Crosslinking and Mechanical Property of Liquid Rubber. III. Curative Effect of Aralkyl and Alicyclic Diols*

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Synopsis

This is the third report on the relationship between the properties and the structure of polyurethane elastomers derived from hydroxyl-terminated liquid polybutadiene (HT-BD). The curative effect of low molecular weight diols was investigated. Previously it was found that the use of aromatic diols presented a processing problem because of its high melting point. To solve this problem, the use of aralkyl diols and alicyclic diols was examined in this paper. The processability was significantly improved by the use of these diols, and the elastomers obtained retained considerably high mechanical properties.

INTRODUCTION

Previously, the relationships between the mechanical properties and the structure of polyurethane elastomers derived from hydroxyl-terminated liquid polybutadiene (HT-BD), aliphatic diols,[1] aromatic diols,[2] and diisocyanates were reported. It was recognized that the mechanical properties of elastomers were enhanced considerably with increase in the molar ratio of low molecular weight diols. Further, the mechanical properties were related to the crosslinking density, the concentration of polar groups, the crystallinity, and other factors.
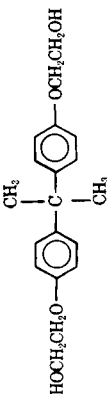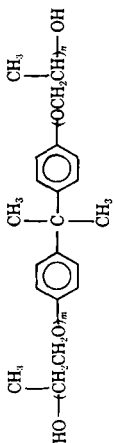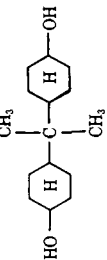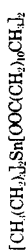
The use of low molecular weight aromatic diols led to stiff elastomers, but they presented a processing problem because of their high melting point. Further, the use of aromatic diols had some problems, such as prolonged curing time and high compression set for their low reactivity.

To circumvent these problems involved in the usage of aromatic diols, aralkyl diols and alicyclic diols, which have aliphatic reactivity, quasi-aromatic structure, and lower melting points, were examined. Using several types of diols, the relationship between the structure and property of polyurethane elastomers derived from HT-BD is discussed on the basis of their tensile property, dynamic viscoelasticity, x-ray diffraction, and so on.

TABLE I
Raw Materials

Material (designation)	Structure	Note	Source
Base polyol			
Hydroxyl-terminated liq. polybutadiene (HT-BD)	trans-1,4 60% cis-1,4 20% vinyl-1,2 20%	OH value 0.85 meq/gr	Idemitsu Petrochemical Co., Ltd. (Poly bd R-45HT)
Diisocyanate			
4,4′-Diphenylmethane diisocyanate (MDI)	OCN—⟨⟩—CH₂—⟨⟩—NCO	mp 38°C	Sumitomo Bayer Urethane Co., Ltd. (Sumidur 44)
2,4-Tolylenediisocyanate (TDI)		mp 19.5–21°C	Nippon Polyurethane Co., Ltd. (Desmodur T-100)
1,6-Hexamethylene diisocyanate (HMDI)	OCN—(CH₂)₆—NCO	bp 140–142°C/20 mm Hg	Sumitomo Bayer Urethane Co., Ltd. (Desmodur H)
Low molecular weight diol			
Ethylene glycol (EG)	HO—CH₂CH₂—OH	bp 197.6°C	reagent grade
Quinol (QL)	HO—⟨⟩—OH	mp 170°C	reagent grade
p-Xylene-α,α′-diol (XD)	HOCH₂—⟨⟩—CH₂OH	mp 119–121°C	reagent grade
1,4-Bis(β-hydroxyethoxy)benzene (BHEB)	HOCH₂CH₂O—⟨⟩—OCH₂CH₂OH	mp 105°C	Mitsui Petrochemical Co., Ltd. (OH value 574, KOH mg/g)
1,4-Bis(β-hydroxyethyl)terephthalate (BHET)	HOCH₂CH₂OC(=O)—⟨⟩—C(=O)OCH₂CH₂OH	mp 110°C	Nippon Soda Ltd. (OH value 442, KOH mg/g)
2,2-Bis(4′-hydroxyphenyl)propane (Bis A)	HO—⟨⟩—C(CH₃)(CH₃)—⟨⟩—OH	mp 156–158°C	reagent grade

Compound	Structure	State/mp	Supplier
2,2-Bis(4'-β-hydroxyethoxyphenyl)propane (Bis A + 2EO)	$HOCH_2CH_2O$—⬡—$C(CH_3)_2$—⬡—OCH_2CH_2OH		AKZO CHEM. (OH value 338)
Bisphenol A base PPG	HO—$(CH_2CH_2O)_m$—⬡—$C(CH_3)_2$—⬡—$(OCH_2CH_2)_n$—OH		
(Bis A + 2PO) $m + n = 2$		liq. at R.T.	Asahi Electro-Chemical Co., Ltd. (OH value 301)
(Bis A + 6PO) $m + n = 6$		liq. at R.T.	Asahi Electro-Chemical Co., Ltd. (OH value 194)
(Bis A + 10PO) $m + n = 10$		liq. at R.T.	Asahi Electro-Chemical Co., Ltd. (OH value 139.6)
1,4-Cyclohexanediol	HO—⬡—OH	mp 112°C	reagent grade
Hydrogenized bisphenol A (H-Bis A)	HO—⬡—$C(CH_3)_2$—⬡—OH	mp 118–121°C	New Japan Chemical Co., Ltd.
Catalyst			
Dibutyltin dilaurate (DBTDL)	$[CH_3(CH_2)_3]_2Sn[OOC(CH_2)_{10}CH_3]_2$	mp 10°C	reagent grade

EXPERIMENTAL

Elastomer Preparation

Raw Material. Chemical characterization of the materials used in this study is presented in Table I.

Preparation. HT-BD and low molecular weight diols were demoistured under reduced pressure before use. Diisocyanates and catalyst were used without further purification. According to the formulations shown in Table II and in the manner described in the previous paper,[1] polyurethane elastomers having various structures were prepared.

Measurements

Measurements were carried out using the same methods as described in the previous paper.[1]

RESULTS AND DISCUSSION

Aromatic low molecular weight diols which have bulkiness, inflexibility, and high cohesive force yield tougher elastomers than aliphatic low molecular weight diols (see Table III). But aromatic diols have some processing problems because of their high melting point and low reactivity. Aralkyl diols which were expected to have similar physical properties to those of aromatic diols and reactivity similar to that of aliphatic diols were examined.

The melting point of aralkyl diols is considerably lower than that of corresponding aromatic diols, and the processing problems can be solved. Pot life when quinol (aromatic) is used as curative is 10 min, while that when xylene diol (aralkyl) is used is 2–3 min, which is nearly equal to that of ethylene glycol (aliphatic). From the viewpoint of pot life, the reactivity of aralkyl diols is almost equal to that of aliphatic diols.

Comparison Between Mechanical Properties of Elastomers Derived from Quinol and Xylene Diol.

The mechanical properties of elastomers derived from quinol and xylene diol are tabulated in Table IV. The mechanical properties of elastomers derived from xylene diol are rather higher than those from quinol. From the fact that the elastomer derived from xylene diol shows a lower compression set, it is believed that more chain extension occurs by the use of aralkyl diols having more reactive aliphatic OH groups.

Figures 1 and 2 show the dynamic viscoelasticity and the wide-angle x-ray diffraction of these elastomers, respectively. From these figures no remarkable difference can be observed. This is reasonable, for the two diols have a similar structure. Therefore, the difference in tensile properties would be caused by a difference in reactivity.

TABLE II
Formulation (Equivalent Ratio)

	1	2	3	4	5	6	7
HT-BD[a]	2.00	1.75	1.50	1.25	1.00	0.75	0.50
Low molecular weight diol	0	0.25	0.50	0.75	1.00	1.25	1.50
Diisocyanate	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Catalyst				varied			

[a] HT-BD = Hydroxyl-terminated liq. polybutadiene.

TABLE III
Curative Effect of Aliphatic Diol (EG) and Aromatic Diol (Bis A)[a]

	EG	Bis A
Hardness, HsA	71	76
100% Modulus, kg/cm^2	31	50
Tensile strength, kg/cm^2	34	59
Elongation at break, %	138	150
T.E.F. value	4.7	8.8
Tear strength, kg/cm	21	28
Compression set, %	23	33
Benzene extract, %	1.6	2.8

[a] Formulation: HT-BD/diol/MDI = 1/1/2 (equivalent ratio). T.E.F. value = total energy function (tensile strength × elongation at break × 10^{-3}); EG = ethylene glycol; Bis A = 2,2-bis(4′-hydroxyphenyl)propane.

TABLE IV
Curative Effect of Quinol and Xylene Diol[a]

	QL	XD
Hardness, HsA	75	80
Tensile strength, kg/cm^2	55	43
Elongation at break, %	100	125
Tear strength, kg/cm	14	20
T.E.F. value	5.5	5.3
Compression set, %	49	15

[a] Formulation: HT-BD/diol/MDI = 1/1/2 (equivalent ratio). T.E.F. value = total energy function (tensile strength × elongation at break × 10^{-3}); QL = quinol; XD = p-xylene-α,α'-diol.

Comparison Between Mechanical Properties of Elastomers Derived from β-Hydroxyethyl Ether Substituent and β-Hydroxyethyl Ester Substituent

The mechanical properties of elastomers derived from quinol, 1,4-bis(β-hydroxyethoxy)benzene, and 1,4-bis(β-hydroxyethyl) terephthalate are tabulated in Table V.

The introduction of β-hydroxyethoxy groups was found to enhance the mechanical properties of the elastomer, while the introduction of β-hydroxyethyl ester groups was less effective. In both cases, the compression set of the elastomers is lowered considerably because of the high reactivity of their OH groups toward aliphatics.

It is well known that ether linkages have lower cohesive energy (1.00 kcal/mole) and higher flexibility than ester linkages (2.90 kcal/mole).[3] Consequently, it is anticipated that the introduction of ether linkages leads to enhanced flexibility
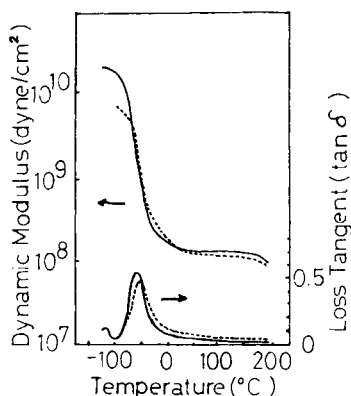
Fig. 1. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (——) QL; (- - - - -) XD.
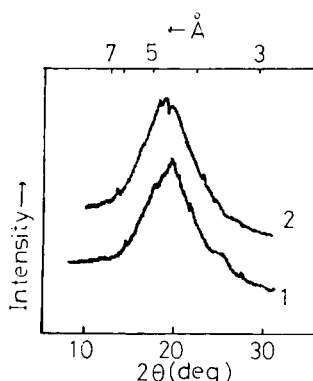

Fig. 2. Effect of diol on wide angle x-ray diffraction intensity; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (1) XD; (2) QL.

of polyurethane elastomers. Contrary to this, the mechanical properties of polyurethane elastomers derived from HT-BD are higher when ether linkages are introduced than when ester linkages are introduced. The contradiction will not be explained until the difference in compatibility of the diols with HT-BD, in morphology, and in other factors is studied.

Figure 3 shows the dynamic viscoelasticity of these elastomers. The decreasing order of dynamic modulus is as follows:

TABLE V
Curative Effect of QL, BHEB, and BHET[a]

	QL	BHEB	BHET
Hardness, HsA	75	75	58
100% Modulus, kg/cm^2	55	56	18
Tensile strength, kg/cm^2	55	62	23
Elongation at break, %	100	150	150
T.E.F. value	5.5	9.3	3.5
Tear strength, kg/cm	14	26	10
Compression set, %	49	33	8

[a] Formulation: HT-BD/diol/MDI = 1/1/2 (equivalent ratio). T.E.F. value = total energy function (tensile strength × elongation at break × 10^{-3}); QL = quinol; BHEB = 1,4-bis(β-hydroxyethoxy)-benzene; BHET = 1,4-bis(β-hydroxyethyl) terephthalate.
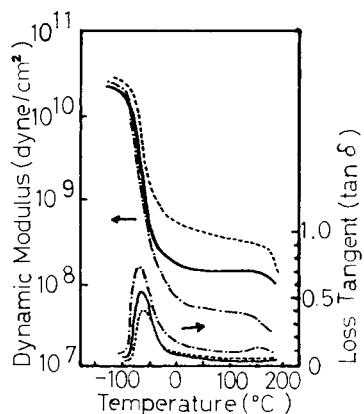
Fig. 3. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2: (——) QL; (- - - -) BHEB; (— · — -) BHET.
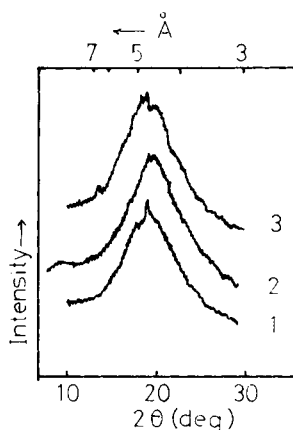

Fig. 4. Effect of diol on wide-angle x-ray diffraction intensity; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (1) BHET; (2) BHEB; (3) QL.

<p style="text-align:center">BHEB cured > QL cured > BHET cured</p>

Figure 4 shows the wide-angle x-ray diffraction of these elastomers. The diffraction intensity of elastomers derived from BHEB is also stronger than that of elastomers derived from BHET.

Figure 5 shows the x-ray diffraction pattern of elastomers derived from HT-BD/BHEB/MDI. In agreement with the result of the diffraction peak in Figure 4, a Debye–Scherrer ring which is attributable to crystallinity can be observed at $2\theta = 19.7°$ ($d = 4.51$ Å).

Comparison Between Mechanical Properties of Elastomers Derived from β-Hydroxyethoxy Substituent and β-Hydroxypropoxy Substituent

The effect of substituent groups was examined also using bisphenol A and its ethylene oxide adduct and propylene oxide adduct. The mechanical properties of elastomers derived from various kinds of diisocyanates are shown in Table VI.
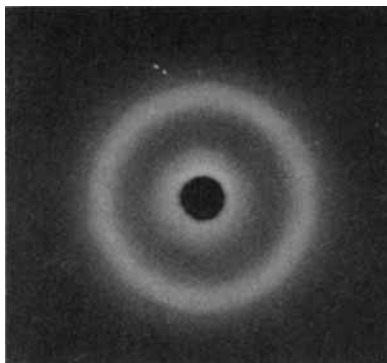
Fig. 5. X-Ray diffraction pattern; HT-BD/BHEB/MDI = 1/1/2 (eq. ratio).

The introduction of β-hydroxyethoxy groups or β-hydroxypropoxy groups affects the mechanical properties of elastomers. That is to say, the mechanical properties are lowered and the elongation at break increases as compared with those from bisphenol A. The compression set of the elastomers derived from alkylene oxide adducts of bisphenol A is lowered considerably because of their high reactivity of aliphatic hydroxyl groups.

The difference in the effect of β-hydroxyethoxy and β-hydroxypropoxy substituents can be explained by the effect of methyl side groups described in the previous paper[1] on the curvature effect of aliphatic diols.

Figure 6 shows the dynamic viscoelasticity of these elastomers. Dynamic modulus is lowered by the introduction of β-hydroxyethoxy or β-hydroxypropoxy groups. In the case of elastomers derived from ethylene oxide adduct, the plateau of the dynamic modulus curve which corresponds to the rubbery state spreads over a wide temperature region.

As shown in Figure 7, the intensity of the wide-angle x-ray diffraction of elastomers derived from EO adduct and PO adduct is rather weakened as compared with that from bisphenol A.

TABLE VI
Curative Effect of Diols Bis A, Bis A + 2EO, and Bis A + 2PO[a]

	Bis A			Bis A + 2EO			Bis A + 2PO		
	MDI	TDI	HMDI	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness, HsA	74	55	49	65	47	45	65	43	31
100% Modulus, kg/cm^2	50	13	8	22	10	6	18	7	4
Tensile strength, kg/cm^2	59	30	16	51	25	17	52	25	12
Elongation at break, %	150	250	275	200	250	300	350	475	450
Tear strength, kg/cm	28	13	9	15	12	8	15	13	6
Compression set, %	33	5	61	10	21	26	21	25	28

[a] Formulation: HT-BD/diol/diisocyanate = 1/1/2 (equivalent ratio). For diol and diisocyanate designations, see Table I.
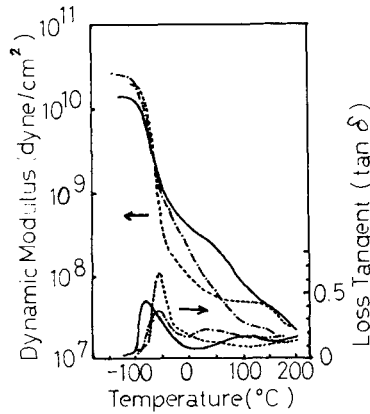
Fig. 6. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (——) Bis A; (- - - - -) Bis A + 2EO; (— · — · —) Bis A + 2PO.

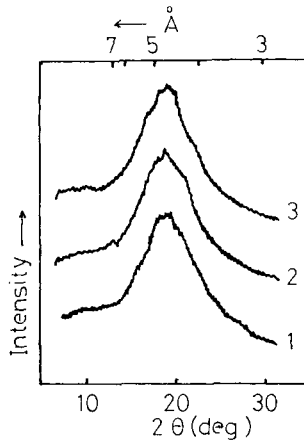Fig. 7. Effect of diol on wide-angle x-ray diffraction intensity; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (1) Bis A + 2PO; (2) Bis A + 2EO; (3) Bis A.

Effect of Average Number of Oxypropyl Groups in Propylene Oxide Adducts

The effect of the average number of oxypropyl groups reacting with OH of bisphenol A on the properties of elastomers was examined. The mechanical properties of elastomers decreases with increase in the average number of oxypropyl groups (Table VII).

Figures 8 and 9 show the relationship between the mechanical properties and the concentrations of polar groups along with the average number of oxypropyl groups. The mechanical properties of elastomers decrease with decrease in the concentrations of urethane groups, diphenylmethane groups, and diphenylpropane groups, which act as hard segments in polymer matrix.

Figure 10 shows the dynamic viscoelasticity of these elastomers. At temperatures above 10°C, dynamic modulus decreases with increase in the average number of oxypropyl groups. This is interpreted by the effect of the concentrations of polar groups described above. On the other hand, at temperatures below 10°C, dynamic modulus increases with increase in the number of oxypropyl
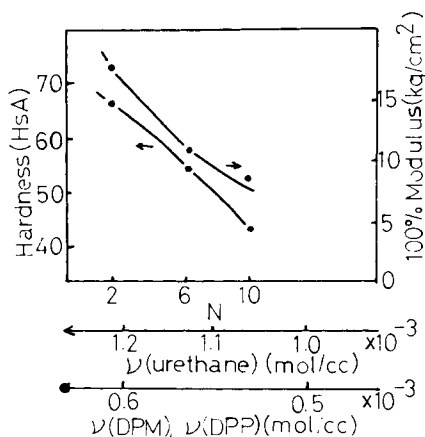
TABLE VII
Curative Effect of Diols Bis A + 2PO, Bis A + 6PO, and Bis A + 10PO[a]

	Bis A + 2PO			Bis A + 6PO			Bis A + 10PO		
	MDI	TDI	HMDI	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness, HsA	65	43	31	55	33	32	43	24	25
100% Modulus, kg/cm^2	18	7	4	11	4	4	9	3	4
Tensile strength, kg/cm^2	52	25	12	32	15	10	18	10	8
Elongation at break, %	350	475	450	475	450	325	300	450	300
Tear strength, kg/cm	15	13	6	13	8	5	13	5	3

[a] Formulation: HT-BD/diol/diisocyanate = 1/1/2 (equivalent ratio). For diol and diisocyanate designations, see Table I.

Fig. 8. Effect of concentration of polar groups on hardness and 100% modulus; HT-BD/diol/di-isocyanate = 1/1/2 (eq. ratio): N = number of oxypropyl groups; ν (urethane) = concentration of urethane groups; ν (DPM) = concentration of diphenylmethane groups; ν (DPP) = concentration of diphenylpropane groups.
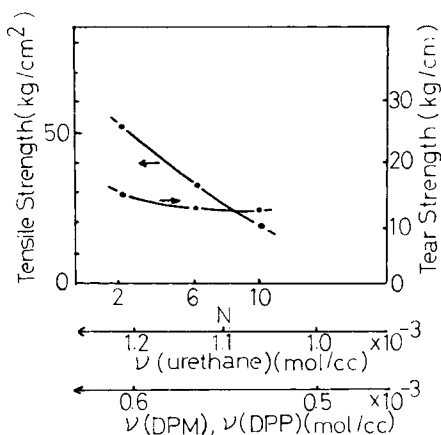

Fig. 9. Effect of concentration of polar groups on tensile strength and tear strength; HT-BD/diol/MDI = 1/1/2 (eq. ratio): N = number of oxypropyl groups; ν (urethane) = concentration of urethane groups; ν (DPM) = concentration of diphenylmethane groups; ν (DPP) = concentration of diphenylpropane groups.

groups. It is said that the glass transition temperature is elevated by an increase in the concentration of oxypropylene groups which have high steric barriers resulting in an increased dynamic modulus. In every case, a loss tangent peak which is ascribed to polybutadiene segments can be observed at about −60° to −70°C. And additional peak can be observed at about 0° to 10°C, and the intensity of the latter peak becomes stronger with increase in the number of oxypropyl groups.

Figure 11 shows the wide-angle x-ray diffraction of these elastomers. It can be seen that the crystallinity of the elastomer decreases with increase in the number of oxypropyl groups. In the case of addition of 2 mole propylene oxide, the lowering of mechanical properties is slight, while with 6 moles propylene oxide, the lowering is remarkable.

In general, an aromatic diol has a high melting point and low reactivity toward isocyanate groups. To improve these disadvantages, the use of alicyclic diols
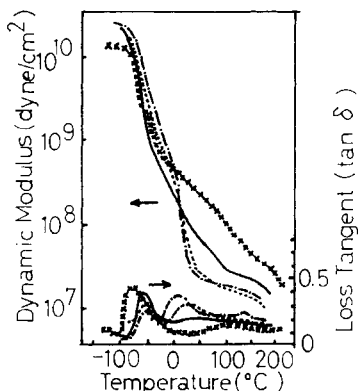
Fig. 10. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (xxxxxx) Bis A; (——) Bis A + 2PO; (- - - - -) Bis A + 6PO; (· — · —) Bis A + 10PO.
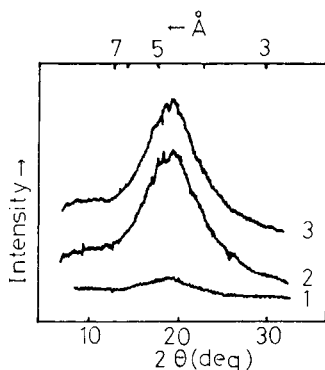

Fig. 11. Effect of diol on wide-angle x-ray diffraction intensity; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (1) Bis A + 6PO; (2) Bis A + 2PO; (3) Bis A.

was attempted. The melting point of alicyclic diols is considerably lower than that of corresponding aromatic diols (Table I). Therefore, the processing problems are improved by the use of alicyclic diols.

Comparison Between Mechanical Properties of Elastomers Derived from Quinol and 1,4-Cyclohexane Diol

The hardness of the elastomers derived from 1,4-cyclohexane diol is lower than that from quinol. But the elongation at break is greater; accordingly, the T.E.F. values, which signify the toughness of elastomers, become greater (see Table VIII). In addition, compression set also improves.

Figure 12 shows the dynamic viscoelasticity of these elastomers. As can be seen from Figure 12, the loss tangent peak of the elastomer derived from 1,4-cyclohexane diol is higher than that from quinol. This result also indicates the toughness of this elastomer.

Figure 13 shows the wide-angle x-ray diffraction. No difference in intensity can be observed.

TABLE VIII
Curative Effect of Diols QL and 1,4-Cyclohexane Diol[a]

	QL			1,4-Cyclohexane diol		
	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness, HsA	75	57	62	67	47	55
100% Modulus, kg/cm^2	55	13	23	28	10	18
Tensile strength, kg/cm^2	55	30	26	42	26	25
Elongation at break, %	100	250	150	175	300	175
T.E.F. value	5.5	7.5	3.9	7.4	7.8	4.4
Tear strength, kg/cm	26	20	18	22	14	14
Compression set, %	49	78	49	29	42	51

[a] Formulation: HT-BD/diol/diisocyanate = 1/1/2 (equivalent ratio). T.E.F. value = total energy function (tensile strength × elongation at break × 10^{-3}); QL = quinol.
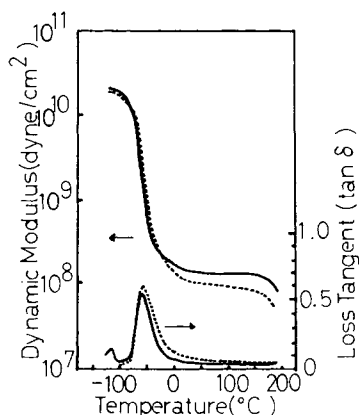

Fig. 12. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (———) QL; (- - - -) 1,4-cyclohexane diol.
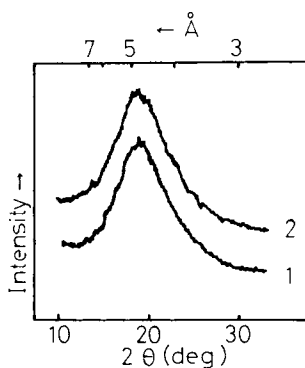

Fig. 13. Effect of diol on wide-angle x-ray diffraction intensity; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (1) 1,4-cyclohexane diol (2) QL.

Comparison Between Mechanical Properties of Elastomers Derived from Bisphenol A and Hydrogenated Bisphenol A

Table IX and Figure 14 show the mechanical properties of elastomers derived from bisphenol A and hydrogenated bisphenol A. In this case, a result similar to that described above is also obtained. That is to say, the elastomer derived from alicyclic diol has lower hardness and higher elongation at break than that

TABLE IX
Curative Effect of Diols Bis A and Hydrogenated Bis A

	Bis A			H-Bis A		
	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness, HsA	74	55	49	70	56	44
100% Modulus, kg/cm^2	50	13	8	30	12	7
Tensile strength, kg/cm^2	59	30	16	60	46	17
Elongation at break, %	150	250	275	250	350	275
T.E.F. value	8.9	7.5	4.4	15.0	16.1	4.7
Tear strength, kg/cm	28	13	9	27	12	5
Compression set, %	33	52	61	25	31	22

[a] Formulation: HT-BD/diol/diisocyanate = 1/1/2 (equivalent ratio). T.E.F. value = total energy function (tensile strength × elongation at break × 10^{-3}); Bis A = 2,2-bis(4'-hydroxyphenyl)propane (bisphenol A); H-Bis A = hydrogenated bisphenol A.

derived from aromatic diol. Toughness and compression set are also improved.

CONCLUSION

The relationships between the mechanical properties and the structure of the polyurethane elastomers derived from HT-BD and several low molecular weight diols and diisocyanates were investigated. The relationships between the molar ratio of low molecular weight diols and the properties of elastomers were similar to those obtained using aliphatic diols in the previous paper.[1]

The curative effect of low molecular weight aromatic diols was also examined in the previous paper.[2] The use of low molecular weight aromatic diols led to stiff elastomers becuase of their bulkiness, inflexibility, and high cohesive force. But they had a processing problem because of their high melting point. Further, the use of aromatic diols had some problems, i.e., prolonged curing time and high compression set because of their low reactivity.

In this paper, in order to improve these problems, the use of alkylene oxide adducts and hydrogenated compounds of aromatic diols was attempted. The melting point of these diols was considerably lowered compared with that of the corresponding aromatic diols. The elastomers obtained by using these diols
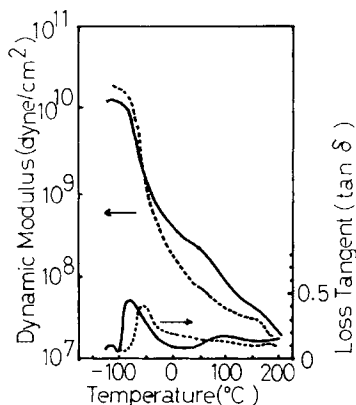

Fig. 14. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2 (eq. ratio): (——) Bis A; (- - - - -) H-Bis A.

showed slightly lower hardness and increased elongation at break compared with that obtained by using aromatic diols. From the viewpoint of T.E.F. value, these elastomers were judged as tough and stiff, for they had high T.E.F. values. Further, the problems such as reactivity, compression set, and benzene extract were also improved.

The use of the alkylene oxide adducts of aromatic diol spread the plateau in the dynamic modulus curve corresponding to the rubbery state and gave an elastomer crystallinity up to the addition of 2 moles propylene oxide. These facts confirm that this adduct is a good chain extender for these systems.

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