

Polyurethane Elastomers Based on Novel Polyether Macrodiols and MDI: Synthesis, Mechanical Properties, and Resistance to Hydrolysis and Oxidation

PATHIRAJA A. GUNATILLAKE,¹ GORDON F. MEIJS,^{1*} EZIO RIZZARDO,¹ RONALD C. CHATELIER,¹ SIMON J. McCARTHY,¹ ARTHUR BRANDWOOD,² and KLAUS SCHINDHELM²

¹CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton Victoria 3168, Australia; ²Centre for Biomedical Engineering, University of New South Wales, P.O. Box 1, Kensington, NSW 2033, Australia

SYNOPSIS

Novel polyurethane elastomers based on 4,4'-diphenylmethanediisocyanate, 1,4-butanediol, and polyether macrodiols that have 6, 8, or 10 methylene groups between the ether oxygens were prepared by two-step solution polymerization. Their mechanical properties and degradation resistance were compared with poly(tetramethylene oxide)-based polyurethanes. The new polyurethanes were more resistant to hydrolysis and to hydrogen peroxide-induced oxidation than were the poly(tetramethylene oxide)-based materials. The poly(octamethylene oxide)-based polyurethane displayed good resistance to sodium hypochlorite. 1,2-Diaminoethane chain-extended polyurethane-ureas were also prepared using the macrodiols poly(hexamethylene oxide) and poly(octamethylene oxide). They were not thermally processable or solvent-castable. Bulk synthesis of novel polyether polyurethanes yielded, in some cases, materials with improved mechanical properties compared with their solution-polymerized counterparts. The outcome of the bulk syntheses was highly dependent, however, on reaction conditions and stoichiometry.

INTRODUCTION

Segmented polyurethane elastomers generally possess excellent mechanical properties and good blood and tissue compatibility. Accordingly, they are frequently used in the construction of medical devices such as cardiac pacemakers, catheters, and heart-assist devices. Polyurethane elastomers are also used in many nonmedical applications including shoe soles, sporting equipment, artificial leathers, and cable insulation.

Segmented polyurethanes are two-phase systems, prepared from diisocyanates, chain extenders, and macrodiols. The diisocyanate and chain extender together form the so-called hard domain, which is dispersed within a matrix of the soft domain, composed of the macrodiol. Phase separation of the hard and soft domains is considered to contribute to the

outstanding mechanical properties of these materials.¹ 4,4'-Diphenylmethanediisocyanate (MDI) is a common diisocyanate for preparing elastomers, while 1,4-butanediol (BDO) is a common chain extender. Macrodiols are usually polyester- or polyether-based. Polyether macrodiols afford elastomers with improved resilience, good performance at relatively low temperatures, and resistance to hydrolytic and microbiological degradation.

Primarily because of the increased resistance to hydrolytic degradation, polyurethanes prepared from poly(tetramethylene oxide) (PTMO) macrodiols are frequently used in biomedical applications. Four commercially significant materials that incorporate this macrodiol are Pellethane[®] 2363-80A (Ref. 2) and various related grades (Dow), Biomer[®] (Ethicon),³ Vialon[®] (Deseret)⁴ and Tecoflex[®] (Thermedics).⁵ Pellethane 2102 is the Dow PTMO-based grade for nonbiomedical applications, such as cable jacketing. Although PTMO-based polyurethanes display a resistance to hydrolysis that is significantly better than poly(ethylene oxide) (PEO)-

* To whom correspondence should be addressed.

based urethanes and their polyester macrodiol counterparts, their overall stability in demanding applications, such as in long-term medical implants, remains an area in which improvement is desirable.⁶

We have recently described conditions for preparing polyether macrodiols that contain 6, 8, or 10 carbon atoms between the ether oxygens by using condensation polymerization.⁷ These polymerizations are catalyzed by sulfuric acid or Nafion-H resin and use 1,6-hexanediol, 1,8-octanediol, or 1,10-decanediol as starting materials. The resulting macrodiols are more hydrophobic than is PTMO or PEO. The purpose of this paper is to report synthetic conditions, mechanical properties, and the relative oxidative and hydrolytic stability of a series of polyurethane elastomers based on MDI, BDO, and these more hydrophobic polyether macrodiols.

Hydrogen peroxide and sodium hypochlorite were chosen as being representative common aqueous oxidative reagents; these reagents have also been implicated in biodeterioration pathways.⁸ Stability toward hydrolysis was assayed under neutral, acidic, and basic conditions. The objective was to ascertain whether improved stability to hydrolysis or oxidation would be imparted by using macrodiols with a greater C/O ratio than that of PTMO, without significantly compromising mechanical properties. We had surmised that as the hydrophobicity of the macrodiol was increased reaction of the polyurethane with aqueous reagents would be retarded; moreover, by reducing the proportion of ether linkages (and therefore the proportion of relatively labile adjacent methylene hydrogens), enhanced oxidative stability might be displayed.

MATERIALS AND METHODS

Pellethane 2363-80A was obtained from Dow Chemicals, while Biomer was obtained from Ethicon. PTMO ($\bar{M}_n = 1000$) was obtained from DuPont under the trade name Terethane. Its hydroxyl number was determined to verify that it was bis(hydroxyl)-terminated. PTMO was dried *in vacuo* for 15 h at 105°C before use.

The macrodiols, α,ω -dihydroxypoly(hexamethylene oxide) (PHMO), α,ω -dihydroxypoly(octamethylene oxide) (POMO), and α,ω -dihydroxypoly(decamethylene oxide) (PDMO) were prepared and dried as described previously.⁷ MDI was distilled under vacuum and the middle fraction (bp 130°C, 0.01 Torr) was used for polymerizations. Dimethylformamide was dried over activated 3 Å molecular

sieves and distilled under nitrogen. A small amount of MDI was added to the distillation pot to remove any amines and residual water. BDO and 1,2-diaminoethane (ED) were dried over activated 3 Å molecular sieves and purified by distillation. The numbering system used in this paper is based on the code (PU-Xy), where X refers to the number of methylenes in the repeating unit of the macrodiol and y refers to the batch number in Table I. Thus, the first entry for a PHMO-based polyurethane in Table I is given the code (PU-6a).

General Method for the Two-Stage Polymerization Procedure

Step 1: Synthesis of the Prepolymer

The macrodiol was placed in a three-necked round-bottom flask fitted with a nitrogen bleed, magnetic stirrer, condenser, and drying tube. The appropriate amount of freshly distilled MDI (150% molar excess), in sufficient anhydrous dimethylformamide to make a 50% w/w solution and stannous octoate (0.01% of total solids), was added to the flask and the mixture was heated to end-cap the macrodiol. The end-capping reaction was carried out for 2 h at 60°C for (PU-4a), 2 h at 80°C for (PU-6a), (PU-6b), and (PU-6e), and 2 h at 90°C for (PU-8a), (PU-8b), and (PU-10a). The isocyanate content of the prepolymer was determined using ASTM method D1638-74.

Step 2: Chain Extension of the Prepolymer

The prepolymer was diluted to 25% (w/v) with anhydrous dimethylformamide. The chain extender BDO (amount based on the free isocyanate content of prepolymer) was then added with stirring under a nitrogen atmosphere as a 10% solution in dimethylformamide. The addition took place at ambient temperature over a period of about 20 min. The solution was then heated to complete the chain-extension reaction. The chain extension was carried out for 4 h at 80°C for (PU-4a), 2 h at 80°C for (PU-6a) and (PU-6b), and 2 h at 90°C for (PU-8a) and (PU-10a). Chain extension with ED (PU-6e) and (PU-8b) was carried out by dropwise addition of a 10% solution of ED in anhydrous dimethylformamide to the prepolymer at 5°C over a period of about 20 min and completing the reaction by stirring at ambient temperature for 1 h.

In all the solution-polymerization experiments, the polymer was isolated by dropwise addition of the diluted (7% w/v in dimethylformamide) poly-

Table I Physical Properties of Polyurethane Elastomers Prepared from MDI, BDO, and Various Soft Segments

Polyurethane	Synthetic Method	Soft Segment	Catalyst (Concentration)	\bar{M}_n (GPC) ^a	\bar{M}_w/\bar{M}_n	Compression Molding Temperature (°C) (Pressure)	Solubility
Pellethane 2363-80A	Bulk	PTMO-1000	Undisclosed	153,000	2.3	180 (8 tons)	DMF at low conc (ca. 1%)
Biomer	Undisclosed	PTMO	Undisclosed	141,000	1.5	Not applicable	
PU-4a	Solution in DMF	PTMO-1000	Stannous octoate (0.015%)	110,000	1.5	160-180 (8 tons)	
PU-4b	Bulk	PTMO-1000	Stannous octoate (0.01%)	212,000	1.9	180 (8 tons)	
PU-4c	Bulk ^b	PTMO-1000	Stannous octoate (0.01%)	98,000	2.0	190 (8 tons)	
PU-6a	Solution in DMF	PHMO-650	Stannous octoate (0.015%)	47,300	2.1	140 (8 tons)	DMF 10%
PU-6b	Solution in DMF	PHMO-2050	Stannous octoate (0.015%)	18,600	1.9	100 (8 tons)	DMF
PU-6c	Bulk	PHMO-860	Stannous octoate (0.01%)	52,900	1.6	Not thermally processable	DMF
PU-6d ^e	Bulk	PHMO-690	Stannous octoate (0.01%)	59,200	1.5	180 (8 tons)	DMF
PU-6e ^d	Solution in DMF	PHMO-650	None	32,000	2.0	Not thermally processable	DMF (limited)
PU-8a	Solution in DMF	POMO-1700	Stannous octoate (0.015%)	25,200	1.9	160-180 (12 tons)	DMF
PU-8b ^d	Solution in DMF	POMO-1700	Stannous octoate (0.015%)	18,600	1.9	Not thermally processable	DMF (swells)
PU-10a	Solution in DMF	PDMO-1270	None	^c	—	160-180 (8 tons)	Swells in DMF
PU-10b	Bulk	PDMO-750	Stannous octoate (0.01%)	34,100	1.6	Not thermally processable	DMF (limited)
PU-10c	Bulk	PDMO-660	Stannous octoate (0.01%)	104,000	1.1	Not thermally processable	DMF (limited)
PU-10d ^e	Bulk	PDMO-660	None	55,300	1.7	200 (8 tons)	DMF

^a Polystyrene-equivalent number-average molecular weight obtained by GPC.

^b The ratio of diisocyanate : PTMO : chain extender used in this experiment was 2.50 : 1.00 : 1.47.

^c An estimate of the molecular weight could not be obtained because a suitable solvent could not be found.

^d The chain extender in this case was ED.

^e The ratio of MDI : macrodiol in these cases was 2.02 : 1; a 2.5 : 1 analog was unprocessable.

mer solution to 10 times its volume of deionized water with stirring. The precipitated polymer was filtered and thoroughly washed with fresh deionized water. It was then dried in a vacuum oven (~ 0.1 Torr) at 45°C for 72 h.

The polyurethanes (**PU-4a**), (**PU-6a**), (**PU-6b**), (**PU-8a**), and (**PU-10a**) were prepared from PTMO of $\bar{M}_n = 1000$, PHMO of $\bar{M}_n = 650$, PHMO of $\bar{M}_n = 2050$, POMO of $\bar{M}_n = 1700$, and PDMO of $\bar{M}_n = 1270$, respectively, using the above procedure. The polyurethane-ureas (**PU-6e**) and (**PU-8b**) were prepared from PHMO of $\bar{M}_n = 650$ and POMO of $\bar{M}_n = 1700$, respectively, and ED.

Bulk Polymerization

These polymerizations were carried out in a glass reaction vessel fitted with a mechanical stirrer, nitrogen bleed, and a condenser. Freshly distilled MDI was placed in the vessel and heated to 60°C under dry nitrogen. When preparing (**PU-4b**), (**PU-4c**), and (**PU-6c**) by bulk polymerization, the melted macrodiol was added to the MDI from an addition funnel over a period of 1 h and reacted for another hour at the same temperature. The isocyanate content of the prepolymer was then determined using ASTM method D1638-74. In the case of (**PU-10d**), PDMO and MDI were placed in the reaction vessel and heated at 100°C for 1 h. The isocyanate content of this prepolymer was not determined due to its insolubility in toluene.

The prepolymer was then degassed under vacuum at 40°C . The amount of the chain extender required to complete the polymerization was added from a syringe and the mixture was stirred at high speed for 1 min. Stannous octoate (0.01%, added as a 2.5% solution in toluene) was then added and stirring was continued for 30 s. The mixture was then poured onto a dish lined with Teflon-coated cloth and cured in an oven at 100°C for 15 h under a flow of dry nitrogen. In the case of the PDMO-based polyurethane (**PU-10d**), the chain extension was carried out at 100°C , but transfer of the molten mixture was difficult since the polymer solidified due to cooling during transfer. Curing in this case was carried out by heating the reaction flask to 100°C under nitrogen; the polymer was removed from the flask after cutting into small pieces.

The polyurethanes (**PU-4b**), (**PU-4c**), (**PU-6c**), (**PU-6d**), (**PU-10b**), (**PU-10c**), and (**PU-10d**) were prepared by the above procedure using PTMO, PHMO, and PDMO as macrodiols. The molecular weight of the macrodiol used in each particular synthesis is shown in Table I. Unless stated

otherwise in this table, the ratio of MDI to macrodiol was 2.5 : 1.

Sample Fabrication

After drying for 15 h *in vacuo*, polyurethanes were compression-molded at temperatures between 100 and 200°C and at a nominal load of either 8 or 12 tons. Biomer was solvent-cast in three layers directly from the 30% dimethylacetamide solution and the sheets were dried at 40°C in a flow of dry nitrogen for 7 days. The flat sheets had dimensions of 60×100 mm and were 1 mm thick. They were cut into several pieces or punched into dumbbells 3 cm in length. The straight (testing) area of the dumbbell was 13×4 mm. All samples were inspected under cross polarizers to determine if internal stress was present. All samples showed no pattern under cross polarizers, indicating that there was no detectable stress.

Degradation Experiments

Dumbbells of polyurethane were encased in a PTFE sheet that was bent once and tied loosely with PTFE tape. The PTFE sheet had holes punched in it to facilitate the circulation of the test solution; each PTFE sheet also had a binary code punched into it for sample identification. This arrangement weighted the sample so that it did not float and prevented samples from adhering to each other; the enveloping was sufficiently loose that exposure of the material to the reagent was unhindered. The treatment time in all the degradation experiments was 24 h.

The hydrolysis experiments (100°C) were carried out by boiling the weighted dumbbells under reflux for 24 h in deionized water, 2M hydrochloric acid, or 5M sodium hydroxide. The 120°C water 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 sufficient to immerse the test specimens. It was then placed in an oven, thermostatted to 120°C . After 24 h, the pressure vessel was cooled rapidly to room temperature and the contents were examined. After these treatments, the dumbbells were rinsed thoroughly with deionized water and dried *in vacuo* at 40°C overnight before being subjected to tensile testing.

Oxidative tests were carried out in a similar manner on dumbbells for 24 h by using either 25% aqueous hydrogen peroxide (prepared by dilution of

30% hydrogen peroxide from May and Baker) or by using sodium hypochlorite from freshly opened bottles (Ajax Chemicals), nominally containing 4% available chlorine.

Evaluation

Mechanical testing was carried out in triplicate with an Instron Model 4032 Universal Testing Machine. A 1 kN load cell was used and the crosshead speed was 500 mm/min.

Gel permeation chromatography was carried out at 80°C with 0.05 M lithium bromide in dimethylformamide as eluent on a Waters Associates chromatograph with 10^5 , 10^3 , and 50 Å μ -Styragel columns. The system was equipped with a refractive index detector and was calibrated with narrow distribution polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

RESULTS AND DISCUSSION

The two-stage solution polymerization method⁹ in dimethylformamide was used initially for the preparation of all polyurethanes. This preparative method gives improved control of structure relative to bulk polymerization, especially when the polymerization is highly exothermic such as when chain extending with diamines. In such cases, reaction in bulk is sometimes too rapid for effective mixing of the reactants and an inhomogeneous product results. The polymerizations were generally catalyzed with stannous octoate and the stoichiometry was generally held constant with a ratio of diisocyanate:macrodilol of 2.5 : 1, although in several of the bulk-synthesized materials, a ratio of 2.02 : 1 was used to reduce hardness and increase processability. The amount of the chain extender was adjusted to maintain the stoichiometry after assaying the isocyanate content of the prepolymer.

4,4'-Methylenediphenyldiisocyanate (MDI) was used as the diisocyanate in all polyurethanes prepared in this study; 1,4-butanediol (BDO) was the chain extender in most cases, although two polyurethane-ureas were prepared with 1,2-diaminoethane (ED). The numbering system used for polyurethanes reported in this paper is outlined in the Materials and Methods section. The commercial medical-grade material, Pellethane 2363-80A, and its solution and bulk polymerized equivalents (**PU-4a**), (**PU-4b**), and (**PU-4c**), prepared from MDI, BDO, and PTMO, were used as reference materials.

The two polyurethane-ureas were compared with Biomer—an ED chain extended polyurethane-urea analog of Pellethane 2363-80A.^{3,10,11}

Synthesis and Mechanical Properties of Polyurethanes Containing α,ω -Dihydroxypoly(tetramethylene oxide) (PTMO)

Pellethane 2363-80A was analyzed by ¹H-NMR spectroscopy to determine the ratios of MDI, PTMO, and BDO in the commercial polymer. Assuming a number-average molecular weight (\bar{M}_n) for the PTMO of 1000², Pellethane 2363-80A was shown by ¹H-NMR spectroscopy to contain MDI, PTMO-1000, and BDO in the approximate ratio 2.5 : 1.0 : 1.5. Accordingly, this stoichiometry was used as a starting point to prepare the novel materials.

When a "laboratory equivalent" (**PU-4a**) of Pellethane 2363-80A was synthesized by the solution polymerization method, the number-average molecular weight of the resulting polymer was 110,000 (Table I). This was approximately 30% lower than that of the commercial material. The material was readily moldable into flat sheets, even though it did not contain antioxidants and processing aids. The sheets were a little harder (Shore 86A) than those prepared from commercial Pellethane 2363-80A and the mechanical properties were significantly inferior (Table II). The laboratory equivalent (**PU-4a**) was much more soluble in dimethylformamide than was commercial Pellethane and was readily solvent-castable, unlike the commercial material. We considered the possibility that a small degree of allophanate cross-linking present in the commercial material, but absent in our solution-polymerized polyurethane (**PU-4a**), caused the differences in solubility and mechanical properties. Bulk synthesis is known to enhance the degree of allophanate cross-linking.¹² Accordingly, two batches of a bulk-synthesized Pellethane equivalent were prepared; one batch (**PU-4b**), had the same stoichiometry of 2.5 : 1.0 : 1.5 as the solution-polymerized material, while the other batch (**PU-4c**) had a small deficiency (2%) of chain extender compared with the stoichiometric amount, so that the excess isocyanate groups could react to form allophanate cross-links.¹² The mechanical properties (Table II) were improved on bulk synthesis and the batch that was prepared with the stoichiometry of 2.5 : 1.0 : 1.5 (**PU-4b**) had similar mechanical properties to commercial Pellethane. The batch that was slightly deficient in chain extender (**PU-4c**) had a low extensibility, probably because of the additional cross-linking.

Table II Mechanical Properties and Shore Hardness of Polyurethane Elastomers

Polyurethane	Synthetic Method	% Hard Segment (w/w)	Fail Stress (MPa)	Fail Strain (%)	Stress at 100% Strain	Set (%)	Shore A Hardness
P80A			30	542	8.2	65	82
Biomer			31	796	4.2	28	64
PU-4a	Solution	44	11	470	7.3	109	86
PU-4b	Bulk	44	31	517	9.8	73	86
PU-4c	Bulk	44	11	296	9.4	51	75
PU-6a	Solution	53	21	238	17	18	90
PU-6b	Solution	27	14	127	12	12	97
PU-6c	Bulk	47	18	345	12	70	80
PU-6d	Bulk	46	16	319	11	57	89
PU-8a	Solution	30	13	320	8	184	93
PU-10a	Solution	36	20	160	21	32	100
PU-10d	Bulk	51	25	284	20	50	97

Synthesis and Mechanical Properties of Polyurethanes Containing α,ω -Dihydroxypoly (hexamethylene oxide) (PHMO)

When the macrodiol, PHMO of $\bar{M}_n = 650$ was reacted with MDI and then chain-extended with BDO using the two-step solution polymerization method, the resulting polymer (**PU-6a**) had a number-average molecular weight of 47,300 and could be compression-molded readily at 140°C (8 tons) to give stress-free sheets (Table I). The material was significantly stronger (Table II) than the PTMO-based solution-polymerized polyurethane (**PU-4a**), although it was inferior to the bulk-synthesized PTMO-based polyurethane (**PU-4b**) or to commercial Pellethane 2363-80A. The ultimate elongation was lower than the PTMO-based materials. The material was also a little harder than its PTMO-based analogs. This is likely to be due to both the reduced percentage of oxygen in the soft segment and the reduced relative mass of soft to hard segments on account of the lower molecular weight of the PHMO macrodiol that was used. It is noteworthy that the polyurethane (**PU-6a**) displayed a relatively low set.

A polyurethane (**PU-6b**), produced from PHMO of higher molecular weight ($\bar{M}_n = 2050$) using the two-step solution polymerization method, was readily compression-molded (Table I), but gave significantly weaker sheets (Table II) than did the material produced with the lower molecular weight PHMO (**PU-6a**). The ease of processing and the mechanical weakness probably result from both the low molecular weight of the polymer and the decreased proportion (by weight) of hard segment in

the polymer. This polymer was not examined for stability to oxidative and hydrolytic attack, because of its poor mechanical properties.

Bulk-synthesized materials were also examined. The polyurethane (**PU-6c**) prepared from PHMO of $\bar{M}_n = 860$ (ratio PHMO:MDI = 2.5 : 1) could not be molded thermally; it could, however, be cast from dimethylformamide. The resulting sheet displayed good mechanical properties; it was generally a softer material than the solution-polymerized PHMO urethane (**PU-6a**). The increased softness and flexibility were likely to be due to the slightly higher molecular weight of the PHMO used in the preparation; this had the effect of increasing the weight fraction of macrodiol to hard segment in the polymer. A polyurethane (**PU-6d**) prepared from a batch of PHMO of $\bar{M}_n = 690$ and a stoichiometry of MDI:PHMO of 2.02 : 1 had similar mechanical properties to the foregoing polyurethane (**PU-6c**), although the material was surprisingly harder (Shore 89A). The weight fraction of macrodiol in this polymer was almost identical to that of the polyurethane (**PU-6c**) prepared with PHMO of lower molecular weight but a higher molar proportion of the macrodiol. The molecular weights of the two polyurethanes (**PU-6c**) and (**PU-6d**) were similar.

When the prepolymer used to prepare the polyurethane (**PU-6a**) containing PHMO of $\bar{M}_n = 650$ was reacted with ED rather than with BDO, the resulting polymer (**PU-6e**) could not be molded thermally, nor was it sufficiently soluble in dimethylformamide or *N,N*-dimethylacetamide to enable solvent-casting. A GPC analysis was carried out on a very dilute solution; the number-average molecular weight was 32,000. Because of the difficulty in fab-

ricating uniform test pieces, we did not determine the mechanical properties of the polymer, nor investigate its stability toward oxidation or hydrolysis.

Synthesis and Mechanical Properties of Polyurethanes Containing α,ω -Dihydroxypoly(octamethylene oxide) (POMO)

Reaction of POMO of $\bar{M}_n = 1700$ with MDI in dimethylformamide gave a prepolymer that was further treated with BDO to afford a polyurethane (**PU-8a**) of molecular weight $\bar{M}_n = 25,200$ that could be compression-molded at 160–180°C (12 tons). The material showed elastomeric properties (Table II), although they were somewhat inferior to those of the PTMO-based polyurethane (**PU-4a**). The polyurethane was harder (Shore 93A) than either the PTMO-based or PHMO-based polyurethanes (**PU-4a**) or (**PU-6a**) of similar composition even though the macrodiol, being of higher molecular weight, represented a greater weight fraction of the polymer (see Table II). It appears that POMO as a soft segment imparts a greater hardness and rigidity to the polyurethane and that POMO is a less flexible or less "soft" macrodiol than is PTMO. This is reflected in its glass transition temperature, which is significantly higher than those of the macrodiols with fewer carbons between the ether linkages (see Table III).

The ED-extended polyurethane prepared from POMO and MDI (**PU-8b**) was neither moldable thermally nor solvent castable, although the material did swell somewhat in dimethylformamide. It was not possible to determine the molecular weight of the polymer by GPC. It appears that the ED-extended, MDI-based polyurethane-ureas derived

from PHMO and higher homologs are of little practical utility owing to the difficulty in fabrication.

Synthesis and Mechanical Properties of Polyurethanes Containing α,ω -Dihydroxypoly(decamethylene oxide) (PDMO)

The polyurethane (**PU-10a**) prepared by two-stage solution polymerization of PDMO of $\bar{M}_n = 1270$, MDI, and BDO gave a material that was thermally processable at 160–180°C (8 tons), but was not soluble in dimethylformamide or dimethylacetamide. Because of the insolubility of the polymer, an estimate of its molecular weight was not obtained. The sheet molded from this polymer was reasonably strong but it tolerated only modest amounts (ca. 160%) of strain before failure. The physical properties quoted in Table II show the polyurethane to be relatively hard and inflexible as perhaps might be anticipated from the low oxygen content of the macrodiol. Bulk polymerization at an isocyanate:macrodiol ($\bar{M}_n = 750$) ratio of 2.5 : 1 gave a material (**PU-10b**) that was not processable either thermally or by solvent-casting. Bulk synthesis using an isocyanate:macrodiol ($\bar{M}_n = 660$) ratio of 2.02 : 1 in the presence of stannous octoate catalyst also gave an unprocessable material (**PU-10c**). When the catalyst was omitted from the reaction, however, a processable urethane (**PU-10d**) was obtained. Presumably, the lower molecular weight of the latter polyurethane ($\bar{M}_n = 55,300$) contributed to its thermal processability. The mechanical properties of this material (**PU-10d**) showed that it was stronger and more extensible than the solution-polymerized PDMO-based polyurethane (**PU-10a**). As well as the difference in the preparative method, there was significantly more of the hard segment present in

Table III Properties of the Pure Macrodiols

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

^a Macrodiols were cast from CH₂Cl₂ (except for PDMO, which was cast from CCl₄) as layers 0.1 mm thick on glass microscope slides.

^b Determined by ¹H-NMR end-group analysis.

^c Measured by DMTA (data from Ref. 13).

^d Air-water contact angle, measured on a modified Kernco G-II contact-angle meter equipped with a micrometer-driven syringe.

* The uneven surface of this film made measurement difficult.

the bulk-synthesized polyurethane (**PU-10d**); this was likely to account for the increase in mechanical strength.

Resistance to Hydrolysis and Oxidation

To examine the effect of reducing the relative number of oxygen atoms in the soft segment on polymer stability, the solution-polymerized polyurethanes prepared from PTMO, PHMO, POMO, and PDMO were assessed by a series of tests involving subsection of the dumbbells prepared from the polymer to drastic hydrolytic conditions, at neutral, high, and low pH. Oxidative stability was assessed by subsection of the materials to refluxing peroxide and hypochlorite. All testing was carried out on triplicate dumbbells for 24 h. The results are reported in Table IV. Reduction in the fail stress of the polymer after treatment was the criterion used to assess stability. The neutral hydrolysis experiment was carried out at 100°C at atmospheric pressure as well as at 120°C in a closed pressure vessel. While most materials were quite stable to water at 100°C for 24 h (Table IV), there was clearly degradation at 120°C. In some respects, since the oxidations were carried out in aqueous solution at 100°C, the 100°C water experiment can be used as a control experiment to separate the effect of the oxidative agent from background hydrolysis resulting from the water in the mixture. The difference between the mechanical properties of untreated polyurethanes and those after treatment with 100°C water, however, was mar-

ginal; in addition, too much credence cannot be placed on the separation of oxidative and hydrolytic effects, since there was no buffering of the solutions to exclude pH variations. The hypochlorite solution was, in fact, quite alkaline at pH = 13.

The data in Table IV show that, although there was little degradation, if any, in water at 100°C over 24 h, subsection of the materials to water at 120°C in a closed vessel for the same period of time was highly discriminatory. Commercial Pellethane 2363-80A was affected most, losing 80% of its strength (fail stress) after treatment, while Biomer lost 45% and the PTMO-based laboratory synthesized material (**PU-4a**) lost 36%. The extreme sensitivity of Pellethane 2363-80A to these conditions may be due to breakage of allophanate cross-links (known to be readily susceptible to hydrolysis,^{12,14} leading to a very significant reduction in mechanical properties compared with the solution-polymerized polyurethane (**PU-4a**) of nominally similar composition; it is perhaps fortuitous that the fail strain of the 120°C water-treated Pellethane 2363-80A is almost identical to that of the laboratory "analog" (**PU-4a**) subjected to the same conditions.

Treatment of the polyurethanes (**PU-6a**) and (**PU-8a**) prepared from PHMO and POMO in 120°C water led to only a 15% reduction in the fail stress, while the polyurethane (**PU-10a**) prepared from PDMO exhibited the lowest reduction in fail stress (5%) of the series. The improved stability of the PHMO-, POMO-, and PDMO-based polyurethanes is probably due to a decreased hydrophilicity

Table IV Resistance to Hydrolysis and Oxidation

Polyurethane	Fail Stress (MPa) [Change Relative to Untreated]						
	Untreated	Water (100°C)	Water (120°C)	HCl	NaOH	H ₂ O ₂	NaOCl
Pellethane 2363-80A	30	29 [-3%]	6 [-80%]	14 [-53%]	19 [-37%]	16 [-47%]	20 [-33%]
Biomer	31	30 [-3%]	17 [-45%]	5 [-84%]	13 [-58%]	0 [-100%]	20 [-35%]
PU-4a	11	10 [-9%]	7 [-36%]	8 [-27%]	8 [-27%]	8 [-27%]	0 ^a [-100%]
PU-6a	19	20 [+5%]	16 [-16%]	17 [-11%]	18 [-5%]	17 [-11%]	12 [-37%]
PU-8a	13	14 [+8%]	11 [-15%]	11 [-15%]	13 [-0%]	12 [-8%]	11 [-15%]
PU-10a	20	19 [-5%]	19 [-5%]	21 [+5%]	17 [-15%]	19 [-5%]	0 ^b [-100%]

^a The material dissolved completely.

^b This polyurethane became brittle.

imparted by fewer oxygens in the macrodiol. Table III lists the hydrophilicity as measured by air-water contact angles of the pure macrodiols. Although POMO has a greater ratio of carbon to oxygen than does PHMO, the hydrolytic stability as measured in this experiment was similar; this can be rationalized on the grounds that the greater molecular weight of the soft segment used to prepare the POMO-based polyurethane (**PU-8a**) leads to an increased oxygen content in the final polymer on a weight basis. The PDMO-based polyurethane is clearly the most resistant to hydrolysis under these conditions; its soft segment is also the most hydrophobic.

The results in Table IV for acid hydrolysis follow the same general pattern, with the PTMO-based materials, Pellethane 2363-80A, Biomer, and the laboratory-synthesized material (**PU-4a**) performing poorly. Biomer, especially, was susceptible to acid hydrolysis. This undoubtedly is a consequence of its polyurethane-urea structure—urea groups are especially prone to acid hydrolysis.¹⁵ Again, it is noteworthy that the novel materials (**PU-6a**), (**PU-8a**), and (**PU-10a**) displayed a good resistance to acid-catalyzed hydrolytic degradation, perhaps again on account of their greater hydrophobicity and consequent resistance to penetration by the reagents.

With sodium hydroxide, the novel materials performed better than the PTMO-based polyurethanes, although the trend within the series PHMO, POMO, and PDMO appears not to be maintained. The reductions in mechanical performance between the samples (**PU-6a**), (**PU-8a**), and (**PU-10a**) after treatment, however, were probably of the order of the experimental errors in determination of the fail stresses. Accordingly, we conclude only that these samples as a group are more resistant to hydroxide than are the PTMO-based samples.

The oxidative tests provided a significant discrimination between materials. The PTMO-based polyurethane-urea, Biomer, proved especially prone to degradation in refluxing 30% hydrogen peroxide, while Pellethane 2363-80A was inferior to its synthetic analog (**PU-4a**) in terms of decrease in fail stress. The final fail stress of the commercial Pellethane, however, was greater than the synthetic analog; this arises because of the superior initial mechanical strength of the commercial material compared with the solution-polymerized PTMO-based polyurethane (**PU-4a**). The novel materials, (**PU-6a**), (**PU-8a**), and (**PU-10a**), showed comparatively little degradation on treatment with hydrogen peroxide. The fewer oxidizable C—H

bonds adjacent to oxygen in the soft segment may account for these observations. There is a trend in the data in Table IV toward increased peroxide stability as the C/O ratio in the soft segment is increased, although the discrimination between the performance of PHMO, POMO, and PDMO in these experiments is too small to affix great significance.

In contrast, there was no correlation between the number of carbons between the ether linkages in the macrodiol and the stability of the polyurethane toward boiling sodium hypochlorite solution (containing 4% available chlorine). The POMO-based polyurethane (**PU-8a**) performed the most satisfactorily. Although hypochlorite is an oxidizing species, the reaction of hypochlorites with polyurethanes is believed not to occur initially at the soft segment; *N*-halogenation may well be the first step.¹⁶ It is noteworthy that the polyurethanes (**PU-4a**) and (**PU-10a**) behaved quite differently in hypochlorite, despite the identical (zero) fail stresses reported in Table IV; the PTMO-based urethane (**PU-4a**) dissolved completely, while the PDMO-based urethane pitted and became very brittle. The other urethanes, unlike those exposed to peroxide, displayed significant surface tack after hypochlorite treatment; we conclude that factors other than hydrophilicity and the availability of oxidizable C—H bonds in the soft segment are the determining factors in the hypochlorite oxidation of these elastomers.

CONCLUSIONS

Thermally moldable polyurethane elastomers were readily prepared from MDI, BDO, and the macrodiols, PHMO, POMO, and PDMO, by solution polymerization. The equivalent polyurethane-ureas, chain extended with ED, however, were not processable thermally or by solvent-casting. The bulk synthesis of a polyurethane-containing PTMO gave a material that had significantly improved mechanical properties over the solution polymerization. However, the properties of other bulk-synthesized materials, especially the processability, appeared to be quite dependent on the formulation and experimental conditions; there is likely, therefore, to be substantial scope for the optimization of properties by minor changes.

With solution-polymerized polyurethanes, the materials became harder as the number of methylenes between oxygens in the macrodiol increased. Generalizations about the other mechanical properties were difficult to make, but it was apparent that the extensibility decreased and that the ma-

terials became less flexible with the incorporation of higher macrodiols, such as PDMO. Two materials based on PHMO, (PU-6a) and (PU-6d), were noteworthy for their good mechanical properties, while being readily processable thermally.

The polyurethanes prepared from the soft segments PHMO, POMO, and PDMO [(PU-6a), (PU-8a), and (PU-10a)] were significantly more resistant to neutral, acidic, and basic hydrolysis than were PTMO-based materials; in addition, they exhibited improved resistance to hydrogen peroxide media at 100°C, relative to laboratory-prepared PTMO-based materials and the commercial standards, Pellethane 2363-80A and Biomer. The POMO-based material (PU-8a) displayed a good tolerance to hot sodium hypochlorite solution.

The suitability of the novel materials incorporating PHMO, POMO, and PDMO is currently being assessed for various demanding applications in which stability is important, including potential use as biomedical materials. For long-term use in implantable devices, both biocompatibility and stability *in vivo* is an important criterion. Results from implant studies and from bio- and hemocompatibility evaluations will be reported separately.

The assistance of Donna McIntosh, Edith Cheong, and Kate Noble is gratefully acknowledged. Support was provided under the Generic Technology component of the Australian Government Industry Research and Development Act 1986, in conjunction with the Medical Engineering Research Association.

REFERENCES

1. W. Meckel, W. Goyert, and W. Wieder, in *Thermoplastic Elastomers. A Comprehensive Review*, N. R. Legge, G. Holden, and H. E. Schroeder, Eds., Hanser, Munich, 1987, p. 13.
2. V. Poirier, in *Synthetic Biomedical Polymers*, M. Szycher and W. J. Robinson, Eds., Technomic, Westport, CT, 1980, p. 73.
3. M. D. Lelah and S. L. Cooper, *Polyurethanes in Medicine*, CRC Press, Boca Raton, FL, 1986, Chap. 3.
4. R. J. Zdrahala, in *Polyurethanes in Biomedical Engineering II*, H. Plank et al., Eds., Elsevier, Amsterdam, 1987, p. 1.
5. M. Szycher, V. Poirier, and D. Dempsy, *Soc. Plast. Eng., Tech. Pap.*, **25**, 743 (1979).
6. M. Szycher, *J. Biomat. Appl.*, **3**, 297 (1988).
7. P. A. Gunatillake, G. F. Meijs, R. C. Chatelier, D. M. McIntosh, and E. Rizzardo, *Polym. Int.*, to appear.
8. M. L. Karnovsky, J. Lazins, and S. Simmons, in *Mononuclear Phagocytes in Immunity, Infection and Pathology*, R. van Furth, Ed., Blackwell, Oxford, 1975, p. 423.
9. D. J. Lyman, *J. Polym. Sci.*, **45**, 49 (1960).
10. J. M. Richards, W. H. McClennen, H. L. C. Meuzelaar, D. E. Gregonis, W. M. Reichert, and M. A. Helle, *Macromolecules*, **18**, 496 (1985).
11. J. Belisle and S. K. Maier, *J. Biomed. Mater. Res.*, **24**, 1585 (1990).
12. R. Arshady and M. H. George, *Polym. Commun.*, **31**, 448 (1990).
13. J. Perena and C. Marco, *Makromol. Chem.*, **181**, 1525 (1980).
14. J. H. Saunders and K. C. Frisch, *Polyurethanes. Chemistry and Technology*, Wiley-Interscience, New York, 1962, p. 322.
15. T. M. Chapman, *J. Polym. Sci. Part A Polym. Chem.*, **27**, 1993 (1989).
16. C. H. Bamford and I. P. Middleton, *Eur. Polym. J.*, **19**, 1027 (1983).

Received September 3, 1991

Accepted November 7, 1991