



Analytical pyrolysis gas chromatography/mass spectrometry (py-GC/MS) of poly(ether urethane)s, poly(ether urea)s and poly(ether urethane-urea)s[☆]

John A. Hiltz^{*}

Defence Research and Development Canada, Atlantic Research Center, Dockyard Laboratory (Atlantic), Building D-20, Station Forces Halifax, PO Box 99,000, B3K 5X5 Halifax, Nova Scotia, Canada

ARTICLE INFO

Article history:

Available online 20 January 2015

Keywords:

Poly(ether urethane)s
Poly(urea)s
Poly(ether urethane-urea)s
Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS)
Polymer analysis

ABSTRACT

The results of a pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) study of several poly(ether urethane), poly(urea), and poly(ether urethane-urea) materials are reported. Mechanisms for the formation of pyrolytic degradation products are proposed. These can be used to differentiate between poly(ether urethane)s, poly(urea)s, and poly(ether urethane-urea)s, as well as between different poly(ether urethane)s, different poly(urea)s or different poly(ether urethane-urea)s. In conjunction with Fourier transform infrared (FT-IR) spectroscopy and thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis, py-GC/MS provides information that allows the characterization and identification of these polymers.

Crown Copyright © 2015 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

Poly(ether urethane)s, poly(ether urea)s and mixed poly(ether urethane-urea)s are used in wide range of applications because of their durability, abrasion resistance, and resistance to oil and chemicals. Typical applications include their use as elastomers, coatings, sealants, adhesives, and foams. These polymers can be either thermoplastics or thermosets.

Poly(ether urethane)s and poly(ether urea)s are phase separated AB block copolymers consisting of urethane or urea rich hard segments and poly(ether) rich soft segments. Hydrogen bonding in the hard segments results in virtual or reversible cross-links in these polymers. The relative proportions of the hard and soft segments, the degree of phase separation (or mixing) and the level of hydrogen bonding in these polymers depend on the nature and relative concentrations of the isocyanates, chain extenders, and polyols used in their preparation.

Poly(ether urethane)s and poly(ether urea)s differ in the nature of the chain extenders and polyols used in their preparation. Poly(ether urethane)s, are made using diol chain extenders and hydroxyl terminated polyols while poly(ether urea)s are made using diamines and amino terminated polyols. Poly(ether urethane-urea)s have both urethane and urea linkages and there-

fore a mixture of hydroxyl and amino terminated chain extenders and polyols are used in their synthesis.

As there is a correlation between the structures and properties of these materials, techniques that allow their characterization are important in material identification to ensure, for instance, that the correct material is used in a particular application or as a first step in determining why the material might have failed in-service. One of these techniques is pyrolysis gas chromatography/mass spectrometry (py-GC/MS).

Three reaction mechanisms have been proposed to account for the products arising from the thermal or pyrolytic degradation of the urethane portion of a poly(urethane) [1–3]. The first is the dissociation of the urethane linkage to form an isocyanate and an alcohol, the second is the formation of a primary amine, an olefin and carbon dioxide (CO₂) via a six-membered transition state and the third is the loss of CO₂ to produce a secondary amine. The mechanisms are shown in Fig. 1.

No evidence of the third mechanism (formation of a secondary amine) was observed in a study of the thermolysis mechanisms of polymethylene polyphenyl isocyanate (PAPI)/propoxylated trimethylol propane (TMP) based model urethanes [4]. This confirmed earlier results found for flexible polyurethane foams [5]. In a py-GC/MS study of poly(ester urethane)s [6], it was noted that the first mechanism (disassociation of the urethane linkage) predominated.

The pyrolytic degradation of the polyols and olefins resulting from the dissociation and concerted degradation of the PAPI-TMP based model compounds were also studied [4,7]. Polyols

[☆] Selected Paper from Pyrolysis 2014, Birmingham, U.K. 19–23 May 2014.

^{*} Tel.: +1 902 427 3425; fax: +1 902 427 3435.

E-mail address: john.hiltz@drdc-rddc.gc.ca

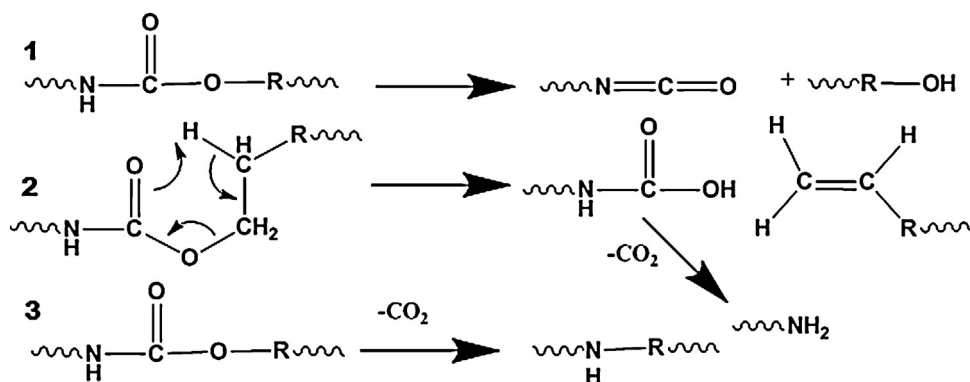


Fig. 1. Thermal degradation mechanisms of poly(urethane)s.

lost water to form either allyl or methyl substituted vinyl ethers. These were the same compounds that arose via the concerted six member transition state. The degradation products of the allyl and methyl vinyl ether terminated polyols were different. The allyl ether degraded to form propene and a keto ether, while the methyl vinyl ether degraded to form propanal and either an allyl ether or a methyl vinyl ether. Using a deuterium labelled TMP in the PAPI-TMP models compounds, no keto ethers were found in the pyrolytic degradation products. Additionally, the levels of deuteration of some pyrolysis products could not be accounted for using only concerted reactions. Free radical reactions were postulated as an explanation for level of deuteration in those products.

The thermal degradation of the poly(ether) portions of these polymers has also been investigated. Lattimer has studied the thermal degradation of both poly(tetrahydrofuran) [8] and

poly(ethylene glycol) [9]. A radical mechanism involving the cleavage of both C–O and C–C bonds was proposed to explain the pyrolysis degradation products.

In this paper, the results of a py-GC/MS study of several poly(ether urethane)s, two poly(ether urea)s and a mixed poly(urethane urea) are reported. Major pyrolytic degradation products are used to identify the compounds, diisocyanates, diols, poly(ether glycol)s, and poly(ether amine)s, used in the preparation of these polymers.

2. Materials and methods

2.1. Materials

The thermoplastic poly(ether urethane) elastomers; Texin 990A, Texin 950D, and Texin 970D (Bayer Polymers, Etobicoke, Ontario,

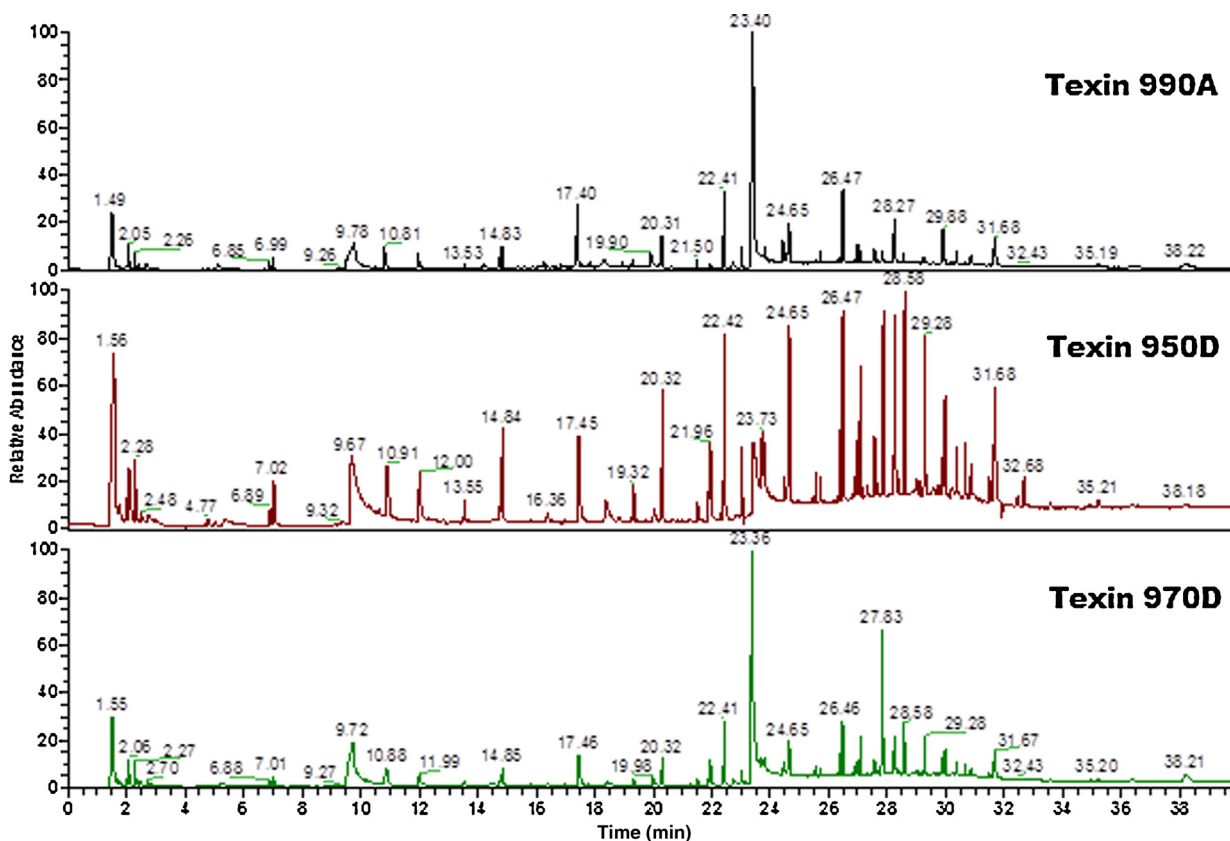


Fig. 2. Pyrograms of the Texin 990A, Texin 950D and Texin 970D samples.

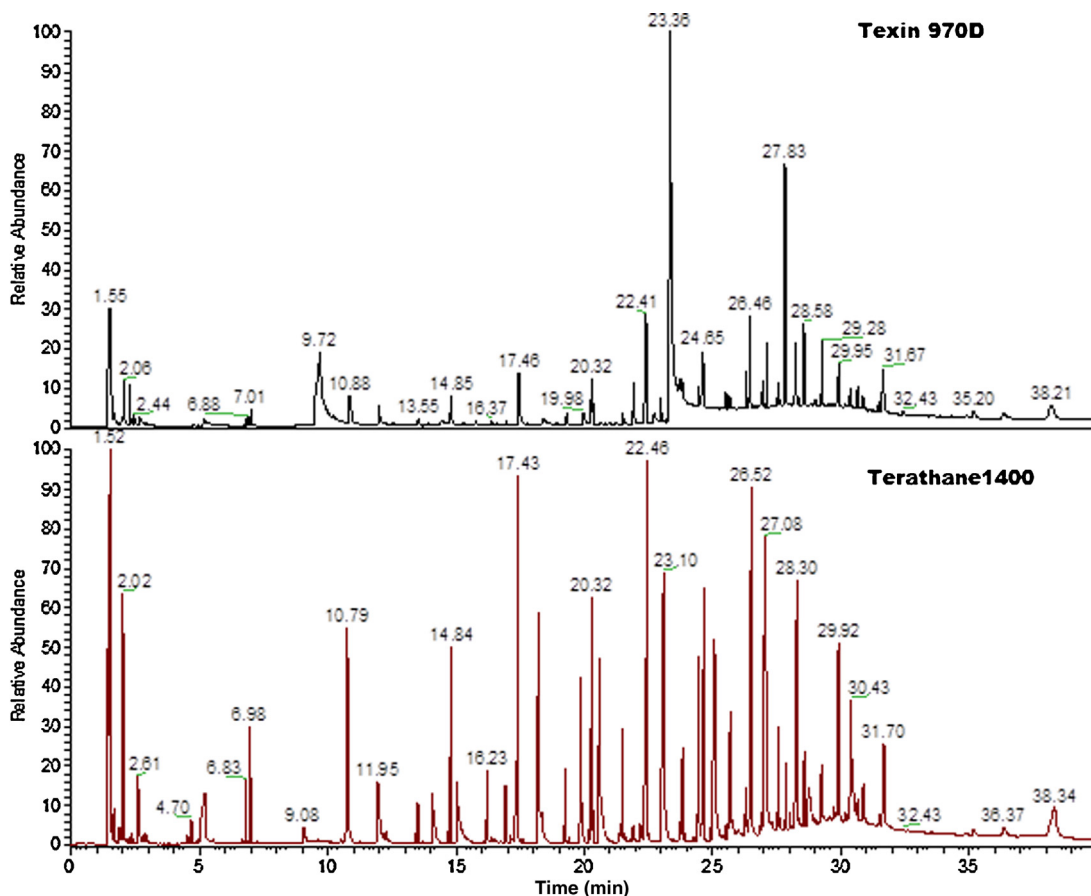


Fig. 3. Pyrograms of Texin 970D and Terathane 1400.

Canada), Elastollan 1195A and Elastollan 1164D (BASF Corporation-Polymers, Wyandotte, Michigan, USA), and Estane 58300 (Lubrizol Advanced Materials, Wickliffe, Ohio, USA), were supplied by the manufacturers. Fourier transform infrared [10] and ^{13}C nuclear magnetic resonance [11] characterization of these elastomers indicated that they were 1-isocyanato-4-[(4-isocyanatophenyl) methyl] benzene or methylene diphenyldiisocyanate (MDI)/1,4-butanediol/poly(tetramethylene ether) glycol based poly(ether urethane)s.

The preparation of the hexamethylene diisocyanate (HDI) based poly(ether urethane) thermoplastic elastomer is described in reference [12]. It was synthesized from two parts HDI, one part diethylene glycol and one part poly(ethylene glycol) in dimethylformamide.

The Dragonshield and Line-X elastomers were supplied by the manufacturers. Product literature indicated that Dragonshield BCTM (Specialty Polymers Inc., Lakewood, Washington, USA) and Line-X[®] XS-350 are poly(urea)s, while Line-X[®] XS-100 (Line-

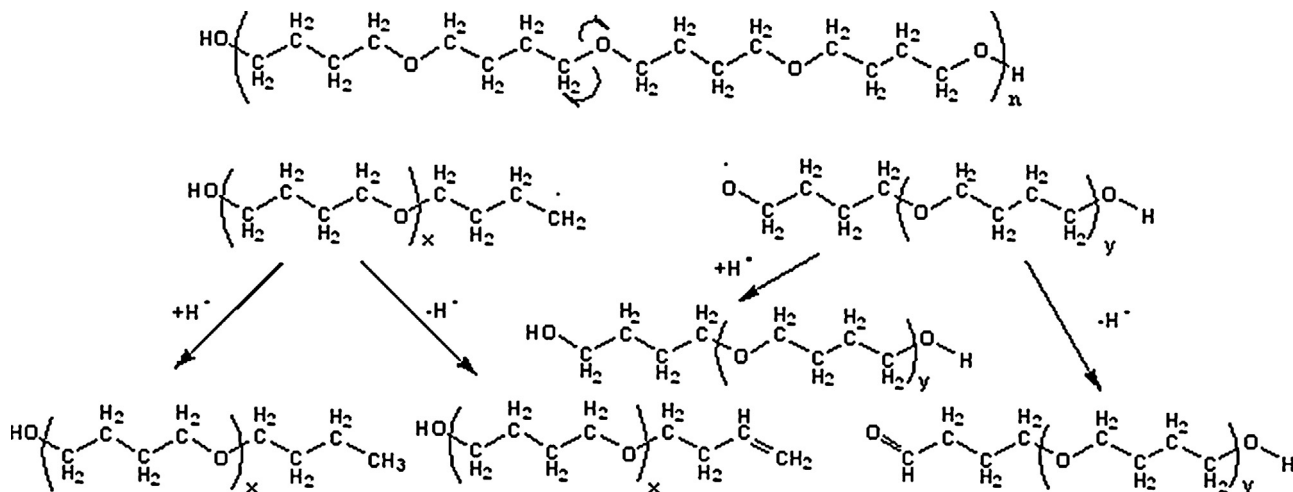


Fig. 4. Thermal degradation pathways for poly(tetramethylene ether) glycol based portions of poly(ether urethane)s resulting from C–O bond cleavage.

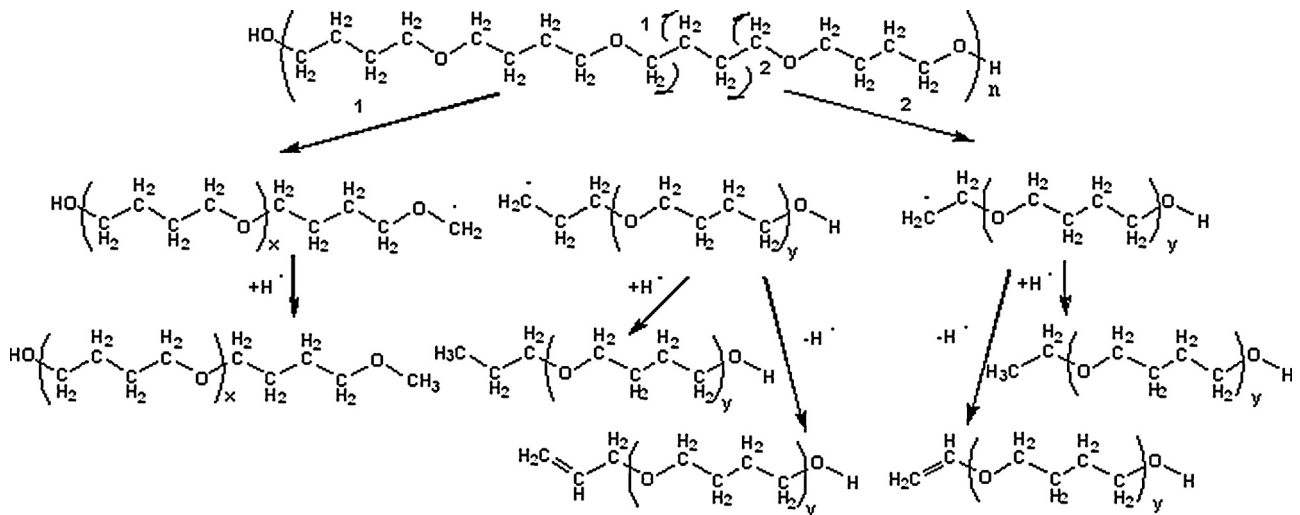


Fig. 5. Thermal degradation pathways for poly(tetramethylene ether) glycol based portions of poly(ether urethane)s resulting from C–C bond cleavage.

X, Huntsville, Alabama, USA) is a mixed poly(urethane/urea). All three were reported to have been prepared using MDI and/or MDI based prepolymers. Dragonsshield was prepared using poly(oxypropylene) diamine, while the Line-X products were prepared with a polyol and diethyltoluenediamine. All three samples were cross-linked elastomers.

Terathane 1400 (Invista) is a poly(tetramethylene ether) glycol with a molecular weight of 1350–1450 g/mol.

2.2. Methods

2.2.1. Pyrolysis gas chromatography/mass spectroscopy

All pyrolyses were carried out in a platinum coil pyroprobe (Pyroprobe 5000, CDS, Oxford, PA). Approximately 0.1 mg of the sample was centered in a 25 mm quartz tube and heated to a final temperature of 700 °C using a heating ramp of 20 °C ms⁻¹. The hold time at the final temperature was 20 s. The pyrolysis products were

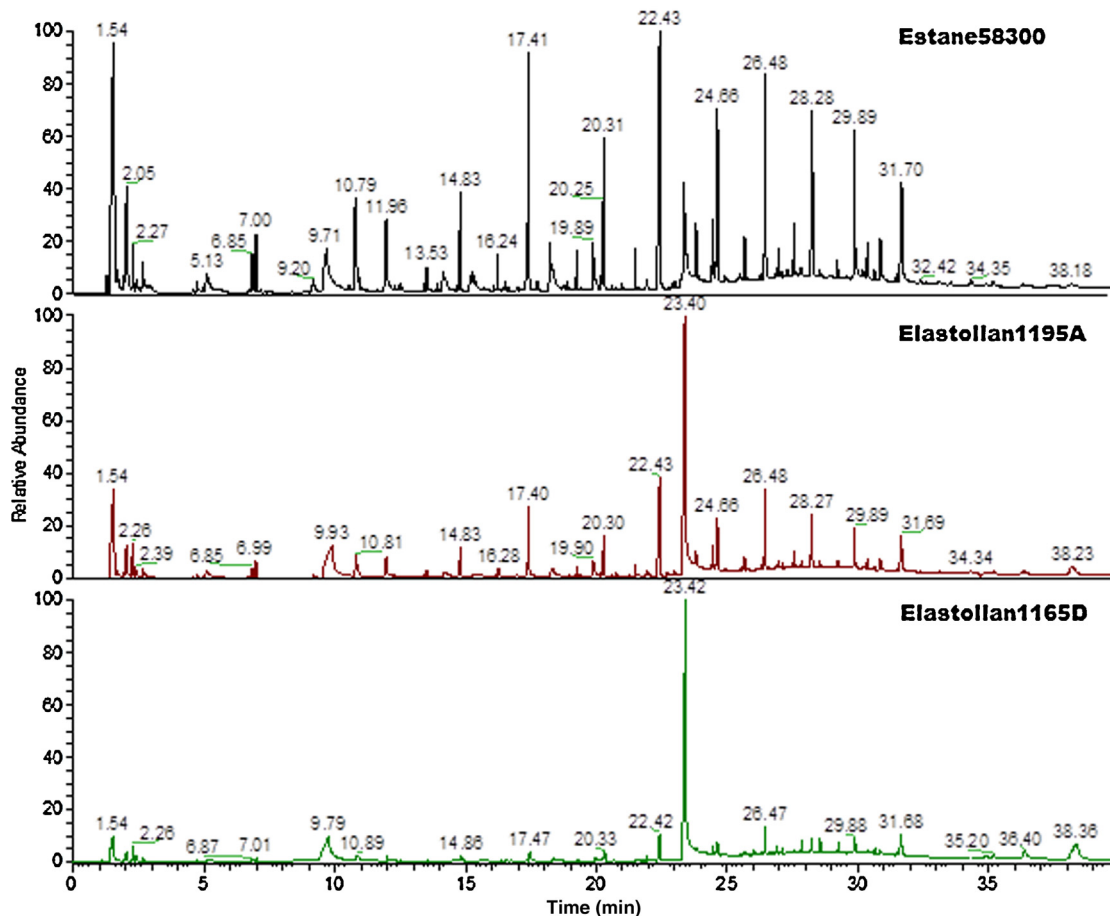


Fig. 6. Pyrograms of the Estane 58300, Elastollan 1195A and Elastollan 1164D samples.

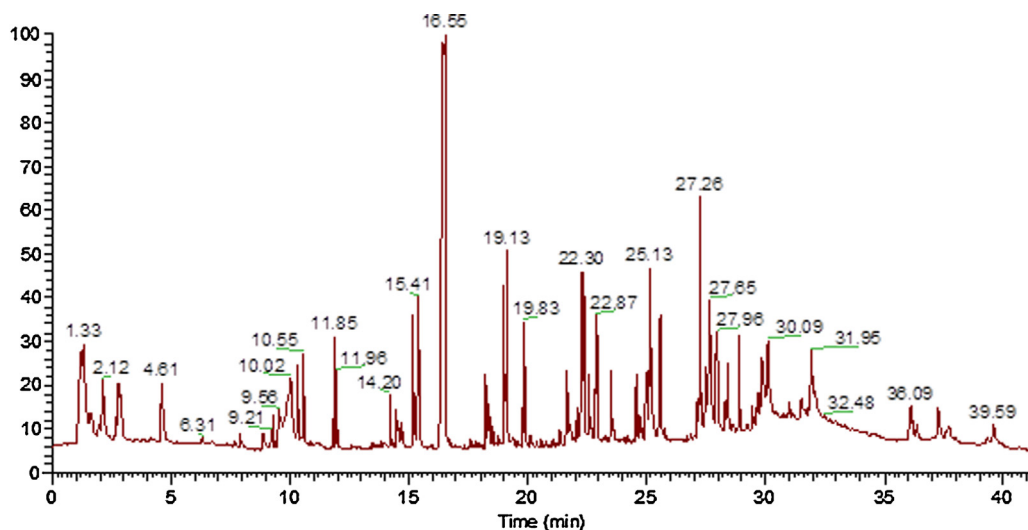


Fig. 7. Pyrogram of a hexamethylene diisocyanate/diethylene glycol/poly(ethylene glycol) based thermoplastic poly(ether urethane).

separated on a 30 m long \times 0.25 mm inside diameter 5% phenyl poly(dimethylsiloxane) capillary column (DB-5, J&W Scientific, Folsom, California). The inlet was set to a split flow of 50 mL min^{-1} , with a split ratio of 50:1. The flow rate of the carrier gas (He) was 1 mL min^{-1} . The heating program used for the gas chromatograph (TSQ Quantum GC, Thermo Scientific) consisted of holding the oven temperature at 40°C for 4 min, then ramping the temperature to 300°C at a rate of $10^\circ\text{C min}^{-1}$, and finally holding the temperature at 300°C for 10 min. Each GC run took 40 min to complete.

A Triple Stage Quadrupole (TSQ Quantum GC, Thermo Scientific) MS/MS was used to detect the pyrolytic degradation products. The MS was used in the full scan mode. Each scan, from 20 atomic mass units (amu) to 500 amu, took approximately 0.5 s.

3. Results and discussion

3.1. Poly(ether urethanes)

The pyrograms of the Texin 990A, Texin 950D and Texin 970D samples are shown in Fig. 2. The compounds released by the pyrolysis of these three thermoplastic polyurethanes were similar although their relative concentrations (responses) vary. Mass spectral identification of the compound giving rise to the broad peaks at ~ 9.7 min in the pyrograms indicated that it was 1,4-butanediol, while the compound at ~ 23.4 min was MDI. These compounds are commonly used in the preparation of poly(ether urethane)s as a chain extender and diisocyanate, respectively, and are released

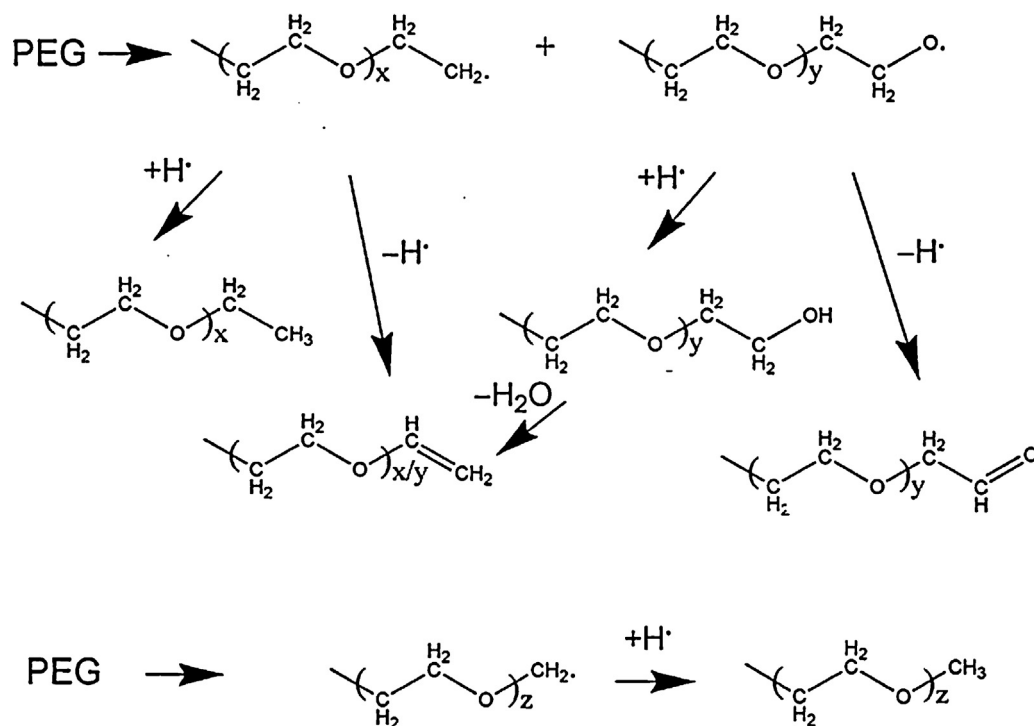


Fig. 8. Thermal degradation pathways for poly(ethylene glycol) (PEG).

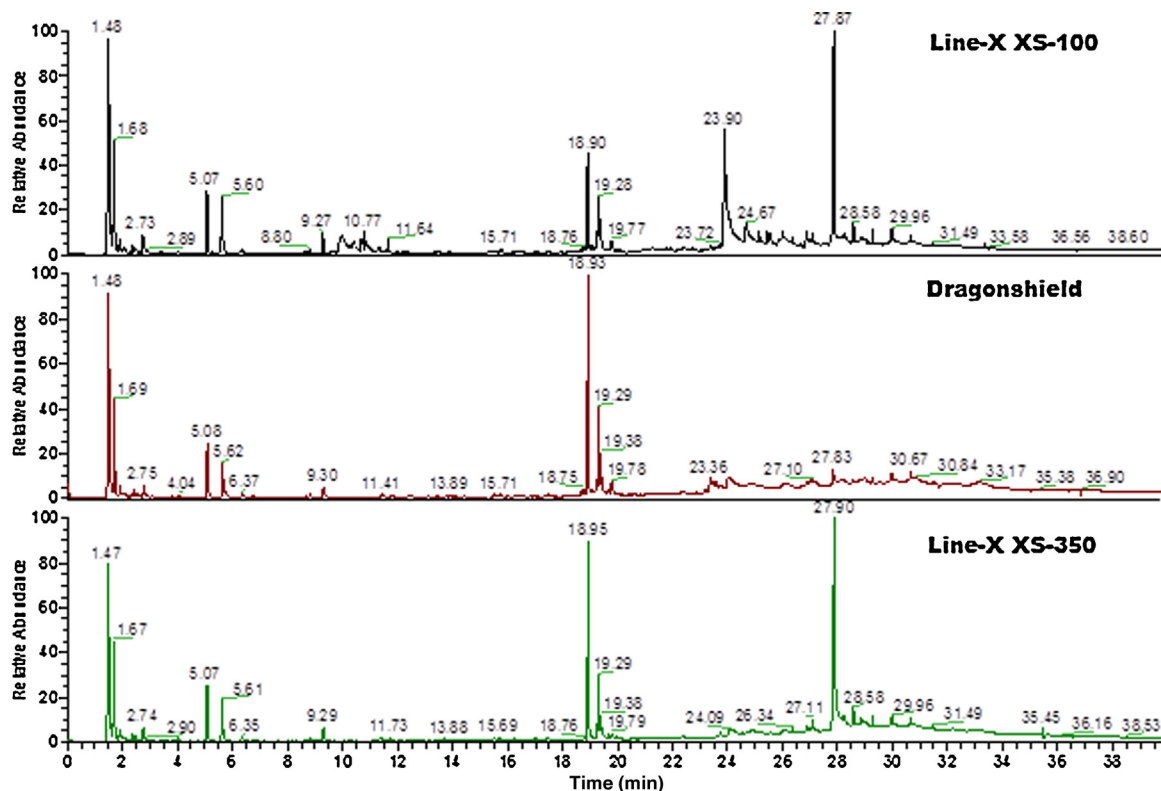


Fig. 9. Pyrograms of the Line-X XS-100, Dragonshield and Line-X XS-350 elastomers.

Table 1

Degradation products arising from pyrolytic degradation of poly(tetramethylene ether) glycol rich soft segment of the Texin thermoplastic elastomers.

Retention time (min)	Compound
1.52	Butane
1.67	Propanal
2.02	Butanal
2.61	1-Butanol
4.70	1-Propoxybutane
5.21	Tetrahydro-2-furanol
6.83	4-Butoxy-1-butene
6.98	<i>n</i> -Butyl ether
11.96	4-Butoxy-1-butanol
14.74	1-Butoxy-4-(4-butoxybutoxy) butene
14.84	1-Butoxy-4-(4-butoxybutoxy) butane

from the thermal degradation of the urethane rich hard segment portion of these polymers (reaction mechanism 1 in Fig. 1).

These polymers also produced a number of degradation products consistent with the degradation of the poly(ether) rich soft segment portion of poly(ether urethane)s. Pyrograms of Texin 970D and Terathane 1400, a commercially available poly(tetramethylene ether) glycol, are shown in Fig. 3. Comparison of the pyrograms indicates that with the exception of the 1,4-butanediol and MDI peaks, the Terathane 1400 and Texin 970D pyrolysis products are similar and confirms that a poly(tetramethylene ether) glycol was used in the preparation of these polymers. Some of the degradation products arising from the poly(tetramethylene ether) glycol portion of these polymers are identified in Table 1.

The thermal degradation of poly(tetramethylene ether) glycols has been studied [8]. The observed degradation products were explained using radical mechanisms involving either C–O bond or C–C bond cleavage. Pathways to the formation of degradation

products arising from either C–O or C–C bond cleavage are shown in Figs. 4 and 5.

The pyrogram of Texin 970D has a large peak at 27.83 min that is not present in the pyrograms of Texin 990A or Texin 950D. Analysis of the mass spectrum of the compound giving rise to this peak indicated that it was 2-(2'-hydroxy-3',5'-ditert-butylphenyl) benzotriazole, an ultraviolet light absorber.

The pyrograms of the Estane 58300, Elastollan 1195A and Elastollan 1164D samples are shown in Fig. 4. The pyrolytic degradation products of these thermoplastic polyurethanes were similar although the relative concentrations (responses) vary from one polymer to the other. They were also similar to those arising from the pyrolysis of the Texin samples. Mass spectral identification of the compound giving rise to the broad peaks at ~9.7 min in the pyrograms indicated that it was 1,4-butanediol, while the compound at ~23.4 min was MDI Fig. 6.

These polymers also produced a number of degradation products consistent with the degradation of the poly(ether) rich soft segment portion of poly(ether urethane)s. Again, the nature of these degradation products was similar to those arising from the pyrolysis of the Texin samples and indicated that poly(tetramethylene ether) glycol was used in the preparation of these polymers.

The pyrograms also provide semi-quantitative information on the relative percentages of the MDI, butanediol and poly(tetramethylene ether) glycol used in the preparation of these Texin, Elastollan and Estane thermoplastic poly(ether urethane). The Shore Type A or Type D Durometer hardness of the polymers are shown in Table 2. Comparing the height of the 1,4-butanediol peak at ~9.7 min, which arises from the pyrolytic degradation of urethane rich hard segment portion of the polymer, to the height of the peak at ~17.4 min, which arises from the thermal degrada-

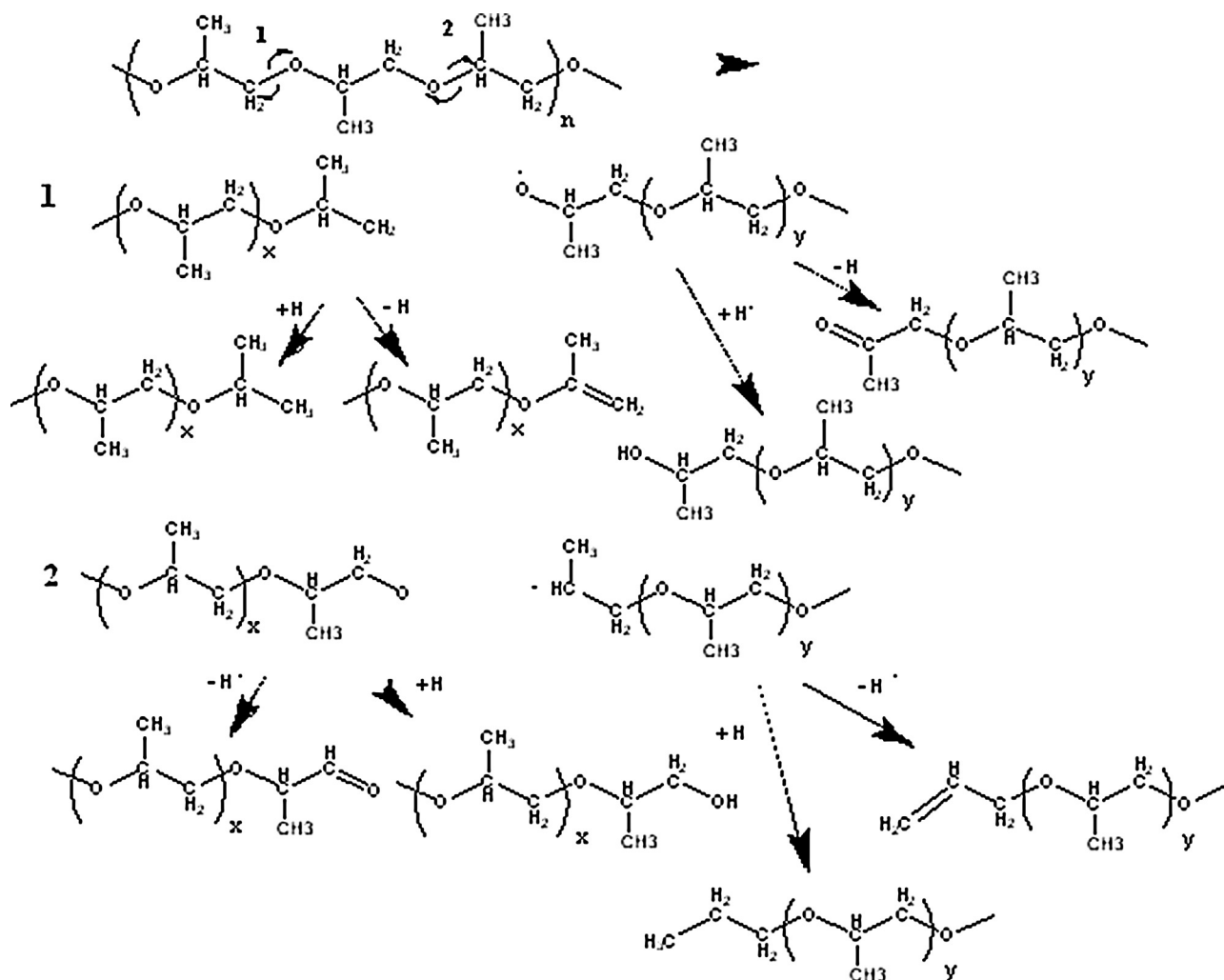


Fig. 10. Thermal degradation pathways of the poly(1,2-propanediol)s resulting from C–O cleavage.

tion of the poly(ether) rich soft segment portion of the polymer, it can be seen that the ratio increases as the hardness of the polymer increases. The Elastollan and Estane samples exhibit the same trend.

The pyrogram of a poly(ether urethane) prepared using hexamethylene diisocyanate (HDI), diethylene glycol (DEG) and

poly(ethylene glycol) (PEG) is shown in Fig. 7. Mass spectra of the peaks at approximately 10.0 min and 16.56 min indicated that they were diethylene glycol and hexamethylene diisocyanate, respectively. These compounds arise from the degradation of urethane rich hard segment portion of the polymer via reaction mechanism 1 in Fig. 1. The majority of the other compounds arise from the

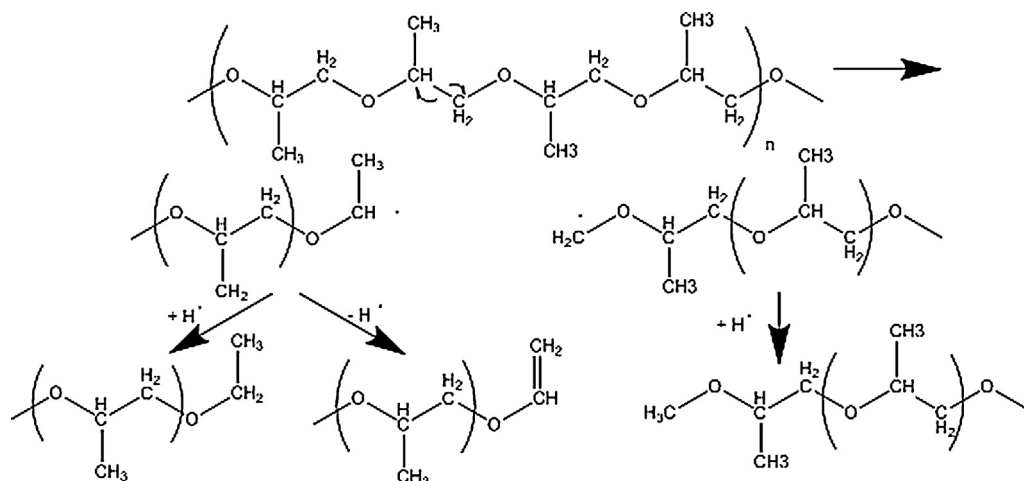


Fig. 11. Thermal degradation pathways of the poly(1,2-propanediol)s resulting from C–C.

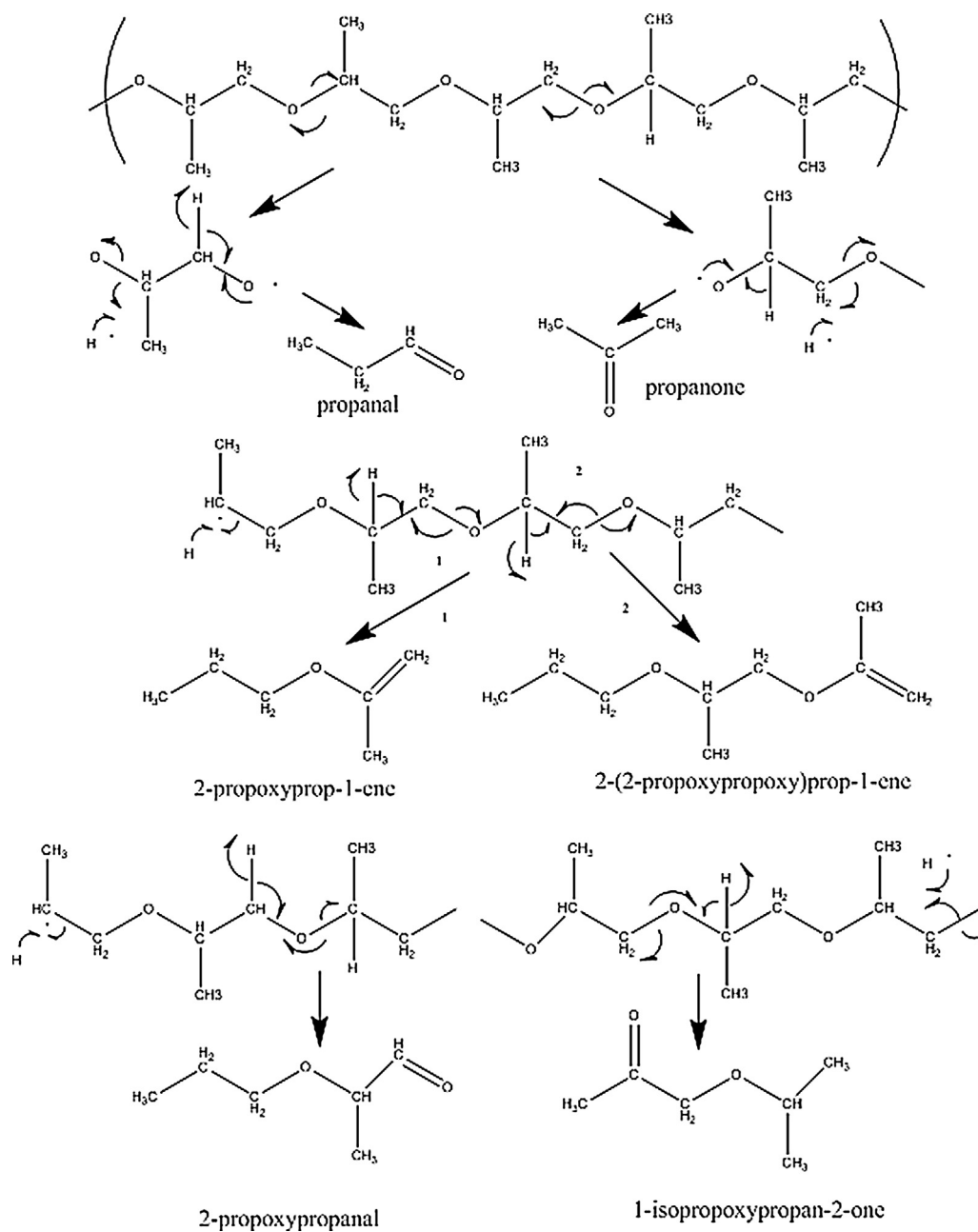


Fig. 12. Thermal degradation pathways of the poly(1,2-propanediol)-based portions of the Dragonshield, Line-X XS-100 and Line-X XS-350 elastomers leading to the formation of products at 1.68 min, 2.73 min, 5.07 min, 5.69 min, and 9.27 min. cleavage.

Table 2

Shore durometer (either Type A or Type D) hardness of the poly(ether urethanes).

Poly(ether urethane)	Shore hardness
Texin 990A	90A
Texin 950D	50D
Texin 970D	70D
Elastollan 1195A	95A
Elastollan 1164D	64D
Estane 58300	80A

Table 3

Degradation products arising from pyrolytic degradation of poly(ethylene glycol) rich soft segment portion of the HDI/DEG/PEG poly(ether urethane).

Retention time (min)	Compound
1.93	2-Methyl-1,3-dioxolane
2.61	2-Ethoxyethanol
2.87	(2-Methoxyethoxy) ethene
4.61	1,2-Diethoxyethane
8.78	2-(2-Methoxyethoxy) ethanol
9.81	2,2'-Oxybis-ethanol
10.23	2-(2-Ethoxyethoxy) ethanol
11.79	1,1'-Oxybis(2-ethoxyethane)

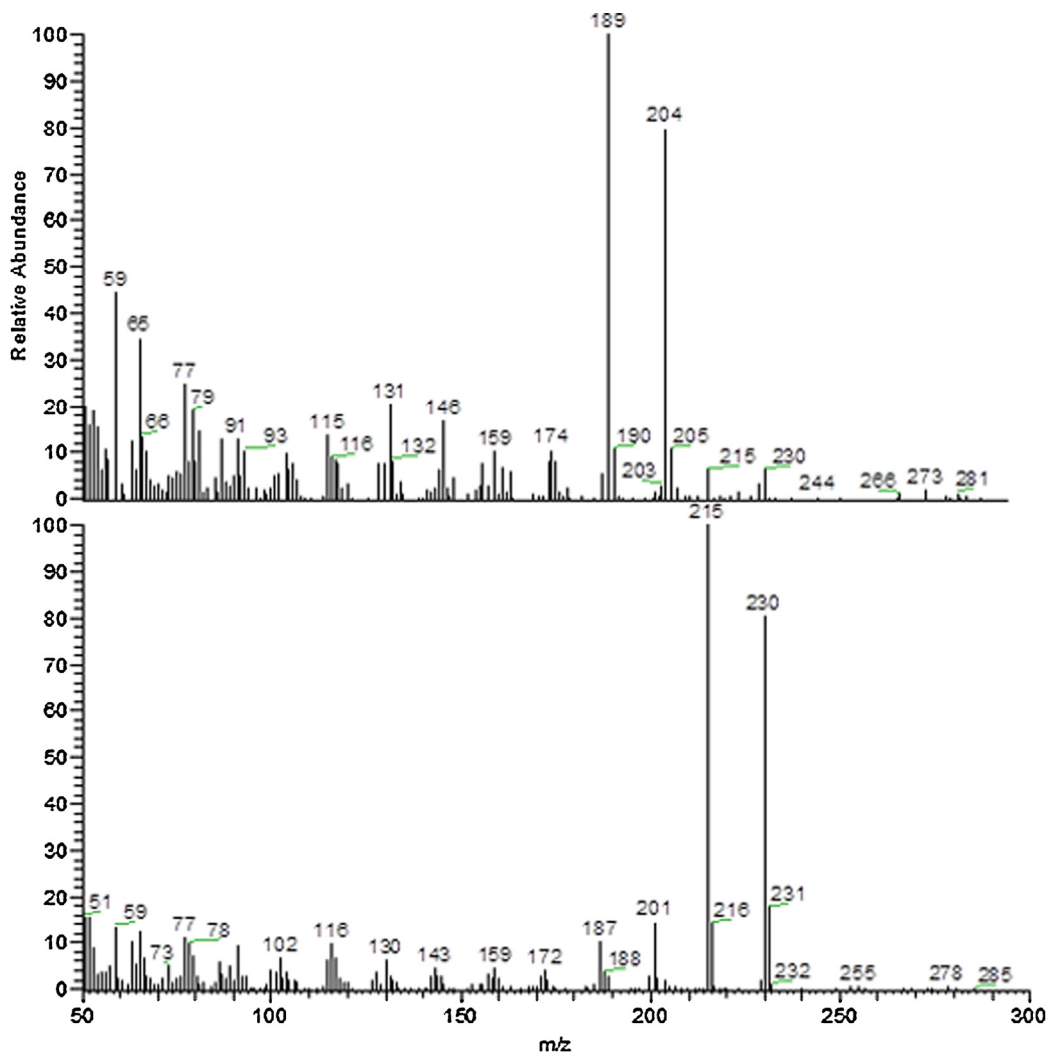


Fig. 13. Mass spectra of the compounds giving rise to the peaks at top: 19.3 min and at bottom: 18.9 min.

degradation of the poly(ethylene glycol) rich soft segment portion of the polymer.

Pathways for the formation of thermal degradation products of PEG are shown in Fig. 8 [9]. These results from either C–O or C–C bond cleavage. Some of the lower molecular weight products resulting from PEG rich portion of the polymer are listed in Table 3 and are consistent with the degradation mechanisms shown in Fig. 8.

4. Poly(urea)s and mixed poly(urethane urea)

Pyrograms of the Line-X XS-100, Dragonshield and Line-X XS-350 elastomers are shown in Fig. 9. The pyrograms of the three elastomers have many similarities. For instance, all three elastomers release degradation products with retention times of approximately 1.48 min, 1.68 min, 2.74 min, 5.07 min, 5.60 min, 9.27 min, 18.90 min, 19.28 min, and 19.77 min. However, there are also differences in the pyrograms. The pyrogram of the Line-X XS-100 elastomer has a degradation product at approximately 9.80 min and a major degradation product at 23.90 min that are not present in the pyrograms of the other two elastomers, while Line-X XS-100 and Line-X XS-350 elastomers have a major degradation product at 27.87 min that is not found in the pyrogram of the Dragonshield elastomer.

Table 4

Degradation products arising from pyrolytic degradation of the poly(1,2-propanediol) rich portions of the Dragonshield, Line-X XS-100 and Line-X XS-350 elastomers.

Retention time (min)	Compound
1.68	Propanal
2.73	2-Propoxyprop-1-ene
5.07	2-Propoxypropanal
5.61	1-Isopropoxypropan-2-one
9.27	2-(2-Propoxypropoxy) prop-1-ene

The compounds giving rise to the peaks at 1.68 min, 2.74 min, 5.07 min, 5.60 min, 9.27 min are shown in Table 4. These compounds are consistent with the thermal degradation of the poly(1,2-propanediol) based polyether portion of the elastomers. General degradation pathways for a poly(1,2-propanediol) based polyether are shown in Figs. 10 and 11 for cleavage of C–O and C–C bonds, respectively. C–O cleavage can lead to the formation of compounds with hydroxyl, propyl, propenyl, isopropyl, and isopropenyl end groups, propanal and propanone, and propanals and propanones with hydroxyl, propyl, propenyl, isopropyl and isopropenyl end groups. Cleavage of C–C bonds results in the formation of degradation products with terminal methyl and ethyl ether groups. Pathways for the formation of the compounds in Table 4 are shown in Fig. 12.

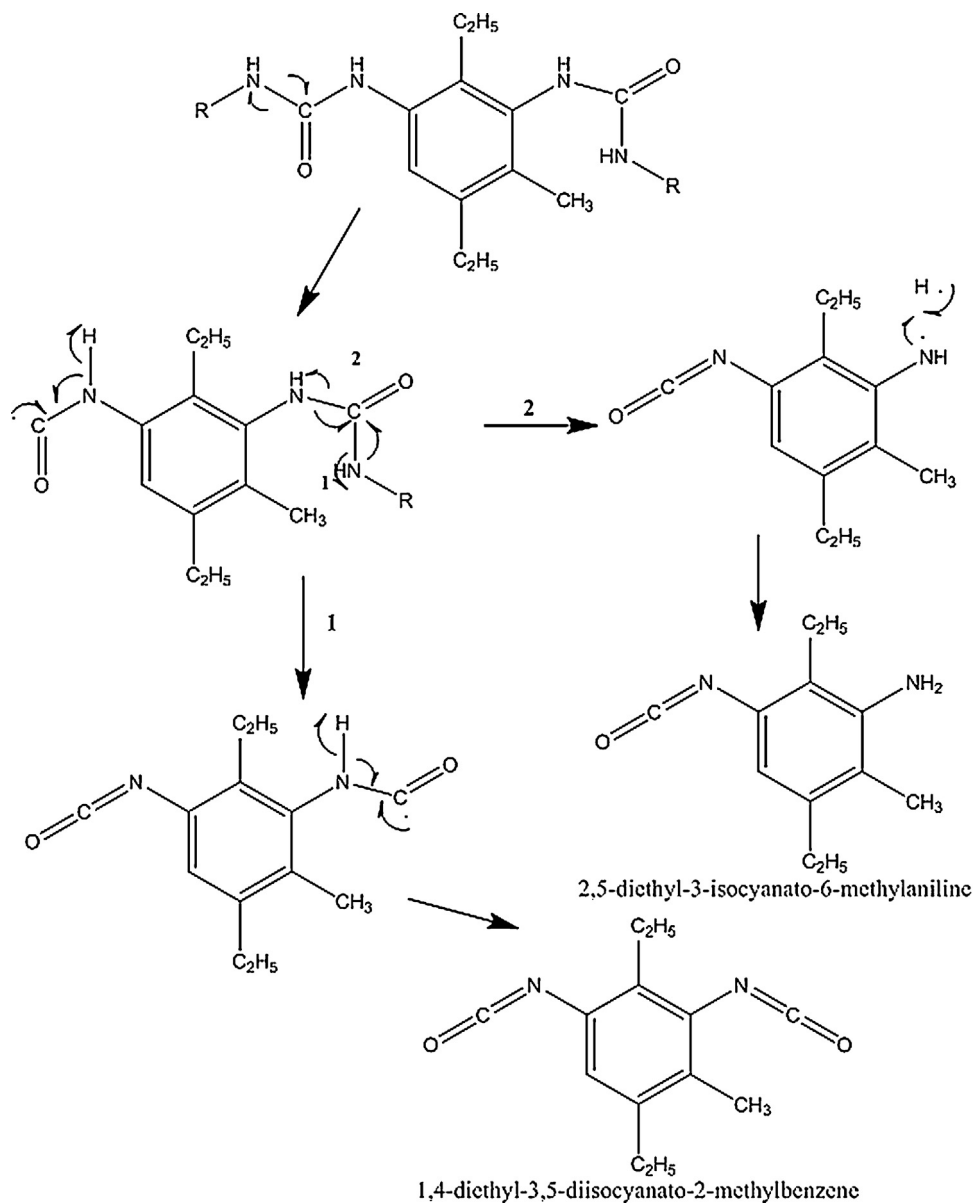


Fig. 14. Pathways for the formation of 1,4-diethyl-3,5-diisocyanato-2-methylbenzene and 2,5-diethyl-3-isocyanato-6-methylaniline from pyrolytic degradation of the Dragonshield, Line-X XS-100 and Line-X XS-350 elastomers.

The mass spectrum of the compound giving rise to the peaks in the pyrograms at ~ 18.9 min is shown in Fig. 13. The compound has a molecular ion at m/e 230 and prominent ions with m/e 215, m/e 201, and m/e 187. Analysis of the mass spectra indicates that it is characteristic of 1,4-diethyl-3,5-diisocyanato-2-methylbenzene. The pathway for the formation of this compound during the pyrolysis of the three elastomers is shown in Fig. 14. The elastomers also have a less intense peak at ~ 19.3 min. The mass spectrum of this compound is shown in Fig. 13. The mass spectrum is characteristic of 2,5-diethyl-3-isocyanato-6-methylaniline. The pathway for the formation of this compound during the pyrolysis of the three elastomers is shown in Fig. 14. These two degradation products in the pyrograms of the three elastomers arise from the diethyltoluenediamine used as a chain extender in their preparation.

Mass spectral analysis of the compound at 9.90 min in the pyrogram of the Line-X XS-100 sample indicated it was diethylene

glycol. Diethylene glycol is listed as one of the starting materials used in the synthesis of Line-X XS-100. It is used as a chain extender in poly(urethane) formulations.

Product literature for these three elastomers indicates that MDI and/or MDI-based prepolymers are used in their formulation. One of the degradation products arising from the pyrolysis of many MDI-based thermoplastic and thermoset polyurethanes is MDI [10]. However, no MDI was detected in the pyrolytic degradation products of the three elastomers studied in this report. The pyrogram of the Line-X XS-100 sample did have a peak at 23.90 min that was identified as 4,4'-diaminodiphenylmethane. The 4,4'-diaminodiphenylmethane arises from the thermal degradation of the portion of the elastomer that incorporated 4,4'-diisocyanatodiphenylmethane (MDI). A pathway for the formation of 4,4'-diaminodiphenylmethane is shown in Fig. 15.

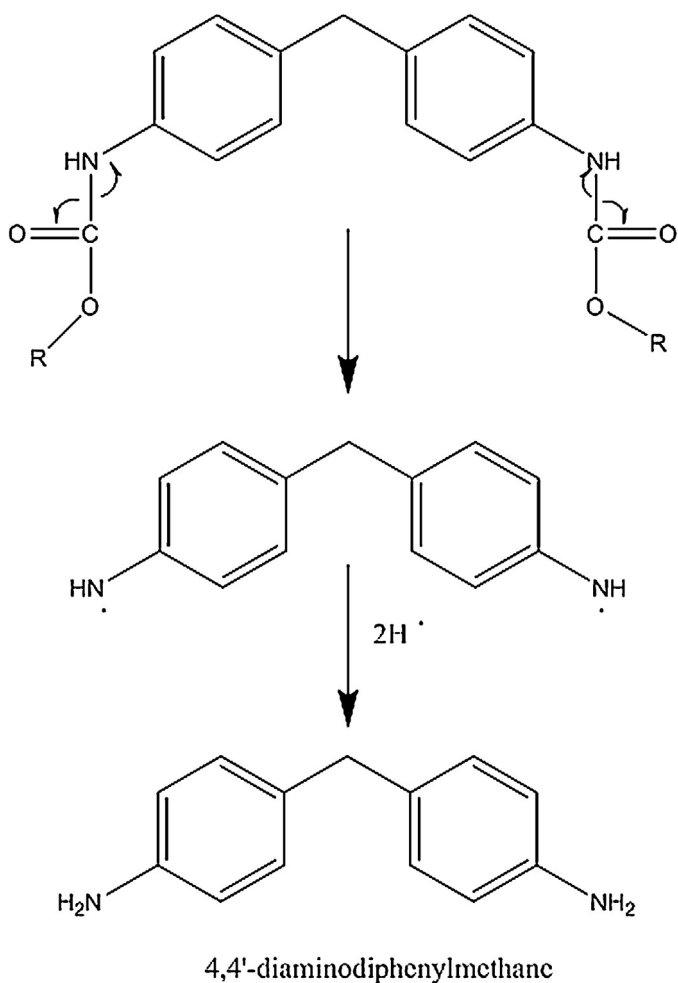


Fig. 15. Pathway for the production of 4,4'-diaminodiphenylmethane during the pyrolytic degradation of the Line-X XS-100 sample.

5. Conclusions

Py-GC/MS has been used to identify the diisocyanates, diols and poly(ether glycol)s used in the preparation of MDI/1,4-butanediol/poly(tetramethylene ether) glycol and HDI/diethylene glycol/poly(ethylene glycol) thermoplastic poly(ether urethane)s. For series of poly(ether urethane)s with varying ratios of diols and poly(ether glycol)s to the diisocyanate, the relative response of the diol to a peak arising from the poly(ether glycol) correlates with the hardness of the polymer. That is, as the ratio of the response of the diol to the poly(ether glycol) degradation product increases,

the hardness of the polymer increases. This is directly related to the proportion of hard and soft segments of these phase separated block copolymers.

The amine terminated polyols used in the poly(urethane urea) and the two poly(urea) formulations could be identified by py-GC/MS. Although the three elastomers studied all contained MDI or MDI based prepolymers, none of them released MDI following pyrolytic degradation. One the poly(urethane urea), released 4,4'-diaminodiphenylmethane, which arises from the degradation of the portion of the polymer where MDI had been incorporated. This is in contrast to MDI based poly(urethane)s where MDI is an identifiable degradation product. However, the three elastomers did release a diisocyanate. This arose from the degradation of the portion of the elastomer where a diamine, diethyltoluenediamine, was incorporated.

Py-GC/MS can be used to differentiate various poly(ether urethane)s, poly(urea)s and poly(urethane urea)s and provide information on the materials used in their preparation. In conjunction with properties, this information is important in the selection of materials for particular applications or in determining why a material failed in an application.

References

- [1] E. Dyer, G.E.J. Newborn, Thermal degradation of carbamates of methylenebis (4-phenyl isocyanate), *J. Am. Chem. Soc.* 80 (1958) 5495–5498.
- [2] E. Dyer, G.C. Wright, Thermal degradation of alkyl N-phenylcarbamates, *J. Am. Chem. Soc.* 81 (1959) 2138–2143.
- [3] E. Dyer, R.E. Read, Thermal degradation of 1-hexadecyl-1-naphthylcarbamate and 1-hexadecyl propyl(1-naphthyl) carbamate, *J. Org. Chem.* 26 (1961) 4388–4394.
- [4] K.J. Voorhees, F.D. Hileman, I.N. Einhorn, J.H. Futrell, An investigation of the thermolysis mechanism of model urethanes, *J. Polym. Sci.: Polym. Chem. Ed.* 16 (1) (1978) 213–228.
- [5] F.D. Hileman, K.J. Voorhees, L.H. Wojcik, M.M. Birky, P.W. Ryan, I.N. Einhorn, Pyrolysis of a flexible urethane foam, *J. Polym. Sci.: Polym. Chem. Ed.* 13 (3) (1975) 571–584.
- [6] H. Ohtani, T. Kimura, K. Okamoto, S. Tsuge, Y. Nagataki, K. Miyata, Characterization of polyurethanes by high-resolution pyrolysis-capillary gas chromatography, *J. Anal. Appl. Pyrolysis* 12 (2) (1987) 115–133.
- [7] K.J. Voorhees, R.P. Lattimer, Mechanisms of pyrolysis for a specifically labeled deuterated urethane, *J. Polym. Sci.: Polym. Chem. Ed.* 20 (6) (1982) 1457–1467.
- [8] R.P. Lattimer, Mass spectral analysis of low-temperature pyrolysis products from poly(tetrahydrofuran), *J. Anal. Appl. Pyrolysis* 57 (1) (2001) 57–76.
- [9] R.P. Lattimer, Mass spectral analysis of low-temperature pyrolysis products from poly(ethylene glycol), *J. Anal. Appl. Pyrolysis* 56 (1) (2000) 61–78.
- [10] J.A. Hiltz, Characterization of Poly(ether)Urethane Thermoplastic Elastomers, DREA-TM -98-222, Defence Research Establishment Atlantic, Dartmouth, NS (CAN), 1998.
- [11] J.A. Hiltz, M. Lumsden, ¹³C NMR Spectroscopy of 4,4-Methylenebis-(Phenylisocyanate)/1,4-Butanediol/Poly(Tetramethylene Ether Glycol) Poly(Ether) Urethanes, DREA-TM-2001-101, Defence Research Establishment Atlantic, Dartmouth, NS (CAN), 2001.
- [12] D. Cook, Phase Mixed Polyurethane Synthesis, DREA CR 2000-076) Defence Research Establishment Atlantic, Dartmouth, Nova Scotia, 2000.