

# Polyurethane Elastomers with Low Modulus and Hardness Based on Novel Copolyether Macrodiols

PATHIRAJA A. GUNATILLAKE, GORDON F. MEIJS, SIMON J. MCCARTHY, NICOLE SHERRIFF

Cooperative Research Centre for Cardiac Technology, CSIRO Division of Chemicals and Polymers, Private bag 10, Rosebank MDC, Victoria 3169, Australia

Received 27 June 1996; accepted 27 July 1996

**ABSTRACT:** A series of copolyether macrodiols was prepared from either 1,10-decanediol or 1,6-hexanediol, by acid-catalyzed condensation polymerization using several comonomers to investigate the effect of copolymerization on reducing macrodiol crystallinity. The comonomers used to disrupt crystallinity included 2,2-diethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, and 1,7-heptanediol. The product copolyethers were identified as hydroxy terminated copoly(alkylene oxides) by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. Based on NMR results, the structures of the copolyethers were established as consisting of blocks of the principal monomer with comonomer 2,2-diethyl-1,3-propanediol incorporated to form only the end structural unit, whereas 1,4-cyclohexanedimethanol incorporated to form the end unit as well as part of the main chain. DSC results confirmed that the copolymerization produced macrodiols with lower crystallinity and lower  $T_g$  than those of the corresponding homopolyethers of the principal monomers, with two exceptions. The exceptions were 1,6-hexanediol/1,10-decanediol, and 1,10-decanediol/1,7-heptanediol copolyethers where no reduction in crystallinity was observed. A series of polyurethane elastomers with a constant hard segment percentage (40 wt %) was prepared using 4,4'-methylenediphenyl diisocyanate and 1,4-butanediol as the hard segment. Tensile test results and Shore hardness measurements demonstrated that copolyether macrodiols produced several polyurethanes with lower modulus and hardness than those of polyurethanes based on homopolyethers of the principal monomers. Of the comonomers studied, 2,2-diethyl-1,3-propanediol-based copolyether produced the polyurethane with the lowest hardness and modulus. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1373–1384, 1997

**Key words:** Copolyether macrodiols; polyurethane elastomers; synthesis; characterization; thermal and mechanical properties

## INTRODUCTION

Polyurethane elastomers are used in medical implants because of their excellent mechanical properties and relatively good hemo and histocompatibilities.<sup>1</sup> These elastomers are segmented copolymers consisting of “soft” segment domains derived

from a macrodiol, and “hard” segment domains derived from a diisocyanate and a chain extender. Generally the two segments are incompatible, resulting in microphase separation, which is primarily responsible for their excellent mechanical properties. The hard-segment structure and weight fraction, soft-segment structure, molecular weight, polydispersity, and crosslinking in either phase influence phase separation and copolymer properties.<sup>2</sup>

Polyurethane elastomers based on polyether macrodiol, poly(tetramethylene oxide) (PTMO) is

---

Correspondence to: Pathiraja A. Gunatillake.  
Contract grant sponsor: Commonwealth Government, Cooperative Research Centres Program.  
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/101373-12

widely used in the construction of implantable medical devices such as pacemakers, defibrillators, catheters, and heart-assist devices. However, it is reported that when implanted for long periods of time the polyurethanes degrade, resulting in surface cracking. This phenomenon, known as environmental stress cracking, is generally accepted to involve an oxidative type degradation centered around the polyether soft segment.<sup>3</sup> Recently, we reported<sup>4</sup> that polyurethanes based on macrodiols developed in our laboratories show significantly improved resistance to stress cracking over that based on PTMO, mainly due to their lower ether oxygen content. These new macrodiols were poly(hexamethylene oxide) (PHMO), poly(octamethylene oxide) (POMO), and poly(decamethylene oxide) (PDMO). Polyurethanes based on these macrodiols generally exhibit higher hardness and modulus relative to those observed for PTMO-based polyurethane having a comparable weight percentage of soft segment.<sup>4</sup> The high modulus and hardness are attributed to increased phase separation resulting from the increased hydrophobicity and paracrystallinity of the soft segment, since the new macrodiols have a higher ratio of methylene groups to ether oxygen than in PTMO.

There is a demand for "soft" and more flexible polyurethane elastomers, especially for medical implant applications. Although one can prepare soft polyurethanes by formulation variations, i.e., by increasing the soft segment content, the resulting polyurethanes are poor in mechanical properties as well as resistance to environmental stress cracking.<sup>5</sup> For example, PTMO-based commercial polyurethane Pellethane 80A is significantly less resistant to stress cracking than the corresponding harder grade Pellethane 55D.<sup>6</sup> In this study we have investigated a different method of preparing soft polyurethanes. This involves synthesis of macrodiols with reduced crystallinity so as to maintain a low level of paracrystallinity in the soft segment of the resulting polyurethane. Such macrodiols were prepared by copolymerizing linear diols such as 1,6-hexanediol with a relatively low level of a branched diol such as 2,2-diethyl-1,3-propanediol, which introduces structural irregularity to the macrodiol structure. The investigation involved 1,6-hexanediol (HD) and 1,10-decanediol (DD) as the two principal monomers, while 1,4-cyclohexanedimethanol (CHDM) and 2,2-diethyl-1,3-propanediol (DEPD) were chosen to introduce irregularity to

the otherwise ordered structures of PHMO and PDMO, the corresponding homopolyethers of the principal monomers. Two other systems involving linear diols with odd and even numbers of methylene groups were also investigated for slight disruption of macrodiol crystallinity. The copolymerization procedure was similar to the method we reported<sup>7</sup> for the synthesis of PHMO and PDMO. This paper reports the synthesis and characterization of such copolyether macrodiols, and synthesis and properties of polyurethane elastomers prepared from them. The biostability of the resulting polyurethanes will be reported elsewhere.

## EXPERIMENTAL

### Materials

1,10-Decanediol, 1,6-hexanediol, 1,7-heptanediol (HPD), and 1,4-cyclohexanedimethanol (Aldrich) were used as received. 2,2-Diethyl-1,3-propanediol (Aldrich) and 4,4'-methylenediphenyl diisocyanate (MDI) were distilled under vacuum and the middle fractions used for experiments. 1,4-Butanediol (BDO) (Aldrich) was dried over activated 3 Å molecular sieves, distilled under vacuum, and the middle fraction used for polymerizations. Poly(hexamethylene oxide) (PHMO) and poly(decamethylene oxide) (PDMO) were prepared by the acid-catalyzed condensation polymerization as reported previously.<sup>7</sup>

### Copolyether Macrodiol Synthesis

The synthesis of the macrodiols was carried out using a method similar to that reported<sup>7</sup> for the synthesis of poly(hexamethylene oxide) by acid-catalyzed condensation polymerization. Unless otherwise indicated, all copolymerizations were carried out using a monomer mixture containing 80 wt % of the principal monomer and 20 wt % of the second comonomer. A typical procedure is as follows.

1,10-Decanediol (80 g, Aldrich) and 1,4-cyclohexanedimethanol (*cis/trans* mixture, 20 g, Aldrich) were placed in a 500 mL two-necked round bottom flask. Concentrated sulfuric acid (1.0 mL) after diluting four times with deionized water, was added to the monomer mixture in the flask at 70°C with rapid stirring and nitrogen bubbling. The flask was then fitted with a distillation head, condenser, and a thermometer. The polymeriza-

tion was carried out for 4.5 h by placing the flask in an oil bath at 170°C and distilling off the condensed water. Bubbling of nitrogen was maintained during the reaction to facilitate faster removal of condensed products. The progress of the polymerization reaction was monitored by analyzing a sample of the crude product by <sup>1</sup>H-NMR spectroscopy.

The molten polymer was added to 1 L of boiling deionized water and refluxed for 15 h. After this period the mixture was allowed to cool to room temperature. Once the polymer layer had solidified, water was decanted off and another 1 L portion of fresh boiling deionized water was added and refluxed for 2 more hours. The process was repeated several times until the washings were neutral as tested by a pH meter. Typically, six such washings were sufficient for complete removal of the acid catalyst. The polymer was dried at 130°C for 4 h under vacuum (0.1 torr). Yield 67 g.

All copolyether macrodiols are designated by using the abbreviation of the principal monomer followed by the abbreviation of the second comonomer. For example, copolyether macrodiol designated as DD-DEPD represents a macrodiol prepared by using 80 : 20 (w/w) mixture of 1,10-decanediol and 2,2-diethyl-1,3-propanediol, respectively. All copolymers were prepared by using 80 : 20 (w/w) mixture of the principal monomer and the comonomer, respectively, and the only exception being DD/CHDM (4 : 6) where the ratio was 40 : 60 (w/w).

### Hydroxyl Number Determination

The hydroxyl number of the purified and dried copolyether macrodiol was determined by phthalic anhydride reflux procedure in accordance with ASTM method D 2849.<sup>8</sup>

### Spectroscopic Analysis

<sup>1</sup>H (200.1 MHz) and <sup>13</sup>C (50.3 MHz) NMR spectra were recorded on a Bruker FT-NMR spectrometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the macrodiols were obtained at ambient temperature from 4 to 10% (w/v) solutions in CDCl<sub>3</sub>.

### Polyurethane Synthesis

All polyurethanes were prepared by using a one-step bulk polymerization procedure. A typical example is described below.

Predried copolyether macrodiol DD-DEPD (40 g, MW 874.52), 1,4-butanediol (4.03 g) and stannous octoate (0.01 wt % of total solids) were placed in a 250 mL polypropylene beaker and degassed at 80°C in an oven under a vacuum of 2 mm Hg for 1.5 h. Molten MDI (22.64 g) was weighed into a wet tared 50 mL polypropylene beaker and quickly poured into the macrodiol mixture while rapidly stirring with a stainless steel spatula under a nitrogen blanket. After stirring for 30 s the viscous polymer was poured onto a Teflon coated metal pan and cured at 100°C for 4 h in an oven under dry nitrogen.

### Size Exclusion Chromatography

Size exclusion chromatography of macrodiols was carried out on a Waters ALC instrument using tetrahydrofuran as the mobile phase at 30°C. The stationary phase consisted of a set of five Ultrastragel columns (10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500 Å). Size exclusion chromatography of polyurethanes was carried out at 80°C with 0.05M lithium bromide in *N,N*-dimethylformamide as eluent on a Waters Associates Chromatograph with two  $\mu$ -Styragel (10<sup>5</sup> and 10<sup>3</sup> Å) and one PLgel (50 Å) columns. Both systems were equipped with a refractive index detector and were calibrated with narrow distribution polystyrene standards. Results are expressed, therefore, as polystyrene-equivalent molecular weights.

### Sample Preparation for Tensile Testing

After drying for 15 h at 65°C *in vacuo* (0.1 torr), polyurethane samples were compression-molded into flat sheets at temperatures between 190 and 200°C under a nominal load of 8 tons. The sheets had dimensions of 60 × 100 mm and were 1 mm thick. They were cut into dumb-bells 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. All samples were stress free and showed no pattern under cross-polarizers. Dumb-bells were stored under ambient conditions for 4 weeks before tensile tests and hardness measurements were carried out.

### Mechanical Properties

Mechanical testing was carried out with an Instron Model 4032 Universal Testing Machine. A

1 kN load cell was used and the crosshead speed was 500 mm/min. The results reported are the median values for six replicates. Hardness measurements were carried out using a Shore A Durometer.

### Differential Scanning Calorimetry

The samples were dried at 65°C for 48 h under vacuum (0.1 torr) and subjected to 10 min annealing at 120°C and rapid cooling to -150°C prior to recording thermograms. DSC thermograms over the temperature range -150 to 240°C were recorded on a Mettler DSC 30 calorimeter linked to a Mettler TC 10A thermal analysis processor. The experiments were carried out at a heating rate of 10°C/min under nitrogen purge. Sample weights were 15–25 mg.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Macrodiols

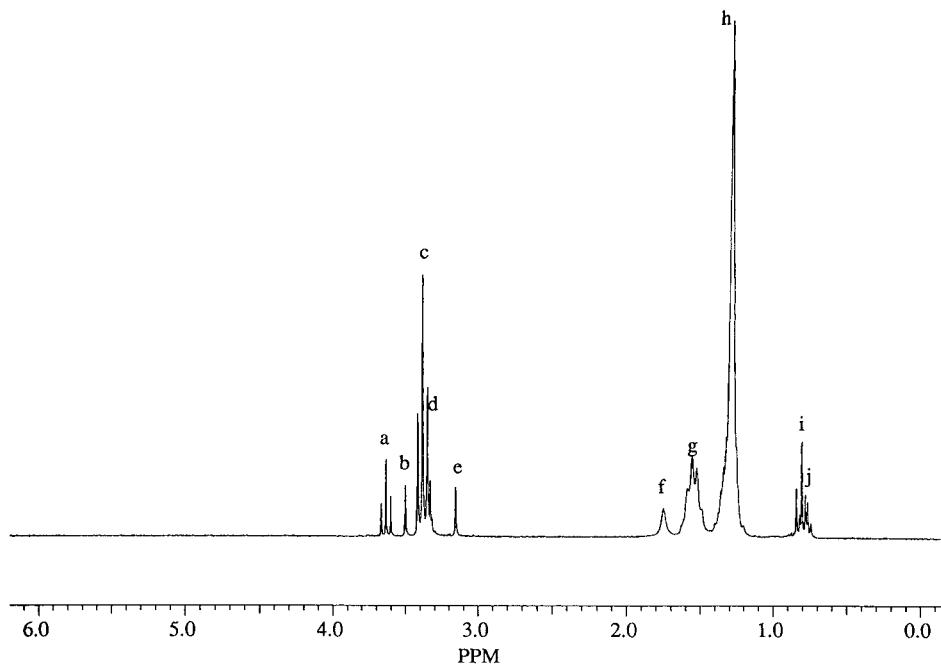
The condensation-copolymerization of 1,10-decanediol (DD) and 2,2-diethyl-1,3-propanediol (DEPD) proceeded with the distillation of condensed water. The reaction mixture turned from colorless to pale yellow as the polymerization progressed. The polymerization was monitored by <sup>1</sup>H-NMR analysis of a sample of the reaction mixture at different reaction times. The progress of the polymerization was indicated by the appearance of new NMR signals due to CH<sub>2</sub> protons adjacent to ether oxygens respectively from the polymerization of DD and DEP (triplet at 3.40 and singlet at 3.15 ppm) which were absent at the start of the polymerization. The signal areas for these two signals increased as the polymerization progressed while the areas of the signals due to methylene groups adjacent to hydroxyl end groups (triplet at 3.63 and singlet at 3.50 ppm, respectively, for DD and DEP) decreased. Further, the SEC analysis of the reaction mixture after 4.5 h of reaction verified that the polymerization reaction has occurred.

Figure 1 shows the <sup>1</sup>H-NMR spectrum of the purified copolymer prepared from DD and DEP. The NMR spectrum is in agreement with the copolymer consisting of structures shown in Scheme 1 where the main chain of the copolymer is derived from DD, while the end functional groups are hydroxyl. The assignment of NMR signals was

based on NMR data for respective monomers as well as those for the homopolymer PDMO.<sup>7</sup>

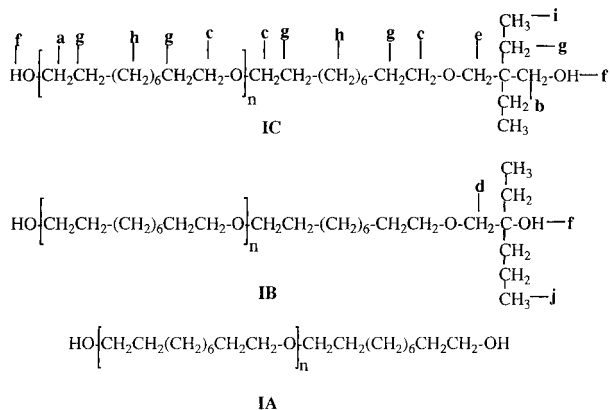
NMR data strongly indicated that the incorporation of 2,2-diethyl-1,3-propanediol to the copolymer is primarily as an end structural unit. If DEP reacted fast the most likely method of its incorporation to the copolyether chain would be to the main structure, and little or no end groups would be resulting from that. The NMR signal (3.15 ppm, signal **e**) area for CH<sub>2</sub> adjacent to ether oxygen and the CH<sub>2</sub> adjacent to end hydroxyl group (3.50 ppm, signal **b**) are equal, further confirming that DEP is present as an end group of the copolyether. The likelihood of the product being a mixture of two homopolymers is very low, since under the same polymerization conditions DEP did not homopolymerize. For example, in a separate experiment this monomer was homopolymerized under identical reaction conditions, but the molecular weight of the product as determined by SEC was only 214. The lower reactivity of DEP is attributed to steric factors. These results clearly demonstrated that under the polymerization conditions employed DEP copolymerizes with DD to give a copolymer with DEP as an end unit, and the absence of any blocks derived from it. It is possible that some polymer chains may have both end units derived from DEP, however, the concentration of such structures would be very low since DD was the major component (75 mol %) in the monomer feed.

The <sup>1</sup>H-NMR results also indicated the presence of three different types of end monomer units. As expected, the major unit is that resulting from DD. The other two end units are derived from DEP. The molar ratio of end units based on DD and DEP, calculated from NMR signal areas, (signals **a** and **b** in Fig. 1) is 2 : 1. The molar ratio of the respective monomers in the feed was 3.08 : 1. Since the copolymerization is step-growth type, if the two monomers had equal reactivity one would expect the end monomer unit molar ratio to be equal to that of the monomer feed. The observed high ratio is consistent with DEP being incorporated to the copolymer as an end unit only, indicating its lower reactivity. The formation of a second type of end unit from DEP (see structure **IB**) is considered to be a result of an ethyl group migration during polymerization. It is well known that diols such as DEP undergo rearrangements involving migration of the ethyl group under acid-catalyzed reaction conditions.<sup>9</sup> This would result in a chain with tertiary hy-



**Figure 1** 200.1 MHz  $^1\text{H}$ -NMR spectrum of purified DD/DEPD copolymer.

droxyl group as shown in structure **IB**. The  $\text{CH}_2$  protons adjacent to ether oxygen of this end monomer unit could be assigned to the singlet (signal **d**, 3.33 ppm) which appears as a shoulder to the triplet at 3.40 ppm. Additionally, the NMR signal **g** assigned to  $\text{CH}_3$  protons appears as two triplets due to the  $\text{CH}_3$  protons of the ethyl and propyl groups. Further confirmation of the end monomer unit structures was obtained by converting the OH end groups of the copolyether to acetyl ester ( $\text{CH}_3\text{COO}$ —) groups by reacting a sample of the copolyether with  $\text{CH}_3\text{COCl}$ /pyridine and analyzing the purified product by  $^1\text{H}$ -NMR.



**Scheme 1**

The  $^1\text{H}$ -NMR spectrum of the acetylated polymer showed chemical shift changes for  $\text{CH}_2$  protons of three different groups. The major spectral change was the downfield shift of NMR signals **a** and **b** to 4.03 and 3.94 ppm, respectively, and an upfield shift of signal **c** to 3.15 ppm, as well as the appearance of a new singlet due to the  $\text{CH}_3$  protons of the acetate group. These observations support the assignments of  $\text{CH}_2$  groups adjacent to hydroxyl end groups; however, the reasons for the upfield shift of signal **c** are not clear.

The composition of the copolymer, estimated based on signal areas, was different from the monomer composition in the feed. The monomer molar ratio DEPD/DD in the feed was 1 : 3.08 and that in the copolymer was 1 : 3.9. This low amount of DEPD in the copolymer is attributed to loss during the purification. During purification the low molecular weight fraction of the copolymer is usually lost into the water layer, since the process involves repeated washing with a large amount of water. It appears that more of the DEPD-containing chains have been lost, presumably due to solubility differences.

$^{13}\text{C}$ -NMR spectroscopy strongly supported the proposed structures in Scheme 1 for the copolymer. The proton decoupled  $^{13}\text{C}$ -NMR spectrum of the copolyether shown in Figure 2 is consistent with structures in scheme 1 and the various sig-

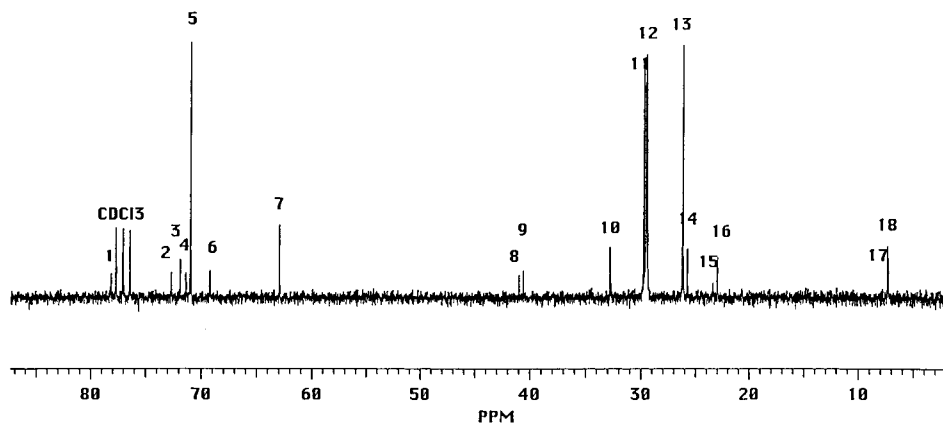


Figure 2 50.3 MHz  $^{13}\text{C}$ -NMR spectrum of purified DD/DEPD copolymer.

nals are assigned as shown in Scheme 2. The signal assignment was based on chemical shift values, comparison with calculated chemical shift values, and by a DEPT (deactivated nuclei enhanced via polarization transfer) experiment. In the DEPT experiment signals 17 and 18 inverted, while 8 and 9 disappeared, and the rest unchanged. This result confirmed that signals 17 and 18 are due to methyl carbons, 8 and 9 quaternary carbons, and all the others methylene carbons.

The copolymerization of HD and DEPD progressed in a similar manner to that of DD-DEPD, except that the cyclic by-product oxepane distilled as expected.<sup>7</sup> The structure of the copolymer was also similar to **I** in that the DEPD incorporated to the copolymer was primarily as an end unit. NMR evidence for the rearranged DEPD unit re-

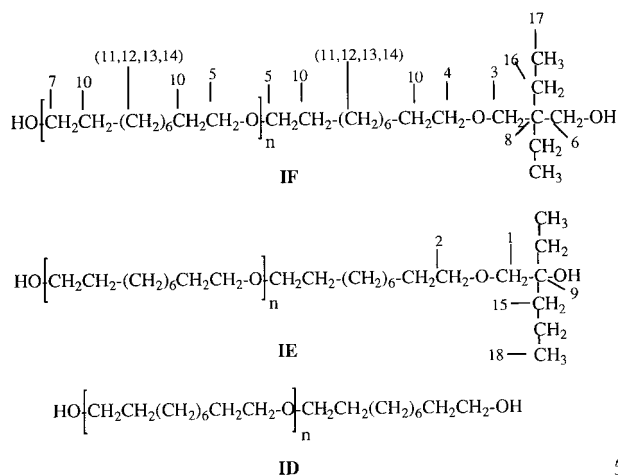
sulting from ethyl group migration was also observed.

Copolymerizations involving CHDM as the second monomer also polymerized in a similar manner.  $^1\text{H}$ -NMR spectrum (Fig. 3) supported structures shown in Scheme 3 for the copolymer prepared from DD and CHDM. The NMR spectrum in the region 3 to 4 ppm shows two sets of doublets each for  $\text{CH}_2$  adjacent to end hydroxyl and ether oxygen since cyclohexanedimethanol used in the copolymerization was a mixture of *cis* and *trans* isomers. Signals due to  $\text{CH}_2$  adjacent to ether oxygen (doublets **t** and **u**) resulting from the polymerization of CHDM showed significantly higher intensity compared to the end  $\text{CH}_2$  signals (signals **q** and **r**) indicating that, unlike the DD-DEPD system, CHDM also incorporated to the copolymer main chain. Since CHDM does not homopolymerize under similar experimental conditions it is very unlikely that blocks of CHDM be present in the copolymer. The observed higher intensity for signals **t** and **u** compared to **q** and **r** supports the presence of copolymer chains of the type **IIb**.

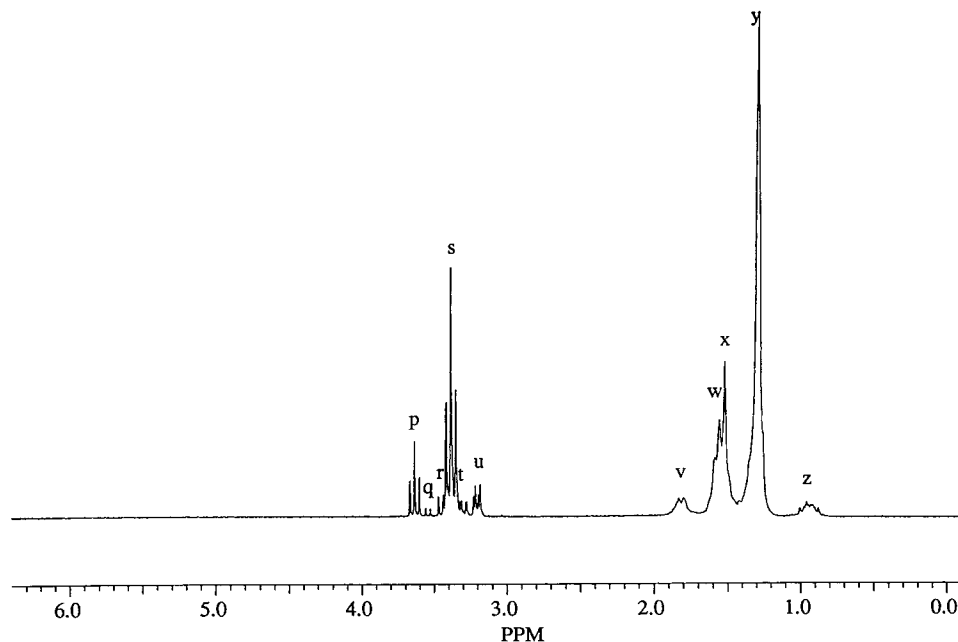
Because of poor base line separation of NMR signals it was not possible to estimate the copolymer composition from NMR results.

Further proof of the copolymer structure was obtained by  $^{13}\text{C}$ -NMR spectroscopy. The  $^{13}\text{C}$ -NMR spectrum of DD-CHDM copolymer shown in Figure 4 is consistent with structures in Scheme 3, and various signals are assigned as shown in **IID**.

Similar results were observed for the copolymerization of HD and CHDM. Copolymer structure was similar to that shown in scheme 3 in that incorporation of CHDM to copolymer main



Scheme 2

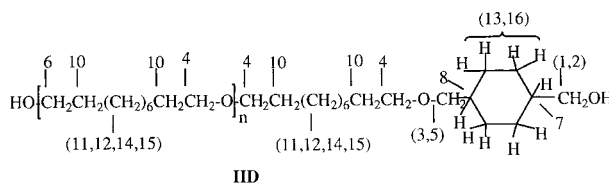


**Figure 3** 200.1 MHz  $^1\text{H}$ -NMR spectrum of purified DD/CHDM copolymer.

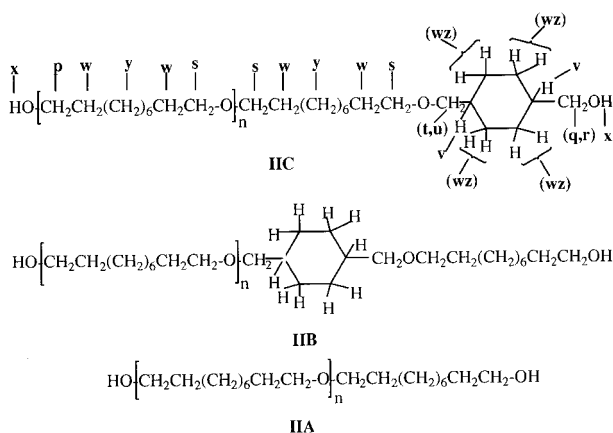
structure as well as end unit was supported by NMR evidence.

The other monomer systems investigated, 1,10-decanediol/1,6-hexanediol and 1,10-decanediol/1,7-heptanediol, also produced copolyethers. The NMR spectra of these copolymers very closely resembled those of their homopolymers, accordingly the analysis of the copolymer composition was not possible. Because of the very close structural similarities, the reactivities of hydroxyl groups of

these monomers are expected to be very similar, therefore the copolymers produced are considered to be random copolymers.



**Scheme 4**



**Scheme 3**

As shown in Table I macrodiols with molecular weights in the 600–2000 range were successfully prepared by this method. Amount of copolymer recovered after purification varied between 55 to 79 g per 100 g of starting monomers, depending on the copolymer system. This variation is a result of the loss during the purification as well as cyclization of 1,6-hexanediol-containing systems. Purification of the copolyether by washing with hot water to remove acid catalyst results in loss of some low molecular material.

Absolute molecular weights of macrodiols were calculated by determining the hydroxyl number of the copolymer, assuming a hydroxyl functionality of 2. Molecular weights estimated by SEC were

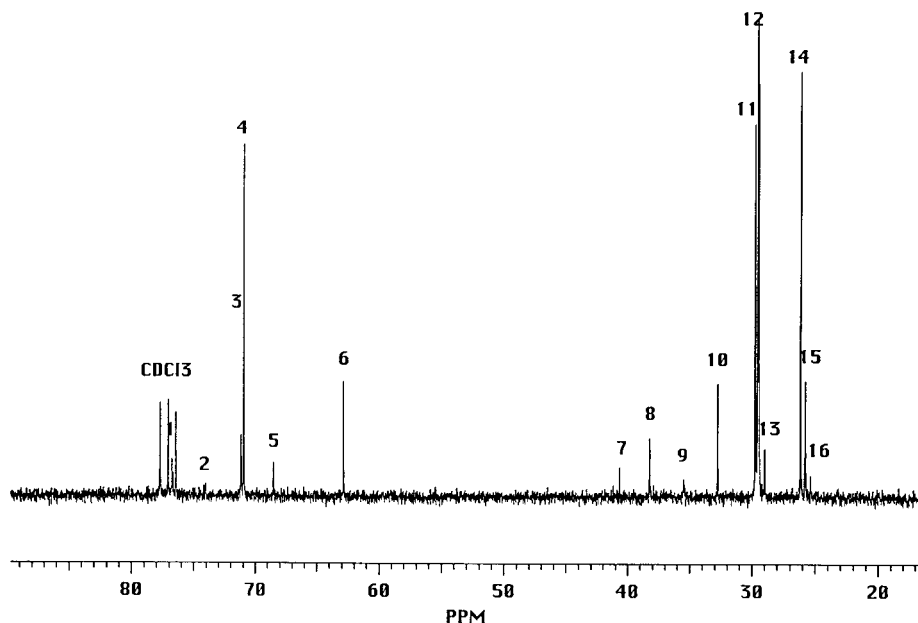


Figure 4 50.3 MHz  $^{13}\text{C}$ -NMR spectrum of purified DD/CHDM copolymer.

significantly higher than those determined by the hydroxyl number method because of the polystyrene standard calibration. Polydispersities were between 1.5 and 1.6, typical of polymers prepared by condensation polymerization.

#### Thermal Analysis of Polyether Macrodiols

Figure 5 shows the DSC traces of a series of copolyethers along with those of the two homopolyethers PHMO and PDMO. DSC results of PHMO and PDMO exhibited sharp melting endotherms peaking at 44.4 and 68.7°C, respectively. The respective glass transition temperatures were observed as very weak transitions with onset temperatures at -61.7 and -41.0°C. On the other hand, copolymers DD/DEPD and DD/CHDM showed multiple melting endotherms. The largest peak centered around 60°C could be assigned to the melting of blocks of DD segments, and the other smaller endotherms could be assigned to less ordered structures resulting from the incorporation of the monomers CHDM and DEPD. Therefore, DSC results support the copolymer structures proposed based on NMR results. Similar effects were observed with the copolyethers HD/DEPD and HD/CHDM. Copolyethers HD/DD and DD/HPD showed sharp melting endotherms, indicating that minor structural changes such as

introduction of diols with an odd number of methylene groups or the slightly different chain lengths did not affect the macrodiol crystallinity.

Table II summarizes the glass transition temperature, peak melting temperature of the main melting endotherm, and the combined heat of fusion of all melting peaks for the series of macrodiols. As indicated by the heat of fusion values, significant reduction in crystallinity was observed for all copolymers with DEPD or CHDM as the comonomer. The two exceptions were the HD/DD and DD/HPD copolyethers demonstrating that the introduction of slight irregularity to the structure did not influence the crystallinity. Copolyethers involving DEPD as the comonomer caused lowering of glass transition temperature by 18.3°C for DD/DEPD and 16.3°C for HD/DEPD from their respective  $T_g$  of homopolyethers. The effect was much less for CHDM comonomer (except when CHDM level was high) showing no change for DD/CHDM and decrease of only 7.4°C for HD/CHDM. The difference may be attributed to the difference in the flexibility of the two comonomers with CHDM being more rigid than DEPD due to its cyclic structure.

#### Polyurethanes Based on Copolymer Macrodiols

A series of polyurethanes were successfully prepared using the copolymer macrodiols. All poly-



**Table I** Molecular Weight and Yield of Various Polyether Macrodiols

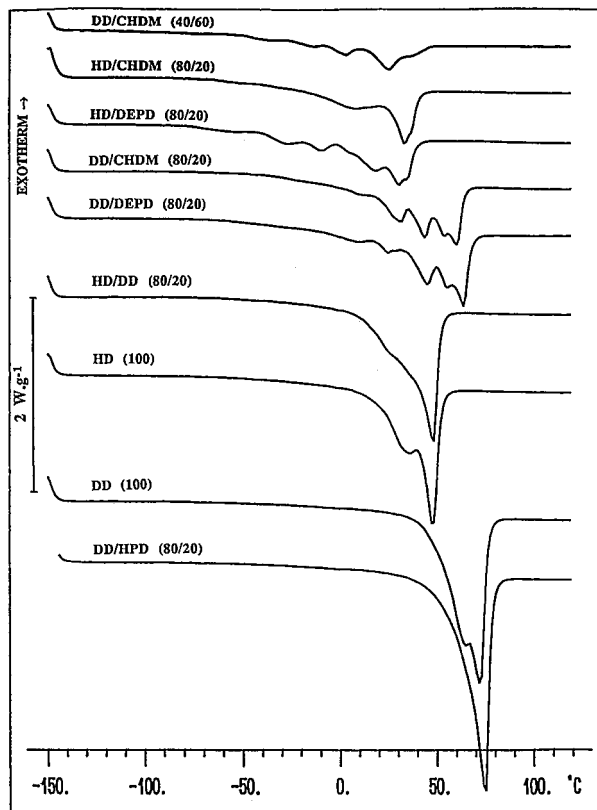
Polyether Macrodiol	Copolymer Yield g/100 g Monomers	$\bar{M}_n$ by Hydroxyl Number Method	SEC Molecular Weights $\bar{M}_n (\bar{M}_w/\bar{M}_n)$
PDMO	80	823	1172 (1.68)
DD/DEPD	79	875	1340 (1.75)
DD/CHDM	67	868	1389 (1.75)
DD/CHDM (4/6)	55	1063	1262 (1.74)
DD/HPD	65	—	2562 (1.75)
PHMO	65	857	1056 (1.63)
HD/DEPD	61	661	998 (1.47)
HD/CHDM	60	1064	1531 (1.81)
HD/DD	69	865	1289 (1.75)

urethanes contained 40 wt % hard segment, which is based on MDI and BDO. The molecular weights of polyurethanes based on copolyether macrodiols were generally lower than those based on the homopolyether macrodiols PDMO and PHMO (Table III). This may be a result of the lower reactivity of the hydroxyl groups attached to the end groups resulting from DEPD and CHDM in the copolyethers. Lower reactivities could be attributed to steric factors.

All polyurethanes were easily thermally processed into flat sheets by compression molding in the temperature range 190–200°C.

As shown by the results in Table IV, copolymerization to reduce the crystallinity of the macrodiols showed a very significant effect on the mechanical properties of the resulting polyurethanes. In the decanediol series, hardness of the polyurethane decreased by about 6 Shore A units as a result of the copolymerization. Likewise, the Young's modulus and stress at 100% elongation decreased, indicating that the polyurethanes are softer than the PDMO-based polyurethane. Polyurethane based on copolyether DD/CHDM (4 : 6) containing higher percentage of CHDM showed very poor mechanical properties. This is a consequence of its low molecular weight. In the hexanediol series only DEPD showed a significant decrease in hardness and modulus. In fact, PU-HD/DEPD was the softest of the polyurethane series. On the other hand, PU-HD/CHDM showed no decrease in hardness and was stiffer than the PHMO-based control material as evidenced by higher modulus and stress at 100% elongation. This may partly be attributed to the relatively higher molecular weight of the copolyether ma-

crodiol used for this sample. Polyurethane PU-HD/DD showed no significantly different properties to those of the control material PU-PHMO, indicating that the introduction of minor structural changes have no significant influence on mechanical properties.

**Figure 5** DSC thermograms of various macrodiols.

**Table II Thermal Transitions and Melting Endotherm Heat of Fusion for Copolyether Macrodiols**

Type of Polyether Macrodiol	$T_g$ (Inset) (°C)	Melting Endotherm Main Peak Temp (°C)	Heat of Fusion (all endotherms) (J/g)
PDMO	-41.0	68.7	180
DD/DEPD	-59.3	59.7	112
DD/CHDM	-41.5	57.9	102
DD/CHDM (4/6)	-50.3	23.9	36.2
DD/HPD	-52.9	69.5	180
PHMO	-61.7	44.4	132.1
HD/DEPD	-78.0	28.5	77.9
HD/CHDM	-69.1	29.8	62.8
HD/DD	-64.2	45.6	142

The ultimate tensile strength and percent elongation at break were significantly lower than those of the corresponding materials based on homopolyethers for both series.

#### Thermal Analysis of Polyurethanes

All polyurethanes were dried at 65°C for 48 h under vacuum and annealed at 120°C for 10 min prior to recording DSC thermograms so as to subject all materials to identical thermal history. Figure 6 shows the DSC thermograms of polyurethanes based on the series of polyether macrodiols. Various thermal transition temperatures and heat-of-fusion values are summarized in Table V. All samples showed a common melting endotherm  $\sim 132^\circ\text{C}$ , attributable to the melting of hard segments with short range order. We have observed that this transition is sensitive to thermal history and typically moves to higher temperatures with

annealing. This phenomenon has been observed by others as well<sup>10</sup> and the endotherm has been attributed to melting of hard domain structure containing predominantly MDI-BDO-MDI segments. Most materials also exhibited high temperature melting endotherms ( $>200^\circ\text{C}$ ) ranging from weak to strong peaks indicative of higher order in the hard segment. Of these only three materials, PU-PDMO, PU-DD/DEPD, and PU-DD/CHDM (40 : 60) showed relatively large peaks with high heat of fusion. Other materials showed only very weak high temperature melting endotherms. This is partly due to differences in the average size of the hard segment length. Although all polyurethanes contained a constant weight percentage of hard segment (40), the average hard segment length varies depending on the molecular weight of the macrodiol.

In general, the DD series-based polyurethanes showed significantly more phase-separated morphology than those based on the HD series. Polyurethane PU-DD/DEPD showed a well-phase separated morphology while PU-DD/CHDM appeared to be less phase-separated (much broader hard segment melting endotherm). The difference may result from the more rigid structure of CHDM relative to that of DEPD. Generally, the DD series-based polyurethanes showed soft segment paracrystallinity consistent with reported results. The less phase-separated morphology for HD copolyether series-based polyurethanes appears to parallel that reported<sup>9</sup> for PHMO- and PDMO-based polyurethanes, where polyurethanes based on the latter showed greater phase separation than those based on the former. It

**Table III Molecular Weights of Polyurethanes Based on Copolyether Macrodiols**

Polyurethanes	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PU-PDMO	48650	1.77
PU-DD/DEPD	25400	1.95
PU-DD/CHDM	29872	1.96
PU-DD/CHDM (4/6)	16101	1.68
PU-PHMO	52000	1.84
PU-HD/DEPD	43290	1.65
PU-HD/CHDM	32400	1.75
PU-HD/DD	51162	1.74

**Table IV Mechanical Properties of Polyurethanes Based on Polyether Macrodiols**

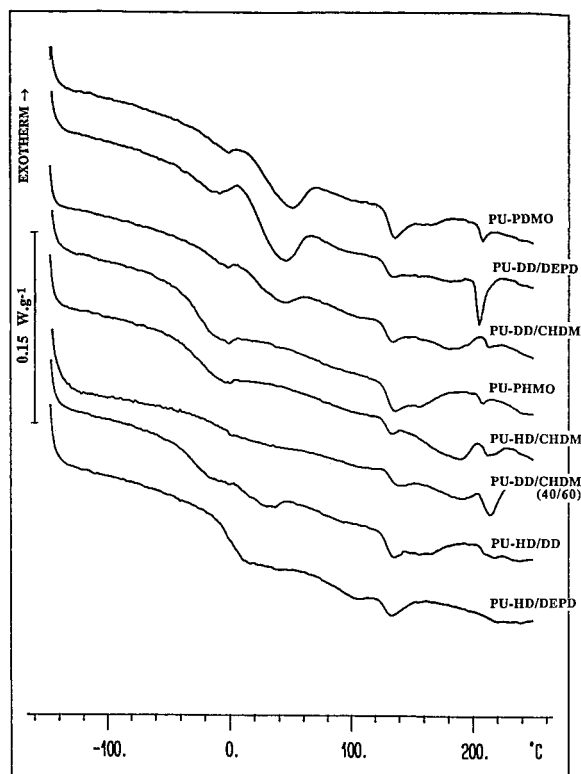
Polyurethane	Hardness (Shore A)	Fail Stress (MPa)	Fail Strain (%)	Stress at 100% Elongation (MPa)	Young's Modulus (MPa)
PU-PDMO	95	32.9	380	15.2	88.8
PU-DD/DEPD	89	14.6	290	11.8	60.3
PU-DD/CHDM	89	18.6	300	14.2	74.8
PU-DD/CHDM (4/6)	90	8.30	14	—	60.4
PU-PHMO	83	15.2	440	7.6	21
PU-HD/DEPD	74	11.0	380	6.8	14.6
PU-HD/CHDM	83	10.3	250	9.8	49
PU-HD/DD	82	17.0	433	8.1	27.2

should also be noted that although the two series of polyurethanes contained the same weight percent of soft segment, the variation of the average length of the hard segment resulting from not having identical macrodiol molecular weights can affect morphology. Furthermore, the difference in reactivity of the hydroxyl groups in the copolyether macrodiols, due to steric factors, may also influence the distribution of the hard segment sequence length.

## CONCLUSIONS

Acid-catalyzed condensation copolymerization was successfully employed to synthesize a series of copolyethers with molecular weights in the 660–1070 range, using 1,10-decanediol and 1,6-hexanediol as the principal monomers, and 2,2-diethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, or 1,7-heptanediol as comonomer to disrupt polyether crystallinity. NMR spectroscopy established the copolyether structure as primarily consisting of blocks of the principal monomer with 2,2-diethyl-1,3-propanediol comonomer forming the chain end unit. On the other hand, 1,4-cyclohexanedimethanol incorporated to form the chain end unit as well as part of the main chain. DSC results of the macrodiols confirmed that the copolymerization significantly reduced the macrodiol crystallinity for copolyethers containing either 2,2-diethyl-1,3-propanediol or 1,4-cyclohexanedimethanol comonomers. However, slight structural modification using comonomers such as 1,7-heptanediol was not effective in reducing polyether crystallinity.

A series of polyurethane elastomers with low modulus and hardness was successfully prepared from these macrodiols. Of the comonomers studied 1,6-hexanediol/2,2-diethyl-1,3-propanediol copolyether was the most effective in producing soft polyurethanes.



**Figure 6** DSC thermograms of polyurethane elastomers based on the series of macrodiols.

**Table V DSC Results of Polyurethanes Based on Polyether Macrodiols**

Polyurethane	Soft Segment $T_g$ (onset) °C	Soft Segment $T_m$ °C (Heat of Fusion, J/g)	Hard Segment Melting Peaks
			Peak Temp, °C (Heat of Fusion, J/g)
PU-PDMO	-32.6	49.5 (8.9)	135.5 (7.8), 207 (1)
PU-DD/DEPD	-41.1	44.0 (9.7)	134 (5.2), 204 (3.2)
PU-DD/CHDM	-45.4	42.5 (4.1)	132 (7), 212.5 (0.6)
PU-DD/CHDM (4/6)	-29.1	—	138 (1.5), 186.2 (2.8), 214.5 (2.8)
PU-PHMO	-37.9	-2.7 (1.0)	135.5 (8.3), 207 (0.4)
PU-HD/DEPD	-12.0	—	102.3 (1.4), 132.2 (7.4)
PU-HD/CHDM	-48.3	4.2 (0.4)	131 (—), 184 (10.5)
PU-HD/DD	-49.7	27.3 (2.8)	134.3 (9.8), 208.4 (0.8)

**REFERENCES**

1. M. D. Lelah and S. L. Cooper, *Polyurethanes in Medicine*, CRC Press, Boca Raton, FL, 1986, Chap. 3.
2. W. Meckel, W. Goyert, and W. Wieder, *Thermoplastic Elastomers. A Comprehensive Review*, N. R. Legge, G. Holden, and H. E. Schroeder, Eds., Hanser, Munich, 1987, p. 13.
3. M. Szycher, *J. Biomat. Appl.*, **3**, 297 (1988).
4. P. A. Gunatillake, G. F. Meijs, E. Z. Rizzardo, R. C. Chatelier, S. J. McCarthy, A. Brandwood, and K. Schindhelm, *J. Appl. Polym. Sci.*, **46**, 319 (1992).
5. A. Brandwood, K. R. Noble, K. Schindhelm, G. F. Meijs, P. A. Gunatillake, R. C. Chatelier, S. J. McCarthy, and E. Rizzardo, *Adv. Biomater., (Biomaterial-Tissue Interfaces)*, **10**, 413–419 (1992).
6. A. Brandwood, G. F. Meijs, P. A. Gunatillake, K. R. Noble, K. Schindhelm, and E. Rizzardo, *J. Biomater. Sci. Polymer Ed.*, **6**, 41 (1994).
7. P. A. Gunatillake, G. F. Meijs, R. C. Chatelier, D. M. McIntosh, and E. Rizzardo, *Polymer Int.*, **27**, 275 (1992).
8. ASTM D 2849-69 Standard Methods of Testing Urethane Foam Polyol Raw Materials, 1969, American Society for Testing and Materials, Philadelphia, PA.
9. T. H. Lowry and K. S. Richardson, *Mechanisms and Theory in Organic Chemistry*, Harper and Row, New York, 1976, p. 286.
10. D. Martin, G. F. Meijs, G. M. Renwick, S. J. McCarthy, and P. A. Gunatillake, *J. Appl. Polym. Sci.*, to appear (1996).