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Synthesis and properties of polyurethanes based on bisphenol-S derivatives

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The relationship between the structure and property of polyurethane elastomer derived from bisphenol-S derivatives/diisocyanate system was studied. The effects of the amount of soft segment of diol, including ester and ether, as well as the effects of structure of diisocyanate on the mechanical properties of elastomer were discussed on the basis of the results obtained from the hardness, tensile strength, elongation, swelling, dynamic mechanical analysis, and X-ray diffraction. Also, the thermal properties of polyurethane elastomer were also investigated by d.s.c. and t.g.a. analyses. The d.s.c. and dynamic properties results demonstrated that the new polyurethanes exhibit a range of glass transition temperatures from − 25 to 48°C, and temperature at loss tan δ peak from 81.0 to 13.7°C. Moreover, t.g.a. results showed that the addition of an ester group increased the thermal stability of polyurethanes. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polyurethane; bisphenol-S; ether linkage)

INTRODUCTION

Polyurethane products have found extensive application in producing elastomers, coatings and foams. However, polyurethane elastomers have a poorer hydrolysis resistance and thermal stability than other elastomers. A number of attempts were made to enhance the performance of polyurethane elastomers[1–12]. For instance, Minoura *et al.*[1,2] reported that the relationship between the property and structure of polyurethane elastomers derived from hydroxyl-terminated polybutadiene (HTBD) and bisphenol-A. Their investigation also indicated that polyurethanes based on aromatic diols have considerably high mechanical properties. However, using aromatic diols would create a processing problem because of their high melting points. Further, using aromatic diols had some other problems, e.g. prolonged curing time and high compression set for their low reactivity.

Although many physico-mechanical studies were performed on elastomeric polyurethanes[13–16], rigid versions have received limited attention, especially for those having more than 70% hard-segment content. Some preliminary studies[17,18] demonstrated that physico-mechanical properties depend on both the hard-to-soft segment ratio and crystallinity. In addition, several investigations[1,2,19,20] indicated that the processibility was elevated by introducing ether and ester linkages which function as a soft segment. For instance, Liaw *et al.* reported that the solubility, processibility and crystallinity of polyamides[19] and polyimides[20] could be improved by introducing the flexible ether linkages.

A number of investigations confirmed that sulfone-containing polymers such as polyethers[21,22], epoxy resins[23,24], polyesters[25] and polyarylates[26], display good physico-mechanical and thermal properties. Since polymer, having a polar sulfone group, has a larger intermolecular force between polymer chains, it has the advantage of resistance to thermal deformation, higher T_g, and thermal stability[21–26]. However, polyurethanes involving bisphenol-S derivatives have only received limited attention.

This study provides comprehensive results of polyurethane derived from bisphenol-S derivatives to determine the contribution of the hard-to-soft segment ratio and crystallinity toward the final properties of the material. Both ether and ester linkages were introduced in polymers, as the soft segment, the solubility and processibility, and thermal stability, respectively, could be improved[1,2,19,20]. Ether linkage was introduced in polymers without much sacrifice of thermal stability. The effects on the physical and thermal properties of introducing the ester and ether linkages into polyurethane are also discussed.

EXPERIMENTS

Materials

Bisphenol-S (BPS, Hailsun Chemical Co., Taiwan) was purified by recrystallization from a mixture of methanol and benzene solvent (1:3, v/v) (1 g with 6 ml of the solvent); m.p. 248°C (Lit[23]. m.p. 248–249.5°C). Ethylene carbonate, 1,2-propylene carbonate, and bromine were supplied by Janssen Chemical Co. The monomer bis[4-(β-hydroxyethoxy) phenyl] sulfone (HEPS) was prepared according to the method reported previously[23,24,27,28]. The solvents were purified by standard methods.

Preparation of monomers

Preparation of H1CEPS (bis[4-(β-hydroxy capronoxyl) ethoxy phenyl] sulfone)[29]. The synthesis procedure of H1CEPS is similar to that of HEPS as described previously[23,24,27]. More specifically, a round-bottomed flask was charged with HEPS (67.6 g, 0.2 mol), ϵ-caprolactone

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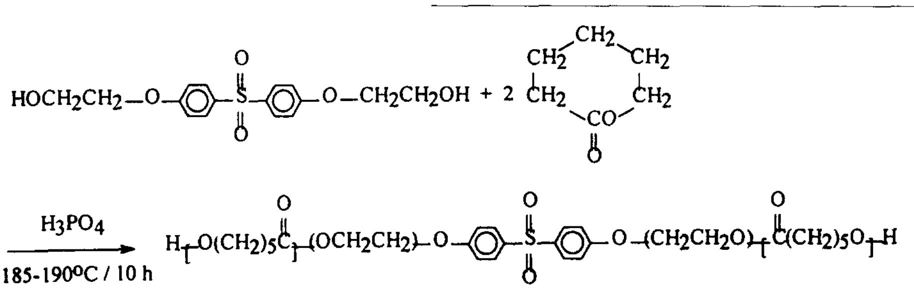
(45.6 g, 0.4 mol) and phosphoric acid (0.01 g) used as a catalyst. The mixture was heated to 185–190°C under nitrogen for 10 h. The waxy solid product was then washed with water several times to remove unreacted ϵ-caprolactone and purified by dissolving it in DMF. Later, it was reprecipitated with water to remove the catalyst. The wax-like product was dried under vacuum at 85°C. The yield was about 95.3%. The reaction took place according to Eq. (1).



H1CEPS (1)

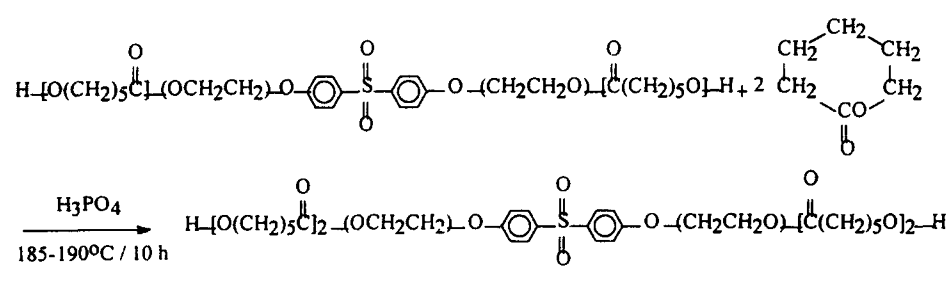
Anal. calcd for $C_{28}H_{38}O_{10}S$: C, 59.36%; H, 6.71%. Found: C, 59.03%; H, 6.87%.

IR spectra exhibit characteristic absorption at 3282 (O–H), 1728 (–COO–) and 1254 cm^{-1} (C–O–C).

^1H n.m.r. (DMSO-d_6), ppm: 7.84 (d, 4H, Ar-H), 7.08 (d, 4H, Ar–H), 4.36–3.95 (m, 8H, -O-CH_2CH_2-OCO–), 3.75 (s, 2H, O–H), 2.25–1.25 (m, 20H, OCO–$(CH_2)_5$–OH).

^{13}C n.m.r. (DMSO-d_6), ppm: 172.74, 161.30, 133.79, 129.25, 115.15, 70.20, 66.46, 63.55, 33.49, 27.94, 24.99, 24.13.

*Preparation of H2CEPS (bis[4-(β-*hydroxy dicapronoxyl) ethoxy phenyl] sulfone) and H3CEPS (bis[4-(β-hydroxy tricapronoxyl) ethoxy phenyl] sulfone). The syntheses procedures of H2CEPS and H3CEPS are similar to that of H1CEPS. Referring to the above procedure, HEPS can be replaced by H1CEPS to obtain a product that, when dried, is a waxy solid, H2CEPS. The yield was about 92.1%. Similarly, a wax solid, H3CEPS, can be obtained by using H2CEPS instead of H1CEPS. The yield was 90.4%. The reaction took place according to Eq. (2) and Eq. (3) for H2CEPS and H3CEPS, respectively. The products were dried and have the following structure:



H2CEPS (2)

Anal. calcd for $C_{40}H_{58}O_{14}S$: C, 60.45%; H, 7.30%. Found: C, 60.16%; H, 7.33%.

IR spectra exhibit characteristic absorption at 3284 (O–H), 1729 (–COO–) and 1256 cm^{-1} (C–O–C).

^1H n.m.r. (DMSO-d_6), ppm: 7.83 (d, 4H, Ar–H), 7.08 (d, 4H, Ar–H), 4.37–3.98 (m, 8H, -O-CH_2CH_2-OCO–), 3.75 (s, 2H, O–H), 2.26–1.28 (m, 40H, OCO–$(CH_2)_5$–OH).

^{13}C n.m.r. (DMSO-d_6), ppm: 172.66, 161.70, 133.79, 129.20, 115.06, 70.15, 66.40, 63.50, 33.43, 27.94, 24.95, 24.09.

Anal. calcd for $C_{52}H_{78}O_{18}S$: C, 61.06%; H, 7.63%. Found: C, 60.85%; H, 7.60%.

IR spectra exhibit characteristic absorption at 3294 (O–H), 1731 (–COO–) and 1237 cm^{-1} (C–O–C).

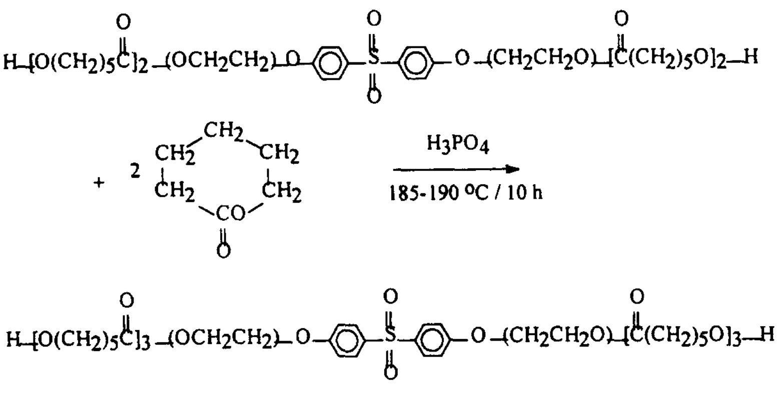
^1H n.m.r. (DMSO-d_6), ppm: 7.84 (d, 4H, Ar–H), 7.08 (d, 4H, Ar–H), 4.35–3.98 (m, 8H, -O-CH_2CH_2-OCO–), 3.98 (s, 2H, O–H), 2.26–1.29 (m, 60H, OCO–$(CH_2)_5$–OH).

^{13}C n.m.r. (DMSO-d_6), ppm: 172.48, 161.69, 133.79, 129.20, 115.08, 69.83, 66.40, 63.48, 33.42, 27.93, 25.03, 24.08.

Polymerization

Preparation of polyurethanes based on H1CEPS, H2CEPS and H3CEPS by bulk polymerization. Polyurethanes based on H1CEPS, H2CEPS or H3CEPS with various diisocyanates were synthesized by bulk polymerization.

A typical example is given below: a 52.4-g (0.05 mol) sample of H2CEPS and dibutyl tin dilaurate (DBTDL) as catalyst were placed in a two-necked flask with a mechanical stirrer, and placed in an oil bath at 120°C under a continuous steady flow of dry nitrogen passing continuously over the mixture. Next, 12.5 g (0.05 mol) of diphenyl methane 4,4′-diisocyanate (MDI) was added to the homogeneous mixture with vigorous stirring. These operations must be carried out as rapidly as possible because quick gelation of the reaction mixture occurred in some formulations. 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 7-day room temperature cure.



H3CEPS (3)

IR spectra exhibit characteristic absorption at 3310 (N–H stretching of urethane group) and 1699 (carbonyl group of urethane group).

^{1}H n.m.r. (DMSO-d_6), ppm: 9.71 (s, 2H, -N*H*C(O)O–), 7.84–7.08 (m, 16H, Ar–H), 4.41–3.98 (m, 10H, -OCH_2CH_2–OCO– and -Ar–CH_2–Ar–), 2.26–1.28 (m, 40H, -(CH_2)$_5$–).

^{13}C n.m.r. (DMSO-d_6), ppm: 172.64, 161.72, 153.54, 137.13, 135.27, 133.69, 129.27, 128.98, 118.24, 115.18, 70.17, 66.79, 63.55, 40.16, 33.28, 28.36, 25.02, 24.21.

In the case of aliphatic diisocyanates and aromatic diisocyanates, DBTDL/diol = 0.03/100 or 0.02/100 (wt./wt.) were used as catalysts[1], respectively.

Measurements

As the infrared absorption band at 2262 cm^{-1} assigned to NCO groups disappeared 1 week after sample preparation, measurements were carried out after more than 7 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 from stress–strain curves (Toyo Baldwin Tensilon UTM-II) at an elongation rate of 25% min^{-1}. Measurements of film specimens (6 mm wide, 80 mm long and *ca.* 2.0 mm thick) were taken at 25°C.

Specific gravity. Specific gravity was calculated by the displacement method on 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 reweighed after rapid surface drying. The equilibrium degree of swelling and sol fraction were calculated using the relations

$$\frac{1}{V_R} = \frac{v_R + v_S}{v_R} = 1 + \frac{\rho_R}{\rho_S}\cdot\frac{\omega_S}{\omega_R} = 1 + \frac{\rho_R}{\rho_S}\cdot\frac{\omega_{S+R} - \omega_R}{\omega_R} \qquad \mathrm{sol}(\%) = \frac{\omega_o - \omega_R}{\omega_o} \times 100$$

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

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

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

Thermal analysis. Thermal gravimetric analyses were performed by 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 diagrams were taken with an X-ray generator (Philips diffractometer system PW1710 Control).

Water absorption. To measure water absorption, film specimens were soaked in de-ionized water at room temperature for 72 h, the surfaces dried with paper towels and then quickly weighed. The films were then 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.

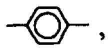
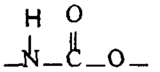
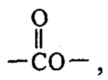
RESULTS AND DISCUSSION

The physical properties of polyurethanes were investigated by X-ray diffraction (XRD), d.s.c., thermogravimetric analysis (t.g.a.), and dynamic mechanical analysis, and tensile strengths, hardnesses, and elongations were also

Table 1 Introduction of polyurethanes

Polymer code	Diisocyanate	Diol	Ratio of ester groups/sulfonyl groups
PUH-1	HDI	H1CEPS	2
PUH-2	HDI	H2CEPS	4
PUH-3	HDI	H3CEPS	6
PUM-1	MDI	H1CEPS	2
PUM-2	MDI	H2CEPS	4
PUM-3	MDI	H3CEPS	6
PUHM-1	HMDI	H1CEPS	2
PUHM-2	HMDI	H2CEPS	4
PUHM-3	HMDI	H3CEPS	6
PUT-1	TDI	H1CEPS	2
PUT-2	TDI	H2CEPS	4
PUT-3	TDI	H3CEPS	6
PUIP-1	IPDI	H1CEPS	2
PUIP-2	IPDI	H2CEPS	4
PUIP-3	IPDI	H3CEPS	6

Table 2 Cohesive engergy density of polar groups[1,2]

Group	Cohesive energy Kcal/mole
 , benzene	3.90
 $-\overset{H}{N}-\overset{O}{\overset{\parallel}{C}}-O-$, urethane	8.50
 $\overset{O}{\overset{\parallel}{-CO-}}$, ester	2.90
$-O-$, ether	1.00

determined. All polyurethane elastomers derived from bisphenol-S derivatives with various diisocyanates are summarized in *Table 1*. Various diisocyanates such as dicyclohexyl methane 4,4′-diisocyanate (HMDI), diphenyl methane 4,4′-diisocyanate (MDI), toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) were used to prepare polyurethane. For each polymer, OH/NCO was fixed at 1.0. The cohesive energy densities of polar groups in the polyurethanes are shown in *Table 2*. On the assumption that the reaction proceeds stoichiometrically, all isocyanate groups were consumed for the formation of urethane groups because the OH/NCO molar ratio is 1.0.

The effects of soft segment/BPS ratio on the hardness of polyurethane based on bisphenol-S are summarized in *Table 3*. This table shows that the hardness of polyurethanes decreased with the increase of the soft segment/BPS ratio.

In other words, the shorter soft segment implies that a higher hardness of polyurethane would be obtained. This result may be due to an increase in polar groups and cohesive energy density[1,2]. As described later in the sections on dynamic thermal mechanical analysis and d.s.c., the lower concentration of polar groups leads to a smaller temperature of loss tangent peak and lower T_g. This is because these polar groups, which have a high cohesive force (see *Table 2*), participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, resulting in a higher hardness. Thus, the MDI- and TDI-based polyurethanes exhibited a higher hardness than the HMDI-, IPDI-, and HDI-based polyurethanes.

In previous work[30,31], the polyester urethanes derived from bisphenol-S were shown to have a somewhat higher hardness and tensile strength, smaller elongation at break, and smaller density than polyether urethanes. The polyurethanes based on bisphenol-S and bisphenol-AF have higher tensile strengths than polyurethanes based on bisphenol A [30,31]. The effects of soft segment/BPS ratio and diisocyanate on the tensile strength and elongation of polyurethanes are also shown in *Table 3*. This table indicates that elongation increased with an increase of soft segment/BPS ratio. As discussed earlier, the TDI- and MDI-based polyurethanes, which contain a higher concentration of polar groups, have a higher tensile strength and lower elongation. *Table 3* also revealed that the HMDI- and IPDI-based polyurethanes have bulky aliphatic rings in the polymer chains, thereby exhibiting a higher mechanical property than the HDI-based polyurethanes. Generally, introducing a soft segment, including ester and ether groups, increases the elongation and decreases the tensile strength.

Figure 1 shows the wide-angle X-ray diffraction of various polyurethanes based on bisphenol-S derivatives and MDI. All polymers were amorphous.

Table 4 summarizes the effects of soft segment/BPS ratio and diisocyanate on the degree of swelling and solvation of polyurethanes. This table revealed that the degree of swelling and solvation of polyurethanes increased with an increase in the soft segment/BPS ratio, irrespective of diisocyanates. This may be ascribed to a decrease in the concentration of the polar groups which act as pseudocrosslinkers[1,2]. Experimental results indicated that all polyurethanes were dissolved when DMSO was used as solvent. We believe that not only the soft segments but also the hard segments swell and solvate because of the high polarity of DMSO and the sulfonyl group. A lower degree of swelling and solvation of the MDI-and TDI-based polyurethanes was observed. The HMDI-, IPDI- and HDI-based polyurethanes exhibited a larger degree of swelling and solvation. The high degree of swelling of the ester-based polyurethanes was due to the polar nature of ester groups. In previous work[30,31], owing to the hydrophilic nature of sulfonyl groups in bisphenol-S-based polyurethanes, the water absorption values for bisphenol-S was shown to be larger than those of the corresponding bisphenol AF-based polyurethanes.

Table 3 Inherent viscosity and mechanical properties of polyurethanes based on bisphenol-S derivatives

Polymer code	η_{inh}^a	Tensile strength (MPa)	Elongation at break (%)	Hardness (HsA)
PUH-1	0.14	9.80	770.00	14
PUH-2	0.13	0.20	1800.00	2
PUH-3	0.15	0.58	3250.00	1
PUM-1	0.25	78.40	1.25	98
PUM-2	0.27	55.30	26.40	20
PUM-3	0.21	6.50	1100.00	6
PUHM-1	0.26	48.30	5.00	98
PUHM-2	0.30	36.10	313.00	18
PUHM-3	0.23	3.90	1650.00	5
PUT-1	0.48	61.70	1.25	95
PUT-2	0.50	41.20	300.00	16
PUT-3	0.44	4.30	1486.00	4
PUIP-1	0.49	31.40	3.75	75
PUIP-2	0.54	28.70	283.00	11
PUIP-3	0.50	3.70	1520.00	4

[a] 0.5 g/dl in *N,N*-dimethylformamide at 30°C

Table 4 Physical properties of polyurethanes based on bisphenol-S derivatives[a]

Polymer code	Swell ($1/V_R$)	Solvation (%)
PUH-1	2.0	0.5
PUH-2	2.3	2.8
PUH-3	4.3	5.5
PUM-1	1.4	0.11
PUM-2	1.7	0.16
PUM-3	2.9	5.1
PUHM-1	2.2	1.6
PUHM-2	2.7	8.0
PUHM-3	4.2	11.1
PUT-1	1.7	0.08
PUT-2	2.3	2.8
PUT-3	3.5	4.5
PUIP-1	2.4	2.3
PUIP-2	2.6	7.3
PUIP-3	4.0	15.4

[a] Benzene was used as a solvent. All polyurethanes were fully soluble in DMSO

The thermal behavior of the polymers was evaluated by t.g.a. and d.s.c. *Table 5* summarizes the results of t.g.a. and d.s.c. analysis of polyurethanes. This table indicates that the MDI- and TDI-based polyurethanes possess a higher thermal stability than HMDI- and IPDI-based polyurethanes. In general, polyurethanes having ester content in their backbones have a larger thermal resistance than polyurethanes having ether content. The glass transition temperatures (T_g) of polyurethanes are also listed in *Table 5*, revealing that T_g decreases with an increase in the soft segment/BPS ratio, irrespective of diisocyanates. Van Bogart *et al.*[32] studied the effects of a soft segment molar mass for a polycaprolactone/HMDI/1,4 butanediol system. Their investigations revealed that increasing the soft segment molar mass at a fixed hard segment length gave rise to an increased tendency for the hard segment domains to be isolated in the soft segment matrix. This phenomenon resulted in a higher degree of phase separation between hard

Table 5 Effect of low molar mass diol and diisocyanate on the thermal properties of polyurethanes[a,b]

Polymer code	Type of diisocyanate and low molar mass diol	T_d^i (°C)[c]	$T_d^{10\%}$ (°C)[d]	T_g (°C)[a]
PUH-1	HDI/H1CEPS	347	359	4
PUH-2	HDI/H2CEPS	348	360	− 12
PUH-3	HDI/H3CEPS	351	361	− 25
PUM-1	MDI/H1CEPS	355	368	41
PUM-2	MDI/H2CEPS	356	370	15
PUM-3	MDI/H3CEPS	361	377	− 9
PUHM-1	HMDI/H1CEPS	349	361	37
PUHM-2	HMDI/H2CEPS	351	362	10
PUHM-3	HMDI/H3CEPS	354	366	− 5
PUT-1	TDI/H1CEPS	347	367	48
PUT-2	TDI/H2CEPS	369	377	12
PUT-3	TDI/H3CEPS	376	386	− 12
PUIP-1	IPDI/H1CEPS	344	359	27
PUIP-2	IPDI/H2CEPS	350	360	9
PUIP-3	IPDI/H3CEPS	349	361	− 15

[a] D.s.c. analyses conducted at a heating rate of 10°C min^{-1}
[b] Thermogravimetric analyses conducted at a heating rate of 10°C min^{-1}in nitrogen
[c] Temperature at initial mass loss recorded on TG at a rate of 10°C min^{-1}
[d] Temperature at 10% mass loss recorded on TG at a rate of 10°C min^{-1}

Table 6 Effect of diol and diisocyanate on the dynamic mechanical properties of polyurethanes

Polymer code	Log E_{max}'' (°C) (α)	Loss tan δ (°C) (α)	Temperature of onset of log E' decline (°C)
PUH-1	27.1	39.3	22.2
PUH-2	5.09	13.7	− 4.4
PUH-3	—[a]	—[a]	—[a]
PUM-1	67.0	78.8	52.0
PUM-2	40.1	54.7	41.0
PUM-3	—[a]	—[a]	—[a]
PUHM-1	60.3	73.9	49.0
PUHM-2	29.4	52.7	16.7
PUHM-3	—[a]	—[a]	—[a]
PUT-1	72.3	80.1	56
PUT-2	—[a]	—[a]	—[a]
PUT-3	—[a]	—[a]	—[a]
PUIP-1	59.5	81.0	51.0
PUIP-2	28.7	55.2	8.0
PUIP-3	—[a]	—[a]	—[a]

[a] Sample was too soft to test its dynamic properties

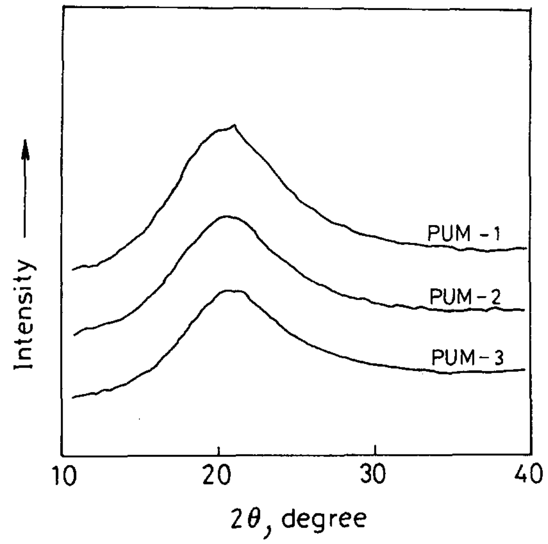


Figure 1 The wide-angle X-ray diffraction curves of polyurethane elastomers for PUM-1, PUM-2 and PUM-3

and soft blocks, and ultimately produced a lower T_g value. *Table 5* shows that the T_g values of polyurethanes based on HDI, HMDI and IPDI were lower than those of TDI and MDI, which is attributed to the stronger hydrogen bonding in the hard block domains. This finding confirms a similar study by Aitken and Jeffs[33].

Dynamic mechanical analysis

The dynamic mechanical behaviors of the polyurethanes derived from bisphenol-S derivatives are displayed in *Table 6*. As found in this table, the onset temperatures of storage modulus (E') decline, loss modulus (E'') and loss tan δ peak all decreased with an increase in ester content. This is reasonable because an increase of ester content would increase the flexibility of polyurethanes, thereby resulting in a lower temperature. In general the MDI- and TDI-based polyurethanes showed higher temperatures in E'', E' and tan δ than HMDI-, IPDI- and HDI-based polyurethanes. This phenomenon may be accounted for

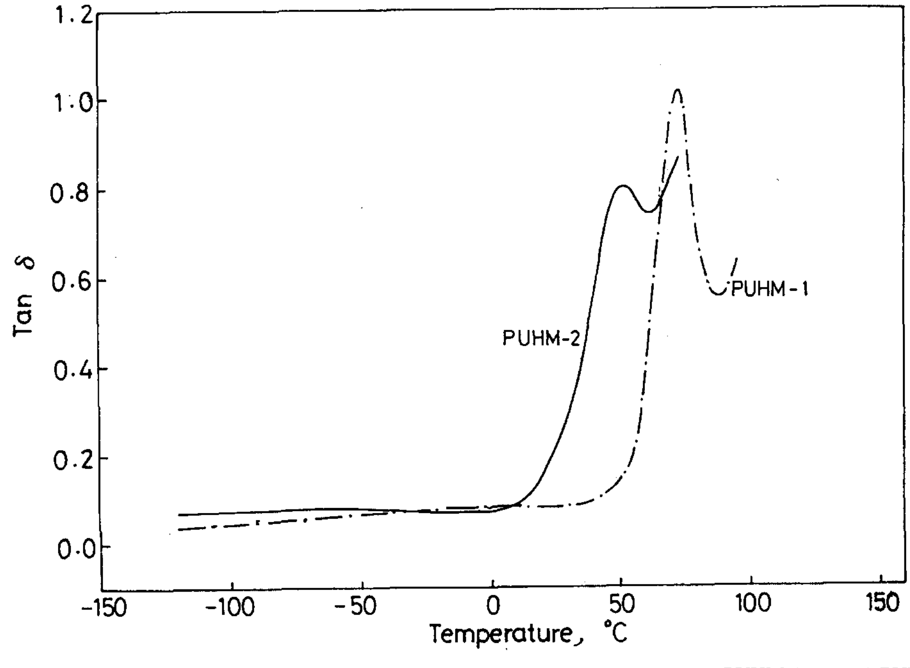


Figure 2 Effects of molar ratio of ε-caprolactone/diisocyanate on the dynamic mechanical property: (- · -) PUHM-1; (——) PUHM-2

through the high concentration of polar groups of the MDI- and TDI-based polyurethanes, thereby making the interaction between the macromolecular chains greater.

Figure 2 shows the dynamic properties of polyurethanes for PUHM-1 and PUHM-2. Both the general shape and the position change proportionately to their ester contents. This figure indicated the tan δ curves became broader with an increase in ester content. This behavior illustrated the small degree of phase separation formed in the polyurethane matrix[3], due to the incompatibility between the components of methylene groups and urethane groups.

CONCLUSIONS

The ester-based diols were prepared by bisphenol-S modified by ethylene carbonate and ϵ-caprolactone. These diols were used to react with HDI, MDI, HMDI, TDI and IPDI to obtain polyurethanes. The polyurethanes based on bisphenol-S derivatives exhibit good mechanical properties because of the additional interaction contributed by the dipolar nature of sulfonyl groups in the polyurethanes. The polyurethanes showed that the increase of ester groups decreased the hardness, tensile strength storage modulus E', solvent resistance and glass transition temperature, and increased the elongation. The t.g.a. results demonstrated that the addition of ester groups increased the thermal stability of polyurethanes. The higher degree of interaction between sulfonyl group and ester group in the ester-based polyurethanes contributed their good physical and thermal properties. Moreover, the high polarity of the sulfonyl group decreased the solvent resistance of polyurethanes.

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