

The Properties of Polyurethanes with Mixed Chain Extenders and Mixed Soft Segments

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SYNOPSIS

Series of polyurethaneurea elastomers were prepared from 4,4'-diphenylmethane diisocyanate, poly(tetramethylene ether) glycol and poly(hexamethylene carbonate) glycol for mixed soft segments, and 1,4-butanediol and isophoronediamine for mixed chain extenders. Characteristics of the copolymers related with compositions were examined. FT-IR spectra showed that most of the urea carbonyl groups associated in hydrogen bonding, while urethane carbonyls only partially did so. Thermal and mechanical properties were investigated through differential scanning calorimetry and tensile testing. These thermal and mechanical properties are discussed from the viewpoint of microphase domain separation of hard and soft segments. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The characteristics of hard and soft segments are important determining factors for the properties of polyurethane (PU) and polyurethaneurea (PUU) elastomers. It is well known and understood that hard and soft segments of PU and PUU segregate into microphase domains separately, and such phenomena cause the polymers to exhibit excellent elastomeric properties. Hard segments, which perform as the strong and reversible physical cross-linking sites, keep the chains from slipping away from each other when stress is applied. So high temperature performance and mechanical strength of PU and PUU are influenced by the stability of the hard segments. The cohesive strength of hard segments can be enhanced by strong interactive forces such as hydrogen bonding or by the crystallization of hard segments. On the other hand, soft segments mainly have to do with low temperature behaviors of PU and PUU. The low glass transition temperature of the soft segments (typically in the range of -60 – -90°C in the homooligomer state) enables PU

and PUU to perform as excellent elastomers even at cold environments.

The properties of PU and PUU can be varied in numerous ways according to the demands of their uses. One of them is to change the ratio of hard and soft segment composition. In general, by increasing hard segment content in PU and PUU structures, elastomers with higher modulus can be obtained. Variation in molecular weights of soft segments also makes differences. Utilizing a compound of different chemical structure, e.g., polyether diol in place of polyester diol for soft segment, or diamine in place of diol for chain extender, is another way of attaining modified properties of PU and PUU.¹⁻³

In this work, we observed the changes in the properties of PUU when one of its components was gradually altered with a compound of different chemical structure. First, we gradually replaced 1,4-butanediol (BD) with isophoronediamine (IPDA), a bulky alicyclic diamine with some methyl side groups. We prepared this series for two different molecular weights of soft segments, 1000 and 2000, which resulted in two different hard segments content, ca. 39 and 24 wt %, respectively. We also partly replaced poly(tetramethylene ether) glycol (PTMG) with poly(hexamethylene carbonate) diol (PHC) for the soft segments. The effects of altered

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structures on the thermal and mechanical properties of PUU were examined, and from the results we tried to explain the effects of structural changes of PUU chains on the microdomain structures of them.

EXPERIMENTAL

Materials

Commercial grade PTMG and PHC of molecular weight 1000 and 2000 (from Kyoken Chemical Works Co.) were used after drying at 90°C for more than 3 h under vacuum. 4,4'-Diphenylmethane diisocyanate (MDI, reagent grade, Tokyo Chemicals Inc.) was melted at 45°C and used after excluding white MDI dimer precipitates in the melts. Reagent grade BD and IPDA (both from Tokyo Chemicals Inc.) were used after immersion of 4-Å molecular sieves for more than a week. *N,N*-dimethylformamide (DMF, Duksan Chemicals, reagent grade) was used as solvent after immersion of 4-Å molecular sieves for more than a week with occasional shaking.

Chemical structures of major compounds are shown in Table I.

Synthesis

Prepolymer method was employed for the synthesis of PUU; an excess amount of MDI was reacted with long chain diol (homooligomer of soft segment), and then reaction with chain extenders was followed.

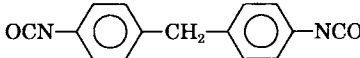
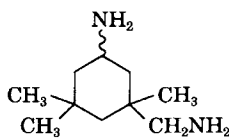
First, a series of PUU with various BD/IPDA compositions was synthesized using PTMG as soft segment. Prepolymer was prepared from the reaction of 1 mol of PTMG and 2.1 mol of MDI at 68°C for

90 min in a stirred vessel. The reaction vessel was constantly purged with dry N₂ gas. Then, 1 mol of chain extenders was added: BD was let in first and reacted for 60–120 min at 68°C in DMF (the reaction time varied with BD/IPDA composition ratio). After cooling the solution of partly chain-extended polyurethane to room temperature, IPDA solution in DMF, which was mixed with a small amount of formic acid (less than 0.03 wt % of final polymer solution weight), was added into the reactor with rapid stirring. Because the reaction between aliphatic amine and aromatic isocyanate was extremely fast, it was difficult to avoid the gelation of the polymer solution without the appropriate use of retarding agents such as formic acid. It was probably due to crosslinking reactions via biuret formation. The solution was stirred for further reaction for 1–2 h, at 68°C. As a final step, 1 mL of methanol was added in order to destroy remaining isocyanate groups. The concentration of the final solution was adjusted to approximately 25% (w/v).

Two sets of the series were prepared using PTMG of two different molecular weights, 1000 and 2000, respectively. The overall [NCO]/[active hydrogen] ratio was kept at 1.05. Hard segment contents of the two sets of PUU samples were approximately 39 and 24 wt % for the PTMG 1000 and PTMG 2000 sets, respectively.

Another series of PUUs were prepared using mixture of PTMG and PHC as soft segments. The BD/IPDA mole ratio for the chain extender was fixed to constant value (= 1/1). MDI (2.1 mol) was made to react with 1 mol of soft segment components, i.e., mixture of PTMG and PHC, at 68°C for 90 min in DMF. The overall reaction scheme after the prepolymer synthesis was similar to that of the previously mentioned series.

Table I Structures and Properties of Major Chemical Compounds Used in the Synthesis

4,4'-Diphenylmethane diisocyanate (MDI)		$T_m = 38^\circ\text{C}$
Isophoronediamine (IPDA)		Mixture of isomers
Poly(tetramethylene ether) glycol (PTMG)	$\text{HO}-(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{O})_n-\text{H}$	$M_n = 1000, 2000; T_m = 23, 28^\circ\text{C}^a$
Poly(hexamethylene carbonate) diol (PHC)	$\text{HO}-\left[(\text{CH}_2)_6-\text{OCO} \right]_n-(\text{CH}_2)_6-\text{OH}$	$M_n = 1000, 2000; T_m = 42, 54^\circ\text{C}^a$

^a Melting temperatures for $M_n = 1000$ and 2000, respectively.

Sample designation and their composition data are listed in Table II. There are four series: H and S denote that hard and soft segment compositions were varied, respectively. -1 and -2 denote the molecular weights of soft segment long chain diols used in the synthesis, corresponding to 1000 and 2000, respectively.

Analysis

FT-IR spectra were taken using Bruker model IFS 88 FT-IR spectrophotometer. PUU was dissolved in tetrahydrofuran, and then cast on an NaCl IR cell to obtain thin films of PUU adequate for the FT-IR spectroscopy. Scanning resolution was 4 cm^{-1} , and 32 scans were averaged to obtain each spectra.

The specimens for the characterization of thermal and mechanical properties were prepared by spreading 25% (w/v) DMF solution onto glass plates, followed by solvent evaporation and drying for 4 h in a convection oven at 80°C .

DSC measurements were carried out by using Mettler TA-3000. The samples of about 9 mg each were melted at 200°C for 2 min and then quenched to -150°C in a DSC cell. Then, they were heated at the rate of $20^\circ\text{C}/\text{min}$ up to 270°C under constant N_2 flow.

The uniaxial stress-strain testing was performed on a Instron Model 1123 tensile testing apparatus at room temperature. The samples had been conditioned at 23°C , 50% relative humidity, for at least 24 h prior to testing. Dimensions of the specimen used were $80 \times 10\text{ mm}$ by size, and $0.16 \pm 0.015\text{ mm}$ thick. The gauge length was 40 mm, and the test was performed at the crosshead speed of 20 cm/min. Measurements of four tests were averaged for each sample.

Relative viscosity η_r was measured by using a Cannon-Fenske type capillary viscometer from 0.2 g/dL DMF solution at 25°C . The average value of three measurements was taken. Intrinsic viscosity $[\eta]$ was obtained by using the equation of Solomon and Ciută,⁴ $[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2}/c$, where η_{sp} is the specific viscosity and c is the concentration of the solution. The results of the viscosity measurements are shown in Table II.

RESULTS AND DISCUSSION

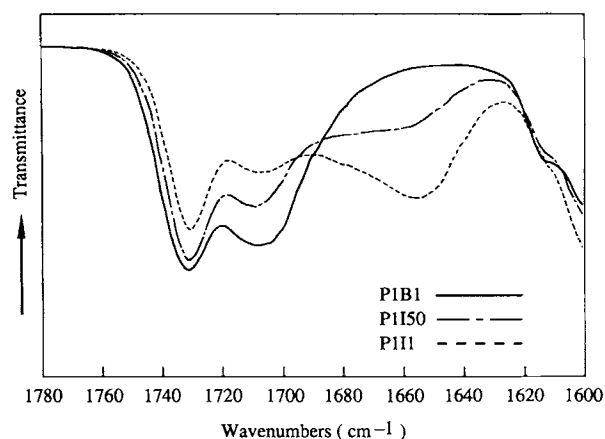
FT-IR Spectra

For each of the obtained FT-IR spectra of PUUs, peaks in the frequency region of $1600\text{--}1780\text{ cm}^{-1}$ of series H-1 and series H-2 are amplified in Figures

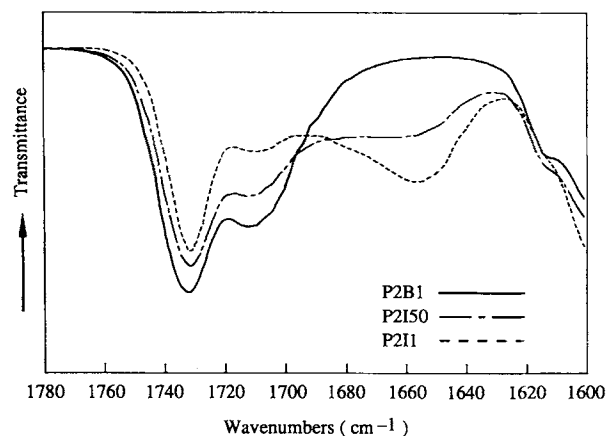
Table II Series of Prepared PUU Samples

Sample	IPDA/BD Mole Ratio	PTMG/PHC Mole Ratio	Hard Segment Content (wt %)	Intrinsic Viscosity (dL/g)
Series H-1				
P1B1	0/100	100/0	38.1	0.545
P1I25	25/75	100/0	38.9	0.756
P1I50	50/50	100/0	39.6	1.368
P1I75	75/25	100/0	40.3	1.089
P1I1	100/0	100/0	41.0	0.873
Series H-2				
P2B1	0/100	100/0	23.5	0.702
P2I25	25/75	100/0	24.1	0.842
P2I50	50/50	100/0	24.7	0.909
P2I75	75/25	100/0	25.4	0.962
P2I1	100/0	100/0	25.8	1.089
Series S-1				
P1-90I50	50/50	90/10	39.6	1.223
P1-70I50	50/50	70/30	39.6	1.011
P1-50I50	50/50	50/50	39.6	1.468
Series S-2				
P2-90I50	50/50	90/10	24.7	0.896
P2-70I50	50/50	70/30	24.7	0.847
P2-50I50	50/50	50/50	24.7	0.927

1 (a) and 1 (b), respectively. Characteristic absorption peaks of urethane and urea carbonyl groups can be observed in this region. For the samples which were chain extended with BD only [P1B1 and P2B1 lines in Figs. 1 (a) and 1 (b)], two distinct peaks are observed, which correspond to urethane carbonyls, non-hydrogen-bonded (1730 cm^{-1}) and hydrogen-bonded (1712 cm^{-1}), respectively.³ From the spectra, it is observed that a certain amount of urethane carbonyls exist in hydrogen-bonded form while the rest of them exist in "free" state form. When 50% of BD is replaced by IPDA [P1I50 and P2I50 lines in Figs. 1 (a) and 1 (b)], another broad peak appears at 1660 cm^{-1} , which corresponds to hydrogen-bonded urea carbonyl. Urea linkage resulted from the reaction of IPDA and MDI. At the same time, the urethane carbonyl peaks are weakened due to the decrease in their concentration. When all of the BDs are replaced by IPDA [P1I1 and P2I1 lines in Figs. 1 (a)



(a)

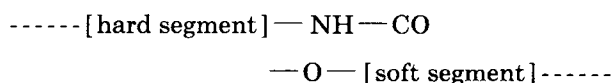


(b)

Figure 1 FT-IR spectra of major samples: (a) series H-1; (b) series H-2.

and 1 (b)], urea carbonyl peak grows more distinct and urethane peaks are all the more weakened.

In both Figures 1 (a) and 1 (b), hydrogen-bonded urethane carbonyl peak shows relatively greater decrease compared with non-hydrogen-bonded urethane carbonyl as the IPDA content is increased. If BD is included in the reaction composition, urethane groups are present both in the hard segments and in the soft segments according to the reaction scheme. But, in the case of PUU, the chain extender of which is solely composed of IPDA [P1I1 and P2I1 lines in Figs. 1 (a) and 1 (b)], the urethane groups are solely made from the reaction of the isocyanate groups of MDI and the hydroxy groups of PTMG. These urethane groups mainly exist in the "borderline" between hard and soft segments:



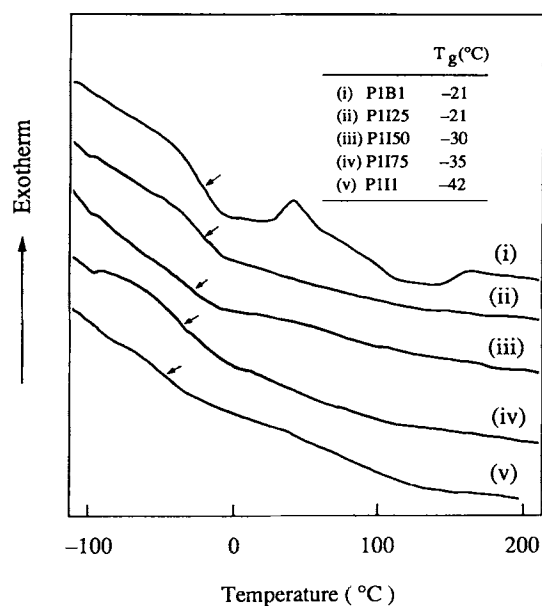
A considerable portion of these "borderline" urethane carbonyls may exist in non-hydrogen-bonded form.⁵

The non-hydrogen-bonded urea carbonyl peak (1695 cm^{-1}) is not seen in both Figures 1 (a) and 1 (b), but the broad hydrogen-bonded urea carbonyl peak (1660 cm^{-1}) shows that most of the urea carbonyls exist in hydrogen-bonded form.

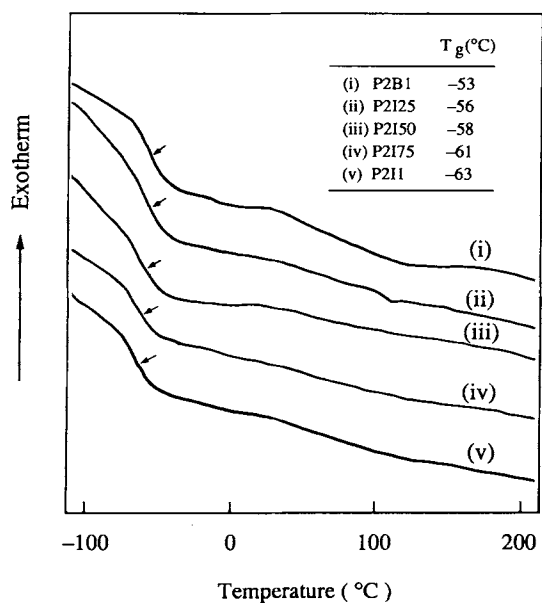
Thermal Characteristics

DSC thermograms of synthesized PUU's are shown in Figures 2 (a) and 2 (b). For the series H-1 (synthesized by using PTMG 1000), the glass transition temperature (T_g) of soft segments decreases as the IPDA content increases [Fig. 2 (a)]. When the concentration of hard segments dissolved in soft domains decreases, T_g of soft segments will tend to shift to its original T_g , which is around -90°C in the case of PTMG.⁶ Thus, the decrease in T_g means that better phase separation is attained as IPDA replaces BD in the polymer. The attainment of better phase separation can be attributed to the increase in urea bond content in the polymer chain. It is reported in several papers that the incorporation of urea linkage in place of urethane linkage substantially enhanced the phase separation between hard and soft segments. Usually the behavior is verified by the decrease in T_g of soft segments, and is mainly due to greater polar interactions between urea groups than between urethane groups and enhanced possibilities of forming hydrogen bonds, as seen in the previous FT-IR section.^{3,7,8}

The PUU samples which were chain extended with BD only (P1B1 and P2B1) have a broad en-



(a)



(b)

Figure 2 DSC thermograms of polyurethaneureas with various chain extender compositions: (a) series H-1; (b) series H-2.

dothorm appearing around 130°C, but it does not appear in other samples in which IPDA was also used as chain extender. This broad endotherm in intermediate temperature is understood as representing the limited short range order according to Seymour and Cooper.^{9,10} This limited short-range order is likely to be of MDI-BD units in the hard segments. By the way, from the disappearance of

the endotherm in the intermediate temperature range, it can be suggested that the incorporation of bulky IPDA units in the hard segments may disrupt the short-range ordering of MDI-BD units. This can be explained from the fact that IPDA has the less flexible ring structure and many side groups, and is the mixture of *cis-trans* isomers.

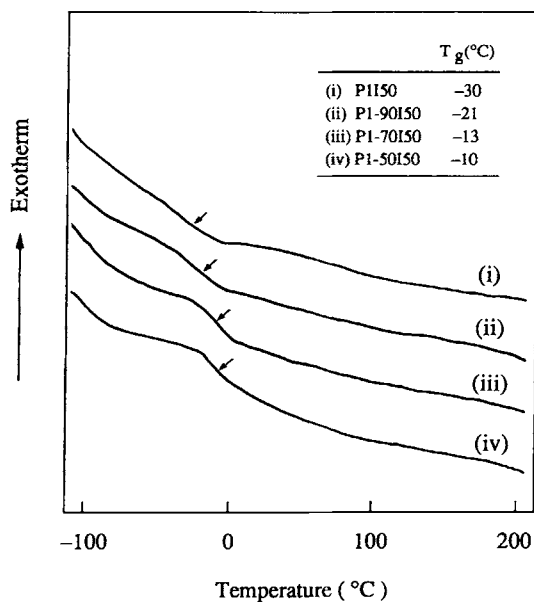
For series H-2 (synthesized by using PTMG 2000), a similar trend in T_g of soft segment was observed [Fig. 2(b)]; T_g of the soft segments decreased as IPDA content was increased. T_g 's are observed in the lower range of temperature compared with that of series H-1, and this is thought to be due to the enhanced phase segregation caused by the PTMG with higher molecular weight.³ The transition observed in the intermediate temperatures (around 130°C) is more obscure in this series mainly due to the lower amount of hard segment.

DSC thermograms of PUUs synthesized at various PTMG/PHC mole ratios and at a fixed IPDA/BD mole ratio (= 1/1) are shown in Figures 3(a) and 3(b). For both series S-1 and S-2, T_g of soft segment shifted to higher temperature as the PHC content in the soft segment was increased. From the fact that the T_g of homo-PHC is higher (reported T_g of PHC is -62°C)⁶ than that of homo-PTMG ($T_g = -90^\circ\text{C}$ for PTMG), the rise in T_g is expected, but the degree of shift is more evident than expected by rule of thumb, especially for series S-2. This is thought to be due to the enhanced phase mixing between hard and soft segments due to the more polar nature of PHC.¹¹

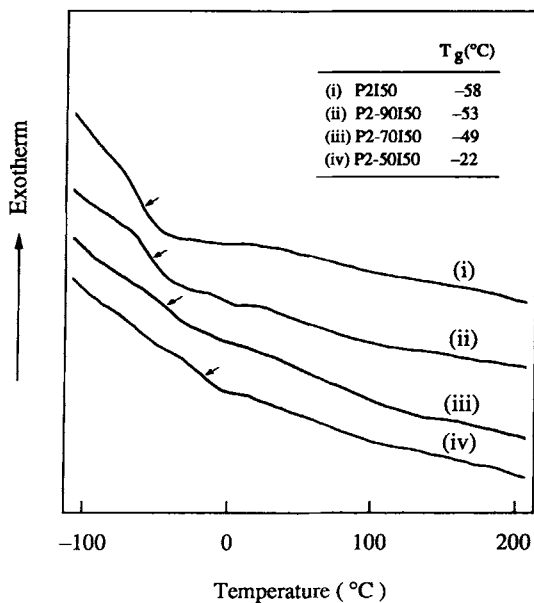
Mechanical Properties

Results of the tensile test are shown in Figure 4. As the chain extender units in the hard segments were gradually changed from BD to IPDA, the modulus showed negative deviation in the intermediate composition of chain extenders. Since the mechanical properties of PUU have much to do with the micro-domain characteristics, the observed mechanical behaviors can be explained from that viewpoint. Structural coincidence is important factor for hard segment domains to be able to form regular arrangements.¹² Thus when two different chain extenders with different structures coexist, the regular arrangement of hard domains can hardly be obtained since their structures are much different with each other to be able to interact favorably with each other. The more evident negative deviation of H-1 series compared with H-2 series might be explained from the fact that H-1 series has higher content of hard segment to manifest the effect of structural changes.

When two PUU samples composed of either BD



(a)



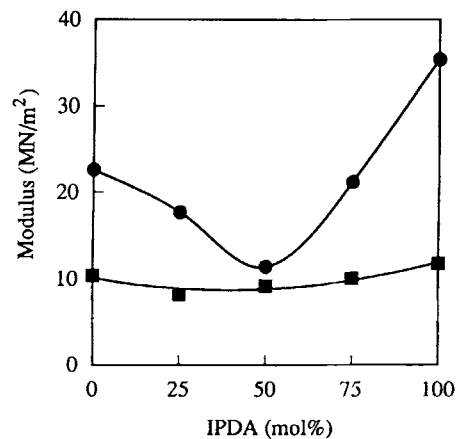
(b)

Figure 3 DSC thermograms of polyurethaneureas with various soft segment compositions: (a) series H-1; (b) series H-2.

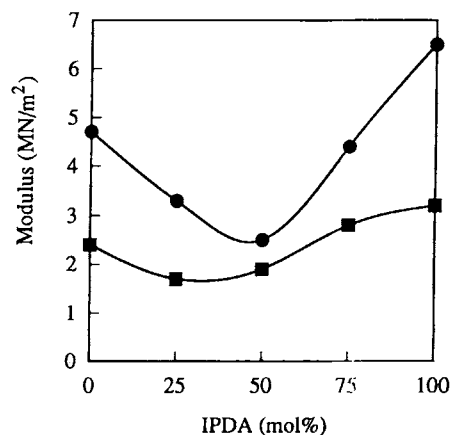
or IPDA as chain extenders are compared, modulus of the IPDA-chain extended PUU is higher than that of BD-chain extended sample. The structure of IPDA is substantially bulky compared with that of BD. Thus, it is likely that close packing of IPDA-chain extended hard segments is less feasible than that of BD-chain extended segments, but, since the cohesive energy of urea groups is much larger than

that of urethane groups, interactions between urea groups resulting from reaction of IPDA and isocyanate might contribute to increasing the modulus of PUUs.¹³

When soft segment compositions are varied, the polymers show a different trend in mechanical properties according to hard segment content (Fig. 5). For series S-1 (with 39 wt % hard segment content), which has shorter soft-segment chain length, the modulus is increased as the content of PHC increased. But in case of series S-2 (with 24 wt % hard segment content), which has longer soft-segment chain length, the change in modulus is relatively small. The carbonate group has much larger cohesive energy than ether group. Thus, the carbonate groups can contribute to enhancing the mechanical strength of the polymers, whereas the carbonate group also



(a)



(b)

Figure 4 Modulus of polyurethaneureas with various IPDA composition in the chain extender: (a) secant modulus at 3% extension; (b) secant modulus at 100% extension [(●) series H-1; (■) series H-2].

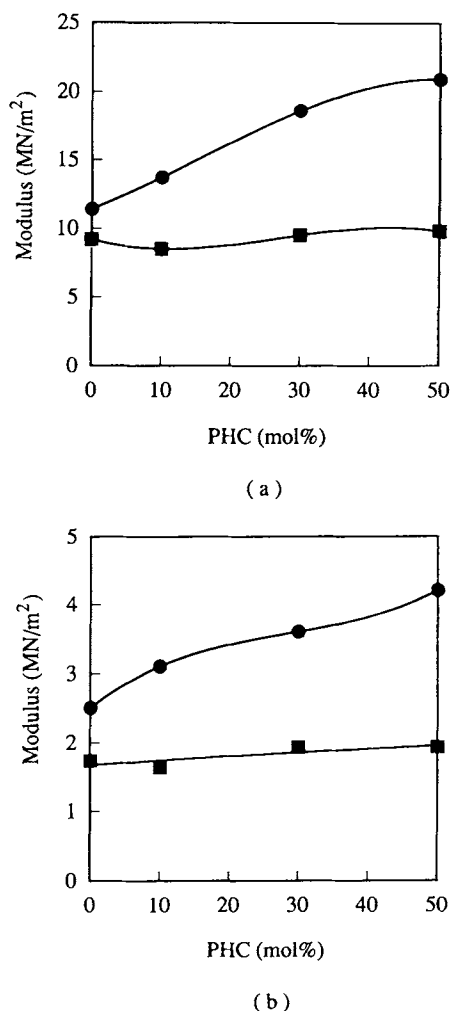


Figure 5 Modulus of polyurethaneureas with various PHC composition in the soft segment: (a) secant modulus at 3% extension; (b) secant modulus at 100% extension [(●) series S-1; (■) series S-2].

has much larger possibility of forming stronger hydrogen-bond with urea or urethane group than ether group can.¹³ That is, it is able to promote phase mixing between soft and hard segments as shown in Figure 3, which, in turn, may decrease the mechanical strength of the polymer by disrupting hard domain stability. Keeping in mind that, with longer soft segment chain length, better phase separation is attained,¹⁴ these two effects might have cancelled each other in the case of series with longer soft segment chain length (MW = 2000). But, for the series with shorter soft segment chain length (MW = 1000), phase separation may not have developed to much extent before any PHC was added. Thus, the extent of phase mixing caused by the incorporation of PHC molecules would have not been as much as that of previous series. Consequently, the

major contribution of the PHC to the mechanical properties of PUUs is likely to be the strengthening effect, and not the "weakening" effect of phase mixing.

CONCLUSION

When the composition of chain extender was altered by gradually replacing BD with IPDA upon synthesis, the structural heterogeneity was brought about by the mixing of two components. It resulted in negative deviation in the modulus of the polymers. IPDA, in spite of its irregular structure, was able to sustain mechanical stability of hard segment, when it was used as a chain extender in the PUU synthesis, possibly due to the bulky structure and strong cohesive force of the urea groups. When the composition of soft segment was varied by partly exchanging PTMG with PHC, the polar properties of carbonate groups in the PHC seemed to increase the phase mixing of hard and soft segments.

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