Synthesis and Characterization of a Series of Poly(alkylene carbonate) Macrodiols and the Effect of Their Structure on the Properties of Polyurethanes

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

Cooperative Research Centre for Cardiac Technology, CSIRO Molecular Science, Private Bag 10, Clayton South MDC, Victoria 3169, Australia

ABSTRACT: A series of polycarbonate and copolycarbonate macrodiols was prepared by using an ester interchange reaction with ethylene carbonate and diols such as 1,6-hexanediol, 1,10-decanediol, 2,2-diethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, and 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane. The diols were chosen to prepare a series of macrodiols with different structural features including linear, branched, rigid, and flexible. The macrodiols were characterized by ^{1}H- and ^{13}C-NMR spectroscopy and DSC. The commercial macrodiol based on 1,6-hexanediol exhibited a high level of crystallinity, while with the exception of 1,10-decanediol–based copolycarbonates all the others were completely amorphous. 1,10-Decanediol–based materials showed partial crystallinity under subambient conditions. 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 polyurethanes based on polycarbonate macrodiols prepared from 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane had the lowest modulus and hardness of the series of polyurethanes. The remaining polyurethanes had high tensile strength with poor elasticity. The morphology of the polyurethanes, as determined by DSC analysis, varied from completely phase-mixed to well phase-separated structures. Polyurethanes based on macrodiols prepared from 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane showed good phase-separated morphology, with sharp hard segment melting endotherms and soft segment glass transitions close to that of the pure soft segment. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1621–1633, 1998

Key words: copolycarbonate macrodiols; siloxane; polyurethane elastomers; synthesis; characterization; thermal and mechanical properties; phase separation

INTRODUCTION

Polyurethane 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. Many polyurethane elastomers exhibit high tensile strength and toughness, characteristic of this class of elastomers, primarily due to their two-phase morphology. Generally, the soft and hard segments undergo microphase separation due to incompatibility resulting in materials with excellent mechanical properties. The hard segment structure and weight fraction, soft segment struc-

ture, molecular weight, polydispersity, and cross-linking in either phase influence phase separation and copolymer properties.[1,2]

In conventional polyurethane elastomers the soft segment is a polyether or a polyester macrodiol. These materials have been the subject of numerous studies using a wide variety of experimental techniques to understand the structure–property relationships.[2] A number of investigations has focused on polyurethanes based on poly(alkylene carbonate)s[3] and nonpolar macrodiols such as polyisobutylene, polybutadiene, and polydimethylsiloxane[4] macrodiols.

Generally, the poly(alkylene carbonate) macrodiol based polyurethanes exhibit high tensile strength, modulus, and low elasticity relative to those based on polyethers. These properties are attributed to the high degree of phase mixing in these materials due to hydrogen bonding between soft segment carbonate groups and hard segment urethane groups. We recently disclosed a range of silicon-based polycarbonate macrodiols (Australian Provisional Patent Application No. PO7002) useful for the preparation of polyurethanes with low modulus and hardness. Although a large number of polycarbonate-based polyurethane formulations have been disclosed in the patent literature,[5] for a range of applications, detailed studies focused on structure–property relationships of the resulting polymers are lacking.

The objectives of the present study were to investigate the effect of poly(alkylene carbonate) macrodiol structure on the properties of resulting polyurethanes and to understand macrodiol structural features required to achieve a balance of phase mixing and separation, leading to materials with low modulus and high ultimate tensile strength. Accordingly, a series of copolycarbonate macrodiols was synthesized by an ester interchange reaction,[6] fully characterized, and subsequently converted to polyurethanes, whose properties were then investigated. Variation in macrodiol structure was achieved by using a range of structurally different diols including 1,6-hexanediol, 1,10-decanediol, 2,2-diethyl-1,3-propanediol, 1,4-cyclohexanedimethanol and 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane. Further variation in structure was achieved by copolymerization involving several combinations of these monomers. This study was part of our on-going investigations to develop degradation resistant, "soft" and more flexible polyurethanes for which there is a current demand, especially for use in implantable medical devices.
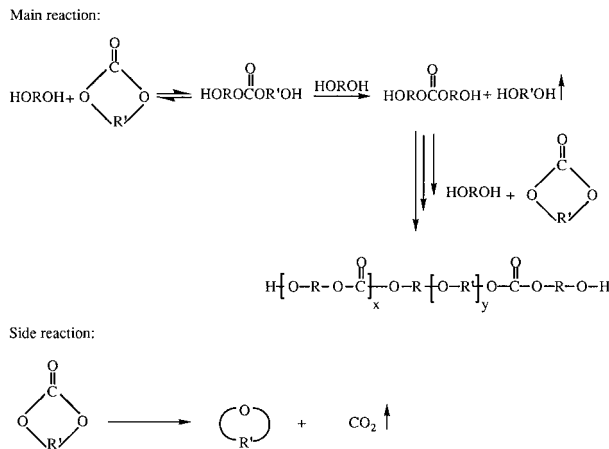
Scheme I

EXPERIMENTAL

Materials

1,10-Decanediol (DD), 1,6-hexanediol (HD), 1,4-cyclohexanedimethanol (CHDM), 2,2-diethyl-1,3-propanediol (DEPD, Aldrich, Milwaukee, WI), and ethylenecarbonate (Aldrich) were used as received. 1,3-Bis(4-hydroxybutyl)-1,1,3,3,-tetramethyldisiloxane (BHTD, Silar Laboratories) and 4,4′-methylenediphenyldiisocyanate (MDI, ICI Australia) were distilled under vacuum and the middle fractions used for experiments. 1,4-Butanediol (BDO, Aldrich) was dried over activated molecular sieves 3 Å, distilled under vacuum, and the middle fraction used for polymerizations. Poly(oxycarbonyloxy-1,6-hexamethylene) macrodiol (Polysciences Inc.) was used after drying (15 h at 105°C and 0.1 Torr vacuum).

Polycarbonate and Copolycarbonate Macrodiol Synthesis

Polycarbonate macrodiols are typically prepared through the polycondensation of diols with phosgene or through the transesterification of diols with carbonates such as ethylene carbonate.[8] Polycarbonate and copolycarbonate macrodiols in this study were prepared by the latter process, which is usually the technically preferred method. The polymerization reaction is usually catalyzed by metals, metal alkoxides, and organometallic compounds.

Stannous-2-ethyl-hexanoate was used as the catalyst in the preparation of macrodiols in this study. The reactions involved are summarized in Scheme I. The polymerization using ethylene car-

bonate proceeds with the evolution of ethylene glycol along with a side reaction involving ethylene glycol to form ethylene oxide units in the polycarbonate chain. Ethylene carbonate is also known to decompose to ethylene oxide and carbon dioxide. However, this has no effect on the macrodiol structure. Polymerization proceeds in a step-growth manner to yield bis(hydroxy-terminated) poly(alkylene carbonate)s. Progress of the polymerization was monitored by SEC and ^{1}H-NMR spectroscopy.

The synthesis of the macrodiols was carried out using a method adopted from that reported[6] by Lai et al. All copolymerizations were carried out using a monomer mixture containing 50/50 wt % of the two comonomers. A typical procedure is as follows.

Ethylene carbonate (50 g), 1,6-hexanediol (25 g), 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane (25 g), and stannous-2-ethyl-hexanoate (0.13 g) catalyst were placed in a 250-mL three-necked round-bottom flask. The flask was then fitted with a fractionation column (filled with glass beads), distillation head, magnetic stirrer bar, condenser, nitrogen inlet, and thermometer. The polymerization was carried out in three stages. In the first stage the reaction mixture was heated to 180°C under a nitrogen flow while maintaining a vacuum of 140 Torr over a period of about 4 h. In the second stage, the reaction temperature was raised to 190°C while increasing the vacuum to 50 Torr and the reaction was continued for 2 more hours. During this period the vacuum was reduced to 10 Torr, stepwise. About 75% of the total distillate was collected during the second stage. In the third stage, the temperature was raised to 200°C and the vacuum reduced to 5 Torr with the nitrogen flow stopped, and reacted for a further 30 min. The reaction was stopped at the end of the third stage by removing the flask from the heating bath and allowing to cool to room temperature under ambient pressure. The progress of the polymerization reaction was monitored by analyzing a sample of the crude product by ^{1}H-NMR spectroscopy and by size-exclusion chromatography. The product polymer was a pale yellow viscous liquid. Yield of the crude polymer was 44.5 g.

The polycarbonate was dissolved in dichloromethane to make a 15% solution and treated with charcoal to remove colored impurities as well as the catalyst residues. The polycarbonate obtained after evaporating the dichloromethane from the filtered solution was further purified by washing with boiling water to remove traces of ethylene glycol and unreacted ethylene carbonate. Boiling water (200 mL) was added to the polymer and stirred for 10 min, allowed to settle and the water was decanted off. This process was repeated three times. The final polymer was then dried at 80°C under vacuum (0.1 Torr) for 15 h. The yield was 40 g.

All polycarbonate and copolycarbonate macrodiols are designated by using abbreviations of the monomer or the comonomers used in the synthesis. For example, a copolycarbonate macrodiol designated as HD/BHTD represents a macrodiol prepared by using 50/50 (w/w) mixture of 1,6-hexanediol and 1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane, respectively. The properties of the macrodiols are summarized in Table I. All polyurethanes are designated by PU-, followed by the macrodiol designation. For example, PU-HD/BHTD represents a polyurethane prepared from the macrodiol HD/BHTD.

Polyurethane Synthesis

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

Predried macrodiol HD/BHTD (25 g, MW 1220), 1,4-butanediol (3.055 g), and stannous 2-ethyl-hexanoate (0.01 wt % of total solids) catalyst were placed in a 250-mL polypropylene beaker and degassed at 80°C in an oven under a vacuum of 2 Torr (1.5 h). Molten MDI (13.61 g) was weighed into a MDI 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 (4 h) in an oven under dry nitrogen.

Hydroxyl Number Determination

The hydroxyl number of the purified and dried macrodiols was determined by phthalic anhydride reflux procedure in accordance with the ASTM method D 2849.[7]

Spectroscopic Analysis

[1]H (200.1 MHz) and [13]C (50.3 MHz)-NMR spectra were recorded on a Bruker FT-NMR spectrometer. ^{1}H and ^{13}C-NMR spectra of the macrodiols

Table I   Poly(alkylene carbonate) Macrodiols

Macrodiol	Yield (g/100 g Monomers)	Mol ratio[a] of Monomers in Feed	Mol ratio[a] of Monomers in Macrodiol	Molar Ratio[a] in End Groups	$\bar{M}_n$[c]	MW by SEC $\bar{M}_n(\bar{M}_w/\bar{M}_n)$
HD	—	—	—	—	893	1519 (2.00)
DEPD	69	—	—	—	1303	1265 (1.2)
HD/DEPD	65	1 : 0.89	1 : 0.66	1 : 0.67	1060	1376 (1.61)
DD/DEPD	70	1 : 1.32	1 : 0.63	1 : 0.67	762	1287 (1.72)
CHDM	65				734	1294 (1.57)
HD/CHDM	68	1 : 0.82	1 : 1.05	1 : 1.20	853	1601 (1.71)
DD/CHDM	75	1 : 1.21	1 : 0.58	1 : 0.50	774	1447 (1.90)
BHTD	60	—	—	—	874	930 (2.23)
HD/BHTD	90	1 : 0.42	1 : 0.42	—[b]	1220	2098 (1.70)

[a] Molar ratio shown follows the order of monomers used in designating macrodiols.
[b] Two end groups are indistinguishable by NMR.
[c] Determined by hydroxyl number method.

were obtained at ambient temperature from 4–10% (w/v) solutions in $CDCl_3$.

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 Ultra-styragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å). Size-exclusion chromatography of polyurethanes was carried out at 80°C, with 0.05 M lithium bromide in N,N-dimethylformamide as eluent on a Waters Associates Chromatograph with two μ-Styragel (10^5 and 10^3 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.

Mechanical Properties

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 dumbbells of 3 cm in length and 1 cm in width; the narrow section as 1.2 cm in length and 0.4 cm in width. All samples were inspected under crosspolarisers to screen for gross residual stress. Dumbbells were stored under ambient conditions for 4 weeks before tensile tests and hardness measurements were carried

out. 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 mean values for five 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) prior to recording thermograms. DSC thermograms over the temperature range −150 to 250°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 a nitrogen purge. Sample weights were 15–25 mg.

RESULTS AND DISCUSSION

Characterization of the Structure of Macrodiols

I NMR

The NMR spectrum of the purified DD/DEPD macrodiol is shown in Figure 1. The signals at 3.58 (triplet) and 3.33 ppm (singlet) due to CH_2 protons adjacent to hydroxyl groups in DD and DEPD, respectively, decreased in intensity while new signals at 4.1 and 3.95 ppm appeared and grew in intensity as the polymerization progressed. Polymer formation was further con-
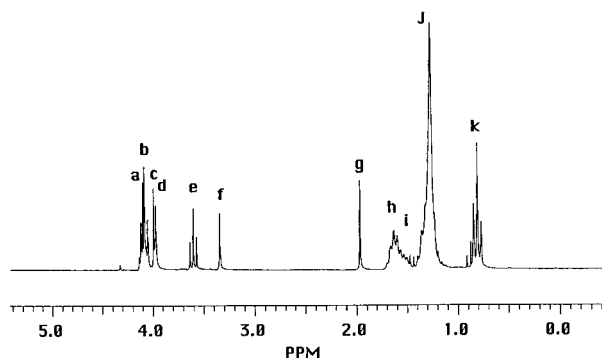
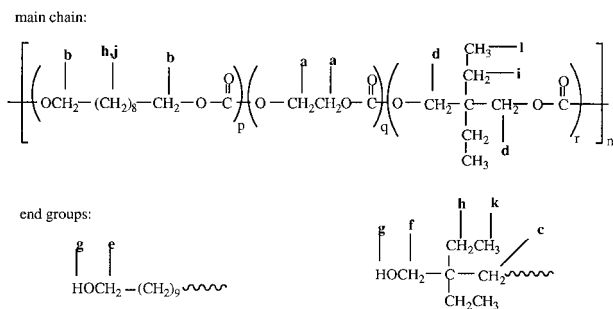**Figure 1** 200.1 MHz ^{1}H-NMR spectrum of purified DD/DEPD copolycarbonate macrodiol.

Figure 2 50.3 MHz proton decoupled ^{13}C-NMR spectrum of purified DD/DEPD copolycarbonate macrodiol.

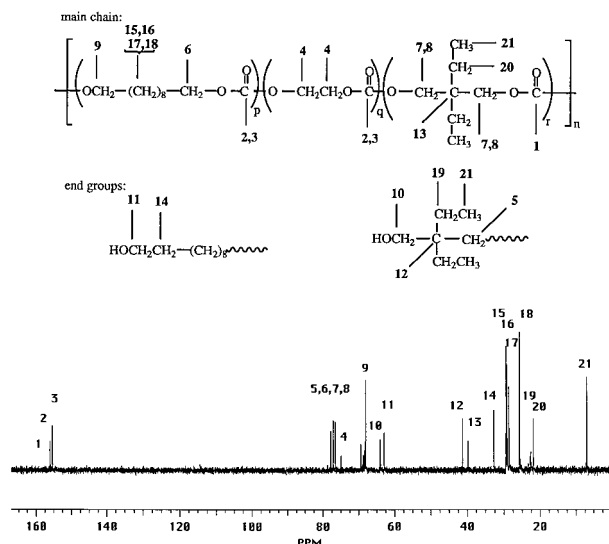firmed by SEC, which showed a broad peak with shorter retention time than the two monomers.

The structure of the macrodiol was established by ^{1}H- and ^{13}C-NMR spectroscopy. The proposed structure (Scheme 2) for the macrodiol main chain was supported by NMR spectroscopy. NMR data was also consistent with the macrodiol having end groups derived from both DD and DEPD. Various ^{1}H-NMR signals (Fig. 1) were assigned, as shown in Scheme II. The signal assignments for this macrodiol and all others in this study were made based on spectral data for the monomers and the corresponding homopolycarbonates (e.g., DEPD in this case), splitting patterns, and chemical shift values. The NMR results also supported the presence of ethylene oxide (OCH_2CH_2) segments in the main structure, as indicated in the literature[6] for polymerizations involving ethylene carbonate. Estimation of the amount of OCH_2CH_2 incorporation was not possible due to signal overlapping.

The approximate molar ratio, calculated from ^{1}H-NMR signal areas, of DD to DEPD in the macrodiol was 1.0 : 0.63 compared with 1.0 : 1.32 in the monomer feed. Because DEPD has a lower boiling point than DD, it is expected that some

DEPD may have distilled over during the distillation of ethylene glycol, resulting in a lower level of DEPD in the copolymer than in the monomer feed. The level of ethylene oxide could not be estimated because of signal overlapping.

An analysis of the ^{13}C-NMR spectra supported the structure in Scheme II for the copolycarbonate. The spectrum with various signal assignments are shown in Figure 2. The signal assignment was based on monomer spectral data, relative chemical shift values, and the results of DEPT (deactivated nuclei enhanced via polarization transfer) experiments (to differentiate methylene, methyl, methyne, and quaternary carbons). The assignment of signals 5 to 8 was tentative due to the very close chemical shift values. However, because of the presence of three different structural units in the repeat unit it is reasonable to expect slight chemical shift differences for the CH_2 groups adjacent to carbonate functional group. Further, the NMR spectrum of the homopolycarbonate prepared from DEPD helped confirm the spectral assignments.

The NMR spectra of the homopolycarbonate DEPD strongly supported the presence of ethylene oxide units as part of the main structure. ^{1}H-NMR spectrum of the polymer showed signals at 4.1 (singlet, OCH_2CH_2), 3.95 (broad singlet, CH_2OCOO of main chain derived from DEPD), 3.35 (singlet, CH_2 adjacent to OH end group), 2.35 (singlet, OH end group), 1.35 (multiplets, CH_2 in ethyl group of DEPD in end units and repeat unit), 0.9 (triplet, CH_3 of end group), and
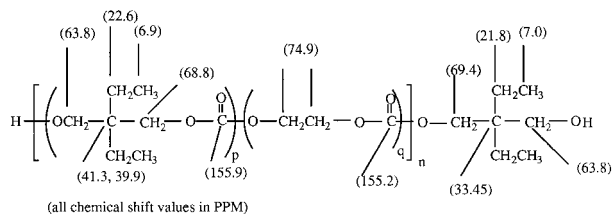
Scheme II
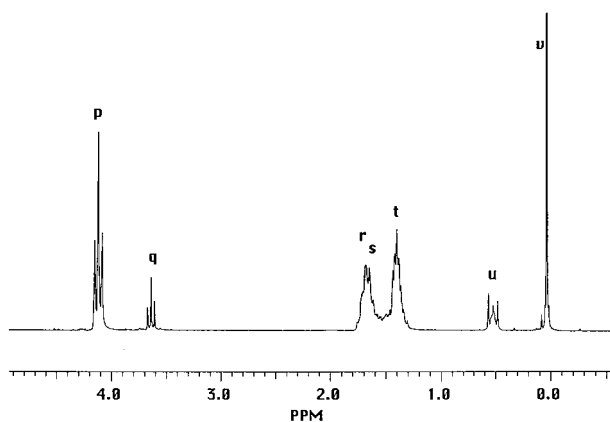
Scheme III

Scheme IV

0.85 ppm (CH_3 of repeat unit). The molar ratio of EO to DEPD in the polymer was 1.0 : 3.3, based on signal areas. ^{13}C-NMR spectral data also supported the proposed structure that is shown in Scheme III, with observed chemical shift values assigned to various carbons in the structure.
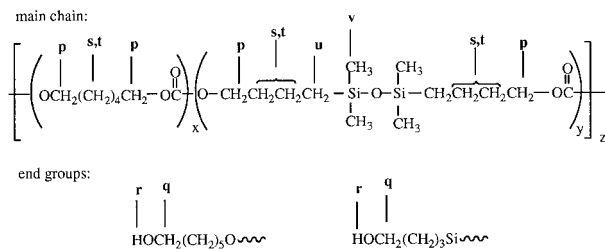
The NMR spectra of the copolycarbonate HD/DEPD showed characteristics indicative of similar structural features. Accordingly, a structure similar to that shown in Scheme II was proposed for the copolymer with end groups resulting from both HD and DEPD. The molar ratio HD : DEPD in the copolymer was 1.0 : 0.66 compared with 1.0 : 0.89 in the monomer feed. The relative loss of DEPD during polymerization was somewhat less in this case compared to DD/DEPD due to boiling point differences. Further support for the structure was obtained from ^{13}C-NMR data.

The structure of the copolycarbonate macrodiol based on HD and BHTD was established, as that shown in Scheme IV, based on NMR results. Figure 3 shows the ^{1}H-NMR spectrum of the copolymer, with various signals being assigned as shown in Scheme IV.

The composition of the copolymer was determined from ^{1}H-NMR signal areas for appropriate signals for the two monomers. The molar ratio of

HD : BHTD in the copolymer was 1.0 : 0.4, which was identical to the monomer molar ratio in the feed. This result indicates that there was no preferential loss of one monomer over the other due to distillation during polymerization. It is interesting to note that in this case there was no incorporation of any ethylene oxide units, as in DEPD-based polycarbonates.

^{13}C-NMR spectral results supported the structure shown in Scheme IV for the copolycarbonate. Figure 4 shows the NMR spectrum with various signal assignments.

The structure of the macrodiol DD/CHDM was established as a random copolycarbonate of DD and CHDM. Unlike copolymerizations involving DEPD, there was no evidence indicating the incorporation of ethylene oxide segments to the copolycarbonate chain, at a level detectable by NMR. Because the CHDM used in the polymerization was a mixture of two isomers (*cis* and *trans* 30/70), the exo-cyclic CH_2 group of CHDM appeared as two sets of doublets. Figure 5 shows the ^{1}H-NMR spectrum of the macrodiol and various signals were assigned as shown in Scheme V.

Figure 3 200.1 MHz ^{1}H-NMR spectrum of purified HD/BHTD copolycarbonate macrodiol.

Figure 4 50.3 MHz proton decoupled ^{13}C-NMR spectrum of purified HD/BHTD copolycarbonate macrodiol.

Figure 5 200.1 MHz ^{1}H-NMR spectrum of purified DD/CHDM copolycarbonate macrodiol.

The assignment of NMR signals in the 3.3 to 4.2 ppm region was relatively easy compared to the 0.8 to 2.0 ppm region where the signal resolution was poor due to many overlapping signals. However, most of the assignments were made based on NMR data of the homopolycarbonate macrodiol of CHDM.

The copolymer composition was estimated using NMR signal areas in the 3.3 to 4.2 ppm region. The DD : CHDM molar ratio in the macrodiol was 1.0 : 0.6 compared with 1.0 : 1.2 in the monomer feed, indicating that a significant amount of CHDM has distilled over during polymerization.

^{13}C-NMR spectral data also supported the structure in Scheme V for the copolycarbonate. Based on the spectral data, the observed chemical shift values for various carbons in the structure are shown in Scheme Va.

The NMR data for the copolycarbonate macrodiol based on HD and CHDM were consistent with the corresponding structure in Scheme V, where HD and CHDM were randomly distributed, with end groups being derived from both monomers. The molar ratio of HD to CHDM in the copolymer was 1.0 : 1.05. It is interesting to note that the

Scheme V

(all chemical shifts in ppm)

Scheme Va

ratio in the monomer feed was only 1.0 : 0.82. This was attributed to relatively higher loss of HD (b.p. 250°C) due to its lower boiling point compared to CHDM (b.p. 283°C).

The commercial polycarbonate macrodiol used in this study was based on 1,6-hexanediol and ^{1}H-NMR spectrum of the product was consistent with structure $H[O(CH_2)_6OCO]_nO(CH_2)_6OH$. Similarly, NMR data of the other two homopolycarbonate macrodiols CHDM and BHTD were consistent with structures $H[OCH_2C_6H_{10}CH_2OCO]_nOCH_2C_6H_{10}CH_2OH$ and $H[O(CH_2)_4Si(CH_3)_2OSi(CH_3)_2(CH_2)_4OCO]_nO(CH_2)_4Si(CH_3)_2OSi(CH_3)_2(CH_2)_4OH$, respectively.

As shown in Table I, polycarbonate macrodiols with molecular weights in the 730 to 1300 range were successfully prepared by this method. The yield of polymer varied between 65 and 90 g per 100 g of monomer, depending on the monomer system. The lower yields were attributed to loss of monomer during polymerization (distilling over) as well as loss of low molecular weight fractions during purification. Because the monomer diols used in the study had different boiling points, it may be necessary to optimize the polymerization conditions to suit each system. The loss of monomer was also reflected in the monomer composition of the copolymer. Except for the HD/BHTD system, all other systems showed a copolymer composition significantly different to that in the monomer feed. The molar ratio of different end groups in copolycarbonate macrodiols was very similar to the monomer composition in the copolymer, as seen by the results in Table I. This is consistent with the step growth nature of the polymerization. Because the hydroxyl groups

in all the monomers are primary, their reactivities appear to be similar, despite other differences such as steric hindrance. Absolute molecular weights of macrodiols were calculated by determining the hydroxyl number of the copolymer, assuming a hydroxyl functionality of 2. With one exception (BHTD), the molecular weights determined by SEC were significantly higher than those determined by the hydroxyl number method, primarily because of the calibration with polystyrene. Polydispersities were between 1.2 and 2.3, which is typical of step-growth polymerizations.

Thermal Analysis of Polycarbonate Macrodiols

Figures 6(a)–(c) show the DSC traces of the series of polycarbonate macrodiols synthesized in this study and a commercial material from Polysciences Ltd. DSC results are summarized in Table II. The commercial material based on HD showed a sharp melting endotherm at 45.5°C as the major peak along with a weaker melting endotherm at 19.2°C, indicative of the presence of a very high crystalline order in the material. The second weak melting endotherm probably results from a less-ordered structure, presumably involving end structural units. A weak glass transition was also observed at −60.1°C.

The macrodiols prepared using DD as one of the comonomers showed some interesting thermal behavior. Both macrodiols DD/DEPD and DD/CHDM showed multiple melting endotherms, as shown by the DSC traces in Figure 6(b) and 6(c). The DSC thermograms for the DD/DEPD macrodiol exhibited a glass transition at −54.4°C, a cold crystallization exotherm at −38.8°C, and a very broad melting endotherm between −25 and 20°C. The enthalpy change for the crystallization peak and the melting peak was very similar. Likewise, DD/CHDM macrodiol showed a glass transition at −49.6°C, a cold crystallization exotherm at −34.0°C, and a melting endotherm at 11.5°C. The ordered structures were presumed to involve decanediol segments. DEPD and CHDM macrodiols are likely to disrupt crystallinity; this was reflected in the homopolycarbonate macrodiols of these monomers that were completely amorphous [see Fig. 6(a) and (b)].

In contrast to the DD cooligomers, all copolycarbonate macrodiols involving HD as a comonomer showed completely amorphous morphology, as indicated by glass transitions with high ΔC_P values and an absence of crystalline melting

peaks (see Table II). The glass transition temperature of the macrodiols varied, depending on the comonomer with BHTD yielding the macrodiol with the lowest T_g (−75.2°C). All three monomers were effective in disrupting the crystallinity of the homopolycarbonates HD and DD. DSC results strongly supported that the macrodiols were random cooligomers of the two monomers. Any homosequence of one monomer forming blocks or homopolymer would have resulted in multiple T_gs or T_ms. Absence of such peaks was taken as strong evidence that these macrodiols are random cooligomers of the respective monomers.

DSC has clearly demonstrated that the copolymerization method employed in this study has produced a range of macrodiols with glass transition temperatures in the −2 to −75°C temperature range, useful for making thermoplastic elastomers. The major structural influence of comonomers DEPD, CHDM, and BHTD, when copolymerized with either HD or DD, was the disruption of the macrodiol crystallinity. In general, monomer diols with nonlinear backbones produced amorphous macrodiols, while those with linear backbones produced macrodiols with paracrystallinity.

Effect of Macrodiol Structure on Polyurethane Properties

### Molecular Weight and Processability

A series of polyurethanes having 40 wt % hard segment based on MDI and BDO was synthesized using these macrodiols. The molecular weights of the polyurethanes are shown in Table III. With the exception of PU-DEPD, all the other polyurethanes had molecular weights in the range 29,000 to 60,000. It was not clear why PU-DEPD had a lower molecular weight.

All polyurethanes were easily thermally processed into flat sheets by compression molding in the temperature range 190 to 200°C. The processed films of materials made from macrodiols with higher molecular weights (> 900) were opaque while the others were clear and transparent.

Mechanical Properties

The mechanical properties of the polyurethanes are summarised in Table IV. The polyurethane prepared from commercial polycarbonate macrodiol (HD) exhibited high tensile strength, low fail strain, and high Young's modulus. Of the other
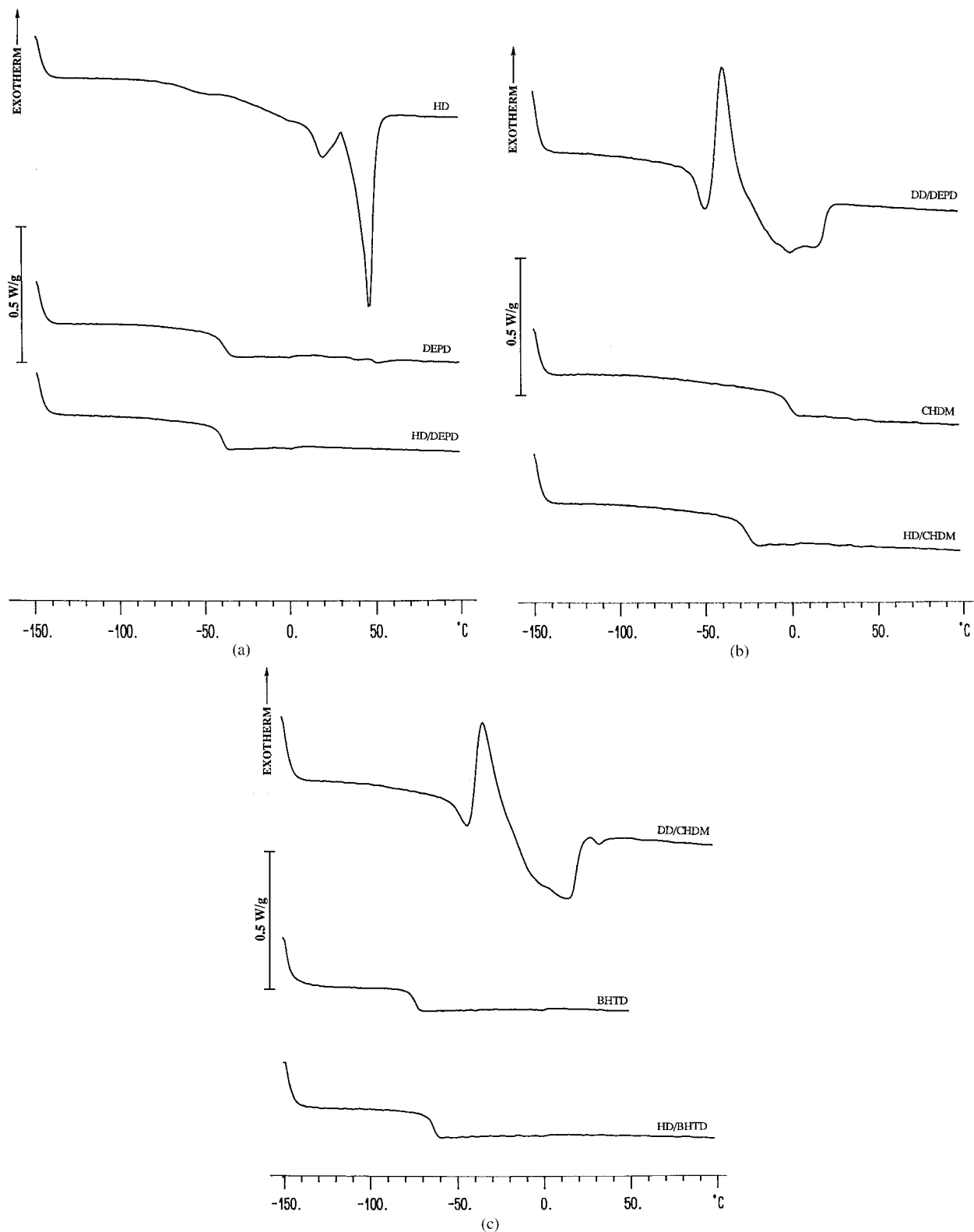
Figure 6 (a) DSC thermograms of polycarbonate macrodiols HD (commercial material), DEPD, and HD/DEPD. (b) DSC thermograms of polycarbonate macrodiols DD/DEPD, CHDM, and HD/CHDM. (c) DSC thermograms of polycarbonate macrodiols DD/CHDM, BHTD, and HD/BHTD.

Table II   DSC Thermal Transition Temperatures and Melting Endotherm Heat of Fusion for Polycarbonate Macrodiols

Macrodiol	T_g (Onset, Midpoint and End, °C)	ΔC_P for Glass Transition (J/gK)	T_m °C and (Heat of Fusion, J/g)
HD[a]	−67.5, −60.1, −52.7	0.14	19.2 and 42.8 (65)
DEPD	−45.8, −40.9, −36.0	0.45	—
HD/DEPD	−46.7, −42.2, −37.8	0.52	—
DD/DEPD	−58.4, −54.4, −50.3	0.61	−1.0 (24.4)
CHDM	−7.4, −2.5, 2.3	0.36	—
HD/CHDM	−32.5, −27.3, −22.0	0.47	—
DD/CHDM	−54.4, −49.6, −44.8	0.52	11.5 (27)
BHTD	−79.1, −75.2, −71.4	0.40	—
HD/BHTD	−69.4, −65.1, −60.8	0.49	—

[a] Commercial material from Polyscience.

three polyurethanes based on homopolycarbonate macrodiols, PU-CHDM showed high tensile strength, very low fail strain, and very high Young's modulus, while PU-DEPD exhibited very poor tensile properties. It was interesting to note that PU-BHTD showed properties characteristic of a typical polyurethane thermoplastic elastomer with good tensile strength, high elongation, and relatively low modulus. These properties are a reflection of phase separation caused by the presence of the hydrophobic siloxane functionality. The poor properties of PU-DEPD could be attributed to its relatively low molecular weight. The high strength, low elongation, and high modulus of PU-CHDM may be a consequence of the somewhat rigid ring structure of CHDM. The influence of the chemical structure on properties was also clearly demonstrated by the Shore hardness measurements shown in Table IV. PU-CHDM was the hardest, while PU-BHTD was the softest in the series.

Table III   Molecular Weights of Polyurethanes Based on Poly(alkylene carbonate) Macrodiols

Polyurethanes	($\bar{M}_n$)	($\bar{M}_w/\bar{M}_n$)
PU-HD	41100	1.89
PU-DEPD	15600	1.72
PU-HD/DEPD	29500	1.63
PU-DD/DEPD	57800	2.79
PU-CHDM	29200	1.91
PU-HD/CHDM	47300	2.53
PU-DD/CHDM	47050	3.27
PU-BHTD	38000	1.92
PU-HD/BHTD	60000	1.94

Copolymerization had a very significant effect on the tensile properties, as shown by the results in Table IV. In the series with 1,6-hexanediol as one comonomer (e.g., PU-HD, PU-HD/DEPD, etc.) the comonomer that gave the softest material with good tensile properties was BHTD. The other two, DEPD and CHDM, although effective in disrupting macrodiol crystallinity, still yielded materials that were quite rigid as seen by the modulus and hardness. Similarly, the DD series of materials exhibited very high modulus along with good tensile strength and moderate elongation. This was partly attributed to the paracrystallinity of the longer alkyl chain of DD, as demonstrated by the DSC results discussed previously. Although not investigated, a copolycarbonate macrodiol containing DD and BHTD would also be expected to show good properties with low modulus. The results, therefore, clearly demonstrated that BHTD was the most useful comonomer to prepare copolycarbonate macrodiols that yields polyurethanes having low modulus and hardness.
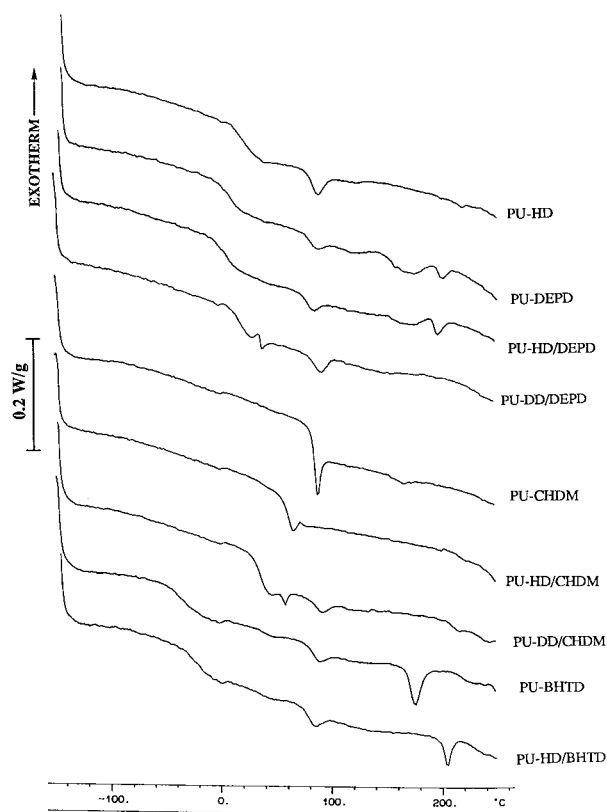
Polyurethane Morphology

DSC results for the polyurethanes (see Fig. 7 and Table V) provided strong evidence to show the effect of soft-segment chemical structure on polyurethane morphology. All DSC traces, with the exception of those for PU-CHDM and PU-HD/CHDM, exhibited a melting endotherm in the 82–92°C temperature range, which can be attributed to order associated with a single MDI unit linking two macrodiol molecules without any BDO chain extender. Similar transitions involving single MDI units have been reported for other sys-

Table IV   Mechanical Properties of Polyurethanes Based on Poly(alkylene carbonate) Macrodiols

Polyurethane	Hardness (Shore A)	Fail Stress (MPa)	Fail Strain (%)	Stress at 100% Elongation (MPa)	Young's Modulus (MPa)
PU-HD-commercial	85	40	180	20.1	144
PU-DEPD	77	6.5	65	—	50
PU-HD/DEPD	77	14	210	13.0	75
PU-DD/DEPD	86	31	250	26.1	165
PU-CHDM	95	44	20	—	457
PU-HD/CHDM	93	40	30	—	452
PU-DD/CHDM	86	38	180	27	259
PU-BHTD	68	20	450	9.5	31
PU-HD/BHTD	74	33	300	13	31

tems.[9,10] In PU-CHDM and PU-HD/CHDM this endotherm was probably slightly shifted and masked by the relatively large glass transition. Of the nine samples analyzed, only four showed any significant crystalline order in the hard segment. Of these PU-BHTD and PU-HD/BHTD were noteworthy because of the sharp melting endotherms observed at 175.9 and 202.8°C, respec-

Figure 7 DSC thermograms of polyurethane elastomers based on the series of polycarbonate macrodiols.

tively, indicating the presence of good phase-separated morphology. These results are consistent with the good mechanical properties observed for both polyurethanes. Similarly, PU-DEPD and PU-HD/DEPD also showed relatively good phase separation. However, the observed multiple endotherms indicated the presence of more than one form of hard segment order. The polyurethane based on the commercial polycarbonate macrodiol showed a typical phase-mixed morphology, characterized by a single glass transition and lack of any crystalline order in the hard segment. Such highly phase-mixed morphology is attributed to the possibility of strong hydrogen bonding interactions between carbonate and urethane functional groups. Similarly, all the polyurethanes based on macrodiols with CHDM as a comonomer exhibited little or no hard-segment order, but a good phase-mixed morphology characterized by the pronounced glass transition.

It should be noted here that the polyurethanes in this study did not have the same average length of the hard segment (only a constant wt %), owing to the fact that the macrodiols did not have identical molecular weights. However, the differences resulting from that would be considered minimal for most materials because they had macrodiol : MDI molar ratios close to 2. The exceptions were the polyurethanes made from macrodiols with molecular weights over 1000 (see Table I).

In all cases, the soft-segment glass transitions were shifted to higher temperatures compared with those of the pure macrodiols. These shifts to higher temperatures, shown in Table V, ranged from 28.9°C to as high as 81°C, indicative of different degrees of phase separation. The two that showed the lowest shifts were PU-BHTD and PU-

Table V DSC Results of Polyurethanes Based on Polycarbonate Macrodiols

Polyurethane	Soft-Segment T_g (Onset, Midpoint End) (°C)			Shift in Soft-Segment T_g (Onset) Relative to That of Pure Macrodiol (°C)	Hard Segment Melting Peaks: Peak Temp, °C (Heat of Fusion, J/g)
PU-HD	7.6,	19.1,	30.5	75.1	86.0 (2.7)
PU-DEPD	−8.0,	2.9,	13.9	37.8	84.5 (1.5), 167.8 (3.7), 199.5 (0.9)
PU-HD/DEPD	−7.0,	5.0,	17.1	39.7	82.8 (1.4), 172.8 (1.6), 197.8 (1.2)
PU-DD/DEPD	9.3,	17.8,	26.4	67.7	37.9 (1.0), 92.9 (2.2)
PU-CHDM	73.6,	81.6,	89.4	81	89.4 (—[a])
PU-HD/CHDM	47.0,	56.5,	66.1	79.5	64.4 (—[a])
PU-DD/CHDM	23.8,	32.9,	42.0	78.2	91.1 (1.3)
PU-BHTD	−50.2,	−32.8,	−15.5	28.9	87.6 (1.2), 175.9 (4.7)
PU-HD/BHTD	−36.4,	−22.4,	−8.5	33	82.9 (1.8), 202.8 (2.1)

[a] Not determined due to overlapping with the glass transition.

HD/BHTD, which is indicative of the relatively good phase-separated morphology. This behavior could be attributed to the chemical structure of BHTD with a flexible siloxane linkage and the typical nonpolar characteristics of materials with such linkages, enhancing the phase separation of soft and hard segments. Siloxanes generally have poor compatibility with the relatively more polar MDI-BDO−based hard segment, which also contributes to phase separation. The other two comonomers DEPD and CHDM, despite being effective in disrupting soft segment crystallinity, appeared to have no significant effect on improving phase separation, although DEPD was marginally better. The steric factors associated with DEPD that may reduce the hydrogen bonding between soft segment carbonate and hard segment urethanes, may be responsible for this difference.

CONCLUSIONS

An ester interchange reaction involving ethylene carbonate and a range of structurally different aliphatic diols was successfully employed to synthesize a series of bishydroxy-terminated polycarbonate and copolycarbonate macrodiols with molecular weights in the 735 to 1300 g/mol range. NMR spectroscopy established that the copolycarbonates were random copolymers of the respective monomers. The copolymer composition of all copolycarbonates, except that from 1,6-hexanediol/1,3-bis(4-hydroxybutyl)-1,1,3,3-tetramethyldisiloxane, was different to that of the monomer feed. This was attributed primarily to differential monomer loss due to distillation during polymerization. DSC results revealed that the macrodiol chemical structure had a significant effect on the glass transition temperature. Generally, the nonlinear monomer diols produced amorphous macrodiols, whereas the linear diols produced macrodiols with paracrystallinity. The series of macrodiols synthesised had T_gs ranging from −2.5 to −75.2°C, making these materials very useful for the preparation of thermoplastic elastomers.

Of the corresponding polyurethanes, those based on macrodiols containing 1,3-bis(4-hydroxybutyl)-1,1,3,3,-tetramethyldisiloxane produced the best materials in terms strength and elasticity. The results clearly demonstrated that the incorporation of siloxane linkages provides structural features required to achieve a good balance of phase separation and mixing to yield polycarbonate macrodiol-based polyurethanes with low modulus (high flexibility) and high strength.

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