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Structural Analysis of Biomer by Pyrolysis Mass Spectrometry and Thermogravimetry

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ABSTRACT: Curie-point pyrolysis mass spectrometry (Py-MS) was used to identify the polymeric components of the poly(ether urethane urea) Biomer, which is widely used in the construction of artificial heart chambers. A comparative study between Biomer and model polymers showed Biomer to be composed of poly(tetramethylene glycol) (PTMG) capped with 4,4′-methylenebis(phenyl isocyanate) (MDI) and chain-extended with ethylenediamine (EDA). As determined from thermogravimetry (TG) and ^{1}H NMR data the PTMG molecular weight appears to be approximately 1000 and the PTMG:MDI molar ratio 2:3. An overall pyrolysis mechanism is proposed which postulates initial scission of urea links followed by cleavage of the urethane bonds and subsequent decomposition of the polyether chains.

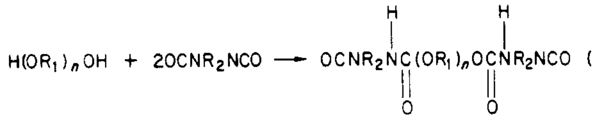
Introduction

Biomer, a segmented poly(ether urethane), is used extensively in the Utah artificial heart.[1] In view of the continuing clinical trials of the artificial heart, the need to elucidate the composition and structure of Biomer is paramount. Knowing the composition and structure will facilitate the analysis of preimplant and postimplant materials and make interpretation of the results more meaningful.

Segmented poly(ether urethanes) are composed of low molecular weight polyethers, diisocyanates, and chain extenders and are synthesized by the following generalized sequence:[2]

a. prepolymerization

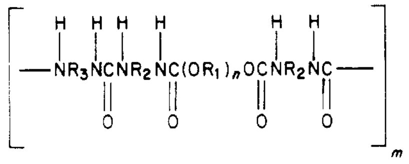
polyether + diisocyanate ⟶ poly(ether urethane)



$$\mathrm{H(OR_1)_{\mathit{n}}OH + 2OCNR_2NCO \longrightarrow OCNR_2\overset{H}{N}\underset{O}{C}(OR_1)_{\mathit{n}}O\underset{O}{C}\overset{H}{N}R_2NCO} \qquad (1)$$

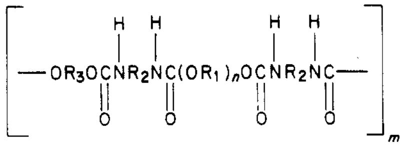
b. chain extension

(i) poly(ether urethane) + diamine ⟶
urea-linked poly(ether urethane)



$$\left[\mathrm{-\overset{H}{N}R_3\overset{H}{N}\underset{O}{C}\overset{H}{N}R_2\overset{H}{N}\underset{O}{C}(OR_1)_{\mathit{n}}O\underset{O}{C}\overset{H}{N}R_2\overset{H}{N}\underset{O}{C}-}\right]_m \qquad (2)$$

(ii) poly(ether urethane) + diol ⟶
urethane-linked poly(ether urethane)



$$\left[\mathrm{-OR_3O\underset{O}{C}\overset{H}{N}R_2\overset{H}{N}\underset{O}{C}(OR_1)_{\mathit{n}}O\underset{O}{C}\overset{H}{N}R_2\overset{H}{N}\underset{O}{C}-}\right]_m \qquad (3)$$

In the production of commercial, segmented poly(ether urethane) (PEUU) both aliphatic (or alicyclic) and aromatic diisocyanates and diamines are used. In general, however, only aliphatic polyethers are used.[2]

Identification of the components used in the synthesis of PEUU's has been attempted by a number of different chromatographic and/or spectroscopic techniques. Traditionally, infrared spectroscopy (IR) has been widely used for polymer characterization. However, the use of IR in analyzing PEUU's is limited by the known difficulty of obtaining information relating to the diisocyanate and diamine constituents.[3] To obtain more complete information, destructive techniques such as hydrolysis followed by analysis of the resultant amines and alcohols[4] and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS)[5] have been employed. These techniques have proven to be capable of providing detailed information but are also time-consuming. Py-GC/MS analysis often requires the use of several different columns, with each analysis taking up to 100 min. Moreover, highly polar, low-volatile pyrolyzates tend to be lost by adsorption on the column.

More recently, pyrolysis mass spectrometry (Py-MS) has been introduced for the analysis of PEUU's. Work reported by Montaudo et al.,[6-9] Dussel et al.,[3] Richards et al.,[10] and Coleman et al.[11] has shown that Py-MS is a fast reliable method for structural analysis of PEUU's. Dussel et al.[3] have shown the ability of pyrolysis field ionization mass spectrometry (Py-FIMS) to identify the polyether, diisocyanate, and aromatic diamine constituents used in the synthesis of PEUU's. However, they reported difficulty in identifying aliphatic diamine chain extenders. Montaudo et al.[6,8] have used Py-MS to detect primary thermal degradation products from polyurethanes and polyureas. Their results indicate that N-monosubstituted polyurethanes and polyureas undergo depolycondensation upon pyrolysis. Montaudo et al.[7,9] have also shown that cyclic and open-chain oligomers produced during pyrolysis of polyurethanes and cyclic oligomers produced during polyurethane synthesis (as reaction by-products) are detectable with Py-MS. Preliminary work done in our laboratory[10,11] used Curie-point Py-MS to analyze Biomer and related model polymers. This resulted in the identification of the diisocyanate, diamine, and polyether constituents.

In spite of the demonstrated ability of Py-MS to identify components in PEUU's, earlier reports show disagreement over the composition of Biomer. Hercules et al.[12] analyzed Biomer using laser pyrolysis/photolysis mass spectrometry. These authors identified the components of Biomer as PTMG capped with 2,4-toluene diisocyanate (TDI) and extended with EDA. Previous work by our group[10] differs in the identity of the diisocyanate, which we found to be MDI.

The composition of PEUU's may be further characterized by thermogravimetry (TG). TG is well suited for characterizing chemical reactions in which one or more of the products are gaseous.[13] Moreover, TG is particularly valuable for quantitating the amount of material involved in the various thermal decomposition reactions. TG of polyurethane foams in an inert atmosphere (pyrolysis) shows a bimodal weight loss in which the first weight loss

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is due to cleavage and decomposition of the urethane links and the second weight loss is due to the thermal decomposition of the polyether segments.[5,14] The similarities in chemical structure between polyurethanes and PEUU's are such that the thermal decomposition may be expected to follow the same scheme. By recording the weight of the PEUU as it is pyrolyzed (in the TG apparatus), one can calculate a polyether to diisocyanate/chain extender ratio.

Experimental Section

Model Polymers. Four model polyethers were used in this study: poly(ethylene glycol) (PEG), MW = 1000; poly(propylene glycol) (PPG), MW = 4000 (Waters Inc.); and two poly(tetramethylene glycols) (PTMG), MW = 970 and 2100 (Teracol, E. I. du Pont de Nemours and Co.).

Model PEUU's were synthesized by following the generalized sequence discussed in the Introduction. Various chain extenders and molecular weight polyethers were used in the syntheses. Two model PEUU's were made by chain extending an MDI capped PTMG 2100 prepolymer with 1,4-butanediol (BD) and 1,2-ethylenediamine (EDA). A third and fourth model were made by extending an MDI capped PTMG 1800 prepolymer with 1,4-butanediamine and an MDI capped PTMG 970 prepolymer with EDA, respectively. In all of the model PEUU's the MDI:PTMG molar ratio was 2:1. The model PEUU's were purified by dissolution in *N*,*N*′-dimethylacetamide (DMAC) and subsequent precipitation in methanol. The precipitates were vacuum-dried.

Sample Preparation. Py-MS Samples. Samples of Biomer were taken from artificial heart ventricles both before and after implantation. Samples of the model polymers were taken from the purified PEUU's and from the polyethers as received from the manufacturer. Milligram amounts of the Biomer and model PEUU's were dissolved in DMAC to form 0.2% (w/v) solutions. Milligram amounts of the polyethers were dissolved in methanol to form 0.2% solutions. To aid in the dissolution of Biomer and the model PEUU's, vortex and ultrasonic mixing were used. All of the solutions were stored in sealed glass vials at 4 °C. Prior to analysis, the samples were exposed to room temperature for 1 h. Five-microliter aliquots of the solutions (10 μg of sample, dry weight) were applied to the ferromagnetic pyrolysis filaments (Curie-point temperature 610 °C) and dried in a heated, filtered air stream under continuous rotation of the filaments. The sample preparation procedure for Curie-point Py-MS analysis has been described in detail in previous publications.[15]

Mass Spectrometer Conditions. Py-MS analyses were performed by using an Extranuclear 5000-1 Curie-point Py-MS system as shown in Figure 1. Samples were heated to the equilibrium temperature of the filament (610 °C) with a temperature rise time of about 5 s and a total heating time of 10 s. The pyrolysis products were ionized by electron ionization at 12-eV electron energy (set value). The quadrupole mass filter was scanned over the range 20–260 amu at a rate of 1000 amu/s. This mass range was repetitively scanned 100 times, and the 100 scans were stored and summed (signal averaging) by a minicomputer system (HP5933A data system). Each sample was analyzed in triplicate.

TG Analysis. Samples for TG analysis were taken from artificial heart ventricles, from selected purified PEUU's and from selected polyethers. Samples were analyzed with a Mettler Thermoanalyzer I system. A 10 ± 0.5 mg sample size was used with helium or nitrogen carrier gas at a flow rate of 100 ± 5 mL/min. Samples were temperature programed from room temperature to 800 °C at 25 °C/min.

Results and Discussion

Figure 2 shows an average pyrolysis mass spectrum of Biomer. The identity of the diisocyanate component is easily deduced. The peaks at *m/z* 250 (M^+), 224 ($M^+ - 26$), and 208 ($M^+ - 42$) are characteristic[3,6,8] of 4,4′-methylenebis(phenyl isocyanate) (MDI).

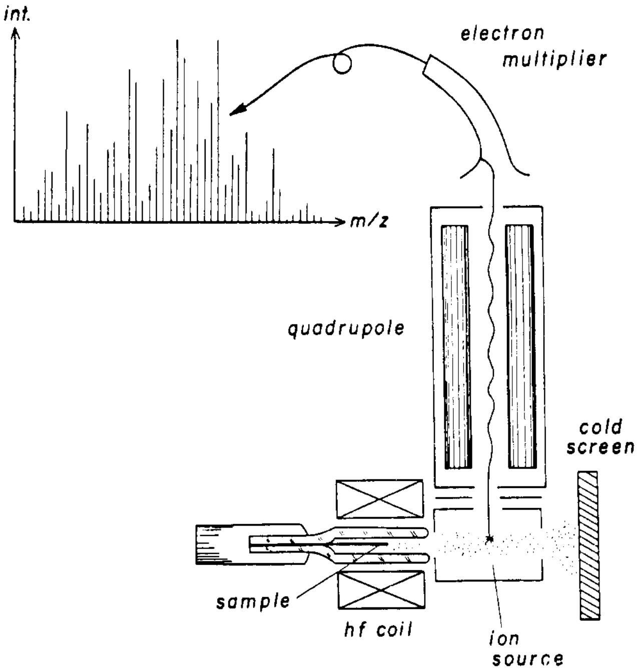


Figure 1. Extranuclear 5000-1 Curie-point Py-MS system. The quadrupole is scanned repetitively, and the consecutive scans are summed by a minicomputer. Analysis conditions: Curie-point temperature, 610 °C; temperature rise time, 5 s; total heating time, 10 s; inlet temperature, 200 °C; electron energy, 12 eV; scanning speed, 1000 amu/s; total scan time, 25 s; number of spectra summed, 100.

The identity of the polyether component is revealed by comparing the Biomer spectrum with the pyrolysis mass spectra of model polyethers. Parts A, B, and C of Figure 3 show the spectra of PEG 1000, PPG 4000, and PTMG 2100, respectively. Several significant peaks are present in each polyether spectrum. Major peaks are seen at *m/z* 89 ($C_4H_9O_2^+$), 73 ($C_4H_9O^+$), 60 ($C_2H_4O_2^+$), and 44 ($C_2H_4O^+$) in the PEG spectrum (Figure 3A). In the PPG spectrum (Figure 3B) major peaks are seen at *m/z* 117 ($C_6H_{13}O_2^+$), 58 ($C_3H_6O^+$), and 42 ($C_3H_6^+$). The PTMG spectrum (Figure 3C) contains key peaks at *m/z* 145 ($C_8H_{17}O_2^+$), 143 ($C_8H_{15}O_2^+$), 129 ($C_8H_{17}O^+$), 73 ($C_4H_9O^+$), and 71 ($C_4H_7O^+$). Comparison of these spectra (Figure 3A–C) with the Biomer spectrum (Figure 2) shows that the greatest degree of similarity exists between the PTMG and Biomer spectra. In the Biomer spectrum the characteristic PTMG peaks at *m/z* 145, 143, 129, 73, and 71 are all present in the proper ratios. This indicates that PTMG is the polyether component used in the synthesis of Biomer.

Comparison of the Biomer spectrum with the pyrolysis mass spectra of model PEUU's enables identification of the chain extender. Parts A, B, and C of Figure 4 show average pyrolysis mass spectra of model PEUU's chain-extended with ethylenediamine (EDA), 1,4-butanediamine (BDA), and 1,4-butanediol (BD), respectively. Each model PEUU was made from an MDI-capped PTMG prepolymer, and the characteristic MDI and PTMG peaks are present in each spectrum. Since these model polymers are derived from the same prepolymer, the differences between spectra are due only to the different chain extenders used. In the spectrum of the EDA-extended PEUU (Figure 4A) there is a large peak at *m/z* 86 which is absent from the spectra of the other two model PEUU's (Figure 4B,C). Likewise, the spectrum of the BDA-extended PEUU (Figure 4B) has a large peak at 114 which is not seen in the spectra of the EDA- or BD-extended PEUU's (Figure 4A,C). Apparently *m/z* 86 is due to the presence of the EDA chain extender, and *m/z* 114 is due to the presence of the BDA chain extender. The peak at *m/z* 30 is present in the spectra of both diamine-extended PEUU's, and it is smaller in the spectrum of the BD-extended PEUU.

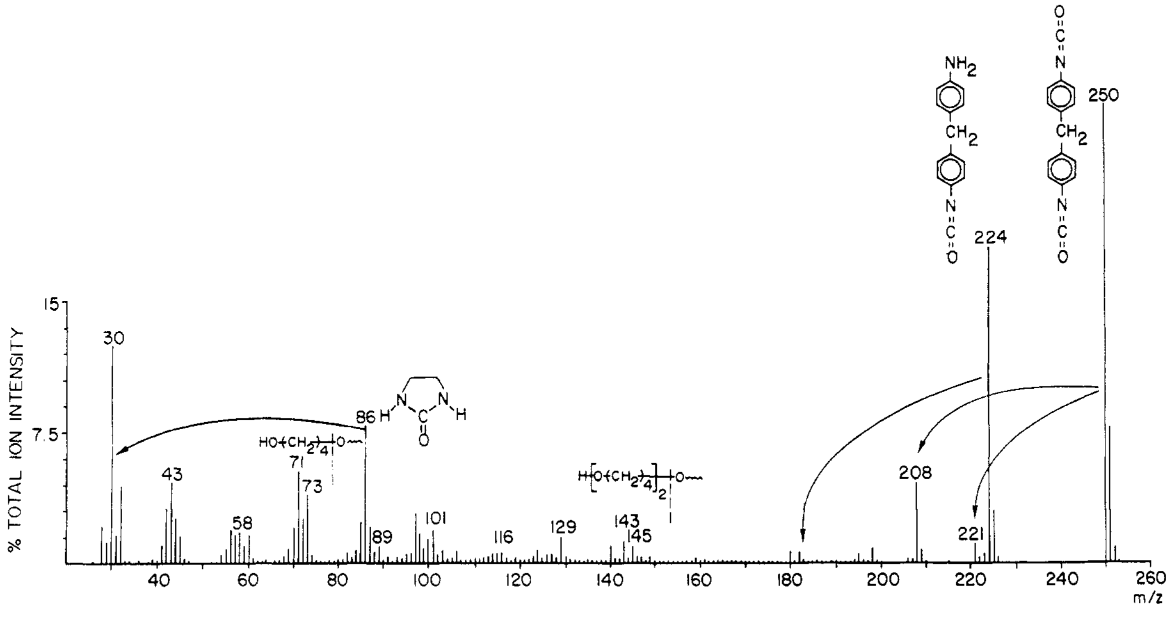


Figure 2. Average (n = 3) pyrolysis mass spectrum of Biomer.

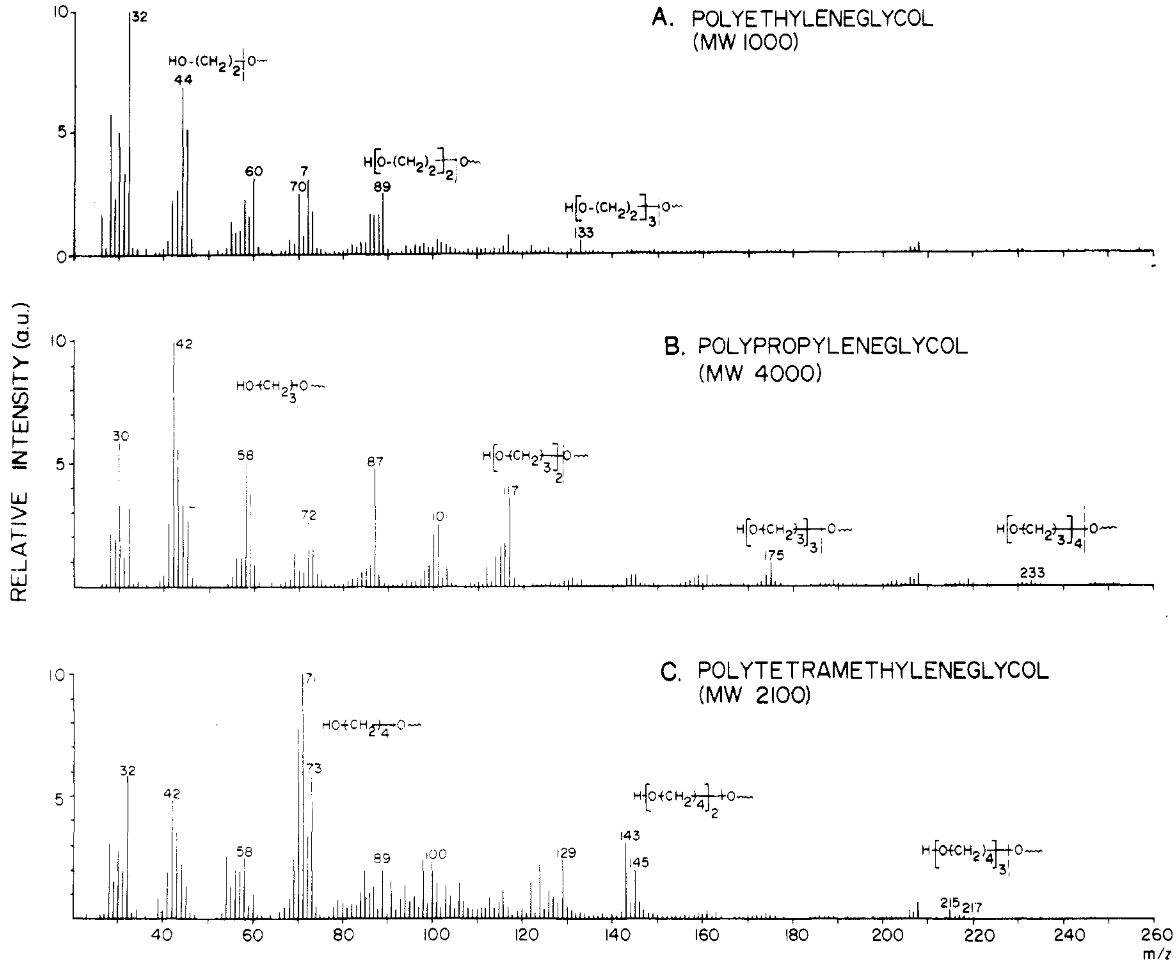
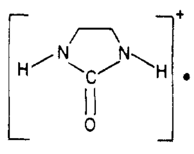
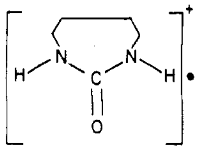


Figure 3. Typical pyrolysis mass spectra of (A) poly(ethylene glycol) 1000 (Waters), (B) poly(propylene glycol) 4000 (Waters), and (C) poly(tetramethylene glycol) 2100 (E. I. du Pont de Nemours). Note the similarities between Figures 3C and 2.

This suggests that m/z 30 is also associated with the diamines. Collision-induced dissociation MS of the m/z 86 ion using a tandem quadrupole MS system (MS/MS) has confirmed that m/z 30 is a fragment of m/z 86 and implies that m/z 114 and 86 may have analogous structures. The MS/MS analysis, which will be described elsewhere,[16] has tentatively identified m/z 86 as 2-imidazolidone (ethyleneurea). On the basis of these data, the structure of m/z 86 and the proposed structures of m/z 114 and 30 are



m/z 86



m/z 114

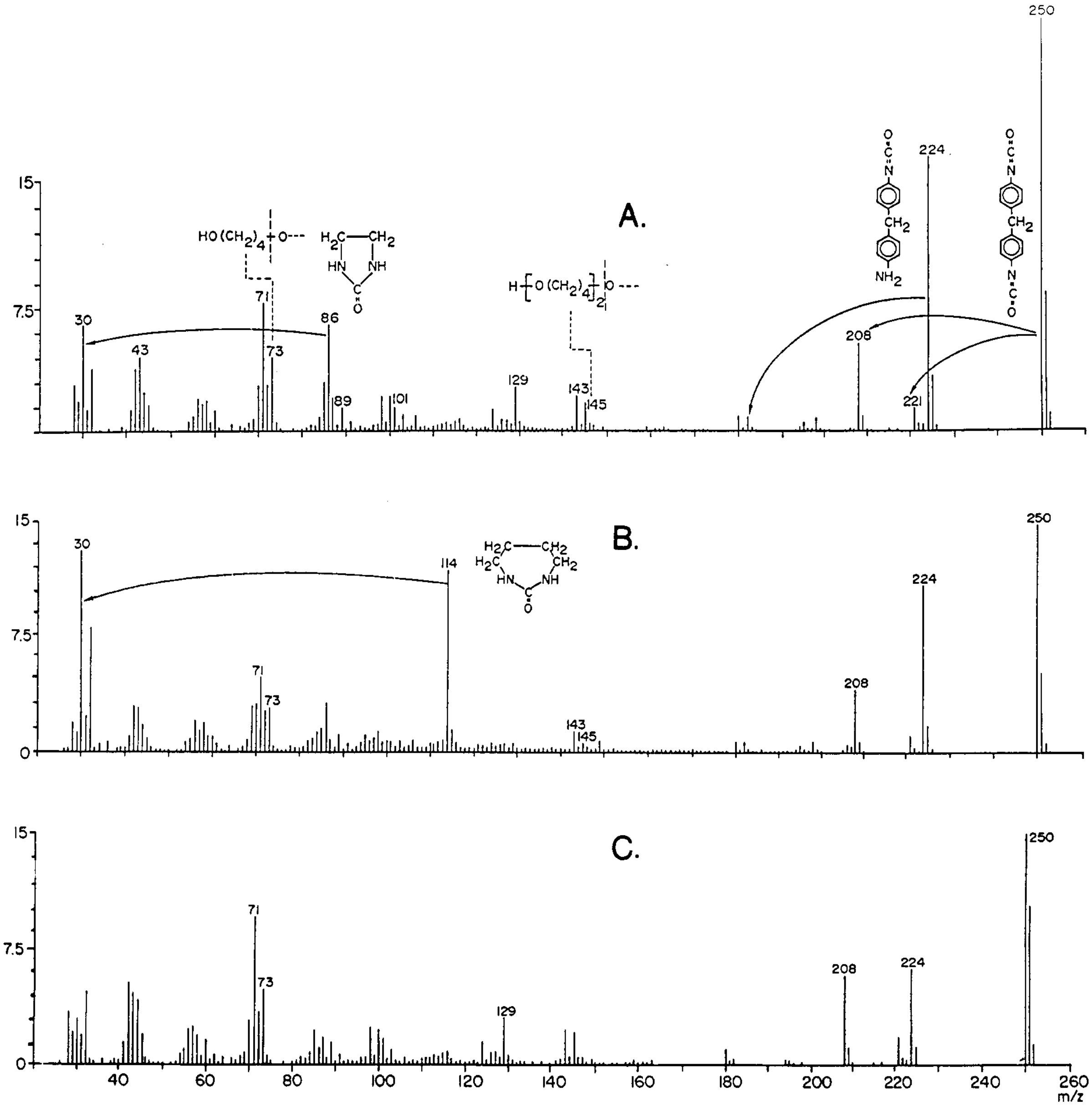


Figure 4. Average ($n = 3$) pyrolysis mass spectra of three model PEUU's. Each is made of PTMG capped with MDI and extended with (A) ethylenediamine, (B) butylenediamine, and (C) butanediol. Parts A and B each contain a peak characteristic of their respective extenders (m/z 86 and 114, respectively). Note the similarities between part A of this figure and the mass spectrum of Biomer (Figure 2).

The spectrum of the BD-extended PEUU (Figure 4C) contains no similarly identifiable peaks which are due to the chain extender. This is apparently due to the characteristic BD peaks being obscured by direct overlap with PTMG-derived peaks.

The Biomer spectrum (Figure 2) shows strong peaks at m/z 86 and 30 which are indicative of the presence of the EDA chain extender. In general, the Biomer spectrum and the spectrum of the EDA-extended model PEUU are strikingly similar. Thus the bulk composition of Biomer is assigned as PTMG capped with MDI and chain extended primarily with EDA. The use of other chain extenders, whose characteristic peaks may be obscured by overlap with PTMG- or MDI-derived peaks (e.g., BD or hydrazine) in combination with EDA is not excluded by the mass spectral data. However, the evidence is strong that EDA is the only extender used.

A typical Biomer thermogram is shown in Figure 5. By comparing the thermogram of Biomer with the thermograms of various polyethers and with the thermograms of model PEUU's with different weight percentages of polyether, it was shown that the first weight loss (300–400 °C) is due to cleavage and degradation of the urethane and

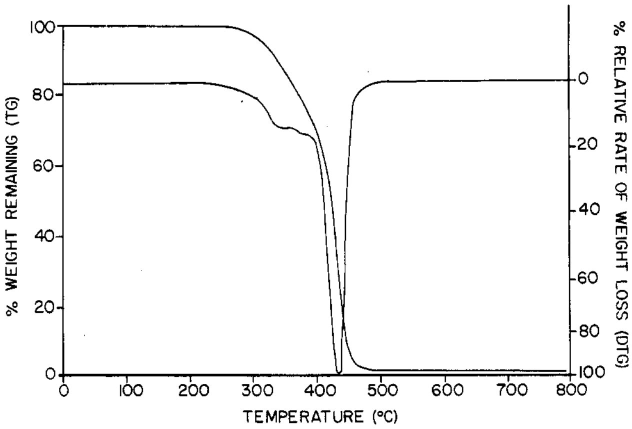


Figure 5. Typical thermogram of Biomer. Two weight losses occur, at 300–400 and 400–450 °C, which are attributed to the decomposition of the urethane/urea segments and the decomposition of the polyether segment, respectively.

urea linkages. From this, it is also shown that the second weight loss (400–450 °C) is due to degradation of the polyether segment. By assuming that the weight loss due to polyether degradation is complete and symmetrical about the point of the maximum rate of weight loss, the amount of polyether present can be determined. This method gave a polyether weight percent of 72 ± 2% for Biomer. When this method was used on PEUU's of known polyether content, the calculated value was within experimental error for a PEUU composed of PTMG 2100, MDI (MDI:PTMG molar ratio = 2:1), and EDA. For a PEUU made with PTMG 970, MDI (MDI:PTMG molar ratio = 2:1), and EDA, the calculated polyether content was about 20% low. ^{1}H NMR data[17] indicate that the PTMG component is 70% by weight of Biomer. This is in good agreement with the value calculated from TG data (see Table I). ^{1}H NMR data also give the PTMG molecular weight as approximately 1000.[17] These Py-MS, TG, and ^{1}H NMR data thus give an approximate PTMG:MDI molar ratio of 2:3 and an overall Biomer composition of [MDI(PTMG1000–MDI)$_2$–EDA–]$_n$.

Combination of the TG and Py-MS data suggests the following four-step pyrolysis mechanism:

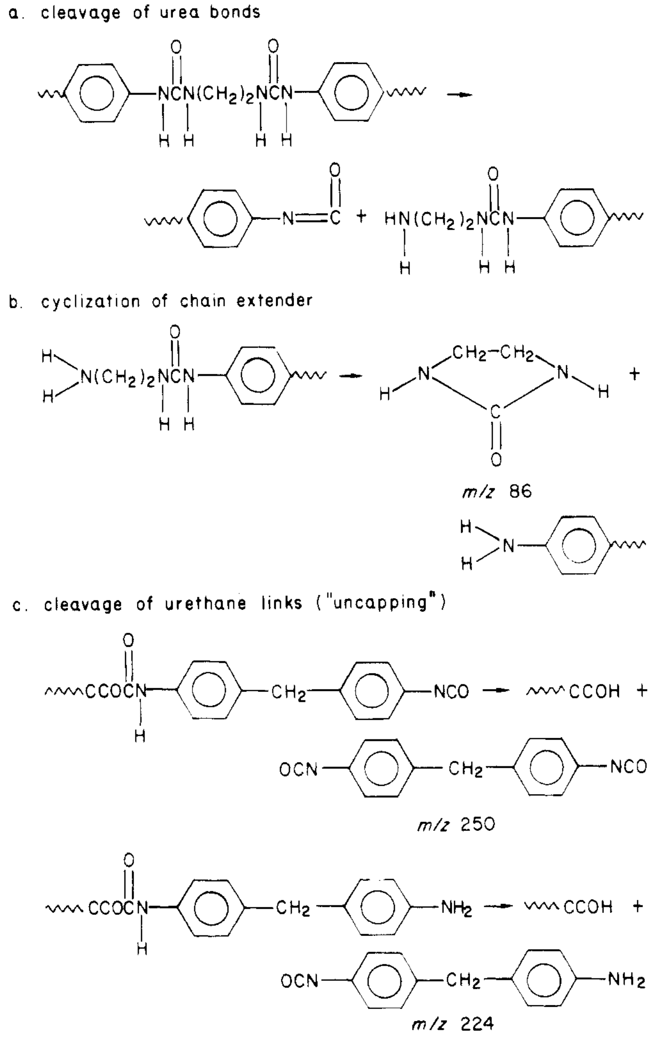


Table I
Polyether Contents of Two Model Polymers and Biomer. Actual Values Calculated from Stoichiometric Ratios Used in Synthesis

sample	calcd polyether wt % TG	calcd polyether wt % ^{1}H NMR	actual polyether wt %
PTMG 970, MDI, and EDA	50 ± 1	n/a	63
PTMG 2100, MDI, and EDA	79 ± 2	n/a	79
Biomer	72 ± 2	70	n/a

Conclusions

Pyrolysis mass spectrometry (Py-MS) of Biomer and related model polymers has unambiguously identified the components used in the synthesis of Biomer. The most probable pyrolysis mechanism appears to involve four consecutive steps: (1) cleavage of urea bonds, (2) cyclization of the chain extender, (3) cleavage of the urethane bonds, and (4) fragmentation of the polyol chains.

The diisocyanate, polyol, and chain-extender moieties are shown to be MDI, PTMG, and EDA, respectively. Determination of the stoichiometry of the components by TG and ^{1}H NMR gives the following approximate composition: [–MDI–PTMG1000–MDI–PTMG1000–MDI–EDA]$_n$.

Registry No. (EDA)·(MDI)·(PTMG) (copolymer), 9053-66-1.

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