The Relative Physical and Thermal Properties of Polyurethane Elastomers: Effect of Chain Extenders of Bisphenols, Diisocyanate, and Polyol Structures

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Received 9 September 1995; accepted 6 December 1996

ABSTRACT: Polyurethane elastomers based on polyols such as polycaprolactone diol of molar mass 2000 and polytetramethylene glycol of molar mass 2000; diisocyanantes such as diphenyl methane 4,4′ diisocyanate and dicyclohexyl methane 4,4′ diisocyanate; and chain extenders such as bisphenol-A, bisphenol-S, bisphenol-AF, and their brominated derivatives were synthesized. The effects of polyol, diisocyanate, and chain extender on the physical and thermal properties were also studied. The polyurethane elastomers were investigated by X-ray diffraction (XRD), differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. Their limiting oxygen indexes (LOIs), solubilities, tensile strengths, hardnesses, and elongations were also determined. XRD analyses revealed that all of the polyurethanes were semicrystalline. However, the addition of bromine atoms in the polyurethanes markedly decreased their degrees of crystallinity. The brominated polyurethane elastomers have good flame retardancy, as indicated by large LOIs. All of the unbrominated polyurethanes showed good mechanical properties and high thermal stabilities. Polyurethanes based on bisphenol-S had lower solvent resistance caused by the dipolar nature of sulfonyl groups in the polymer chains. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1251–1265, 1997

Key words: polyurethane elastomers; bisphenol-S; bisphenol-AF; bisphenol-A; polycaprolactone diol; PTMG; LOI; bromination; dynamic mechanical analysis; chain extender

INTRODUCTION

Polyurethane (PU) products have found extensive application in manufacturing elastomers, coatings, and foams. A number of attempts[1–11] have been made to improve the physical and thermal properties of the polyurethanes. Also, the physical and thermal properties of polyurethanes were varied by varying the compositions of polyurethanes.[1–11]

Barikani and Hepburn[12,13] examined the effects of the structures of different types of chain extenders and diisocyanates on the thermal stability properties of polyurethanes based on polycaprolactone diol. In their investigation, the thermal stabilities of these polyurethane elastomers were enhanced considerably with the addition of low molar mass diols used as chain extenders. However, a systematical study for the effect of chemical structures of chain extenders and diisocyanates on the thermal stabilities of polyurethanes is incomplete. Minoura et al.[4,5] investigated the relationships between the mechanical properties and structures of polyurethane elastomers derived from hydroxy-terminated liquid polybutadiene (HT-BD), aliphatic diol, aromatic diols, and diisocyanates. These results confirmed that the

Journal of Applied Polymer Science, Vol. 66, 1251–1265 (1997)

CCC 0021-8995/97/071251-15

mechanical properties are related to the crosslinking density, the concentration of polar groups, the crystallinity, and other factors. The study of PU mechanical properties has received considerable attention.[14] Pandya et al.[14] indicated that mechanical properties display profound changes in the regions of the glass transition temperature. They contended that these changes can be considered as the most important material characteristic of a polymer. Several investigators[15–25] demonstrated that polymers based on bisphenols, such as bisphenol-S, bisphenol-A, and bisphenol-AF, show high thermal stability. However, a systematical explanation of the effect of bisphenols used as chain extenders on the properties of polyurethanes has not yet been provided.

In addition, reduction of flammability for the polymer is also important. Conventional techniques[26–28] that impart flame retardancy into the polyurethanes include chemical modification and physical blending with phosphorus and/or halogen compounds. It is well known that polymers derived from chemical modification show better thermal stabilities and mechanical properties than those derived from chemically unmodified compounds. Therefore, applying brominated low molar mass diols to improve flame retardancy, while maintaining thermal and mechanical properties of polyurethanes, is also of interest. In this work, a systematic investigation is made of the effect of chemical structures of chain extenders on the physical and thermal properties of polyurethanes. In addition, the fire retardancy of these polymers is also investigated.

EXPERIMENTAL

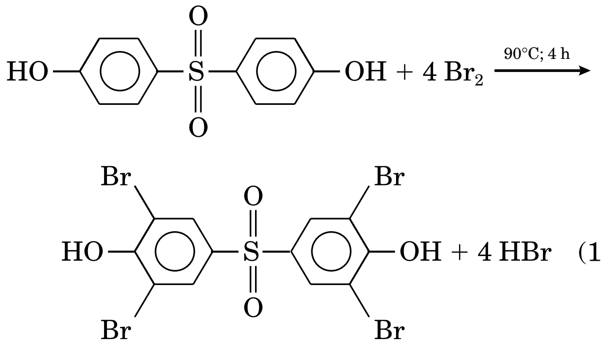
Materials

Polycaprolactone diol of molar mass 2000 (Janssen Chem. Co.), polytetramethylene glycol of molar mass 2000 (Janssen Chem. Co.), diphenyl methane 4,4′ diisocyanate (MDI) (TCI Co.), dicyclohexyl methane 4,4′ diisocyanate (HMDI) (Merck Co.), and dibutyl tin dilaurate (DBTDL) as a catalyst (TCI Co.) were used as received without further purification. Bisphenol-S (Hailsun Chemical Co.) was purified by recrystallization from a mixture of methanol and benzene solvent (1 : 3 v/v) (1 g with 6 mL of the solvent); mp 248°C[17] (ref. 29; mp 248–249.5°C). Bisphenol-AF was recrystallized from benzene; mp 163–165°C (ref. 19; mp 163–164°C). Commercial bisphenol-A was also recrystallized from benzene; mp 155–156°C (ref. 30; mp 154–155°C). Bromine was purchased from Merck Co.

Preparation of Monomers

Preparation of 3,3′,5,5′-tetrabromobisphenol S[17]

A round-bottomed flask (1 L) equipped with dropping funnel was charged with bisphenol S (54 g, 0.216 mol) and distilled water (300 mL). While the suspension was heated from 30 to 90°C, bromine (139.3 g, 0.872 mol) was added to the reaction flask through the dropping funnel over a period of 40 min. The temperature was maintained at about 90°C for 4 h. Following completion of the reaction, the crude product was washed with an aqueous sodium sulfite solution and then washed with distilled water to remove residual hydrogen bromide. The final product was dried in vacuum at 60°C for 24 h. A white powder of mp 289°C was obtained. (Lit.[17,31] mp 289°C). The yield was over 91%. The reaction took place according to eq. (1).

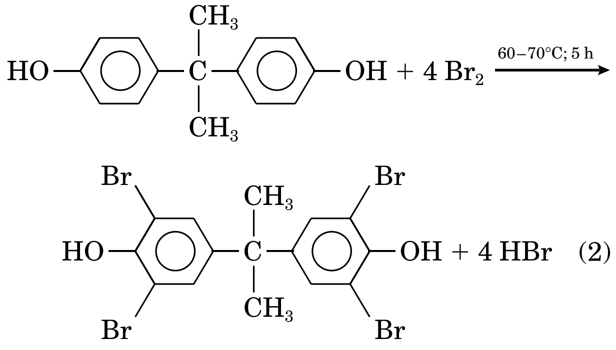


(1)

3,3′,5,5′-Tetrabromo bisphenol-S (TBBPS)

Preparation of 3,3′,5,5′-tetrabromobisphenol A[32]

A round-bottomed flask (1 L) equipped with a dropping funnel was charged with bisphenol A (45 g, 0.216 mol) and distilled water (600 mL). While the suspension was heated from 30 to 60°C, bromine (139.3 g, 0.872 mol) was added to the reaction flask through the dropping funnel over a period of 40 min. The temperature was maintained at about 60–70°C for 5 h. Following completion of the reaction, the crude product was washed with aqueous sodium sulfite solution and then washed with distilled water to remove residual hydrogen bromide. The final product was dried in vacuo at 60°C for 24 h. A white powder of mp 174–176°C was subsequently obtained. The yield was over 93.6%. The reaction took place according to eq. (2).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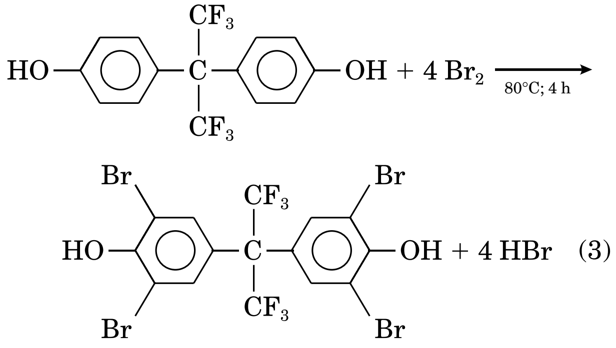
3,3′,5,5′-Tetrabromo bisphenol-A

Preparation of 3,3′,5,5′-tetrabromobisphenol AF[33]

A round-bottomed flask (1 L) equipped with a dropping funnel was charged with bisphenol AF (33.6 g, 0.1 mol) and distilled water (500 mL). While the suspension was heated from 30 to 80°C, bromine (65 g, 0.41 mol) was added to the reaction flask through the dropping funnel over a period of 40 min. The temperature was maintained at about 80°C for 4 h. Following completion of the reaction, the crude product was washed with aqueous sodium sulfite solution and distilled water to remove residual hydrogen bromide.

The final product was dried *in vacuo* at 60°C for 24 h. A white powder of mp 256°C was subsequently obtained. The yield was over 94%. The reaction took place according to eq. (3).


(3)

3,3′,5,5′-Tetrabromo bisphenol-AF

Polymerization

Chemical characterization of the materials used as chain extenders in this study is presented in Table I. Polyols such as polycaprolactone diol and PTMG and chain extenders were dried under reduced pressure at 80°C for 4 h before use. Diisocyanates such as HMDI and MDI (mp 38°C) were purchased from TCI Co., Ltd. According to the formulation in Table II, polyurethane elastomers having various structures were synthesized. Synthetic procedures for the preparation of these elastomers are described as follows. One equivalent of polyol and dibutyl tin dilaurate (DBTDL) as catalyst were placed in a two-necked flask with a mechanical stirrer and immersed in an oil bath at 120°C under a steady continuous flow of dry nitrogen.

Two equivalents of diisocyanate were then charged through a dropping funnel into the homogeneous mixture with vigorous stirring for a period of 5–10 min. After the addition of diisocyanate, the NCO-terminated prepolymer was formed. Then, one equivalent of the chain extender was added to the NCO-terminated prepolymer with vigorous stirring for 30–90 min. The viscous reaction mixture obtained was degassed under reduced pressure and cast on a mold (treated with silicon release agent) and heated to a fixed cure temperature. The mixture was cured at 120°C for 5 h in a press mold, with an additional seven-day room-temperature cure. In the case of the HMDI and MDI systems, DBTDL : diol = 0.03/100 or 0.02/100 (w/w) were used as catalysts, respectively.[4,5]

Measurements

As the infrared absorption band at 2262 cm^{-1} assigned to NCO groups disappeared one week after sample preparation, all measurements were carried out after more than seven days had passed since preparation.

Hardness

Hardness was measured on an A-type spring hardness tester according to JIS K6301.

Tensile Properties

Tensile strength and elongation at break were determined according to stress–strain curves (Toyo Baldwin Tensilon UTM-II) at an elongation rate of 25% min^{-1}. Measurements were taken at 25°C with film specimens (6 mm wide, 80 mm long, and ca. 2.0 mm thick), and the average of at least five individual determinations was taken.

Specific Gravity

Specific gravity was calculated by displacement method with water.

Swelling and Sol Fraction

The equilibrium degree of swelling of each elastomer was determined by immersing a small sample (20 × 20 × 2 mm) in 100 mL solvent (benzene or DMSO) for 50 h at room temperature and reweighing after rapid surface drying. The equilibrium degrees of swelling and sol fraction were calculated using the following relations:[4,5]

$$\frac{1}{V_R} = \frac{v_R + v_S}{v_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{\omega_S}{\omega_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{\omega_{S+R} - \omega_R}{\omega_R}$$

$$\mathrm{sol}\,(\%) = \frac{\omega_O - \omega_R}{\omega_O} \times 100$$

where $1/V_R$ is equilibrium degree of swelling, sol (%) is sol fraction, v_R is volume fraction of elastomer component in the swollen sample, v_S is volume fraction of solvent in the swollen sample, ω_R is weight of dry sample after swelling, ω_S is weight of solvent contained within swollen sample, ω_{S+R} is weight of swollen sample, ω_O is original weight of sample before swelling, ρ_R is density of dry sample before swelling, and ρ_S is density of solvent (0.87865 for benzene and 1.1014 for DMSO at 20°C).

Dynamic Thermal Mechanical Analysis

Dynamic mechanical measurements were taken on a Du Pont 983 DMA unit at a frequency of 1 Hz, ranging in temperatures from −150 to 150°C at a heating rate of about 5°C min^{-1}. The sample size was approximately 60 × 10 × 2 mm.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) traces were obtained on a Du Pont 9000 system. Measurement was taken over the range of −100 to 300°C at a heating rate of 10°C min^{-1}.

Thermal Analysis

Thermal gravimetric analyses (TGAs) were performed using a thermal analyzer (ULVAC, Sinku-Riko, Model 7000) at a heating rate of 10°C min^{-1} in nitrogen atmosphere. The weight of samples tested was about 100 mg.

X-ray Diffraction

X-ray diffraction (XRD) diagrams were taken with an X-ray generator (Phillips model Diffractometer system PW1710 Control). Polymers were measured as films.

Limited Oxygen Index

The LOI was determined on a SUGA instrument according to JIS K7201.

Water Absorption

To measure water absorption, film specimens were soaked in deionized water at room temperature for 72 h, blotted with paper towels, and then weighed immediately. Next, the films were placed on watch glasses and dried in vacuum at 30°C for 48 h. After reweighing the films on a microbalance, the water absorption was calculated.

RESULTS AND DISCUSSION

All polyurethanes derived from various chain extenders, diisocyanate, and polyol were synthesized in a two-step procedure. The equation for the first step involves the formation of an isocyanate end-capped monomeric soft segment (I), which is then chain extended with a diol in the second step to yield the (AB)n multiple block copolymer structure.

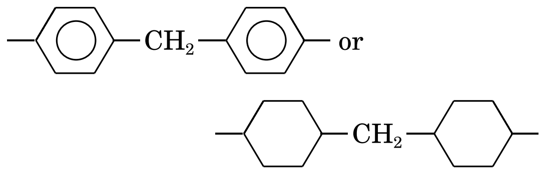
Step 1 (end-capping):

$$2\,\mathrm{OCN{-}R_1{-}NCO} + \mathrm{HO}\sim\sim\sim\mathrm{OH} \longrightarrow$$
$$\mathrm{OCN}\!+\!\!\left[\mathrm{R_1{-}NHCOO}\sim\sim\sim\mathrm{OOCHN}\right]\!\!+\!\mathrm{R_1{-}NCO}$$

I

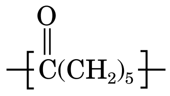
where

R_1 =



and

$$\sim\sim\sim = \left[\mathrm{CH_2CH_2CH_2CH_2O}\right]_{n-1}\!\!-\!(\mathrm{CH_2})_4- \text{ or}$$



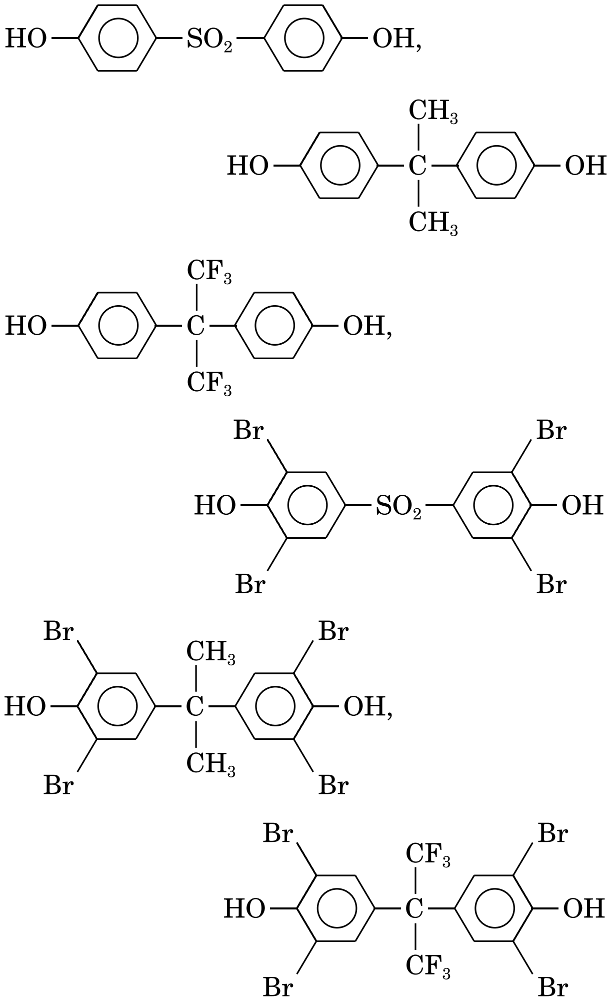
$$\left[\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{C}}}(\mathrm{CH_2})_5\right]$$

Step 2 (chain extension):

$$\mathrm{I} + \mathrm{HO{-}R_2{-}OH} \longrightarrow$$

$$\left[\mathrm{OR_2OOCNH{-}\!(R_1{-}NHCOO} \sim\!\sim\!\sim \mathrm{OOCHN)\!{-}R_1{-}NHCO}\right]_n$$

where $HO—R_2—OH$ =

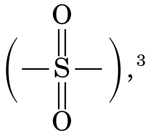


Physical Properties

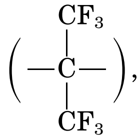
Hardness, density, tensile strength, and elongation at break of the polyurethanes, based on low molar mass diols, diisocyanate (MDI or HMDI), and polyol (polycaprolactone or polytetramethylene glycol) are listed in Table III. For each polymer, NCO : OH was fixed at 1 : 1.

This table reveals that polyester urethanes derived from bisphenols have a somewhat higher hardness and tensile strength, smaller elongation at break, and smaller density than polyether urethanes. This phenomenon may be due to that urethane NH—ester carbonyl hydrogen bonds are stronger than urethane NH—ether oxygen bonds.[34] It is also well known that ether linkages have a higher flexibility and lower cohesive energy (1.00 kcal/mol) than ester linkages (2.90 kcal/mol).[35] Consequently, it is anticipated that the introduction of ether linkages leads to enhanced flexibility and reduces the tensile strength of polyurethane elastomers.[36] That is, the mechanical properties of polyurethane elastomers derived either from MDI or HMDI are higher when ester linkages are introduced. It was also found that MDI-based polyurethanes (PU-7–PU-12) have higher tensile strengths than HMDI-based polyurethanes (PU-1–PU-6). This may be due to an increase in the concentration of polar groups (urethane groups and phenyl groups), which have higher cohesive forces and function as constituents of the secondary interchain bondings.[4,5] The cohesive forces participate in intermolecular hydrogen bonding and restrict the rotation of the polymer segments, thereby resulting in enhanced mechanical properties. This effect results in a decrease in elongation at breaking.

Results in Table III clearly indicate that the polyurethanes based on bisphenol S and bisphenol AF have higher tensile strengths than polyurethanes based on bisphenol A. A comparison of the tensile strengths of polyurethanes reveals that a difference in properties may be attributed to the polar nature of the sulfone group



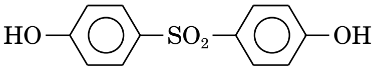
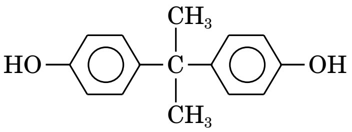
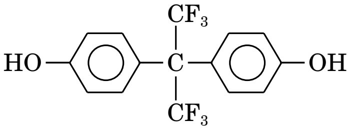
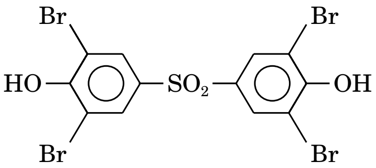
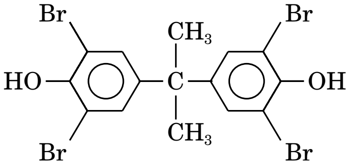
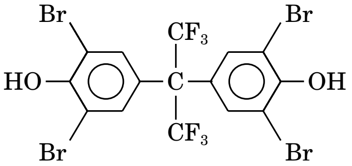
$\left(—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}—\right)$,[37] and the gem-di(trifluoro methyl) group



$\left(—\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}—\right)$, as compared to the nonpolar gem-dimethyl in bisphenol A. These polar groups may participate in intermolecular interaction and compensate for the disadvantage of reduction in the polymer symmetry, thereby resulting in a higher tensile strength. Table III shows that all the polyurethanes derived from brominated bisphenols (PU-13–PU-24) have a lower hardness and tensile strength than the polyurethanes derived from nonbrominated bisphenols (PU-1–PU-12). The decrease in such mechanical property of polyurethanes based on brominated bisphenols can be accounted for by an increase of free volume caused by bromine substitution.[37,38]

The physical properties of polyurethanes in

Table I Structures of Various Chain Extenders

Chain Extender	Structures		C (%)	H (%)	O (%)
Bisphenol-S		Calcd	—	—	—
		Found	—	—	—
Bisphenol-A		Calcd	—	—	—
		Found	—	—	—
Bisphenol-AF		Calcd	—	—	—
		Found	—	—	—
Brominated Bisphenol-S		Calcd	25.47	1.06	11.31
		Found	25.62	1.16	11.28
Brominated Bisphenol-A		Calcd	33.09	2.20	5.88
		Found	33.08	2.21	5.88
Brominated Bisphenol-AF		Calcd	27.60	0.90	4.91
		Found	27.60	1.00	4.90

various solvent absorptions and solvations are summarized in Table IV. The absorption and swelling ability of the polyether urethanes are higher than that of polyester urethanes when water or benzene are used as solvents. This effect can be elucidated by the degree of phase mixing in polyurethanes. Polyether urethanes are assumed to have a higher tendency to phase separation than that of polyester urethanes because urethane NH—ether oxygen bonds are weaker than urethane NH—ester carbonyl hydrogen bonds. Results in this study also indicated that MDI-based polyurethanes have a better solvent resistance than HMDI-based polyurethanes when benzene and water are used as solvents. A comparison of the solvent absorption values of MDI-based polurethanes and HMDI-based polyurethanes in benzene and water reveals that a difference in values may be attributed to the higher concentration of polar groups which function as pseudo-crosslinkages in MDI-based polyurethanes.

The water absorption values for bisphenol AF based polyurethanes are lower than those of the corresponding bisphenol-S- and bisphenol-A-based polyurethanes. This effect may be due to the hydrophobic nature of fluorinated groups in bisphenol-AF-based polyurethanes. Similar hydrophobic behaviors have been found in other fluorinated polymers.[23,24]

Table IV clearly indicates that all of the polyurethanes based on brominated bisphenols have a higher water absorption and swelling values when water and benzene are used as solvents. This finding may be accounted for by an increase of their overall hydrophilicity and free volume brought about by bromine substitution.[33,39] Similarly, the degree of swelling increases with an increasing concentration of polar groups in polyure-

Table II Introduction of Polyurethanes

Polymer Code	Diisocyanates	Polyol	Chain Extender
PU-1	HMDI	PCL	Bisphenol-S
PU-2	HMDI	PCL	Bisphenol-A
PU-3	HMDI	PCL	Bisphenol-AF
PU-4	HMDI	PTMG	Bisphenol-S
PU-5	HMDI	PTMG	Bisphenol-A
PU-6	HMDI	PTMG	Bisphenol-AF
PU-7	MDI	PCL	Bisphenol-S
PU-8	MDI	PCL	Bisphenol-A
PU-9	MDI	PCL	Bisphenol-AF
PU-10	MDI	PTMG	Bisphenol-S
PU-11	MDI	PTMG	Bisphenol-A
PU-12	MDI	PTMG	Bisphenol-AF
PU-13	HMDI	PCL	Brominated bisphenol-S
PU-14	HMDI	PCL	Brominated bisphenol-A
PU-15	HMDI	PCL	Brominated bisphenol-AF
PU-16	HMDI	PTMG	Brominated bisphenol-S
PU-17	HMDI	PTMG	Brominated bisphenol-A
PU-18	HMDI	PTMG	Brominated bisphenol-AF
PU-19	MDI	PCL	Brominated bisphenol-S
PU-20	MDI	PCL	Brominated bisphenol-A
PU-21	MDI	PCL	Brominated bisphenol-AF
PU-22	MDI	PTMG	Brominated bisphenol-S
PU-23	MDI	PTMG	Brominated bisphenol-A
PU-24	MDI	PTMG	Brominated bisphenol-AF

thanes when DMSO was used as solvent, as shown in Table IV. Not only the soft segments but also the hard segments swell because of the high polarity of DMSO. However, the degree of swelling of polyurethanes, when benzene was used as a swelling solvent at low concentration of polar groups, is higher than that of polyurethanes when DMSO was used. This phenomenon has also been found by Minoura et al.[4,5] for polyurethane based on hydroxy-terminated polybutadiene.

Figure 1 shows the wide-angle XRD intensity of polyurethanes for PU-1, PU-4, PU-13, and PU-16. This figure indicated that the crystalline lattices of polyurethanes were varied with various compositions. Debye–Scherrer rings, which suggest the existence of crystalline regions, can be observed at $2\theta = 19.0$ degrees ($d = 4.67$ Å) and 21.7 degrees ($d = 4.10$ Å) for PU-4 and PU-1, respectively. The other peak for the unbrominated-bisphenols-based polyurethane (PU-1 and PU-4) was observed at $2\theta = 24.3$ degrees (i.e., $d = 3.66$ Å). The observation of $2\theta = 24.3$ degrees may be due to the crystalline structure of the hard domains in the polyurethane. A comparison of the curves of PU-13 and PU-16 reveals that the decrease of mechanical properties of polyurethane elastomers derived from brominated bisphenols (see Table III) can be ascribed not only to an increase of free volume of bromine atom but also to a decrease of crystalline region in the polymer matrix.

The effects of chain extenders, polyol, and diisocyanate on the degree of crystallinity of polyurethanes are summarized in Table V.

This table reveals that the addition of bisphenols (PU-1–PU-12) slightly affect the degree of crystallinity. Polyurethanes such as PU-1, PU-4, PU-7, and PU-10 containing a sulfonyl group that has a small van der Waals radius have relatively large degrees of crystallinity. Polyurethanes based on bisphenol A containing the isopropyl group and based on bisphenol AF containing the hexafluoro propane group have smaller degrees of crystallinity. Brominated polyurethanes (PU-13–PU-24) have smaller degrees of crystallinity than unbrominated polyurethanes (PU-1–PU-12). Nagata et al.[23] observed that polyamides incorporating halogen substituents on the ring led to a decreased crystallinity because of their larger van der Waals radius.

Thermal Properties

Effects of chain extenders on the thermal properties of polyurethanes are shown in Table VI. As

Table III Effects of Chain Extenders, Polyols, and Diisocyanates on the Mechanical Properties of Polyurethanes

Polymer Code	Hardness (HsA)	Tensile Strength (MPa)	Elongation at Break	Density (g cm^{-3})
PU-1	98	27	8.3	1.25
PU-2	98	18	7.1	1.22
PU-3	97	31	7.1	1.30
PU-4	75	24	8.7	1.40
PU-5	79	23	9.9	1.34
PU-6	78	26	13.1	1.44
PU-7	91	62	8.8	1.32
PU-8	89	38	8.2	1.25
PU-9	85	75	7.7	1.38
PU-10	57	33	11.9	1.40
PU-11	58	31	14.2	1.35
PU-12	56	35	15.8	1.41
PU-13	96	20	4.1	1.64
PU-14	97	22	3.8	1.61
PU-15	97	25	5.2	1.69
PU-16	35	11	1.8	1.62
PU-17	12	14	2.1	1.56
PU-18	26	16	3.1	1.65
PU-19	96	45	6.3	1.55
PU-20	96	43	6.1	1.48
PU-21	92	60	11.4	1.63
PU-22	65	23	7.1	1.59
PU-23	30	25	8.4	1.50
PU-24	50	32	12.3	1.64

shown in this table, the T_g values of the polyester urethanes are 15–30°C higher than those of polyether urethanes. Figure 2 indicates that T_g of PU-8 (BPA : PCL : MDI) is 18°C higher than that of PU-3 (BPA : PCL : HMDI). All MDI-based polyurethanes exhibit the same behavior as compared to the corresponding HMDI-based polyurethanes. This result had also been found by Aitken and Jeffs[40] for polyurethanes based on MDI and HMDI. In addition, MDI-based polyurethanes have a stronger hydrogen bondings in the hard block domains. As shown in Table VI, T_g values for bisphenol-S-based polyurethanes are higher than those of the corresponding bisphenol-A-based polyurethanes. As discussed earlier, this phenomena is because of the increase in intermolecular forces due to the sulfone groups. T_g values for the bisphenol AF-based polyurethanes are somewhat higher than those for the bisphenol-S-based polyurethanes. This phenomenon may be due to the fluorinated groups in the polymer chains. The effects of bromine substitution of bisphenols on the T_g of polyurethanes are summarized in Table VI. This table indicated that PU-16 (TBBPS : PTMG : HMDI) has a somewhat higher T_g value than PU-4 (BPS : PTMG : HMDI). Almost all brominated bisphenols based polyurethanes display the same phenomenon. This result may be accounted for by the decrease of the chain flexibility caused by increased steric hindrance brought about by bromine substitution. This increase in steric hindrance compensates for the disadvantage of the increase in free volume from bromine substitution, thereby raising the T_g values. A similar observation was also found by Marks[20] for copolycarbonates based on bisphenol A and tetrabromobisphenol A.

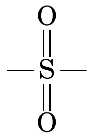
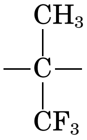
The thermal stability of the polyurethanes was studied by thermogravimetry. Table VI also summarizes the initial decomposition temperatures observed by TGAs (T_d^i) and temperatures ($T_d^{10\%}$), where 10% mass loss was observed. This table also presents the maximum decomposition temperatures ($T_d^{\max}$) and mass residues at 700°C. Figure 3 shows the TG curves used in this study to obtain the data included in Table VI, along with mass loss data for PU-3 and PU-18.

Inspection of these two thermograms indicates

Table IV Effects of Chain Extenders, Polyols, and Diisocyanates on the Physical Properties of Polyurethanes

	Benzene		DMSO		
Polymer Code	Swelling ($1/V_R$)	Sol (%)	Swelling ($1/V_R$)	Sol (%)	Water Absorption (%)
PU-1	9.79	79.44	3.43	44.27	1.56
PU-2	9.52	28.24	2.57	25.27	1.46
PU-3	10.19	43.82	2.73	27.01	1.45
PU-4	16.42	38.02	1.92	9.75	2.51
PU-5	20.86	12.33	1.98	11.54	1.73
PU-6	28.73	13.23	1.87	4.15	1.60
PU-7	5.51	2.64	4.14	40.32	0.48
PU-8	5.83	2.81	4.56	33.35	0.43
PU-9	5.01	2.96	5.02	47.72	0.41
PU-10	9.18	16.05	4.44	9.95	2.40
PU-11	8.00	5.83	4.77	7.86	0.87
PU-12	11.18	33.46	3.09	12.74	0.56
PU-13	10.10	9.67	3.15	34.67	2.08
PU-14	14.21	58.48	2.23	24.76	1.84
PU-15	14.39	11.92	2.51	27.82	1.84
PU-16	21.16	59.84	2.87	20.26	5.19
PU-17	18.60	50.47	3.20	18.09	6.93
PU-18	12.82	85.53	2.03	9.68	3.06
PU-19	7.82	22.97	4.13	22.77	2.60
PU-20	8.09	19.49	3.31	27.87	1.45
PU-21	8.28	27.05	3.53	25.75	1.15
PU-22	5.21	4.92	3.02	17.92	3.64
PU-23	19.19	58.87	4.07	13.89	2.52
PU-24	12.49	19.31	3.49	20.62	2.22

that brominated aromatic bisphenols based polyurethanes are less stable than unbrominated bisphenols based polyurethanes; however, the former have a higher char yield.[41,42] This is to be expected since a substitution in the aromatic rings reduces stability. The mass losses corresponding to the liberation of HBr are apparently evident for the brominated bisphenols based polyurethanes.

The LOI values determined are also shown in Table VI. All brominated bisphenols based polyurethanes have a higher degree of fire resistance than their corresponding unbrominated bisphenols based polyurethanes. Kapuscinska and Pearce[41] reported that halogen imparts flame retardancy to polyamides, thereby resulting in higher LOI values. Their investigation demonstrated that polyester urethanes have a higher fire resistance than polyether urethanes. This behavior is possible due to the higher hydrogen-to-carbon ratio and lower oxygen-to-carbon ratio of the polyester segment than of the polyether segments. The LOI values of bisphenol-S[43] and bisphenol-AF-based[22–24] polyurethanes are higher than those of their corresponding polyurethanes based on bisphenol-A. This phenomenon may be due to the presence of the  $-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$ group and  $-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}-$ group in addition to the phenyl rings.

Dynamic Mechanical Analysis

Influence of the Diisocyanates Structures on Thermal Stability

The effect of chemical structures of various diisocyanates on the thermal stability of their polyurethane elastomers was found by comparing two different types of PU elastomers in which the variable was the type of diisocyanate, such as HMDI and MDI. These results are summarized in Table VII. Figure 4 shows the DMA curves used in this study to obtain the data for PU-2 and PU-8.

From this figure, the HMDI-based polyurethanes demonstrated a relatively higher loss tan δ temperature, loss modulus (E'') temperature, and temperature of onset of storage modulus (E') than MDI-based polyurethanes. This result indicates that thermal stability of HMDI-based polyurethanes is higher than that of MDI-based polyurethanes. However, from the viewpoint of chemical structures, it is expected that MDI-based polyurethanes have higher thermal stability because they contain benzene rings, which have high cohesive energy and bulkiness. This anomalous behavior may indicate that long soft segments of HMDI, together with that of low molar mass diol, form tight crystalline structures.

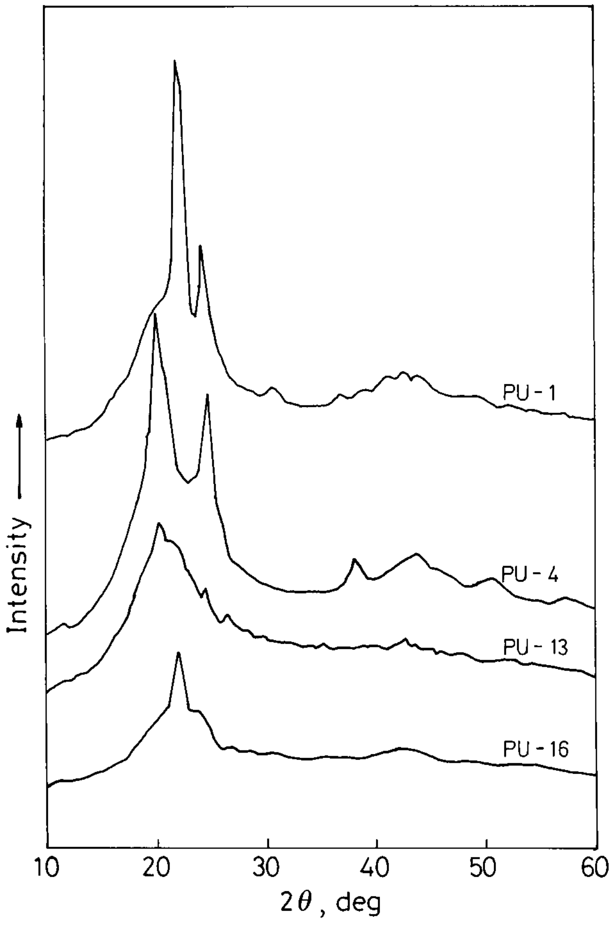


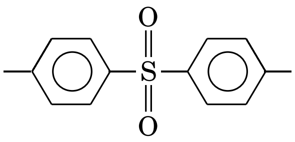
Figure 1 Effects of chain extenders and polyol on wide-angle XRD intensity of polyurethanes for PU-1, PU-4, PU-13, and PU-16.

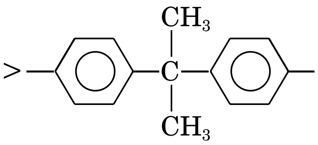
Table V Effects of Chain Extender, Polyol, and Diisocyanate on the Degree of Crystallinity of Polyurethanes

Polymer Code	Crystallinity (%)
PU-1	59.6
PU-2	53.2
PU-3	57.9
PU-4	61.0
PU-5	59.3
PU-6	60.1
PU-7	58.3
PU-8	58.4
PU-9	58.6
PU-10	61.1
PU-11	58.1
PU-12	55.8
PU-13	46.3
PU-14	41.4
PU-15	44.7
PU-16	44.2
PU-17	45.3
PU-18	34.1
PU-19	45.5
PU-20	38.8
PU-21	38.9
PU-22	57.4
PU-23	39.8
PU-24	44.4

Influence of the Chain Extender Structures on the Thermal Stability

The influence of the chain extender structures on the thermal stability of polyurethanes was also studied as shown in Table VII. This table denotes loss modulus (E'') and tan δ as a means of observing the dependence of temperature stability on chain extender structures. From Table VII, the order of decreasing thermal stability is as follows:





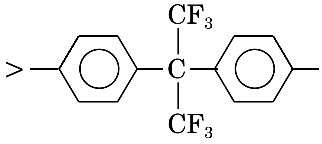
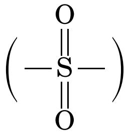
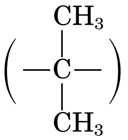


Table VI Effects of Chain Extenders, Polyols, and Diisocyanates on the Thermal Properties of Polyurethanes

Polymer Code	T_g (°C)[a]	T_d^i (°C)[b]	$T_d^{10\%}$ (°C)[c]	$T_d^{\max}$ (°C)[d]	Residue at 700°C (%)	LOI
PU-1	−41	256	356	409	3.8	25.5
PU-2	−49	265	361	417	2.9	25.0
PU-3	−40	268	359	408	4.0	30.0
PU-4	−68	256	358	409	3.3	23.8
PU-5	−71	289	364	417	2.9	23.0
PU-6	−65	260	356	411	3.1	24.0
PU-7	−33	251	359	406	6.0	25.0
PU-8	−31	277	361	412	2.7	23.5
PU-9	−30	250	357	411	2.3	24.5
PU-10	−58	255	349	413	3.1	22.5
PU-11	−61	251	351	409	7.4	22.0
PU-12	−57	258	357	416	5.8	23.5
PU-13	−40	255	298	307	6.0	34.0
PU-14	−45	262	304	311	5.6	30.0
PU-15	−38	265	306	315	6.4	33.0
PU-16	−56	230	277	298	1.5	36.5
PU-17	−62	250	290	310	2.1	33.0
PU-18	−56	252	292	304	2.8	36.0
PU-19	−34	255	290	300	8.4	30.0
PU-20	−32	258	306	311	6.2	31.0
PU-21	−32	265	302	316	4.5	31.5
PU-22	−66	246	285	300	3.5	26.0
PU-23	−71	258	300	307	9.6	25.5
PU-24	−52	263	304	310	8.2	28.0

[a] DSC analyses conducted at a heating rate of 10°C min^{-1} in nitrogen.
[b] T_d^i is the temperature at which initial loss of mass was observed.
[c] $T_d^{10\%}$ is the temperature at which 10% loss of mass was observed.
[d] $T_d^{\max}$ is the temperature at which maximum loss of mass was observed.

This phenomenon may be due to the polar nature of sulfone groups  $\left(-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\right)$ in bisphenol-S-based polyurethanes, as compared to the nonpolar nature of the isopropyl groups  $\left(-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\right)$ in bisphenol-A-based polyurethanes. A comparison of the results between bisphenol-A-based polyurethanes and bisphenol-AF-based polyurethanes reveals that the bisphenol-A types have higher thermal stabilities than bisphenol-AF-based polyurethanes. This finding indicates that the introduction of fluorine atoms instead of hydrogen atoms increases the pliability of polymer films. The lower thermal stability of the bisphenol-AF-based polyurethanes is presumably attributed to the weaker intermolecular forces between the polymer chains. As mentioned above, the order of decreasing thermal stability is actually related to the degree of crystallinity (Table V).

Influence of the Introduction of Bromine Atoms on Thermal Stability

The influences of the introduction of bromine atoms on the thermal stability of polyurethanes are also shown in Table VII. Figure 5 shows the dynamic properties of polyurethanes for PU-7 (BPS:MDI:PCL) and PU-19 (TBBPS:MDI:PCL). In this figure, the introduction of bromine atoms (PU-19) decreased the temperature of loss tangent peaks simultaneously and broadened the loss of tangent peaks of the polyurethanes. The broadened loss tangent peak implies that phase separation is formed in the polymer matrix.[44]

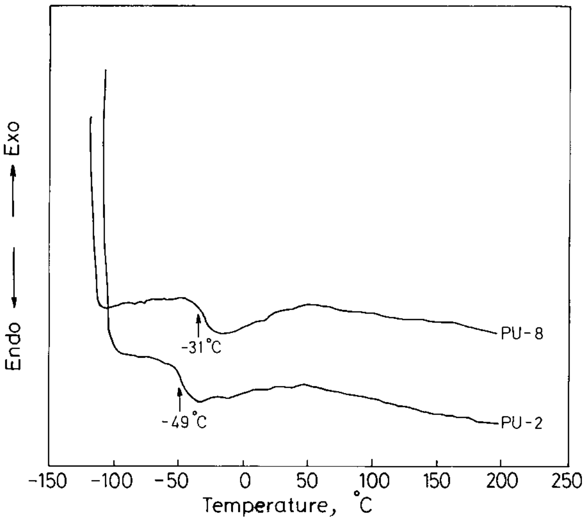


Figure 2 DSC curves of polyurethanes for PU-2 and PU-8, conducted at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

This phenomenon indicates that the increase in free volume of the polymer chain, due to bromine substitution, increases the difficulty of interaction between the polymer chains, thereby decreasing dynamic mechanical properties. The mechanism for the decrease of the interaction between the polymer chains is elucidated in Figure 6. The figure shows that the interaction between dipolar sulfonyl groups and ester or urethane groups was reduced by the bromine substituents, which have large van der Waals radii. This interaction contributes to the increase in the degree of phase separation.

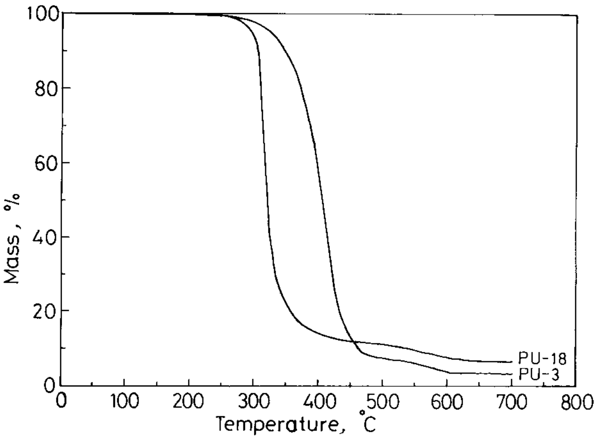


Figure 3 Thermogravimetric curves of polyurethanes for PU-3 and PU-18, conducted at a heating rate of 10°C min^{-1} in an air atmosphere.

Table VII Effects of Chain Extender, Polyol and Diisocyanate on the Dynamic Mechanical Properties of Polyurethanes

Polymer Code	Type of Diisocyanate	Log $E''^{\max}$ (°C)	Loss tan δ (°C)
PU-1	HMDI	26.9	53.0
PU-2	HMDI	−8.9	50.0
PU-3	HMDI	−9.7	47.0
PU-4	HMDI	−59.2	−31.4
PU-5	HMDI	−48.3	−30.0
PU-6	HMDI	−51.0	−32.1
PU-7	MDI	19.4	36.8
PU-8	MDI	11.9	31.1
PU-9	MDI	−5.7	6.3
PU-10	MDI	−45.3	−33.4
PU-11	MDI	−40.5	−24.7
PU-12	MDI	−47.3	−33.5
PU-13	HMDI	2.4	27.6
PU-14	HMDI	−2.8	22.1
PU-15	HMDI	0.9	26.0
PU-16[a]	HMDI	—	—
PU-17[a]	HMDI	—	—
PU-18[a]	HMDI	—	—
PU-19	MDI	−32.2	−16.7
PU-20	MDI	−5.7	1.2
PU-21	MDI	−17.9	−10.7
PU-22	MDI	−59.9	−45.0
PU-23	MDI	−38.3	−26.1
PU-24	MDI	−41.1	−28.9

[a] Samples were too soft to be prepared at room temperature.

CONCLUSION

Polyurethane elastomers were synthesized by chemical extension using bisphenols and their brominated derivatives. Results obtained from the analysis of mechanical properties demonstrated that the BPS and BPAF-based polyurethanes have higher tensile strengths than BPA-based polyurethanes. The MDI-based polyurethanes, which have a higher concentration of polar groups, exhibited better tensile strengths than HMDI-based polyurethanes. However, the MDI-based polyurethanes have a lower elongation value. The polyester urethanes have a somewhat higher hardness and tensile strength, as well as a smaller elongation at break and smaller density. The addition of bromine atoms in polyurethane decreases their mechanical properties. The water absorption and swelling values of the polyether urethanes are higher than those of polyester urethanes. The introduction of bromine

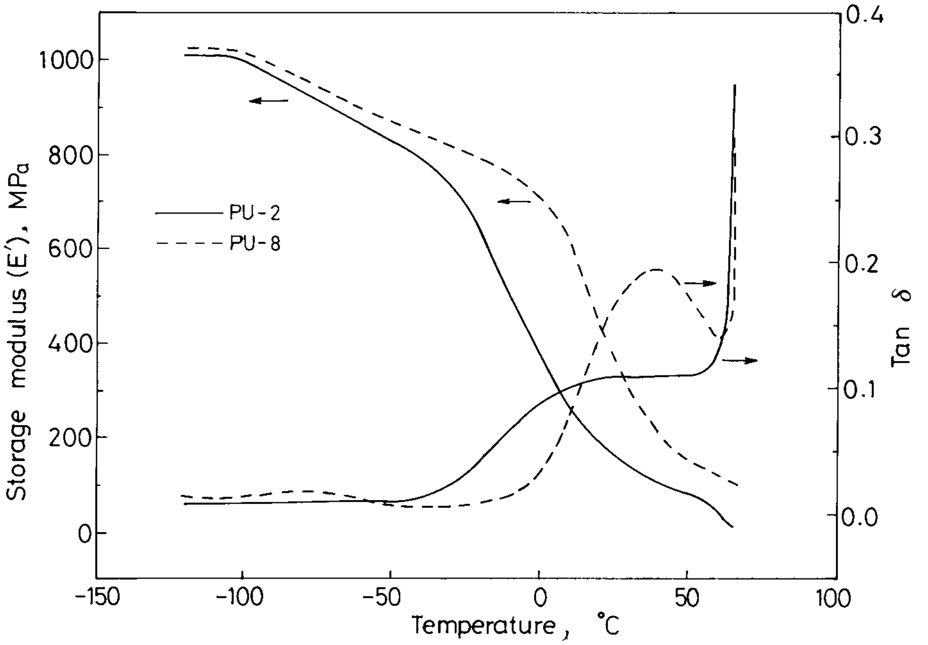


Figure 4 Effects of diisocyanate on dynamic mechanical property (polycaprolactone diol : bisphenol-A : diisocyanate): (——) HMDI for PU-2; (---) MDI for PU-8.

atoms in polyurethane increases the water absorption and solvation of polyurethanes because of their higher polarity and larger free volume.

The physical properties of polyurethane elastomers derived from MDI were better than those derived from HMDI. The BPS-based polyurethanes, having dipolar sulfonyl groups in the polymer chains, show higher solvation and water absorption values.

XRD patterns analysis reveals that the poly-

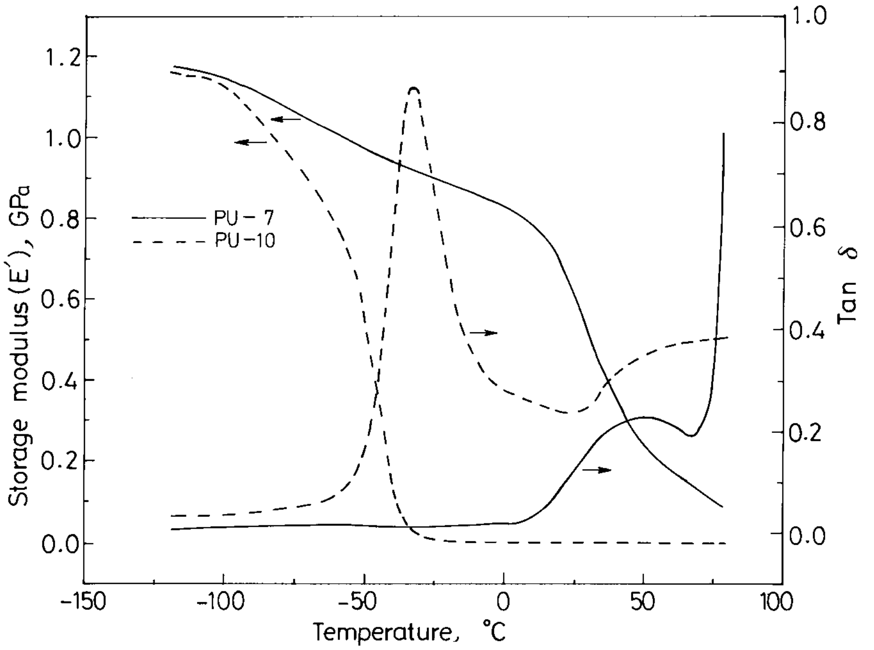


Figure 5 Effects of bromination on dynamic mechanical properties (Polyol : chain extender : MDI): (——) BPS for PU-7; (---) TBBPS for PU-19.

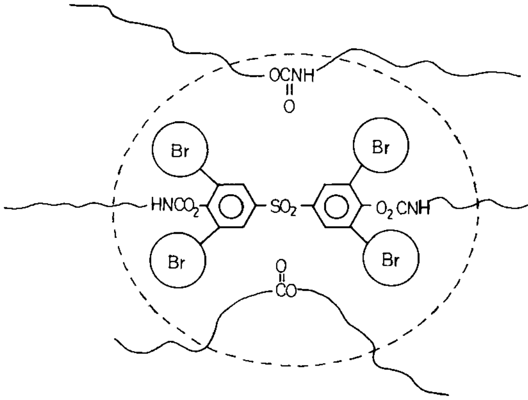


Figure 6 The intermolecular interaction in polar polymers: dipolar sulfonyl group-ester group and dipolar sulfonyl group–urethane group in the brominated bisphenol-S-based polyurethanes.

urethanes containing a sulfonyl group have relatively higher degrees of crystallinity. The polyurethanes incorporating bromine substituent on the ring led to decreased crystallinity. DSC analysis revealed that the T_g values of the polyester urethanes are 15–30°C higher than those of polyether urethanes. All the MDI-based polyurethanes have higher T_g values than the HMDI-based polyurethanes. The BPS and BPAF-based polyurethanes exhibit high T_g values. The TGA and LOI values show that the introduction of bromine atoms increases the flame retardancy and decreases the thermal stability of polyurethanes.

The dynamic properties of the MDI-based polyurethanes were lower than those of the HMDI-based polyurethanes. The BPS-based polyurethanes have higher dynamic properties than the BPA and BPAF-based polyurethanes when polyester diol was used. However, applying the same condition for the BPS-based polyurethanes shows lower dynamic properties. This result implies that the interaction between ester groups and dipolar sulfonyl groups improved the dynamic properties. The introduction of bromine atoms broadens the tan δ peak.

The author would like to thank the National Science Council of the Republic of China for financial support under grant NSC-85-2216-E011-006 and S.P. Lin and C.C. Huang for their technical assistance.

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