Synthesis and Characterization of Segmented Polyurethanes Containing Aromatic Diol Chain Extenders

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ABSTRACT: A series of segmented polyurethanes (SPUs), based on hexamethylene diisocyanate (HDI) and polytetramethylene glycol (PTMG) as soft segments and then extended with alkylene di(4-hydroxybenzoate), HB as hard segments, were synthesized in this study. The effect of the number of methylene units in HB (from 2 to 6) on the microphase separation of the SPUs was evaluated by means of a differential scanning calorimeter (DSC) and a polarized optical microscope (POM). The kinetic reaction between HB and HDI was determined by Fourier transform infrared spectroscopy. The rate constants of the second-order kinetics showed that the reactions of HDI and HB with odd numbers of methylene units appeared to be faster than those with even numbers of methylene units. The results from POM showed that the SPUs with even numbers of methylene units in the HB have a higher degree of phase separation between the hard and soft segments than those with odd numbers of methylene units in HB. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 539–546, 1997

Key words: segmented polyurethane; microphase separation; alkylene di(4-hydroxybenzoate); sott segments; hard segments
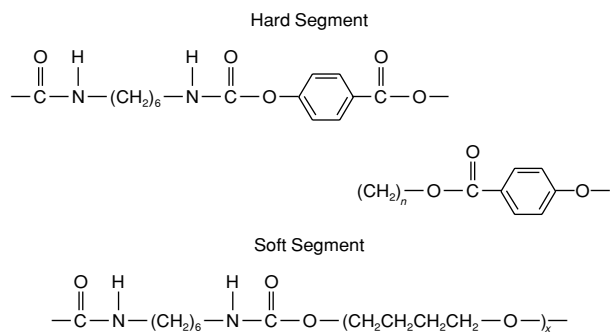
INTRODUCTION

Polyurethane (PU) is a fascinating class of polymers which, through the variations of the hard and soft segments, can exhibit diverse physiochemical properties. It has been suggested for use as biomaterials since 1967[1] due to its strong mechanical properties and good tissue and blood compatibility. Recent advances of this class of materials have been reviewed by Gogolewski[2] and Cooper,[3] and most efforts have been made to improve the blood-contacting properties of PU biomaterials.[4–9] However, the frequently used diisocyanates are 4,4'-diphenylmethylene diisocya-

nate (MDI) and toluene diisocyanate (TDI), which are respectively converted into the toxic, mutagenic, and carcinogenic diamine 4,4'-methylenedianiline (MDA)[10–12] and toluene-diamine (TDA)[13] after degradation.

The other problem of MDI-based polyurethanes is the commercially unfavorable yellowing upon exposure to UV radiation or heat.[14,15] In order to solve the yellowing and degradation problems of the aromatic polyurethanes, the research has focused on the development of biomedical-grade polyurethane elastomers based on aliphatic diisocyanates. In 1979, the second-generation biomedical-grade polyurethane was introduced under the trade named Tecoflex®, which was synthesized from the aliphatic 4,4'-methylene dicyclohexyl diisocyanate (H_{12}MDI). It has been reported that the polymer is less water and heat stable than its

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Hard Segment

Soft Segment

Scheme 1

Figure 1 Variations of $(NCO)_0/(NCO)$ with time for the reaction of HB and HDI at 70°C.
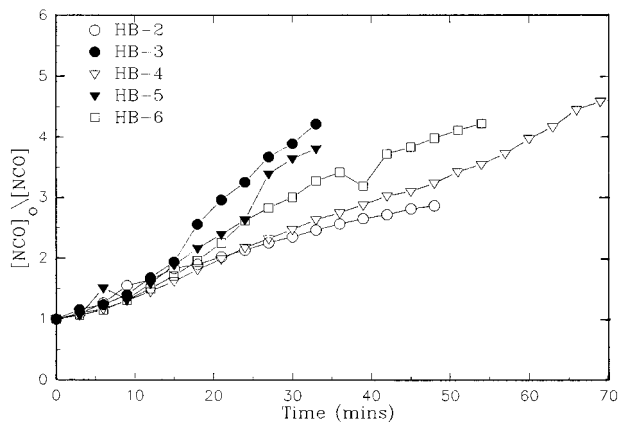
aromatic analog Pellethane.[15] This seems to be due to the lack of regularity in the hard segments, as the polymer was produced from the mixture of $H_{12}MDI$ isomers. In order to overcome the yellowing and toxic problems of MDI-based polyurethanes, the new biomedical-grade polyurethanes based on 1,6-hexamethylene diisocyanate (HDI), less toxic than MDI and more pure than $H_{12}MDI$, were synthesized in our laboratory. With concern that the aliphatic diisocyanate might reduce mechanical properties and thermal stability, efforts were then made to synthesize nontoxic aromatic diols, alkylene di(4-hydroxybenzoate), as the chain extenders. (When degraded, the residue compound is 4-hydroxy benzoic acid.) Since the reactivity of a commonly used aromatic diisocyanate with an aliphatic diol is higher than that of an aliphatic diisocyanate with an aromatic diol, the reaction kinetics between HDI and the aromatic diols were studied primarily. The degree of phase separation by varying the methylene units in the aromatic diols in polyurethanes will be discussed.

EXPERIMENTAL

Materials and Synthesis

A series of methylene units (from 2 to 6) in alkylene di(4-hydroxybenzoate), HB, were synthe-

sized by adopting the procedures described in references 16 and 17.

Polyurethanes were prepared by a conventional two-step solution polymerization method, reacting the aliphatic 1,6-hexamethylene diisocyanate (Aldrich) with a polyether diol, polytetramethylene glycol (PTMG, MW = 1000, Aldrich), to form a soft-block segment. The resultant prepolymer was then extended with an aromatic alkylene di(4-hydroxybenzoate) (HB), to form a hard-block segment. Scheme 1 shows the chemical structures of the hard and soft segments in SPU. The whole polymerization process was as follows. Polyether diols PTMG were dehydrated in a vacuum at 120°C for 3 hours. Then, the calculated amount of HDI in 20 wt % of dimethylformamide (Merck, dried over 4 Å molecular sieves prior to use) was added and the reaction was kept at 110°C for 2 hours under a nitrogen atmosphere. Then, the temperature was decreased to 80°C and a solution of chain extenders and catalyst (1 wt % of dibutyltin dilaurate, DBTDL, Aldrich) in 10 wt % of DMF was added to the prepolymer mixture dropwise for 10 hours. The polymer was precipitated by quenching the reaction mixture in

Table I   The Second-order Rate Constants of Different HB Reacted with HDI at 70°C

	HB-2	HB-3	HB-4	HB-5	HB-6
Intercept	1.121	0.669	0.889	0.726	0.867
Slope (min^{-1})	0.039	0.106	0.052	0.089	0.066
k ($min^{-1} M^{-1}$)	5.85	15.89	7.80	13.34	9.90
R	0.989	0.987	0.998	0.975	0.991

$[HDI]_0 = 6.67 \times 10^{-3} M$.

Table II   Compositions and Properties of Segmented Polyetherurethanes

|	Molar Ratio			T_g (°C)		Ave. MW	
Polymer	HDI	PTMG	HB	T_{gs}	T_{gh}	M_n	M_w
PU-PTMG-2	2	1	1	−76.5	80.0	5200	11000
PU-PTMG-3	2	1	1	−59.5	62.0	16300	24500
PU-PTMG-4	2	1	1	−60.9	91.0	18100	34500
PU-PTMG-5	2	1	1	−56.6	—	17600	39500
PU-PTMG-6	2	1	1	−61.7	61.0	22500	42000
PU-PTMG-2-0.5	2	0.5	1.5	−76.3	80.0		
PU-PTMG-2-1.25	2	1.25	0.75	−77.2	100.0		
PU-PTMG-2-1.5	2	1.5	0.5	−77.1	—		

70 : 30 v/v cold water : ethanol. White precipitate was obtained with a typical yield of 85%. The unreacted residue was extracted with ethanol. The final products were dried in a vacuum oven at 50°C for 10 hours.

In the kinetic studies, a molar ratio of 0.1 mmol HDI and 0.1 mmol HB was dissolved in 15 mL of DMF. Before the injection of the sample into a solution IR cell with a temperature controller (from Specac, Cambridge Electronic Industries), 6 wt % of the catalyst DBTDL was added. Infrared spectra were recorded at 70°C with a Perkin-Elmer FTIR 2000 Fourier transform infrared spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Characterization

The thermograms of polymers were determined with the use of a differential scanning calorimeter (DSC-7, Perkin-Elmer) at a heating rate of 20°C/ min under helium. The glass transition temperatures were taken at the midpoint of the abrupt heat-capacity jump. The DSC was calibrated with a pure indium standard. A polarized light microscope (Olympus BHSP) was used to determine the morphological textures of the crystalline domains. A solution of 1 wt % in DMF was cast on pretreated glass coverslips which were cleaned thoroughly with chromic acid, followed by water and detergents under sonication, and then washed with ethanol and dried under vacuum at 45°C. The molecular weights of the polymers were characterized by gel permeation chromatography (GPC). The GPC was performed in a Hewlett Packard 1050 system equipped with a variable UV detector and a 1047 refractive index detector. Samples were eluted through three PL-gel columns in series at 70°C using DMF as an eluent. Ten polystyrene standards (Polysciences, Inc.) were used to calibrate the material system used.
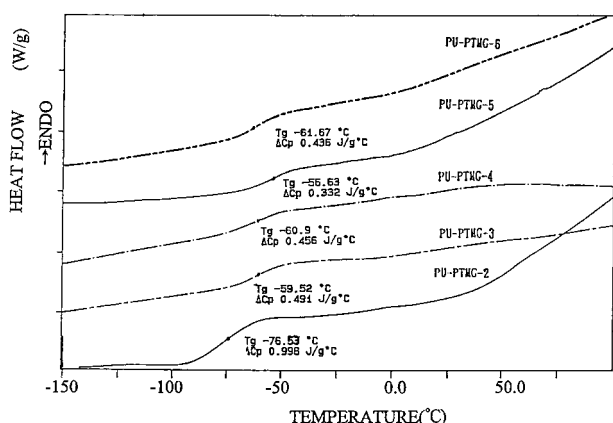
Figure 2   DSC thermograms for PU-PTMG-HB over the low-temperature range.
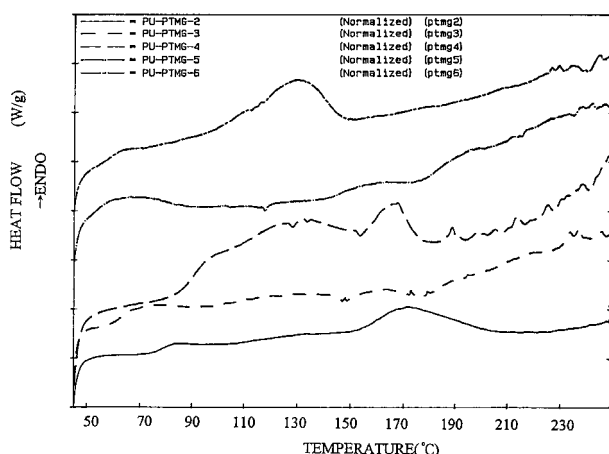
Figure 3   DSC thermograms for PU-PTMG-HB over the high-temperature range.
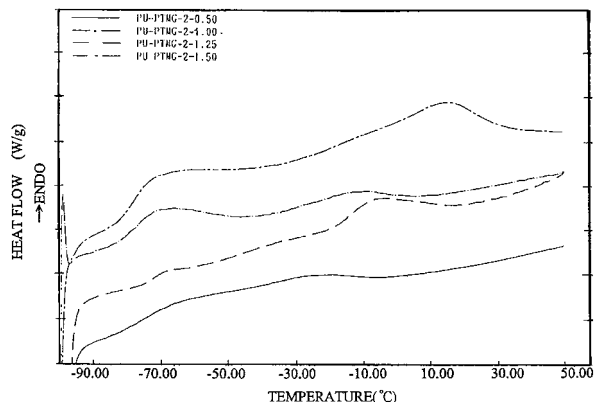
Figure 4 DSC thermograms for PU-PTMG-2 with different PTMG contents over the low-temperature range.

RESULTS AND DISCUSSION

### Synthesis of Segmented Polyetherurethanes (SPU)

A significant effort was made in this study to develop an aliphatic thermoplastic polyurethane elastomer with physical properties comparable to high-performance aromatic-based polyurethanes. Typically, the reaction of an isocyanate with an alcohol is essentially a nucleophilic attack of the alcohol on the carbon atom of the isocyanate group, followed by a 1,3 shift of the hydrogen atom. The reactivity of an aromatic diol with an aliphatic diisocyanate is much less than that of an aliphatic diol with an aromatic diisocyanate. Therefore, only the hard segments, HDI and HB, were chosen for the kinetic study.

The reactions were carried out in an IR solution cell with a temperature controller at 70°C. The characteristic absorbance of NCO functional groups appeared at 2276 cm^{-1} and decreased with time, and the peak area under 2325–2150 cm^{-1} was used to represent the concentration of NCO functional groups. The simple second-order kinetic model was used to simulate the reaction.[18] The plot of the initial NCO concentration over the concentration at time t [$(NCO)_0/(NCO)_t$ vs. time]
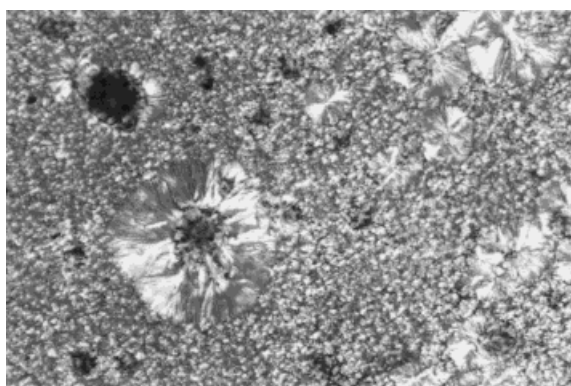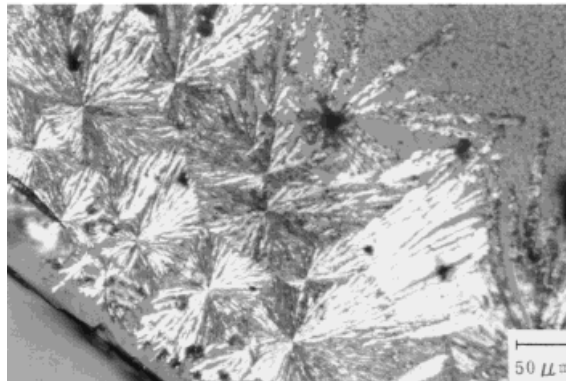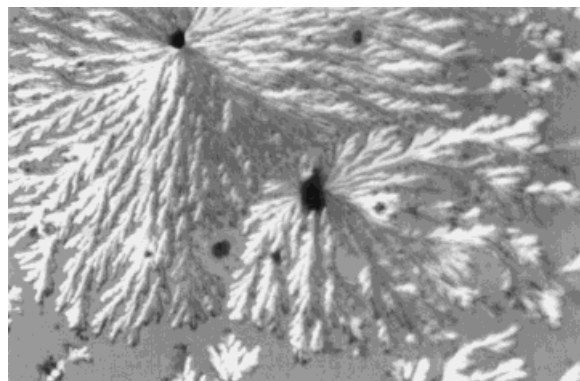

(a) HDI-HB-2
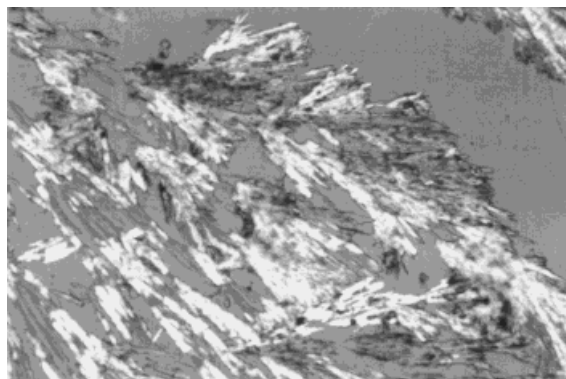
(c) PU-PTMG-3
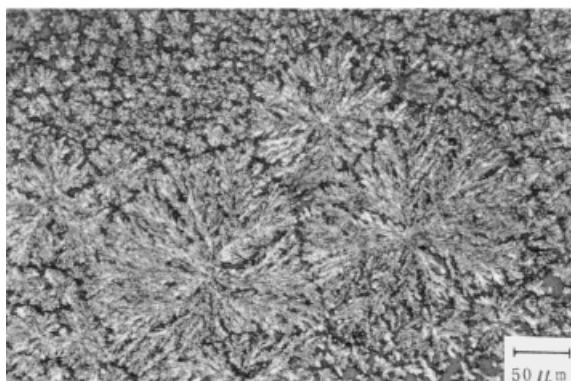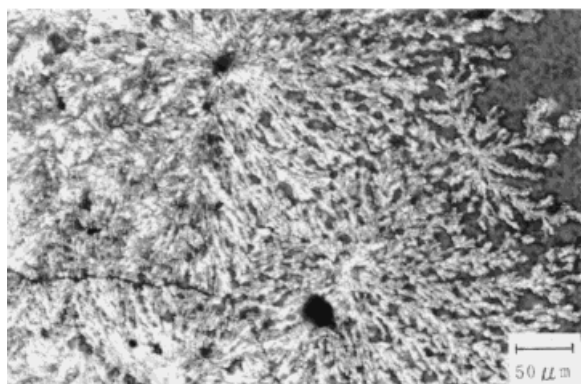

(b) PU-PTMG-2

(d) PU-PTMG-4

Figure 5 Polarized-light micrographs for PU-PTMG-HB.

(e) PU-PTMG-5

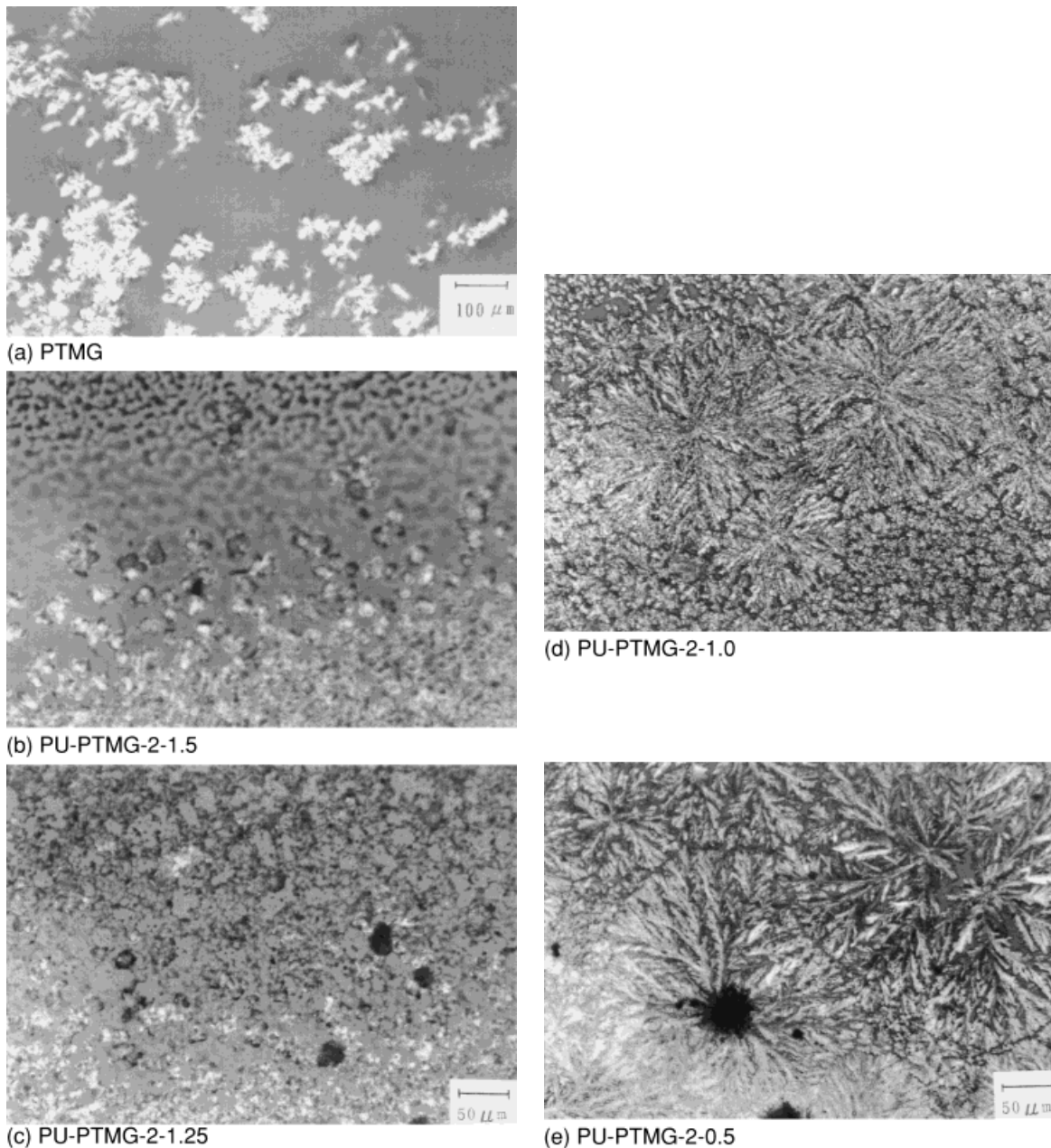(f) PU-PTMG-6

Figure 5 (*Continued from the previous page*)

was indicated in Fig. 1. The rate constants, k, were obtained from the slopes of the plots. Values of the slopes and the intercepts were summarized in Table I with linear regression (R) values. These second-order rate constants were comparatively the same order as those of the uncatalyzed reaction of phenyl isocyanate with aliphatic diols[19] and ten times larger than those of the catalyzed reaction of HDI with dicarboxylic acids.[20] The rate constants for odd numbers of methylene units in HB, HB-odd, seem larger than those for even numbers of methylene units, HB-even. This suggests that the reactivity of HDI with HB-even is poorer than with HB-odd, especially for HB-2. The result is similar to the reported reaction for the uncatalyzed polyesterification of adipic acid, where ethylene glycol showed the slowest reaction, followed by 1,12-dodecamethyene glycol and then by 1,10-decamethylene glycol.[21] However, the odd−even effect on the reaction rate constant was not found in the literature.

In Table II, SPUs with the molar ratio of 2 : 1 : 1 of HDI : PTMG : HB were synthesized, and the numeral after PTMG indicates the number of methylene units in the HB. We found that the slowest reaction rate of HB-2 and HDI resulted in the lowest molecular weight of PU-PTMG-2. Furthermore, PU-PTMG-2 was systematically synthesized by varying the molar ratio between PTMG and HB-2 with HDI fixed at two moles. The numeral after 2 in Table II represents the molar composition of PTMG. No precipitate was found if the HB-2 was less than 0.5 moles or higher than 1.5 moles. We believe that at low HB-2 content, the reacted products (most are the soft segments) are soluble in the nonsolvent system we used. For the SPUs with high contents of HB-2, the molecular weight was not high enough to allow the polymer to be precipitated. This is mainly due to the low reactivity between HDI and HB-2. Due to the relatively low molecular weight in our synthesized SPUs, the more complex catalytic system will be tried in our further work.

Differential Scanning Calorimetry (DSC)

For experimental convenience, the DSC scans were separately run at two temperature ranges, i.e., $-100°$ to $100°C$ for the soft segment transitions and $50°$ to $250°C$ for the hard segment transitions. The thermograms for the PU−PTMG−HB series are illustrated in Fig. 2. Since the increase of soft-segment glass transition temperatures from pure PTMG ($\sim -85°C$) is an indication of the phase mixing between the hard-segment units and the soft-segment phase,[22–24] we concluded from Table II that PU-PTMG-2, having the lowest T_{gs} value of $-76.5°C$, showed the greatest phase separation between the hard and soft segments; and PU-PTMG-5, with the highest T_{gs} value of $-56.6°C$, indicated the best phase-mixing effect. The observation of T_g and T_m for the soft segment phase was reproducible even after the heating and cooling cycle. Higher temperature thermal transitions were not as easily observed as those for the soft segment phases. The T_{gh}s for the hard-segments were in the range of 60 to 90°C after fast-heating the samples to 120°C for 3 min, followed by quenching them to 50°C.

The endothermic peaks corresponding to melting behavior were ambiguous, except for those SPUs with the even numbers of methylene units (Fig. 3). The observed effects of the number of methylene units in HB of SPUs are similar to

Figure 6 Polarized-light micrographs for PU-PTMG-2 with different PTMG contents.

those found in small compounds,[25] where the even number of methylene units showed a higher degree of crystallinity. Owing to the high crystallinity in their hard segments and slightly low T_g in their soft segments, we concluded that those SPUs with even numbers of methylene units formed better phase separation of the hard and soft segments. The same results were observed in segmented poly(urethaneureas) (SPUUs) with various aliphatic diamine chain extenders.[26] The

SPUUs containing diamines with an odd number of methylene units also showed a remarkable degree of phase-mixing between the hard and soft segments.

On variation of molar compositions of PTMG and HB-2, the T_g of the four samples remains at about $-76° \sim -77°C$ for the soft-segment transition as tabulated in Table II. The values of melting points increase with increasing soft segment content and close to the T_m of pure PTMG, i.e.,
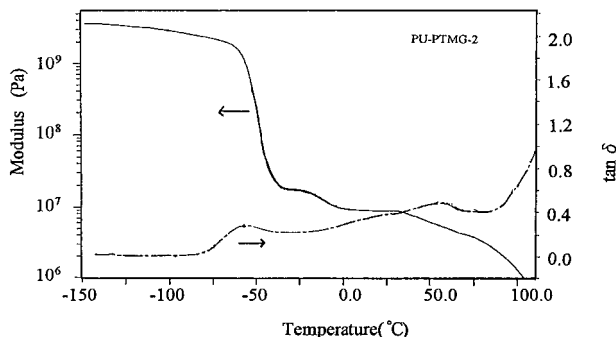
Figure 7 Storage modulus and tan δ for PU-PTMG-2.

23°C as shown in Fig. 4. The degree of phase separation also goes hand in hand with the increase in the soft-segment contents. Furthermore, the endothermic peak in the region of the hard-segment phase becomes pronounced when the composition of hard segments is increased. Increasing the hard segment content results in an increased degree of crystallinity; on the other hand, the tendency of hard segments to form the continuous phase is also increased.

Optical Microscopy

An optical microscope was used to study the effect of the number of methylene units in HB and the composition of SPU on the crystalline texture and on the phase separation. Figure 5 shows the optical micrographs of PU–PTMG with different methylene units. Since the experimental temperature was fixed at room temperature, which is above the melting point of the soft segment of SPUs, the observed textures can be attributed to the hard segment domain. Although complete spherulite texture was not obtained for the PU–PTMG–HB system, it is clear that the system with an even number of methylene units in HB exhibits a more distinguished spherulitic texture as shown in Figure 5. Moreover, phase separation in the continuous phase can be seen in PU–PTMG-4 and PU–PTMG-6. This was consistent with the findings from our DSC studies, which showed that systems with even numbers of methylene had lower T_{gs}s due to the exclusion of the hard segments from the soft segment phases. On the other hand, increasing the soft segment content in PU–PTMG-2 resulted in a decreased degree of crystallinity of hard segment domains and an increased degree of phase separation as shown

in Fig. 6. In the high PTMG contents, i.e., PU–PTMG-2-1.25 and PU–PTMG-2-1.5, the texture on the surface looks like that of a pure PTMG; and the microphase separation becomes prominent.

CONCLUSIONS

A series of new polyetherurethane biomaterials were successfully synthesized using the aliphatic diisocyanate HDI with aromatic diol HB as a chain extender. The promising characteristics of this chemical design are the reduced toxicity upon degradation and the reduced degree of yellowing upon exposure to UV radiation. The reactivity of HDI with HB-odd was higher than that with HB-even. The slowest reaction rate of HB-2 and HDI resulted in the lowest molecular weight of PU–PTMG-2. Phase separation phenomena of SPUs with HB-even were more distinguished than those of SPUs with HB-odd, due to faster reaction rates and higher conversions of HDI and HB-odd, resulting in more homogenous distributions between the hard and soft segments. Since the aliphatic polyurethanes usually lack desired mechanical properties, the preliminary test of storage modulus of PU–PTMG-2 in the low temperature range, as shown in Fig. 7, seems comparable to the commercially used Biomer®.

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