos 2400 mass spectrometer system (The BFGoodrich Co.). About 1 mg of the dry polymer was placed in a Pyrex pyrolysis tube and flash pyrolyzed at 550°C in the coil probe of a CDS 100 Pyroprobe unit. The pyrolyzates were swept through a heated (250°C) 2-ft transfer line to the jet separator and into the ion source using a helium carrier gas stream. Accurate mass measurements were performed by peak matching at resolution ($M/\Delta M$) of 10,000. For these measurements the temperature of the Pyroprobe was slowly increased by manual adjustments until the ion signal to be measured appeared on the oscilloscope screen with sufficient intensity to be matched against the appropriate perfluorokerosene reference peak. Accurate mass measurements were made with an electron impact ionization energy of either 70 or 50 eV.

RESULTS AND DISCUSSION

The pyrolysis mass spectrum of Biomer lot BSP (Fig. 1) contains several peaks which are characteristic of its polymeric components. The peaks at m/z 250, 224, 221, and 208 are characteristic of 4,4′-methylenebis (phenyl isocyanate) (MDI); the peaks at m/z 143, 145, 71, and 73 are characteristic of poly(tetramethylene glycol) (PTMG) and the peak at m/z 86 is characteristic of the ethylene diamine (EDA) chain extender. High resolution mass measurements (Table I) support these assignments. Also, there is a large peak at m/z 32. This peak is likely due to background (methanol or O_2) since subsequent analyses of the same material have not produced a similarly large peak at m/z 32. The small peak at m/z 149 is from phthalate background contamination.

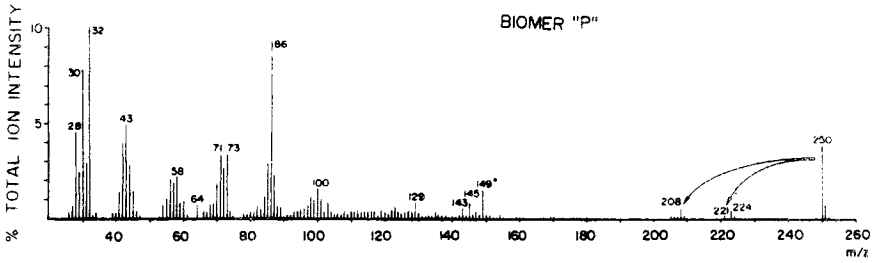


Fig. 1. Average ($n = 3$) pyrolysis mass spectrum of Biomer P. The symbol * indicates a phthalate contaminant. All spectra in Figures 1–6 were obtained on the Extranuclear 5000-1 instrument.

TABLE I
Atomic compositions of pyrolysis products from Biomer and Lycra Spandex

Measured[a] Mass	Atomic Composition	Calculated[b] Mass	Origin of Ion
250.0743	$C_{15}H_{10}N_2O_2$	250.0742	MDI
224.0946	$C_{14}H_{12}N_2O$	224.0950	MDI
208.0762	$C_{14}H_{10}NO$	208.0762	MDI
86.0480	$C_3H_6N_2O$	86.0480	EDA
145.1227	$C_8H_{17}O_2$	145.1228	TMG
143.1073	$C_8H_{15}O_2$	143.1072	TMG
73.0654	C_4H_9O	73.0653	TMG
71.0497	C_4H_7O	71.0497	TMG
382.2859	$C_{26}H_{38}O_2$	382.2872	AO
339.2319	$C_{23}H_{31}O_2$	339.2324	AO
213.1729	$C_{12}H_{23}NO_2$	213.1729	Amine
198.1494	$C_{11}H_{20}NO_2$	198.1494	Amine
165[c]	$(C_8H_{18}N^{37}Cl)$	—	Amine
163[c]	$(C_8H_{18}N^{35}Cl)$	—	Amine
150[c]	$(C_7H_{15}N^{37}Cl)$	—	Amine
148[c]	$(C_7H_{15}N^{35}Cl)$	—	Amine
127.1361	$C_8H_{17}N$	127.1361	Amine
114.1283	$C_7H_{16}N$	114.1283	Amine
108[c]	$(C_4H_9N^{37}Cl)$	—	Amine
106[c]	$(C_4H_9N^{35}Cl)$	—	Amine

[a] Measured by peak matching in electron impact mode (70 or 50 eV) at a resolution $M/\Delta M$ approx. 10000.

[b] Based on the given atomic composition.

[c] Nominal mass only; signal too weak and transient for accurate measurement at high resolution.

The pyrolysis mass spectrum of Biomer lot BSQ (Fig. 2) shows many similarities with the previous Biomer lot BSP spectrum (Fig. 1). Figure 2 contains the peaks which are characteristic of MDI, PTMG, EDA, and a phenolic antioxidant, 4,4′-butylidene-bis-(6-*t*-butyl-*m*-cresol) (not shown in Fig. 1). This antioxidant is practically nontoxic.[17] However, several peaks are present which are not present in the spectrum of Biomer lot BSP. These include m/z 213, 198, 140, 127, 114, 163, 165, 148, 150, 106, and 108 (Table I).

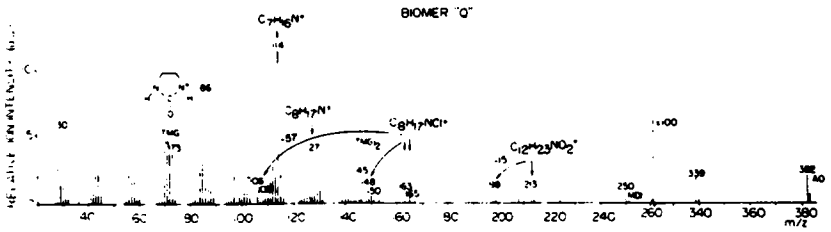


Fig. 2. Typical pyrolysis mass spectrum of Biomer Q. Compare with the pyrolysis mass spectrum of Biomer P (Fig. 1).

When these spectral differences were first encountered, several possibilities were considered, including contamination, manufacturing changes, polymer degradation during storage, and batch variations.[15] After reviewing our library of spectra and further analysis, it was found that this mass spectral difference is due to lot-to-lot variations. In subsequent discussion we will call lot BSP "Biomer P" and lot BSQ "Biomer Q." Our analyses have shown that Biomer lots BSL, BSM, BSR, and BSS are similar to Biomer Q. Thus far, BSP is the only lot that has been found which lacks the additional peaks (*m/z* 213, 198, 140, etc.).

Initial speculation on the nature of these peaks centered on possible chain extenders other than EDA which may be present. This was supported in part by previous work by our group,[14] which indicated that *m/z* 114 is characteristic of a 1,4-butanediamine chain extender. High resolution mass measurements of Biomer Q (Table I) show that *m/z* 114 has an atomic composition of $C_7H_{16}N$. If *m/z* 114 were due to a butane diamine chain extender, one would expect that it would be analogous in composition to *m/z* 86 ($C_3H_6N_2O$), which is due to the EDA chain extender.[14] Since this is not the case, it is clear that *m/z* 114 is not due to a butanediamine chain extender.

As was found for *m/z* 114, the remaining unknown peaks do not fit into any known or predicted Py-MS patterns for different possible chain extenders. However, the accurate mass measurements (Table I) indicate that several of the peaks have atomic compositions which are related to one another by common pyrolytic and electron impact fragmentations. Also, the presence of chlorine is indicated by the arrangement and the ratio of intensities of the peaks at *m/z* 165/163, 150/148, and 108/106. The ions at *m/z* 114, 127, 198, and 213 are at least partially derived from residuals in the Biomer, since these ions appeared as volatiles in the high resolution experiments at approx. 150°C. (This temperature is lower than that necessary for the onset of pyrolysis.) Also the material responsible for these ions can be extracted from the polymer with acetone and detected by either EI or FAB-MS. The suspected chlorine-containing ions (*m/z* 106/108, 148/150, 163/165) only appeared in the higher temperature pyrolyzate. However, it was not possible to determine atomic compositions for these ions, since the signals were too weak and transient to measure masses accurately at high resolution. Our evidence suggests that all of these nitrogen-containing ions may be due to a quaternary ammonium chloride salt that is present as a residual in the polymer. Quaternary amine antistatic agents or tertiary amine catalysts may be the source(s) of these spectral features.

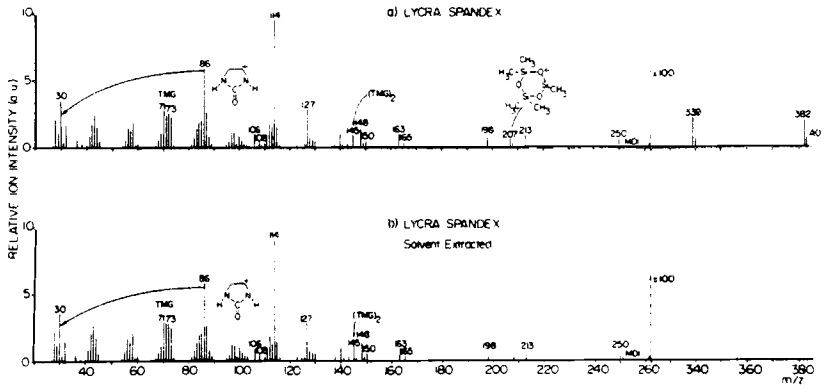


Fig. 3. Typical pyrolysis mass spectra of (a) Lycra Spandex and (b) Lycra Spandex after solvent extraction. Note the absence of the silicone and antioxidant peaks in part (b).

The slow heating rate of the Py-HRMS measurements gave substantial information about the time/temperature behavior of the components in Biomer. However, this information is beyond the scope of the paper and will be presented elsewhere.

In Figure 3, pyrolysis mass spectra of Lycra Spandex and solvent extracted Lycra Spandex are shown. Both spectra contain the characteristic MDI, PTMG, and EDA peaks. The peaks which are related to the chloride salt are also present. The spectrum of Lycra Spandex [Fig. 3(a)] has a peak at m/z 207 which is characteristic of polydimethylsiloxane and also peaks at m/z 339 and 382 for the antioxidant. Upon solvent extraction of Lycra Spandex, this silicone oil and antioxidant are removed, as demonstrated by the absence of the characteristic ions in Figure 3(b).

The pyrolysis mass spectra of "Medical grade" and "Industrial grade" Pellethane [Figs. 4(a) and 4(b), respectively] contain peaks characteristic of MDI and PTMG building blocks. There are no peaks which are characteristic of an EDA or similar diamine chain extender. However, it is possible that

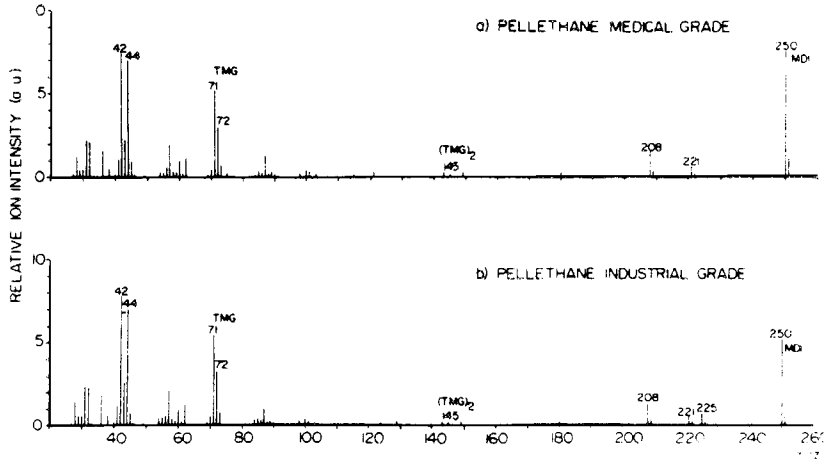


Fig. 4. Typical pyrolysis mass spectra of (a) medical grade Pellethane, and (b) industrial grade Pellethane.

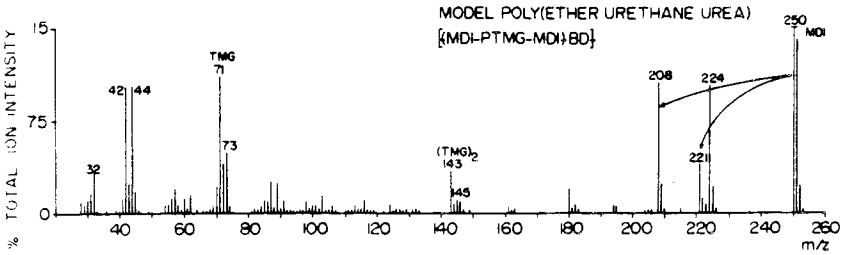


Fig. 5. Averaged (n = 3) pyrolysis mass spectrum of a model polyurethane composed of PTMG (MW = 600) capped with MDI and extended with BD. Analysis conditions are the same as for all other samples in this report, except the inlet temperature was 200°C. The higher inlet temperature results in relatively higher intensity of the MDI related ions.

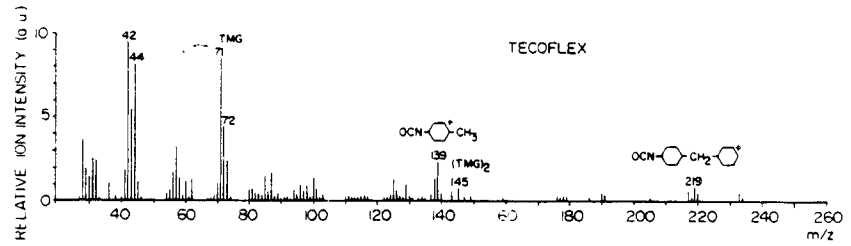


Fig. 6. Typical pyrolysis mass spectrum of Tecoflex.

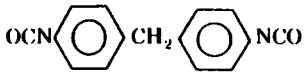
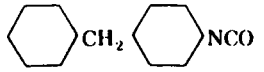
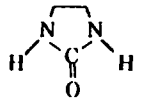
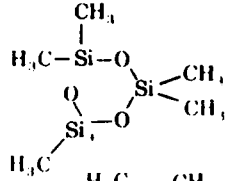
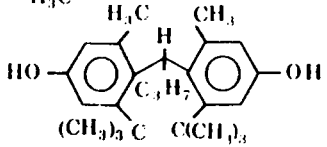
butanediol (BD) was used as a chain extender. The presence of a butanediol chain extender would be difficult to detect qualitatively since its key peaks (m/z 42/44, 71/72/73) would be obscured by the characteristic PTMG peaks. However, comparison of the spectra in Figure 4 with the spectrum of a model polyurethane analyzed in a previous study[18] (Fig. 5) aids in the identification of the chain extender used in Pellethane. The model polyurethane was made by capping PTMG (MW = 600) with MDI and extending this prepolymer with BD. The high degree of similarity between the spectra in Figures 4 and 5 (especially the correspondence of the peaks at m/z 42/44 and m/z 71/72/73) strongly suggests that BD is the chain extender used in the production of Pellethane. The spectrum of the industrial grade Pellethane [Fig. 4(b)] has a peak at m/z 225 which is probably due to butyldiphenyl amine, an antioxidant.

The pyrolysis mass spectrum of Tecoflex (Fig. 6) contains peaks which are characteristic of PTMG building blocks. The peaks in the higher mass range, m/z 219 and 139, are characteristic[4] of 4,4'-diisocyanotodicyclohexylmethane (Hylene W or HW). As was seen in the Pellethane spectra, there are no peaks which indicate the presence of a diamine chain extender. However, the spectral pattern at m/z 42/44 and m/z 71/73 is similar to the pattern found in the Pellethane spectra and the model polyurethane spectrum (Figs. 4 and 5). This strongly suggests that BD is used as a chain extender in Tecoflex.

CONCLUSIONS

The combination of Curie-point pyrolysis mass spectrometry with high resolution mass spectrometry has identified the components used in the syntheses of Biomer, Lycra Spandex, Pellethane, and Tecoflex. A summary of

TABLE II
Proposed structures of major pyrolysis products from Biomer, Lycra Spandex, Pellethane, and Tecoflex

m/z	Structure	Source (proposed)	Samples which Contain this Ion	Reference
250		MDI	All except Tecoflex	12
219		HW	Tecoflex	12
139		HW	Tecoflex	12
71/73	C_4H_7O/C_4H_9O	PTMG	All	14
143/145	$C_8H_{15}O_2/C_8H_{17}O_2$	PTMG	All	14
86		EDA	Biomer, Lycra Spandex	14
42/44	C_2H_2O/C_2H_4O	BD	Pellethane/Tecoflex	—
207		poly(dimethylsiloxane)	Lycra Spandex	16
382		Antioxidant	Biomer, Lycra Spandex	—
225		Antioxidant	Pellethane	—

the spectra structure correlations is shown in Table II. Also, the antioxidant found in Biomer and Lycra Spandex has been identified. The antioxidant is essentially nontoxic. An antioxidant in Pellethane and an antistatic agent or residual catalyst in Biomer and Lycra Spandex were tentatively identified.

This study demonstrates the utility of Curie-point Py-MS and Py-HRMS as tools for quality control. Knowing the identity of the components, additives, and impurities in implant materials will enable users of these materials to make more intelligent decisions about their use. While this work is not intended to serve as a selection method for implant materials, it demonstrates the ability of Py-MS in combination with HRMS to detect components and additives in PEUUs and shows that these techniques can be valuable tools for the quality control of implant materials. Furthermore, the results presented indicate the need for the establishment of standardized test methods for implant materials. Both Py-MS and Py-HRMS are excellent candidates for inclusion in such testing protocol.

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