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Synthesis and Properties of Thermotropic Liquid Crystalline Polyurethane Elastomers (II): Effect of Structure of Chain Extender Containing Imide Unit

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Abstract : We synthesized polyurethane elastomers containing imide unit for the first time. The polyurethane elastomers were prepared from poly(oxytetramethylene)glycol (PTMG) as a polyol of M_w 1000, 4,4'-diphenylmethane diisocyanate (MDI) as a diisocyanate, and chain extenders containing imide unit. The chain extenders are novel type of diols such as N,N-bis(6-hydroxyhexyl)-3,4,3',4'-biphenyldicarboxyimide (BHHDI) and N,N'-bis[4-(6-hydroxyhexyloxy)phenyl]-3,4,3',4'-biphenyldicarboxyimide (BHPDI). Both of the chain extenders have a flexible spacer of 6-methylene units and imide group, but a phenyl group between the flexible spacer and the imide moiety exists only in the dihydroxy compound BHPDI. The effects of the chemical structure of the chain extenders and hard segment content on the thermal and mechanical properties were studied. The thermal and mechanical properties of polyurethane elastomers were investigated by differential scanning calorimetry, dynamic mechanical thermal analysis, and tensilemeter. In the polyurethane elastomers (MHHs and MHP's) the thermal stability, tensile strength, and initial modulus increase as the hard segment content is increased, whereas elongation at break reduces with increasing hard segment content. The chain extender BHPDI gives a polyurethane elastomer of higher thermal stability and mechanical properties than the chain extender BHHDI composed of imide unit and flexible spacer. This is attributed to different structural features of the chain extender.

Introduction

In ensuing years the urethane polymer-forming system has received intensive attention resulting in the synthesis of many specialized forms, in particular plastics and rubbers in solid and cellular form, surface coatings, adhesives and fibres.[1] Polyurethanes can contain a high concentration of polar groups, in particular the urethane group resulting from isocyanate-hydroxyl reactions, as well as ester, urea, and other groups. The interactions[2-11] between these polar entities are of great importance in determining the properties of polyurethanes of all types, and especially the polyurethane block copolymers where local concentrations of polar groups occur together. The summed interactions between hard segments containing many urethane or urea groups, hydrogen bonding and dipole-dipole interactions can be great enough to provide a pseudo crosslinked network structure between linear polyurethane chains,[12] so that the polymer has the physical characteristics and mechanical behaviour of a covalently crosslinked network at room temperature.

Polyurethane elastomers from these are now used for the very wide number of applications due to their unique property of combining high strength with high hardness and high modulus plus high elongation at break. Also certain polyurethane elastomers combined with flexibility and overall resistance to most types of aliphatic and aromatic fluids give them a unique property combination not possessed by any other rubber or plastic.[1,13]

In the previous works,[14,15] we prepared thermoplastic polyurethane elastomers from 4,4'-diphe-

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nylmethane diisocyanate (MDI), 1,4-butane diol (BD) as a chain extender, and poly(propylene) glycol (PPG) (or poly(oxytetramethylene)glycol (PTMG)) as a polyol of M_w 2000. The effects of hard segment content and block length on the properties of polyurethane elastomers were investigated. We also synthesized thermotropic polyurethane elastomers from 4,4'-diphenylmethane diisocyanate (MDI), poly(oxytetramethylene)glycol (PTMG) as a polyol of M_w 1000, and N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboxyimide (or N,N'-bis[4-(6-hydroxyhexyloxy)phenyl]-3,4,3',4'-biphenyldicarboxyimide) as a new type of chain extender. The effects of hard segment content and the flexible spacer length in a chain extender on the liquid crystallinity and properties of polyurethane elastomers were examined.

The object of this research is to investigate the synthesis and properties of polyurethane elastomers containing imide unit. Introduction of liquid crystalline properties in the polyurethane elastomers is intended by incorporating hard-segment containing rigid imide unit in the backbone. In addition, relationship between the structure of chain extenders and liquid crystallinity is examined in detail.

In this study, we firstly synthesized two kinds of diols. One is that with a imide group, a flexible spacer, and a phenyl group between the imide moiety and the flexible spacer. The other is that with a imide moiety and a flexible spacer, but not having the phenyl group between the imide group and the flexible spacer. Then, polyurethane elastomers were prepared from PTMG as a polyol, MDI as a diisocyanate, and the diol compounds as a chain extender. The effects of the hard segment content and chemical structure of a chain extender on the properties of polyurethane elastomers were investigated. Their structures and thermal properties were examined by using fourier tarnsform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (^{1}H-NMR), differential scanning calorimetry (DSC), polarized optical microscope with a hot stage (POM), and dynamic mechanical thermal analyzer (DMTA). Mechanical and elastic properties were also examined using an Instron.

Experimental

Materials. Poly(oxytetramethylene)glycol (PTMG, M_w 1000, BASF) was used after being dried under vacuum at 80 °C. 1,4-Diphenylmethane diisocyanate (MDI, Aldrich) was used without further purification. 1,4-Aminophenol (Aldrich), 6-aminohe-xanol, 4,4'-biphthalic anhydride (Tokyo Kasei. Co.), and 6-chloro-1-hexanol (Aldrich) were used as received. N,N-Dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were dried over molecular sieves and distilled under reduced pressure.

Synthesis of Dihydroxy Compounds as a Chain Extender.

N,N'-Bis(6-hydroxyhexyl)-3,4,3',4'-biphenyldicarboxyimide (BHHDI) : 6-Aminohexanol (0.046 mol) was added to a solution of 4,4'-biphthalic anhydride (0.023 mol) in 35 mL of DMF, and the reaction mixture was stirred for 24 hr at room temperature. Then, acetic anhydride (40 mL) and pyridine (8 mL) were added to the mixture, which was refluxed for 5 hr. The reaction solution was cooled and poured into distilled water to precipitate the product. The solid product was collected by filtration and washed thoroughly with water. The resulting product N,N-bis(6-acetoxyhexyl)-3,4,3',4'-biphenyldicarboxyimide (BAcHDI) was recrystallized from ethanol three thimes and dried at 70 °C in vacuum. *p*-Toluenesulfonic acid was added into a solution of BAcHDI in methanol and refluxed for 5 hr. After cooling, the dihydroxy compound BHHDI was filtered off and recrystallized from 1,4-dioxane three times: Yield 80%; mp 110 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.37-1.71 (16H, m), 3.41-3.45 (4H, m), 3.56-3.65 (4H, t), 4.40-4.44 (2H, t), 8.18 (2H, d), 8.31 (4H, d).

N,N'-Bis[4-(6-hydroxyhexyloxy)phenyl]-3,4,3',4'-biphenyldicarboxyimide (BHPDI) : 1,4-Amino-phenol (0.046 mol) and 4,4'-biphthalic anhydride (0.023 mol) were mixed in 35 mL of NMP. The mixture was reacted for 14 hr at 90 °C, then poured into methanol. The precipitate N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboxyimide (BPDI) was filtered off and recrystallized from DMF. The reaction of BPDI with 6-chloro-1-hexa-nol is described elsewhere.[15] The

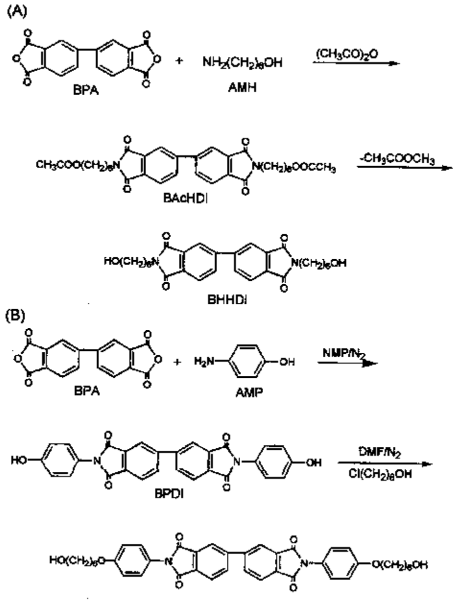
BPDI (0.0013 mol)/DMF (40 mL) solution was placed in a 250 mL three-necked flask equipped with a dropping funnel, a reflux condenser, and heated to 80 °C. Then, 6-chloro-1-hexanol (0.0026 mol) was added dropwise. The reaction was continued by refluxing for 15 hr and poured into distillated water. The precipitated material BHPDI was filtered off and recrystallized from DMF: Yield 65%; mp 141°C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 1.13-1.25 (16H, m), 3.46-3.64 (4H, m), 4.05-4.09 (4H, t), 4.25-4.29 (2H, t), 6.92-6.95 (4H, d), 7.02-7.06 (4H, d), 7.11-7.14 (2H, d), 7.18-7.23 (4H, d).

Synthesis of Polyurethane Elastomers. Into a 250 mL four-necked flask equipped with a condenser, thermometer, magnetic stirrer and nitrogen inlet-outlet, MDI (1.1 mmol) was placed. PTMG (M_w, 1000)(0.33-0.84 mmol) and DMF (15-20 mL) was introduced. The flask was placed in an oil bath and the reaction mixture was stirred at 80 °C for 2 hr under nitrogen atmosphere. Then dihydroxy compound (BHPDI or BHHDI) (0.26-0.77 mmol) and DMF (15 mL) were added, and the reaction was continued for 24 hr at 100 °C. The product was precipitated out by pouring the reaction mixture into methanol. The precipitated product was filtered off, washed three times with methanol, and dried at 70 °C in vacuum.

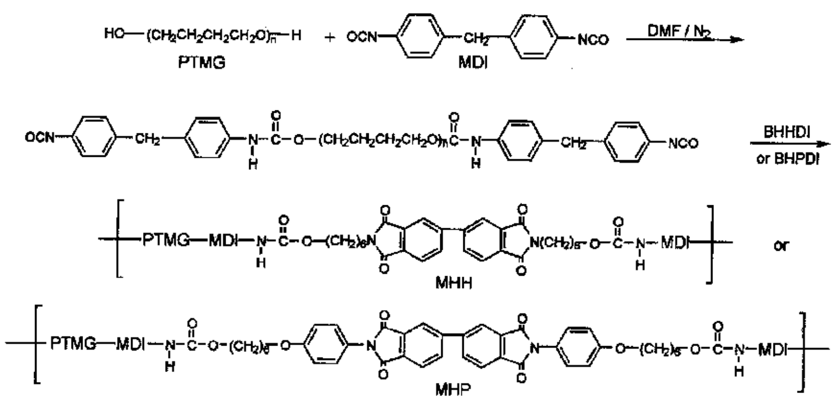
Measurements. The ^{1}H-NMR spectra were recorded on a Varian Unity Plus 300 spectrometer. The concentration of the polymer solutions was about 15%. NMR tube (5 mm) was used in a spinning mode. The samples were prepared by using DMSO-d_6 and hexamethylenedisiloxane (HMDS) as an internal reference. To confirm the structure of the synthesized chain extenders and polymers, infrared spectroscopy was performed by using a Fourier transform infrared spectrometer (Impact 400D, Nicolet). For each sample, 32 scans at 2 cm^{-1} resolution was collected in the absorption mode. The thermal behavior of samples was examined by using a DSC 220C (Seiko) at a heating rate of 10 °C/min under a nitrogen atmosphere. The dynamic mechanical thermal behaviors of polymers were measured by a DMTA (Mk III, Rheometric Scientific). The DMTA was operated from −80 to 250 °C at a heating rate of 3 °C/min. And a frequency was 2 Hz. The films with dimensions of $8 \times 3 \times 0.5$ mm^3 were prepared by solvent casting for all DMTA measurement. The tensile test was carried out with a Tinius Olsen 1000 on dumbbell specimens of cross-sectional area 3×0.5 mm^2 at room temperature. The cross-head speed was 20 mm/min. The stress-strain hysteresis test was carried out with the same tester as above, at room temperature. The sample was clamped in the tester and subjected to successive maximum 300%.

Results and Discussion

The dihydroxy compounds containing the imide moiety, N,N'-bis[4-(6-hydroxyhexyloxy) phenyl]-3,4,3',4'-biphenyldicarboxyimide (BHPDI) and N,N'-bis(6-hydroxyhexyl)-3,4,3',4'-biphenyldicarboxyimide (BHHDI), were synthesized in a two step procedure starting from 4,4'-biphthalic anhydride (BPA) as shown in Scheme I. The compounds as chain extenders were obtained in 65−88% yields. Structures of the resulting compounds were confirmed by ^{1}H NMR spectrum on a



Scheme I. Synthesis of dihydroxy compounds. (A) N, N'-bis(6-hydroxyhexyl)-3,4,3',4'-biphenyldicarboxyimide (BHHDI) and (B) N,N'-bis[4-(6-hydroxyhexyloxy) phenyl]-3,4,3',4'-biphenyldicarboxyimide (BHPDI).



Scheme II. Synthesis of polyurethane elastomers MHH's and MHP's.

DMSO-d_6 solution at 50 °C.

The polyurethane elastomers were synthesized from 4,4'-diphenylmethane diisocyanate (MDI) as a diisocyanate, poly(oxytetramethylene)glycol (PTMG) as a polyol of M_w 1000, and chain extenders containing imide unit (BHHDI or BHPDI) as shown in Scheme II. These polymers were designated as MHH series or MHP series. As a representative case, MHP50 is a polyurethane elastomer consisting of MDI, PTMG, BHPDI, and 50 wt% of hard segment content. Yield and intrinsic viscosity of the resulting polymers are shown in Table I. The polymers with high molecular weights indicated by intrinsic viscosity of 0.59 to 0.70 dL/g were obtained in 76 - 80% yields.

The structure of the resulting polyurethane was identified with FT-IR spectroscopy. As shown in Figure 1, the typical IR spectrum of the polyurethane elastomer MHH65 at room temperature showed the bands near 3330 cm^{-1} (N-H stretching), 1700 cm^{-1} (C=O stretching), 1540 cm^{-1} (C-N-H bending), and 1280 cm^{-1} (N-C-O stretching).

DSC thermograms of the polyurethane elastomers MHH's and MHP's are presented in Figure 2. In DSC scans of the polyurethanes, the glass transition is not observed, whereas the transition can be observed through dynamic mechanical thermal measurement mentioned below. Two endothermic peaks are detected at 136 °C and 154, 129 and 161 °C, respectively, in the MHH50 and MHH65. But, in the MHH35 cotaining 35 wt% of hard segment content one broad endothermic peak is detected at 129 °C. For the MHP's

Table I. Composition and Properties of Polyurethane Elastomers MHH's and MHP's

PUA	Composition (Molar Ratio) MDI/BHHDI/ PTMG(BHPDI)	Hard Segment Contents (%)	η_{inh}[a] (dL/g)	Yield (%)
MHH35	1.00/0.30/0.70	35	0.70	80
MHH50	1.00/0.50/0.50	50	0.68	77
MHH65	1.00/0.67/0.33	65	0.67	80
MHP35	1.00/0.24/0.76	35	0.69	76
MHP50	1.00/0.44/0.56	50	0.61	80
MHP65	1.00/0.64/0.36	65	0.59	79

[a] Solvent: DMF; concentration: 0.5 g/dL.

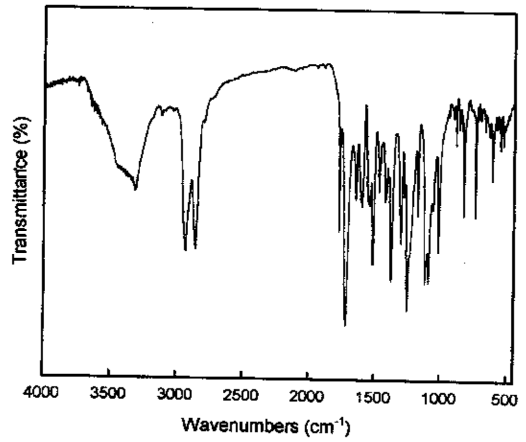


Figure 1. FT-IR spectrum of a polyurethane elastomer MHH65 at room temperature.

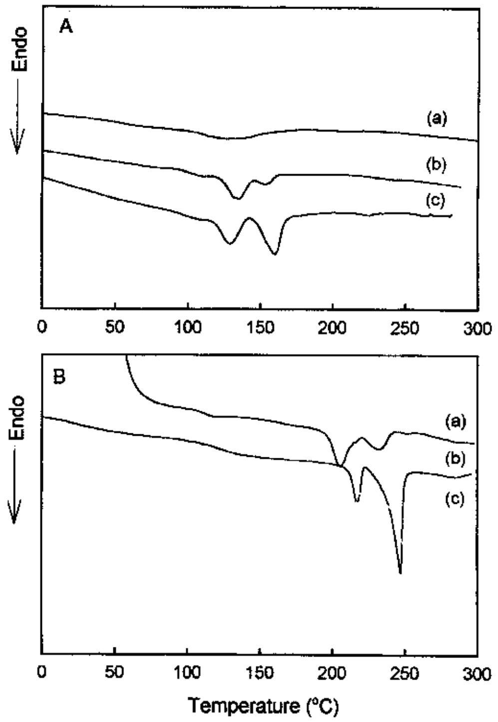


Figure 2. DSC thermograms for polyurethane elastomers. (A) MHH's and (B) MHP's: (a) 35, (b) 50, and (c) 65 wt% of hard segment content.

series, two endothermic peaks were detected at 207 °C and 234, 215 and 246 °C, 211 and 254 °C, respectively, in the 35, 50, and 65 wt% composition of hard segment. The peak appearing at the lower temperature might be associated with a crystal-crystal transition since the polarizing microscope observation did not reveal any melting transition in this temperature range. The endothermic peaks positioned at the higher temperature were found to the melting transition temperature confirmed by the polarizing microscope, associated with disordering processes which occur in the urethane hard segment domains. The main endothermic peaks shifted to higher temperature and the heat of fusion (ΔH_m) increased as the hard segment content is increased from 35 to 65%. The data in Table II demonstrate the effects of hard segment content and chemical structure of chain extender on the transition temperature. Both the MHH's and MHP's series of polyurethanes show an increase in melting temperature T_m with increasing hard segment content. In addition, value of T_m in the MHP's series with BHPDI component is higher than that of in the MHH's series with BHHDI component.

Table II. Thermal Properties of Polyurethane Elastomers MHH's and MHP's

PUA	Phase Transition Temperature[a]			
	T_{m1} (°C)	T_{m2} (°C)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)
MHH35	129	–	7.3	7.9
MHH50	136	154	5.8	21.0
MHH65	129	161	4.8	22.9
MHP35	207	234	5.2	–
MHP50	215	246	8	1.6
MHP65	211	254	6.5	9.2

[a] Determined by DSC measurement at a heating rate of 10 °C/min.

For the polyurethanes an importance of intermolecular hydrogen bonds resulting from urethane linkages was found out and it was revealed that the intermolecular hydrogen bonds play an important role in the stability and liquid crystal behavior of molecules.[16-19] Hydrogen bonding was studied by analyzing the FT-IR data of a curve-fitting in the carbonyl region which corresponds to the hydrogen-bonded carbonyl group near 1702-1717 cm^{-1} and the free carbonyl group near 1730 cm^{-1}. In the previous papers[14,15] the detail works of the curve fitting of the carbonyl region with the various hard segment contents for the polyurethanes were performed. It was revealed that the hydrogen-bonded carbonyl region for the polyurethanes with higher hard segment content was larger than that of the polyurethanes with lower hard segment content. In the polyurethane elastomers consisting of PTMG, MDI, and chain extender with imide group, MHP50 and MHP65 containing chain extender BHPDI showed liquid crystal behavior, but MHP35 and MHH's containing chain extender BHHDI did not show liquid crystallinity. Their liquid crystal behavior will be described in detail elsewhere.[15]

Polyurethane elastomers consisting of MDI, PTMG of M_w 1000, BHPDI as a chain extender exhibited stable liquid crystalline phases and high thermal stabilities compared with polyurethanes

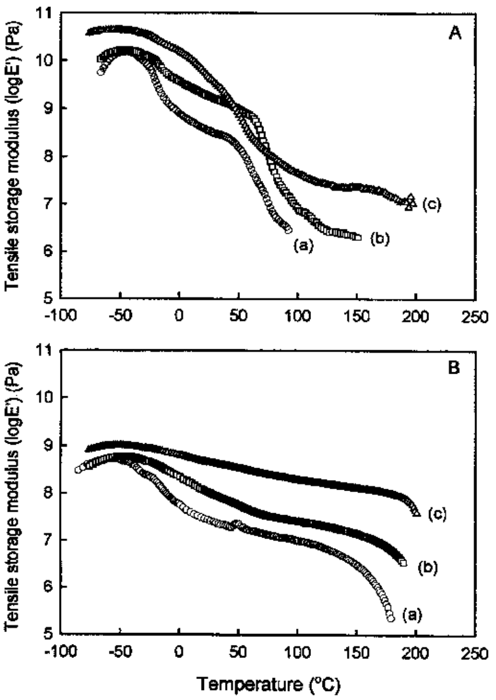


Figure 3. Tensile storage modulus for polyurethane elastomers. (A) MHH's and (B) MHP's: (a) 35, (b) 50, and (c) 65 wt% of hard segment content.

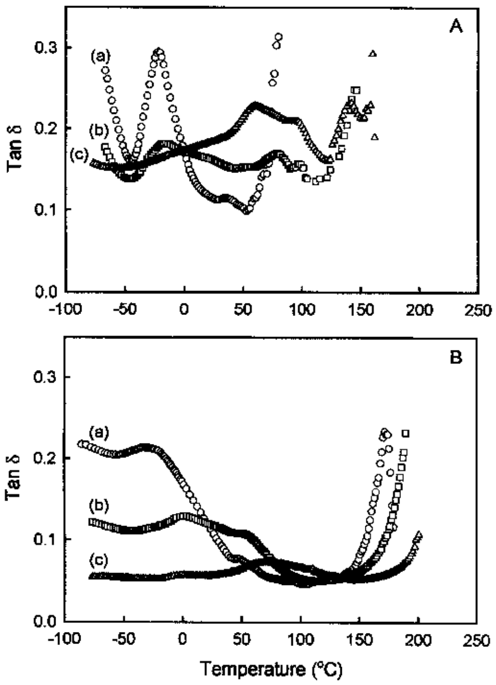


Figure 4. Tan δ for polyurethane elastomers. (A) MHH's and (B) MHP's: (a) 35, (b) 50, and (c) 65 wt% of hard segment content.

prepared in the previous papers.[14,15] For example, the polyurethanes containing imide unit showed the nematic texture, melting temperatures ranged from 207 to 254 °C, and 10% weight-loss temperatures ranged from 284 to 334 °C. The results were much higher than those of the polyurethanes without imide unit.

It has been known that dynamic mechanical thermal analysis (DMTA) is a rapid technique for measuring the change in modulus (the storage and loss modulus) over a wide range of temperature, providing considerable information on the position of transitions and the mechanical properties such as the glassy state and the rubbery plateau modulus of polymers.[13,20] Figure 3 shows the storage modulus (log E') over the range −100 to 250 °C for the two polyurethane elastomers (MHH's and MHP's) in which the variable is the hard segment content and the chemical structure of the chain extender. From the data it is obvious that as the hard segment content increases from 35 to 65% the thermal stability of polyurethane elastomers is enhanced and the chain extender BHPDI with the phenyl group between the imide unit and the flexible spacer gives a polyurethane elastomer of higher thermal stability than the chain extender BHHDI as a diol composed of imide unit and flexible spacer. The temperature at which the log E' shows significant change is considered to indicate the temperature limit of thermal stability of the polyurethane elastomers.[13] That is to say, the maximum values imply the limit of thermal stability of polyurethane elasomers. For example, polyurethane elastomers MHH's start to lose thermal stability at 95, 150, and 195 °C, respectively, as the hard segment content is increased. Polyurethane elastomers MHP's start to lose thermal stability at 145, 175, and 195 °C, respectively, as increasing the hard segment content. And, the modulus of the almost plateau region increased and extended to higher temperature as the hard segment content increased.

Figure 4 shows the tan δ as a function of temperature for two polyurethane elastomers with the same PTMG soft segment and MDI, but different chain extender. The tan δ curves show at least two peaks: One transition peak of hard segment shifted to higher temperature and the other transition peak corresponding to the glass transition of PTMG soft segment phase broadened as the hard segment content is increased. These phenomena indicate a partially phase mixed morphology with increasing the hard segment content. From the results of the storage modulus and tan δ measurement, it is found that significant transitions were shown for polyurethane elastomers MHH's containing a chain extender BHHDI and phase mixings were indicated for two polyurethane elastomers as the hard segment is increased.

The tensile properties of a polymer are also measured to provide information on the mechanical properties of a polymer. The stress-strain properties of the polyurethanes MHH's and MHP's are shown in Figure 5. From the results, Young's modulus, ultimate tensile strength, and elongation at berak are obtained. These data show that an increase in the hard segment content or the incorporation of rigid imide unit leads to a higher Young's modulus and lower elongation at failure. It can be seen that tensile strength and initial modulus increase as the hard segment content is increased, whereas elongation at break reduce with increasing hard segment content. For the MHH's series elongation at break more slowly reduce with increasing hard segment content.

In the polyurethane, hard segment crystallization has been found to increase stress hysteresis, permanent set, and tensile strength.[20] It was revealed that stress hysteresis is a function of domain ductility and restructuring, and the nature of the mixed hard and soft segment interfacial regions,[21] unlike the low strain Young's modulus which depends on the rigidity and morphology of the hard segment domains. Figure 6 shows a typical stress-strain hysteresis for polyurethane elastomers MHP35 and MHP50. Their elongation at which the retraction curve returns to zero stress decreased with increasing hard segment content, but in the same strain region the stress increased.

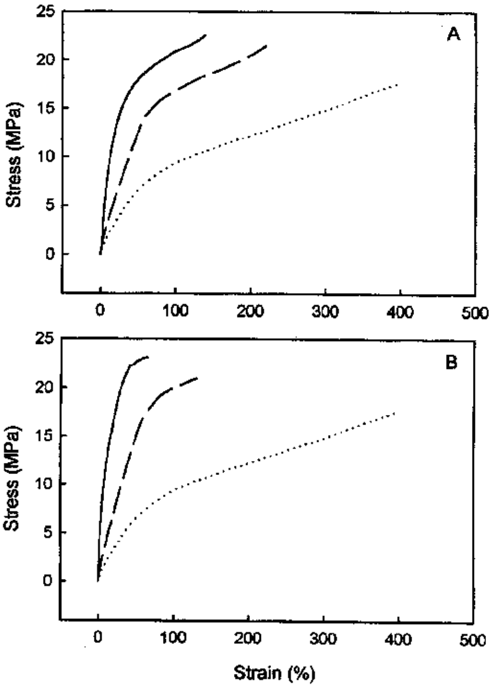


Figure 5. Tensile stress-strain behavior for polyurethane elastomers. (A) MHH's and (B) MHP's: (a) 35, (b) 50, and (c) 65 wt% of hard segment content.

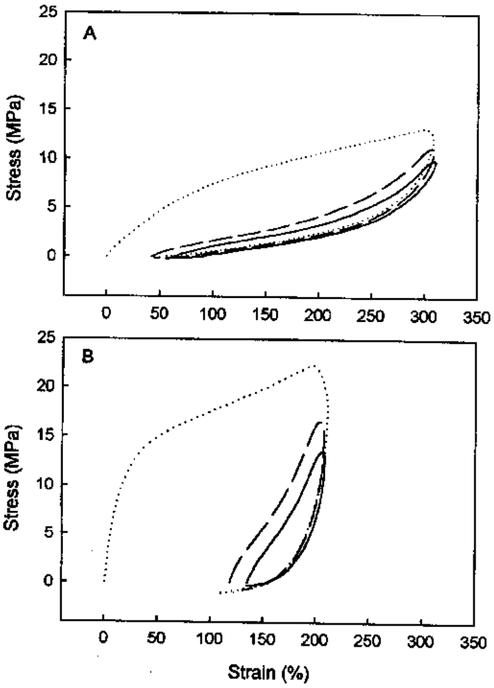


Figure 6. Stress-strain hysteresis curves for polyurethane elastomers. (A) MHP35 and (B) MHP50.

From the tensile retraction behavior it was found that the polyurethane elastomers having lower hard segment content exhibited good elastomeric behavior.

Conclusions

A series of new polyurethane elastomers were successfully synthesized using the chain extender with imide group. By combining imide group and flexible spacer the polyurethane elastomers exhibit good mechanical and elastic properties. The main endothermic peaks shifted to higher temperature and the heat of fusion (ΔH_m) increased as the hard segment content is increased from 35 to 65% in the DSC thermograms. In the tan δ curves one transition peak of hard segment shifted to higher temperature and the other transition peak corresponding to the glass transition of PTMG soft segment phase broadened as the hard segment content is increased. These phenomena indicate a partially phase mixed morphology with increasing the hard segment content. The tensile strength and initial modulus of the polyurethanes increased as the hard segment content is increased, whereas elongation at break reduced with increasing hard segment content. In the stress-strain hysteresis of polyurethane elastomers their elongation at which the retraction curve returns to zero stress decreased with increasing hard segment content. From the tensile retraction behavior it was found that the polyurethane elastomers having lower hard segment content exhibited good elastomeric behavior. Increasing the rigidity of the chain extender when changing from BHHDI to BHPDI results in a increase in thermal stability. These depend upon different structural features of the chain extender. A polyurethane elastomer prepared from the chain extender BHHDI is inferior in tensile properties to the polyurethane elastomer containing the chain extender BHPDI. The incorporation of rigid imide units into polyurethane elastomers improved mechanical properties and thermal stabilities.

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