Novel Polyetherurethaneurea Elastomers Based on α,α,α',α'-Tetramethyl-m-xylenediisocyanate: Synthesis, Characterization, Processability, and Hydrolytic Stability

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SYNOPSIS

A series of novel polyetherurethaneurea elastomers based on m-TMXDI, polyether macrodiols containing 4, 6, 8, or 10 methylene groups between the ether linkages, and aliphatic and aromatic diamines was prepared by two-step solution polymerization. All the materials were thermally processable at 120–160°C except one that was solvent-castable. Mechanical properties and hydrolytic stability (at neutral pH) were found to depend on the macrodiol and chain extender. Poly(tetramethylene oxide)-based polyetherurethaneureas that were chain-extended with primary aliphatic diamines, other than 1,3-propanediamine, exhibited significantly better mechanical properties than those chain-extended with secondary aliphatic or aromatic diamines. The mechanical properties and hydrolytic stability of polyetherurethaneureas containing poly(hexa-, octa-, or decamethylene oxide) and 1,6-hexamethylenediamine were considerably better than those containing 1,2-ethylenediamine. The hydrolytic stability increased with the increasing C/O ratio of the macrodiol. With poly(hexamethylene oxide)-based materials, the phase separation between soft and hard domains was higher than that of the other materials as determined by DSC. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well recognized that the good mechanical properties of polyurethane elastomers are a direct result of their two-phase microstructure.[1,2] Typically, these materials consist of glassy or crystalline "hard"-segment domains dispersed throughout a continuous rubbery "soft"-segment amorphous phase. The soft-segment domains impart elastomeric properties, whereas the hard-segment domains act to reinforce the copolymer mechanically. The hard-segment structure and weight fraction, soft-segment structure, molecular weight, polydispersity, and cross-linking in either phase influence microphase separation in these copolymers. Because of their excellent mechanical properties, such as abrasion resistance and high flexural strength, and good biocompatibility, polyurethanes are frequently used in medical implants.

We have initiated research efforts in our laboratories to synthesize improved polyurethanes for use in medical implants. Recently, we reported[3] the synthesis and characterization of a series of polyetherurethanes based on 4,4'-methylene diphenyl diisocyanate (MDI) and novel polyether macrodiols. In that study, the effect of the macrodiol structure on mechanical properties and resistance to hydrolysis and oxidation was investigated. The present study is concerned with the synthesis and characterization of polyetherurethaneureas based on α,α,α',α'-tetramethyl-m-xylenediisocyanate (m-TMXDI) (I), a series of polyether macrodiols and diamine chain extenders. TMXDI has not been used commonly in polyurethane synthesis, and by virtue of its steric hindrance around the isocyanate groups, it would appear to be a suitable candidate for pre-

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paring polyurethanes with outstanding hydrolysis resistance. This is one of the several properties required of a material for use in long-term medical implants:

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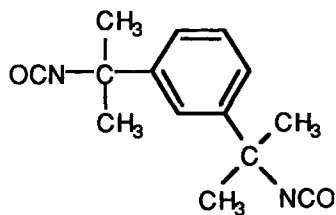
(I)

m-TMXDI is a hindered diisocyanate produced by American Cyanamid.[4] This diisocyanate has characteristics typical of an aliphatic diisocyanate because of the lack of conjugation of the aromatic ring with the isocyanate groups. The reactivity of *m*-TMXDI is similar to that of hexamethylene diisocyanate.[4] These characteristics give polyether-urethaneurea elastomers prepared from *m*-TMXDI many useful properties including resistance to weathering, hydrolytic stability, and high elongation. Chang and Saxon[5,6] discussed the advantages of *m*-TMXDI over conventional diisocyanates such as 4,4'-methylene diphenyl diisocyanate and toluene diisocyanate.

The synthesis and applications of a limited range of polyurethanes from both *para* and *meta* isomers of TMXDI have appeared in the literature.[7-11] Beumel and Stack reported[12] on the dynamic mechanical properties of *p*-TMXDI-based elastomers chain-extended with the aromatic diamine, diethyltoluenediamine (DETDA). The two-step bulk prepolymer method of synthesis has been used in these studies; a range of aromatic diamines has been employed as chain extenders. Although Saxon and Chang[5,6] indicated that aliphatic diamines are too reactive for cast polyurethane elastomer formulations, the details of such studies have not yet appeared in the literature.

Unlike many conventional diisocyanates, TMXDI does not undergo side reactions to form allophanate and biuret linkages during polyurethane synthesis, presumably because of steric hindrance accorded by the methyl groups on the carbons α to the isocyanate groups. The formation of allophanate and biuret linkages causes cross-linking and branching, resulting in polyurethanes with greater structural complexity. Furthermore, such cross-linked materials are often unprocessable. The absence of these side reactions makes *m*-TMXDI an ideal diisocyanate for the synthesis of well-defined

linear polyurethane elastomers that are useful for the study of structure–property relationships. In this paper, we report the synthesis, characterization, processability, and hydrolytic stability of polyetherurethaneurea elastomers based on *m*-TMXDI, a series of polyether macrodiols that contain 4, 6, 8, or 10 methylene groups between the ether oxygens and both aliphatic and aromatic diamine chain extenders. The main objective of the present study is to investigate the effect of the number of methylene groups between the ether linkages in the macrodiols on processability, mechanical properties, and hydrolytic stability of the corresponding polyetherurethaneureas. We have recently described conditions for preparing polyether macrodiols that contain 6, 8, or 10 methylene groups between the ether oxygens.[13]

EXPERIMENTAL

Materials

m-TMXDI (complementary sample from Cyanamid Australia Pty. Ltd.) was dried over activated 3 Å molecular sieves and purified by distillation under nitrogen at reduced pressure. The middle fraction collected at 120°C (0.05 Torr) was used for polymerizations. *N,N*-Dimethylformamide (DMF) (Aldrich) was dried over activated 3 Å molecular sieves for 7 days and was then distilled under a reduced pressure of nitrogen. A small amount of MDI was added to the distillation flask to react with impurities such as amines that may be present in DMF. The middle fraction was used in polymerization experiments. The catalyst dibutyltindilaurate (Eastman Kodak) was used as received.

1,2-Ethanediamine (EDA), 1,3-propanediamine (1,3-PDA), 1,4-butanediamine (1,4-BDA), *p*-xylenediamine (*p*-XDA), and 1,6-hexanediamine (HDA) (all from Aldrich) were purified by distillation, and the middle fractions collected were used as chain extenders. Except for HDA and *p*-XDA, all amines were dried over activated 3 Å molecular sieves for at least 3 days prior to distillation. *N,N'*-Dimethylethylenediamine (DMEDA, Tokyo Kasei) was dried over activated 3 Å molecular sieves for 3 days and distilled under nitrogen; the fraction boiling at 118°C was used for chain-extension experiments. Diethyltoluenediamine (DETDA, Ethyl Corp.) was purified by distillation prior to use in polymerizations. 1,6-Hexanediol, 1,8-octanediol, and 1,10-decanediol (Aldrich) were purified by distillation under vacuum. Concentrated sulfuric acid, Na-

fion catalyst (acid form, equiv wt 1100, 10–35 mesh, C.G. Processing) and absolute ethanol were used as received.

Poly(alkylene oxide)s

Poly(tetramethylene oxide) (PTMO, Terathane-1000 from Du Pont) was dried by heating at 105°C under a vacuum of 0.1 Torr for 15 h prior to use in polymerizations. Poly(hexamethylene oxide) (PHMO), poly(octamethylene oxide) (POMO), and poly(decamethylene oxide) (PDMO) were synthesized by the acid-catalyzed (concentrated sulfuric acid or Nafion-H resin) polymerization of diols according to procedures reported previously.[13] Typical sulfuric acid and Nafion-catalyzed polymerizations are described below. 1,6-Hexanediol (200 g) was placed in a 500 mL round-bottom flask and heated under vacuum (0.1 Torr) at 100°C for 1 h. The flask was cooled to 50°C and fitted with a nitrogen bleed, Dean-Stark trap, and condenser. Concentrated sulfuric acid (2.2 mL) was added dropwise with stirring, and the reaction mixture was heated at 170°C under a controlled flow (100 mL/min) of dry nitrogen. Polymers with different molecular weights were obtained by varying the time of heating. The reaction times to prepare PHMO with molecular weights of 570, 1190, and 2100 were 3.5, 6, and 9 h, respectively.

The polymerized reaction mixture was poured into a warm, saturated solution of calcium hydroxide to neutralize the sulfuric acid catalyst. The mixture was allowed to cool to ambient temperature while stirring and the precipitated macrodiol was filtered and thoroughly washed with water. The macrodiol was dried in a vacuum oven at 45°C for 48 h. The dried product was dissolved in hot ethanol, filtered while hot to remove any remaining calcium sulfate, and was purified by recrystallization from a 70/30 (v/v) mixture of ethanol and water and dried in a vacuum oven at 45°C for 48 h.

A similar experimental procedure was followed for the preparation of POMO and PDMO. The reaction times at 170°C to prepare POMO with molecular weights of 1170 and 2050 were 9 and 12 h, respectively. However, the recrystallizations were carried out from absolute ethanol. PDMO (MW 1270) and POMO (MW 850) were prepared according to the procedures described in a patent application.[14]

Synthesis of Polyetherurethaneurea Elastomers

The polyetherurethaneurea elastomers were synthesized by the two-step solution polymerization method[15] using DMF as the solvent. All glassware was dried in an oven at 105°C overnight followed by flame drying prior to polymerization. A typical polymerization was carried out as follows:

The dried PTMO (MW 975, 113.0 g, 0.1158 mol) was placed in a three-necked round-bottom flask fitted with a dry nitrogen inlet, condenser, magnetic stirrer, and drying tube. m-TMXDI (58.28 g, 0.2385 mol) and DMF (172.4 g) were added at ambient temperature under nitrogen. Dibutyltindilaurate (added as an $\sim$ 1% solution in toluene to make 0.015% by weight of total solids) was added and the mixture was heated at 90°C for 4 h. The isocyanate content of the prepolymer solution was determined according to ASTM method D1638-74.[16]

The prepolymer solution (153.2 g) was placed in a three-necked round-bottom flask fitted with a mechanical stirrer, condenser, nitrogen inlet, and drying tube. The prepolymer was diluted to 25% solids content with DMF, and HDA (5.921 g) was added as a 10% solution in DMF with stirring over a period of about 5 min. The chain extension was carried out for 2 h at 90°C. The polymer solution was diluted with DMF to about 7% solids content and added dropwise into a large excess of deionized water. The precipitated polymer was washed with fresh deionized water overnight and then dried in a vacuum oven (0.1 Torr) at 45°C for 3 days.

The polyetherurethaneurea elastomers are designated by the monomers used in their preparation. For example, PTMO-975-EDA refers to an elastomer synthesized from m-TMXDI, PTMO with a molecular weight of 975 and EDA. The molar ratio of the diisocyanate to the macrodiol was 2.5 : 1 in all cases, except PTMO-975-EDA and PTMO-975-HDA, where the ratio was 2.0 : 1. The chain extender was added to maintain the stoichiometric balance based on the experimentally determined isocyanate content. The commercial materials Pellethane 2363-80A™ and Biomer™ (lot number BSZ 038, 30% solution in N,N-dimethylacetamide) were obtained from Dow Chemical and Ethicon, respectively. Pellethane 2363-80A is a polyetherurethane based on PTMO (MW 1000), MDI, and 1,4-butanediol. The solution grade Biomer, a polyetherurethaneurea, is based on PTMO (MW 2000), MDI, and a mixture of diamines, primarily ethylenediamine.

Size-Exclusion Chromatography (SEC)

SEC of polyetherurethaneureas was carried out on a Waters Associates chromatograph using 0.05 M lithium bromide in dimethylformamide as the mobile phase at 80°C. The flow rate was 1.0 mL/min. The

stationary phase consisted of a set of two μ Styragel HT columns (10^5 and 10^3 Å) and one PLgel (100 Å) column. The SEC system was calibrated with polystyrene standards.

Sample Preparation

After drying for 15 h *in vacuo*, polyetherurethaneureas were compression-molded into flat sheets at temperatures between 120 and 160°C and at pressures of between 1.3 and 2.7 MPa. Solvent casting was carried out from a 10% solution in DMF at 40°C in a flow of dry nitrogen. The sheets had dimensions of 60 × 100 mm and were 1 mm thick. They were cut into dumbbells of 3 cm in length and 1 cm in width; the narrow section was 1.2 cm in length and 0.4 cm in width. All samples were inspected under cross-polarizers to determine if internal stress was present. Unless specifically mentioned otherwise, all samples were stress free and showed no pattern under cross-polarizers.

Mechanical Properties

Stress–strain measurements were carried out on triplicate dumbbells with an Instron Model 4032 Universal Testing Machine. A 1 kN load cell was used and the crosshead speed was 500 mm/min.

Testing for Hydrolytic Stability

Dumbbells punched from polyetherurethaneurea sheets were encased in a PTFE sheet that was bent once and tied loosely with PTFE tape. The PTFE sheet had holes punched into it to facilitate the circulation of water; each PTFE sheet also had a binary code punched into it to facilitate sample identification. This arrangement weighted the sample so that it did not float and prevented samples from adhering to each other; the envelope was sufficiently loose so that exposure of the material to water was unhindered. The dumbbells were in complete contact with water and did not come out of the cage during testing. The hydrolysis experiments at 100°C were carried out by boiling the weighted dumbbells under reflux for 24 h in deionized water, while the 120°C hydrolysis experiments were carried out by placing the weighted dumbbells into a metal pressure vessel that was lined with glass. The pressure vessel was then filled to one-third of its capacity with water, which was ample to immerse the test specimens. It was then placed in an oven, thermostated to 120°C. After 24 h, the pressure vessel was cooled rapidly to room temperature and the contents were examined.

The dumbbells were rinsed thoroughly with deionized water and dried *in vacuo* at 40°C overnight before being subjected to tensile testing.

DSC Analysis

DSC thermograms over the temperature range −120–240°C were recorded on a Mettler DSC 30 calorimeter linked to Mettler TC 10A thermal analysis processor. The experiments were carried out at a heating rate of 5°C/min under a N_2 purge. Sample weights were 20 ± 4 mg. The samples were dried in a vacuum oven at 45°C for 24 h prior to analysis.

Spectroscopic Analysis

FTIR spectra of polymers were recorded on a Bomem Michelson series spectrometer using thin-film samples. Prepolymers were directly applied as thin films on NaCl plates and analyzed. In the case of polyetherurethaneureas, a 2% solution of the polymer in DMF was deposited as a thin film on a NaCl plate, and then the solvent was evaporated in a vacuum oven at 45°C overnight.

RESULTS AND DISCUSSION

Syntheses of Prepolymers

End-capping reactions to prepare prepolymers were monitored by analysis of the isocyanate content and by FTIR and ^{13}C-NMR spectroscopy. Analysis of the isocyanate content of the prepolymers at the end of the end-capping reaction (Table I) indicated that the content of "free" isocyanate was lower than would be expected on the basis of reactant stoichiometry, but the differences were small with the exception of PHMO-2100. The content of "free" isocyanate is defined as the concentration of isocyanate groups able to undergo the chain-extension reaction. The small differences may be attributed to possible side reactions involving adventitious impurities present in the system that can react with the isocyanate groups. Another possible reason for low isocyanate content would be the formation of allophanate linkages. However, analysis of the prepolymer prepared from PHMO-975 by IR and ^{13}C-NMR spectroscopy revealed no allophanate linkages. *m*-TMXDI and PTMO-975 were reacted in the presence of dibutyltindilaurate (0.015%) at 100°C, and samples (thin film between NaCl plates) of the reaction mixture were analyzed by FTIR spectroscopy at different time intervals. The peak

**Table I   Isocyanate Content of Prepolymers
Prepared from m-TMXDI and
Various Macrodiols**

Macrodiol (MD)	Molar Ratio (m-TMXDI : MD)	NCO (%)[a]	
		Theory[b]	Expt[c]
PTMO-975	2 : 1	3.00	2.78
PHMO-1190	2.5 : 1	3.42	3.35
PHMO-2100	2.5 : 1	2.32	1.83
POMO-1170	2.5 : 1	3.48	3.15
POMO-2050	2.5 : 1	2.36	2.27
PDMO-1270	2.5 : 1	3.20	3.14

[a] Grams of NCO per 100 g of prepolymer solution.

[b] The isocyanate content calculated based on the stoichiometry of reactants.

[c] The isocyanate content determined by using ASTM method D1638-74.

heights of absorption bands at 1722 cm^{-1} (urethane C=O) and 2258 cm^{-1} (isocyanate C=O) were used to monitor the end-capping reaction. The ratio of the height of the peak at 1722 cm^{-1} to that of the peak at 2258 cm^{-1} reached a value of 0.31 after 2 h of reaction and remained constant for up to 24 h of reaction at 100°C. This result suggests the absence of side reactions such as allophanate formation in this system. Further support was obtained by analyzing the prepolymer by ^{13}C-NMR spectroscopy, which showed only two peaks at 153.7 (C of isocyanate) and 156.1 ppm (C of urea carbonyl) in the carbonyl region of the spectrum. If a significant amount of allophanate linkages were present, a third peak in this region would be expected. The absence of allophanate linkages in this system may be attributed to steric hindrance from the methyl groups for the reaction between urethane N — H and NCO to form such linkages.

m-TMXDI prepolymers have advantages over those prepared from aromatic diisocyanates such as MDI because of the absence of side reactions. The advantages include good storage stability and usefulness in synthesis of linear polyurethanes. The good storage stability of m-TMXDI prepolymers has been demonstrated by Saxon and Chang.[5] We also have observed that the prepolymer solutions can be stored at ambient temperature in closed containers without gel formation.

Chain Extension of Prepolymers

The chain extensions were carried out by adding the diamine as a 10% (w/v) solution in DMF to the prepolymer solutions and heating to about 80°C for 2 h. Unlike the prepolymers prepared from more reactive diisocyanates such as MDI, m-TMXDI-based prepolymers did not form gels or precipitate during the chain-extension reaction, using either aliphatic or aromatic diamines. This is attributed to the low reactivity of the hindered isocyanate groups of m-TMXDI as well as to the absence of side reactions such as allophanate and biuret formation. The chain-extension reactions were usually complete in 2–3 h, and longer reaction times showed no significant increase in the molecular weights of polyetherurethaneureas as determined by SEC. On the other hand, preparation of m-TMXDI-based polyetherurethaneureas by bulk polymerization was not successful due to the difficulty in uniformly mixing the diamine chain extenders with the prepolymers in the chain-extension step. The liquid prepolymers immediately solidified upon addition of small amounts of the diamine, making further mixing impossible. The resulting polymers were low in molecular weight and high in polydispersity. To avoid this, all polyetherurethaneureas reported in this paper were prepared by the two-step solution polymerization technique.

The PTMO-based polymers were white rubbery materials soluble in solvents such as DMF, dimethylsulfoxide, tetrahydrofuran, and methylene chloride. In solvents such as ethanol, the materials softened but did not dissolve completely. The PHMO-based materials were off-white solids that were only soluble in DMF and dimethylsulfoxide. Their solubility in these solvents as lower than that of the PTMO-based materials. Likewise, the POMO- and PDMO-based materials were white solids and were soluble only in hot DMF and dimethylsulfoxide.

High molecular weight polyetherurethaneureas were prepared in high yield (> 90%) as shown in Table II by the solution polymerization method. In the PTMO series, all the diamine chain extenders, except DETDA, produced polymers with molecular weights exceeding 100,000. The low molecular weight in the case of DETDA may be a consequence of its lower reactivity due to steric hindrance. The molecular weights of the polyetherurethaneureas prepared from PHMO and POMO macrodiols were in the 45,000–94,000 range; these were lower than those of the PTMO series. This may be attributed to the lower solubilities of the PHMO- and POMO-based polyurethanes compared with those containing PTMO; the PHMO- and PDMO-based materials precipitated from DMF when cooled to room temperature. It should be noted that the molecular weights reported in Table II are relative to polysty-

Table II Molecular Weights, Yields, and Optimum Processing Temperatures of Polyetherurethaneureas Prepared from m-TMXDI

	MW by SEC		Yield (%)	Hard Segment (Wt %)	Processing Temperature (°C)
Material	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$			
PTMO-975-EDA[a]	175,000	1.44	97	37	140
PTMO-975-1,3-PDA	101,000	2.01	95	43	140
PTMO-975-1,4-BDA	223,500	1.36	90	43	140
PTMO-975-HDA[a]	114,500	1.38	97	39	140
PTMO-975-DMEDA	128,000	1.73	91	43	120
PTMO-975-p-XDA	196,400	1.48	92	45	160
PTMO-975-DETDA	44,000	1.76	96	52	140
PHMO-570-EDA	71,000	1.77	96	55	160
PHMO-570-HDA	63,400	2.2	95	57	140
PHMO-1190-EDA	57,800	2.11	96	36	160
PHMO-1190-HDA	94,000	2.04	98	39	160
PHMO-2100-HDA	53,100	1.58	97	26	140
POMO-850-HDA	68,500	1.49	92	46	140
POMO-1170-HDA	47,700	1.71	94	40	120
POMO-1170-EDA	44,700	1.71	95	37	120
POMO-2050-EDA	b	b	99	26	160
POMO-2050-HDA	b	b	92	28	140
PDMO-1270-HDA	b	b	93	38	140

[a] Melt-processed samples showed high internal stress.
[b] Not determined due to insolubility in DMF.

rene standards. It has been previously reported[17] that the absolute number-average molecular weights of polyurethanes prepared from MDI, PTMO, and 1,4-butanediol (BDO) are about 20% lower than those determined by SEC calibrated with polystyrene standards. Accordingly, the molecular weights of the polyetherurethaneureas reported in Table II may be overestimated somewhat.

Thermal Processability

All the polyetherurethaneureas were compression-molded into 1 mm-thick sheets at a temperature between 120 and 160°C. Optimum processing temperatures are listed in Table II. The optimum processing temperatures were determined by examining the test sheets, pressed at different temperatures between 100 and 180°C, for transparency, uniformity, and degree of internal stress. The internal stress in sheets was estimated by visualizing through cross-polarizers as birefringence. Deterioration of mechanical properties and polymer yellowing were experienced after processing at temperatures above 160°C. Near and below 120°C, there was insufficient fusing and mixing of the polymer to produce clear

and stress-free sheets. In the PTMO series, all polyetherurethaneureas, except PTMO-975-EDA and PTMO-975-HDA, gave sheets with very little internal stress, as evidenced by little or no birefringence when inspected under cross-polarizers. PTMO-975-EDA and PTMO-975-HDA were solvent-cast to give stress-free sheets for stress–strain measurements. Compression-molded sheets obtained from materials based on PHMO, POMO, and PDMO showed very low internal stress when viewed through cross-polarizers. These sheets were used for stress–strain measurements.

Mechanical Properties of Polyetherurethaneureas Based on α,ω-Dihydroxypoly(tetramethylene oxide)

A series of polyetherurethaneureas were prepared from m-TMXDI and PTMO-975 with a number of different diamines including primary and secondary aliphatic diamines and primary aromatic diamines. Polyetherurethaneureas with good mechanical properties were obtained as shown in Table III. Table III also shows the properties of two medical-grade polyurethanes, Biomer and Pellethane 2363-

Table III   Mechanical Properties of *m*-TMXDI-based Polyetherurethaneureas

Material	Fail Stress (MPa)	Fail Strain (%)	Stress at 100% Elongation (MPa)	Set (%)	Hardness (Shore A)
PTMO-975-EDA	27	1280	8.0	25	74
PTMO-975-1,3-PDA	13	730	2.0	60	72
PTMO-975-1,4-BDA	24	510	4.7	50	74
PTMO-975-HDA	17	460	5.6	65	72
PTMO-975-DMEDA	12	1690	1.4	25	56
PTMO-975-p-XDA	17	550	a	85	80
PTMO-975-DETDA	13	380	9.2	75	a
PHMO-570-EDA	12	200	9.0	35	a
PHMO-570-HDA	25	390	12	18	91
PHMO-1190-EDA	6.3	300	24	15	85
PHMO-1190-HDA	26	980	12	20	80
PHMO-2100-HDA	18	590	8.0	170	84
POMO-1170-EDA	22	1030	11	20	98
POMO-1170-HDA	23	920	13	40	86
POMO-2050-EDA	9.3	80	49	30	a
POMO-2050-HDA	25	590	11	184	97
PDMO-1270-HDA	20	310	15	85	a
Pellethane 2363-80A[b]	30	580	7.7	77	82
Biomer[b]	31	800	4.2	28	64

[a] Not determined.
[b] Commercial material.

80A (see Experimental section). Properties of PTMO-975-EDA and PTMO-975-1,4-BDA were comparable to those of Biomer and Pellethane 2363-80A. PTMO-975-EDA showed the best mechanical properties of the series. The results show that the number of methylene groups in primary aliphatic diamine chain extenders has a significant effect on the mechanical properties. The material with the odd number of methylene groups (PTMO-975-1,3-PDA) showed the lowest fail stress of the four materials studied. These results are consistent with the literature results.[18] In general, mechanical properties of polyurethanes containing chain extenders with an even number of methylene groups have better mechanical properties than those with an odd number of methylene groups; this is attributed to the ease of hard-segment crystallization when the number of methylene groups is even.[18] In materials containing chain extenders with an even number of methylene groups, the fail stress, fail strain, and modulus at 100% elongation gradually decreased, whereas the set increased from 25 to 65% when the number of methylene groups was increased from 2 to 6. There was no significant difference in the hard-

ness. The effect of the difference in the proportion of hard segment on the mechanical properties is considered negligible since the hard-segment content varied in a narrow range (37 and 43%), (see Table II). The difference in molecular weights of the polyetherurethaneureas may also have an effect, but it is considered unlikely to be significant since molecular weights exceeding about 25,000 are known to have little effect on mechanical properties of polyurethanes.[18,19]

The polyetherurethaneurea that contained the secondary aliphatic diamine chain extender DMED showed the lowest fail stress, modulus at 100% elongation, and set in the series. The material was very elastomeric, showing a fail strain of 1690%—highest in the series. Comparison of the properties of this material with those of PTMO-975-EDA indicates that a methyl group on each nitrogen of the diamine prevents hydrogen bonding in the hard-segment urea linkages, thus affecting crystallinity and mechanical properties.

The polyetherurethaneurea containing *p*-xylenediamine chain extender (PTMO-975-*p*-XDA) exhibited mechanical properties similar to those of

PTMO-975-HDA. The material was the hardest in the series even though its hard-segment content was comparable to the other materials in the series (see Table II). The aromatic ring of p-XDA may enhance the hardness of the polyetherurethaneurea by contributing to $\pi-\pi$ bonding interactions.

The polyetherurethaneurea (PTMO-975-DETDA) containing the sterically hindered aromatic diamine chain extender showed poor mechanical properties compared with those containing primary aliphatic diamines. The lower molecular weight of the polyurethane as well as the weaker hydrogen bonding due to steric hindrance may be responsible for the poor properties.

Mechanical Properties of Polyetherurethaneureas Based on α,ω-Dihydroxypoly(hexamethylene oxide)s

In the PHMO series, the polyetherurethaneureas containing hexamethylenediamine as chain extender showed better mechanical properties than those containing ethylenediamine, with PHMO-1190-HDA showing the best mechanical properties in this series (see Table III). This trend was the opposite of that observed for the PTMO series.

Increasing the molecular weight of the macrodiol significantly affected the mechanical properties of the materials containing EDA, whereas the effect was not so significant for those materials containing HDA. When the macrodiol molecular weight was increased from 570 to 1190, the fail stress decreased by 48% (see results in Table III for PHMO-570-EDA and PTMO-1190-EDA). On the other hand, with HDA, there was no systematic change in fail stress as the molecular weight of the macrodiol increased. Except PHMO-2100-HDA, all the other materials showed lower tensile set values than the PTMO series; the low proportion of hard segment in this material may be responsible for the high set. In general, the PHMO-based polyetherurethaneureas showed high moduli compared with the PTMO series, indicating the inherent lower flexibility of PHMO. PHMO is more hydrophobic than is PTMO (see Table IV) and, accordingly, the PHMO-based materials show higher phase separation, which may also contribute to high moduli.

Mechanical Properties of Polyetherurethaneureas Based on α,ω-Dihydroxypoly(octamethylene oxide) and α,ω-Dihydroxypoly(decamethylene oxide)

As with the PHMO-based materials, POMO-based polyetherurethaneureas containing HDA showed better mechanical properties than did those containing EDA (see Table III). The difference in properties was more significant with the higher molecular weight macrodiols than with the low molecular weight ones. With the exception of tensile set, there was no significant difference in mechanical properties of materials containing HDA when the molecular weight of POMO was increased. However, in materials containing EDA, the increase in molecular weight made the materials very stiff, showing a fail strain of only 80%. Although the reasons for this behavior are not clear, a high degree of crystallinity in both hard and soft segments may have contributed to the low fail strain. Except for the low fail strain, the mechanical properties of the PDMO-based polyetherurethaneurea were similar to those of POMO and PHMO-based materials with similar macrodiol molecular weight.

The effect of varying the number of methylene

Table IV Properties of the Pure Macrodiols

Macrodiol[a]	$\bar{M}_n$[b]	T_g^c (°C)	T_m (°C)	Contact Angle[d]		
				Sessile	Advancing	Receding
PTMO	975	−72	39	28	34	24
PHMO	1190	−47	60	30	42	< 10[e]
POMO	1170	−24	72	67	74	29
PDMO	1270	−32	75	75	85	48

[a] Macrodiols were cast from dichloromethane (except for PDMO, which was cast from carbon tetrachloride) as layers 0.1 mm thick on glass microscope slides.
[b] Molecular weights were determined by ^{1}H-NMR end-group analysis and vapor pressure osmometry (see Ref. 13).
[c] Measured by DMTA (data from Ref. 18).
[d] Air-water contact angle, measured on a modified Kernco G-11 contact-angle meter equipped with a micrometer-driven syringe.
[e] The uneven surface of this film made measurement difficult.

groups between the ether oxygens in the macrodiol on the mechanical properties of the corresponding polyetherurethaneureas can be illustrated by comparing the properties of PTMO-975-HDA, PHMO-1190-HDA, POMO-1170-HDA, and PDMO-1270-HDA (Table III). The effect of the variation of the hard-segment proportion and the macrodiol molecular weight on the mechanical properties of the four materials reported here is considered insignificant, since the percent hard segment varied in a narrow range (38–40 wt %) and the macrodiol molecular weights only varied between 975–1270. The PHMO- and POMO-based polyetherurethaneureas have the best mechanical properties (viz., high fail stress and fail strain, and low tensile set). It appears that there is an optimum combination of diisocyanate, chain extender, and macrodiol for good extensibility in this series. Furthermore, the mechanical properties are not a simple function of the number of CH_2 groups; rather, there are other factors such as the degree of phase separation and crystallinity in the soft-segment domains.

Hydrolytic Stability of m-TMXDI-Based Polyetherurethaneureas

The hydrolytic stability of the polyetherurethaneureas was investigated in water at 100 and 120°C over a period of 24 h and assessed by measuring fail stress before and after treatment. These results are shown in Table V.

In the PTMO series, the polyetherurethaneureas containing EDA, 1,4-BDA, and DMEDA were untestable for mechanical properties after both tests, indicating severe degradation. The materials containing HDA and p-XDA showed relatively better resistance. These two materials were likely to be more hydrophobic than were the other materials in the series because of the high CH_2 content in HDA and the aromatic ring in p-XDA. The high fail stress of the untreated materials appears to have no effect on the stability under the conditions used in the study; the materials with the high initial fail stresses (PTMO-975-EDA and PTMO-975-1,4-BDA) lost all strength in both tests.

As with the PTMO series, the polyetherurethaneurea containing HDA was more stable hydrolytically than those containing EDA in the PHMO series. Likewise, the same trend was observed with the POMO-based materials (see Table V). PDMO-1270-HDA exhibited good resistance to water at 100°C, but lost a lot of strength at 120°C. In general, the polyetherurethaneureas containing HDA showed better hydrolytic resistance than did the other materials. The higher hydrocarbon content in this chain extender may make the hard segment of the HDA-chain-extended polyetherurethaneureas more hydrophobic than those chain-extended with EDA.

Table V   Hydrolytic Stability of m-TMXDI-Based Polyetherurethaneureas

Material	Untreated Fail Stress (MPa)	100°C (H₂O) Fail Stress (MPa)	100°C (H₂O) % Change in Fail Stress	120°C (H₂O) Fail Stress (MPa)	120°C (H₂O) % Change in Fail Stress
PTMO-975-EDA	27	3.4	−87	0	−100
PTMO-975-1,4-BDA	24	0	−100	0	−100
PTMO-975-HDA	17	8.3	−51	4.1	−76
PTMO-975-DMED	12	0	−100	0	−100
PTMO-975-p-XDA	17	20	+22	6.6	−60
PTMO-975-DETDA	13	6.6	−50	0	−100
PHMO-570-EDA	12	8.3	−28	0	−100
PHMO-2100-HDA	18	16	−9	11	−41
POMO-1170-EDA	22	15	−35	0	−100
POMO-1170-HDA	23	18	−24	13	−42
POMO-2050-HDA	25	24	−4	15	−40
PDMO-1270-HDA	20	19	−3	0	−100
Controls					
Pellethane 2363-80A	30	29	−2	5.5	−82
Biomer	31	30	−3	17	−44

Increasing the number of methylene groups between the ether oxygens in the macrodiol also improved the resistance to hydrolysis in the 100°C water test. In the 120°C water test, the trend was, however, followed only up to POMO. Surprisingly, PDMO became brittle and lost almost all of its strength. Improved resistance can be attributed to the increasing hydrophobicity of the polyetherurethaneureas due to the macrodiol; PDMO is more hydrophobic than is PTMO because of its higher C/O ratio. The relative hydrophobicity among the four macrodiols showed the increasing order PTMO < PHMO < POMO < PDMO as determined by contact-angle measurements (see Table IV).

Several of the novel polyetherurethaneureas showed hydrolytic resistance comparable or slightly better than the commercial polyurethanes, Pellethane 2363-80A and Biomer, the latter which is an MDI-based polyetherurethaneurea. The commercial polyurethanes were used for comparison mainly because of their applications as biomaterials. In the 100°C water test, POMO-2050-HDA and PDMO-1270-HDA showed hydrolytic stability similar to Pellethane 2363-80A and Biomer. In the 120°C water test, POMO-2050-HDA exhibited resistance similar to Biomer, but better resistance than Pellethane 2363-80A. On the other hand, PDMO-1270-HDA lost almost all of its strength in the 120°C water test.

Infrared Analysis

Four polyetherurethaneureas with the same hard-segment composition but with different soft seg-

ments were analyzed by IR spectroscopy to study the effect of varying the C/O ratio in the soft segment on the extent of hydrogen bonding. The studies showed that there was no measurable difference. The IR spectrum of POMO-1170-HDA is shown in Figure 1. The IR spectra of PTMO-975-HDA, PHMO-1190-HDA, and PDMO-1270-HDA are qualitatively very similar to the spectrum shown in Figure 1. The assignments of several important peaks are shown in Figure 1.

Thermal Analysis

Thermal transitions of m-TMXDI-based polyetherurethaneureas were determined by DSC analysis of samples prepared from thin sheets. Table VI summarizes the transitions for the soft and hard segments. The soft-segment glass transition temperatures (T_g) of all the materials, except those containing PHMO, were substantially higher than the T_g values of the corresponding pure soft segments; the glass transition temperatures of pure PTMO, PHMO, POMO, and PDMO are -72, -47, -24, and $-32°C$, respectively[20] (see Table IV). Such deviations of T_g are generally considered[21] to result from hard- and soft-segment mixing. In addition, microphase separation causes anchoring of the macrodiol segments in the phase boundary, which can also raise T_g. These results indicate that the PHMO-based materials show the least amount of phase mixing between the soft and the hard segments. Except for PDMO-1270-HDA, all other materials tested showed melting endotherms in the 217–230°C temperature range. These transitions are
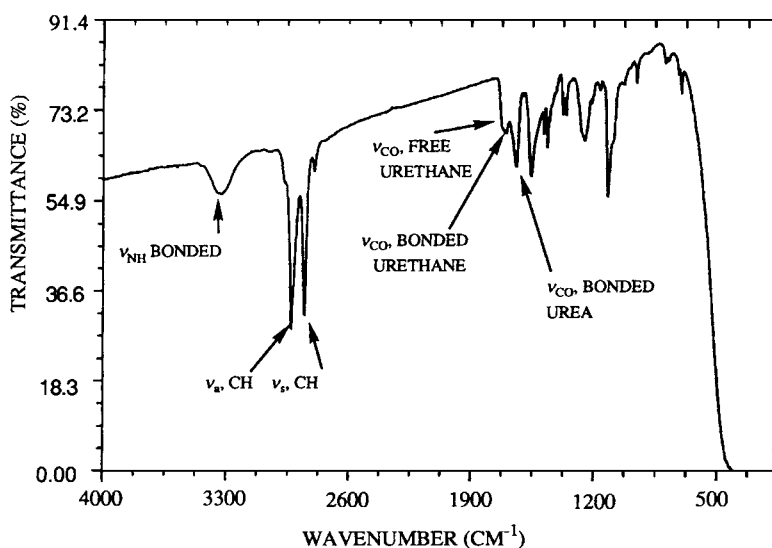

Figure 1   Infrared spectrum of POMO-1170-HDA.

attributed to the melting of crystalline regions of the hard segment. Except for PHMO-2100-HDA, the other materials showed no glass transition detectable by DSC for the hard segment, indicating high crystallinity.

The glass transition temperature (T_g) of the polyetherurethaneurea soft segment generally showed a tendency to increase as the number of methylene groups between the ether oxygens of the macrodiol was increased in the 4–10 range (see Table VI). The PTMO-based materials showed a T_g of about $-55°C$ irrespective of the type of the chain extender. However, in the PHMO series, the T_g varied between -18 and $-57°C$, showing a dependency of T_g on the molecular weight of the macrodiol as well as the type of chain extender. In this series, the T_g did not follow a trend when the molecular weight of the macrodiol was increased from 570 to 2100, but the T_g decreased from -51 to $-57°C$ when the macrodiol molecular weight was increased from 570 to 1190 and then increased to $-18°C$ for PHMO-2100. PHMO-2100-HDA also showed a melting endotherm, indicating a significant amount of crystallinity in the soft-segment domains. The high T_g for this material may indicate that the amorphous soft-segment regions are mostly in the phase boundary region. The presence of soft-segment crystallinity was also observed by Wang and Cooper[21] for polyetherurethaneureas prepared from MDI, PTMO-2000, and EDA. The materials containing lower molecular weight PHMO showed no soft-segment melting endotherms, indicating the absence of crystalline domains in the soft segment.

As with the PHMO-based polyetherurethaneureas, the T_g of materials containing POMO increased with increasing molecular weight of the macrodiol, and the material containing the higher molecular weight POMO showed a melting endotherm at $74°C$ (see Table VI). The PDMO-1270-HDA showed a T_g at $-15°C$ and a large melting endotherm at $58°C$ with a shoulder at $46°C$. The presence of a soft-segment melting endotherm is indicative of soft-segment crystallinity that increases as the number of the methylene groups between the ether oxygens increases.

CONCLUSIONS

A series of novel polyetherurethaneureas was synthesized from m-TMXDI, polyether macrodiols containing 4, 6, 8, or 10 methylene groups between the ether linkages, and aliphatic and aromatic diamines, by using the two-step solution polymerization. The resulting materials were tested for their processability, mechanical properties, and hydrolytic stability. DSC and IR spectroscopy were also used to characterize the materials.

The end-capping reaction of m-TMXDI to form the prepolymer proceeded without detectable allophanate formation. The chain extension with aliphatic and aromatic diamines yielded medium-to-high molecular weight materials in high yield ($> 90\%$). All polyetherurethaneureas were thermally processable in the 120–160°C temperature range, except the one prepared from m-TMXDI, PTMO-975, and EDA.

The mechanical properties were observed to depend primarily on the number of methylene groups between ether oxygens of the macrodiol and the type

Table VI   Thermal Transitions of m-TMXDI-Based Polyetherurethaneureas

| Material | Soft Segment | | Hard Segment | |
	T_g (°C) (onset, end)	T_m (°C)	T_g (°C)	T_m (°C)
PTMO-975-EDA	-55 ($-64, -45$)			220
PTMO-975-HDA	-57 ($-67, -47$)			217
PHMO-570-EDA	-42 ($-44, -37$)			218
PHMO-570-HDA	-51 ($-59, -43$)			220
PHMO-1186-HDA	-57 ($-65, -57$)			
PHMO-2100-HDA	-18 ($-20, -15$)	46.4	142	223
POMO-850-HDA	-44 ($-46, -34$)			
POMO-2050-HDA	-18 ($-20, -2$)	74		230
PDMO-1270-HDA	-15 ($-21, +10$)	58 (47)		

of chain extender. In the PTMO series, materials containing primary aliphatic diamine chain extenders, except 1,3-PDA, exhibited mechanical properties better than those containing secondary aliphatic or aromatic diamines.

TMXDI-containing polyetherurethaneureas containing novel soft-segments PHMO, POMO, and PDMO, showed very good mechanical properties when the chain extender was HDA. In contrast to what was observed in the PTMO-based materials, EDA chain-extended materials showed poor mechanical properties with the exception of the material containing POMO-1170 and EDA. The best mechanical properties are obtained when the macrodiol molecular weight was around 1000.

In general, polyetherurethaneureas containing HDA as the chain extender were more resistant to hydrolysis (at neutral pH) than were the other materials tested. Hydrolytic stability increased with the increasing C/O ratio of the macrodiol, although the PDMO-based material became brittle on vigorous hydrolysis.

The PHMO-based materials showed the least amount of phase mixing between hard and soft segments. This is reflected by the small difference in T_g observed for the pure macrodiol and that for the soft segment in the corresponding polyetherurethaneurea. There was no significant difference in the extent of hydrogen bonding, detectable by IR, between the samples containing the four different soft segments.

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