Crosslinking and Mechanical Property of Liquid Rubber. II. Curative Effect of Aromatic Diols

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Synopsis

The relationships between the properties and structure of polyurethane elastomers derived from hydroxyl-terminated liquid polybutadiene (HT-BD), several low molecular weight aromatic diols, and diisocyanates were studied. The curative effects of the diols were examined by such means as tensile properties, dynamic viscoelasticity, x-ray diffraction, and others. It was found that the properties of the elastomers derived from HT-BD were greatly affected by the structure of low molecular weight chain extender diol. These results were interpreted by the steric effect, crystallinity, and the concentration of polar groups.

INTRODUCTION

In the previous paper,[1] the relationship between the structure and property of polyurethane elastomers derived from HT-BD (hydroxyl-terminated liquid polybutadiene), aliphatic diols, and diisocyanates was reported. It was recognized that the mechanical properties of elastomers were enhanced considerably with an increase in the molar ratio of low molecular weight diol. Further, the mechanical properties were related to the crosslinking density, the concentration of polar groups, the crystallinity, and others. In this paper, the curative effects of aromatic diols are discussed.

By analogy of the result with phenol,[2] the reactivity of aromatic diols to isocyanates would be rather low because their hydroxyl groups are not as nucleophilic. Urethane groups derived from aromatic diols are expected to be unstable to heating since the blocked isocyanates which regenerate the isocyanate groups by heating are generally being synthesized with phenol.[3] Further, there is a processing problem because most of aromatic diols have high melting points. For these reasons, the cases employing aromatic diols as chain extenders of polyurethane elastomers have hardly been seen.[4] From the structural viewpoint, an elastomer derived from aromatic diol is anticipated to be stiff because of its bulkiness, inflexibility, and high cohesive force. Although there are some problems for practical use, it would be interesting to investigate these systems.

Using several types of diols, the relationship between the structure and

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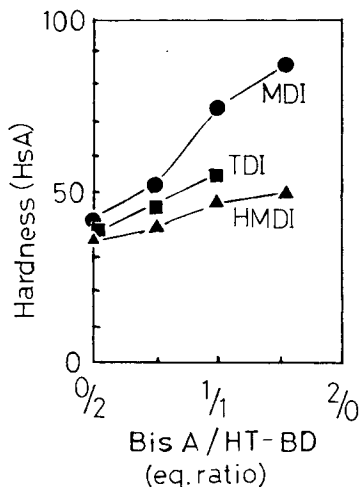
Fig. 1. Effect of diol ratio on hardness.

property of polyurethane elastomers derived from HT-BD will be discussed on the results of dynamic viscoelasticity, x-ray diffraction, and others.

EXPERIMENTAL

Elastomer Preparation

Raw Material. The materials used in this study are characterized in Table I.

Preparation. Hydroxyl-terminated liquid polybutadiene (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 in the same methods described in the previous paper.[1]

RESULTS AND DISCUSSION

Effect of Molar Ratio of Bisphenol A on Properties of Polyurethane Elastomers Cured with MDI, TDI, and HMDI

The HT-BD-derived polyurethane elastomers cured with MDI, TDI, or HMDI, varying the amount of bisphenol A to HT-BD at fixed NCO/OH ratio, were investigated.

The mechanical properties such as hardness, 100% modulus, tensile strength, elongation at break, tear strength, compression set, and benzene extract are shown in Figures 1–7.

The relationships between the molar ratio of low molecular weight diol, R, and

TABLE I
Materials

Material (designation)	Structure	Notes	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/g	Idemitsu Petrochemical Co., Ltd. (Poly bd R-45HT)
	Diisocyanate		
4,4'-Diphenylmethane diisocyanate (MDI)	$OCN-\bigcirc-CH_2-\bigcirc-NCO$	mp 38°C	Sumitomo Bayer Urethane Co., Ltd. (Sumidur 44)
2,4-Tolylene diisocyanate (TDI)	$OCN-\bigcirc(CH_3)(NCO)$	mp 19.5 −21°C	Nippon Polyurethane Co., Ltd. (Desmodur T-100)
1,6-Hexamethylene diisocyanate (HMDI)	$OCN-(CH_2)_6-NCO$	bp 140–142°C/20mmHg	Sumitomo Bayer Urethane Co., Ltd. (Desmodur H)
	Low Molecular Weight Diol		
Ethylene glycol (EG)	$HO-CH_2CH_2-OH$	bp 197.6°C	reagent grade
Catechol (CL)	$\bigcirc(OH)(OH)$	mp 105°C	reagent grade
Resorcinol (RL)	$HO-\bigcirc-OH$	mp 109–111°C	reagent grade
Quinol (QL)	$HO-\bigcirc-OH$	mp 170°C	reagent grade
2,2-Bis(4'-hydroxyphenyl)propane (Bis A)	$HO-\bigcirc-C(CH_3)_2-\bigcirc-OH$	mp 156–158°C	reagent grade
	Catalyst		
Dibutyltin dilaurate (DBTDL)	$[CH_3(CH_2)_3]_2Sn[OOC(CH_2)_{10}CH_3]_2$	mp 10°C	reagent grade

TABLE II
Formulation (Equivalent Ratio)

	1	2	3	4	5	7	8
HT-BD	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 - - - - - - - - - - - - - - - - - -						
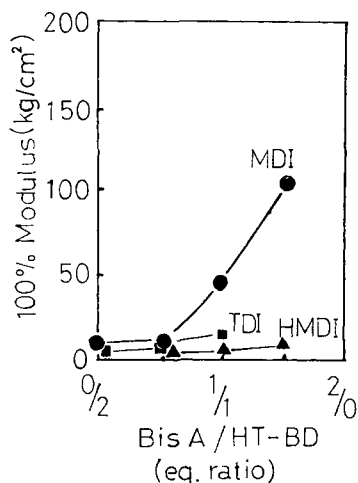
Fig. 2. Effect of diol ratio on 100% modulus.
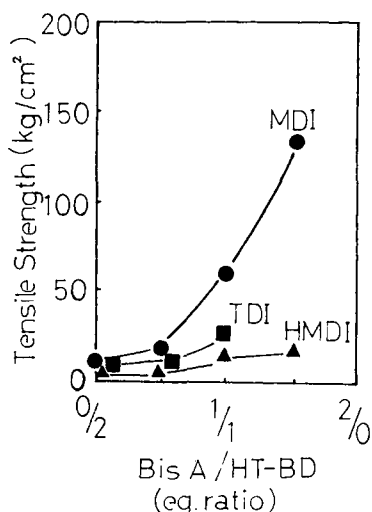
Fig. 3. Effect of diol ratio on tensile strength.

the properties of elastomers are similar to those obtained using the aliphatic diols described in the previous paper.[1] Namely, mechanical properties such as hardness, 100% modulus, tensile strength, and tear strength increase with increase in the molar ratio R. The curve of elongation at break has a maximum with increasing molar ratio R. Compression set increases and benzene extract decreases with increase in the molar ratio R.
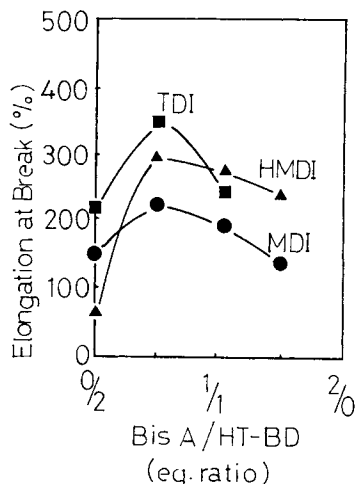
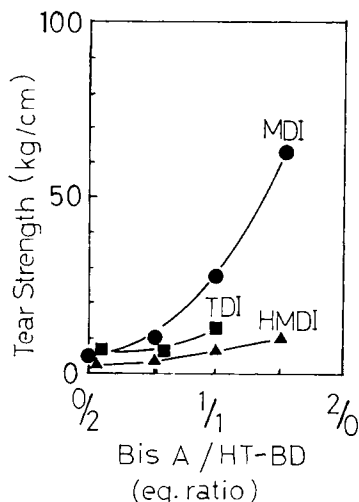Fig. 4. Effect of diol ratio on elongation at break.

Fig. 5. Effect of diol ratio on tear strength.

In all other aromatic diols used, tendencies similar to those of bisphenol A were observed.

These behaviors could be interpreted by crosslinking density, the concentration of polar groups and the crystallinity as described previously in the case of aliphatic diols.

Comparison Between Bisphenol A and Ethylene Glycol

The curative effect of aromatic diol (bisphenol A, Bis A) is tabulated in Table III along with that of aliphatic diol (ethylene glycol, EG). The superiority of the mechanical properties of Bis A over those of EG is probably due to the bulkiness, inflexibility, and the high cohesive force of aromatic rings. The compression set and benzene extract of elastomers derived from aromatic diols are higher than those from aliphatic diols. These could be ascribed to the incompleteness in chain extension reaction arising from the low reactivity of aromatic diols.
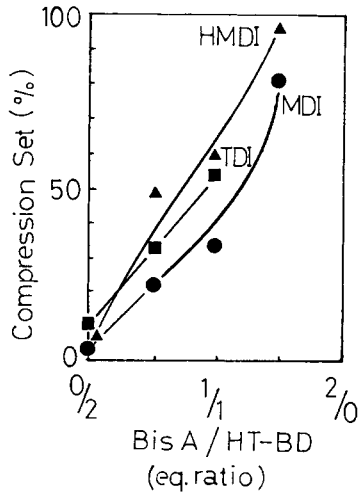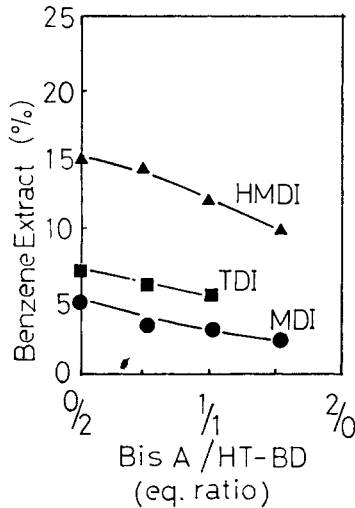
Fig. 6. Effect of diol ratio on compression set.

Fig. 7. Effect of diol ratio on benzene extract.

Effect of *o*-, *m*-, and *p*-Dihydroxybenzenes on the Properties of Elastomers

The effect of dihydroxybenzenes on the properties of elastomers was investigated using three isomers, catechol (ortho), resorcinol (meta), and quinol (para). In all systems cured with diisocyanate, the increasing order of hardness, 100% modulus, tensile strength and tear strength of elastomers was as follows (Table IV):   catechol cured < resorcinol cured < quinol cured.   The poor mechanical properties with the meta and orthoisomers can be ascribed to the disturbed orientation of polymer segments and the sterically hindered intermolecular forces and crystallization.

Figure 8 shows the result of the wide-angle x-ray diffraction on the elastomers derived from catechol, resorcinol, and quinol.   In every diffraction diagram, a strong peak can be observed at $2\theta = 19°$ ($d = 5.22$ Å).   The diffraction intensity decreased as follows: para isomer > meta isomer > ortho isomer.   Therefore,

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

	EG	Bis A
Hardness, HsA	71	76
100% modulus, kg/cm^2	30.5	50.2
Tensile strength, kg/cm^2	34.0	58.6
Elongation at break, %	138	150
T. E. F. value[b]	4.7	8.8
Tear strength, kg/cm	20.6	28.4
Compression set, %	22.9	33.4
Benzene extract, %	1.6	2.8

[a] Formulation: HT-BD/diol/MDI = 1/1/2 (eq. ratio).
[b] Total energy function (tensile strength × elongation at break × 10^{-3}).

TABLE IV
Effect of Steric Structure of Low Molecular Weight Diols on Properties of Elastomers

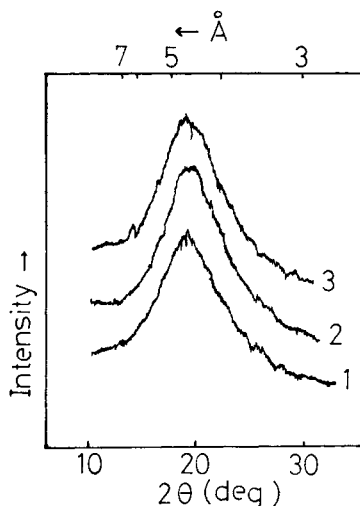|	Catechol (o-)			Resorcinol (m-)			Quinol (p-)		
Property	MDI	TDI	HMDI	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness, HsA	68	52	47	70	50	62	75	57	62
100% modulus, kg/cm^2	28	12	10	34	11	20	55	13	23
Tensile strength, kg/cm^2	44	24	16	52	26	22	55	30	26
Elongation at break, %	225	350	250	200	300	250	100	250	150
Tear strength, kg/cm	18	15	9	25	18	16	26	20	18

Fig. 8. Effect of diol ratio on wide-angle x-ray diffraction intensity HT-BD/diol/MDI = 1/1/2: (1) CL (o-); (2) RL (m-); (3) QL (p-).

the difference in the mechanical properties of the elastomers derived from the isomers could be ascribed to the difference in the crystallinity of polymer segments.

Figure 9 shows the x-ray diffraction pattern of HT-BD/QL/MDI elastomer system. A Debye-Sherrer ring due to the crystalline region can be seen also at $2\theta = 19°$ ($d = 5.22$ Å).

Figure 10 shows the dynamic viscoelasticity results of the elastomers derived from three dihydroxybenzene isomers. In the low-temperature region, the dy-
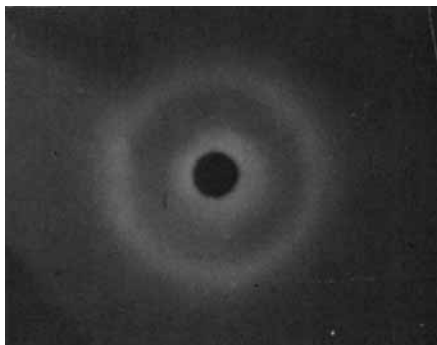
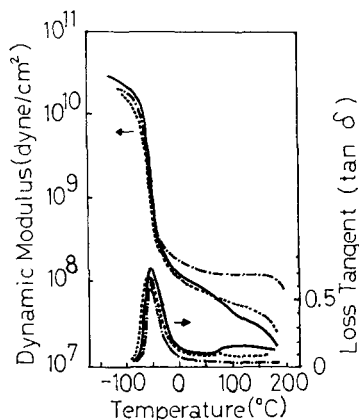Fig. 9. X-Ray diffraction pattern; HT-BD/QL/MDI = 1/1/2.

Fig. 10. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2: (——) CL
(o-); (- - -) RL (m-); (· — · — ·) QL (p-).

namic modulus of the elastomers is nearly same, but they are significantly different in the high-temperature region.

The influence of the symmetric effect on the melting point of polymers has already been investigated with poly(tetraethylene terephthalate) (mp 232°C) and poly(tetramethylene isophthalate) (mp 152°C)[5]. After the rotation around the chain axis, the conformation of the meta isomer becomes different, while that of the paraisomer still remains as it was before the rotation. Therefore, the meta isomer attains much more entropy after obtaining mobility so that the melting point of the polymer becomes lower. In the present cases of catechol and resorcinol, the lowered dynamic modulus in the high-temperature region can also be explained in the same manner.

Comparison Between Phenylene Skeleton and Diphenyl Skeleton

The mechanical properties of elastomers derived from quinol and Bis A are tabulated in Table V. The mechanical properties of the elastomers derived from Bis A are superior to those from quinol, because of the bulkiness and stiffness of the diphenylpropane skeletons.

Figure 11 shows the dynamic viscoelasticity results. When quinol is used, the wide plateau, which corresponds to the rubbery states, can be observed. In the

TABLE V
Mechanical Properties of Elastomers Derived from Quinol (QL) and Bisphenol A (Bis A)

Property	QL	Bis A
Hardness, HsA	75	76
100% modulus, kg/cm^2	55.4	50.2
Tensile strength, kg/cm^2	55.4	58.6
Elongation at break, %	100	150
T. E. F. value	5.5	8.8
Tear strength, kg/cm	25.9	28.4
Compression set, %	49.3	33.4

case of Bis A, the dynamic modulus is rather high in the lower-temperature region but decreases greatly with increase in temperature.

Figure 12 shows the wide-angle x-ray diffraction intensities of these elastomers. No difference in their intensities can be observed.
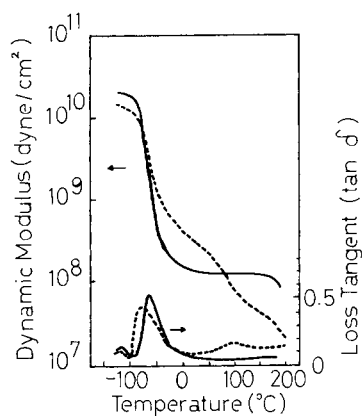

Fig. 11. Effect of diol on dynamic mechanical property; HT-BD/diol/MDI = 1/1/2; (——) QL; (- - -) Bis A.
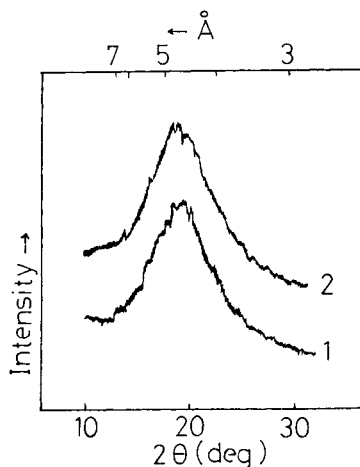

Fig. 12. Effect of diol on wide-angle x-ray diffraction intensity: (1) Bis A; (2) QL.

CONCLUSIONS

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

Of the ortho, meta, and para isomers of dihydroxylbenzene, the para isomer produced the stiffest elastomer. The effects of the isomers is ascribed to the difference in crystallinity and steric effect.

The mechanical properties of elastomers derived from bisphenol A were superior to those derived from quinol. This is ascribed to the bulkiness and stiffness of the diphenylpropane skeleton. With quinol, the dynamic modulus curve had a wide plateau which corresponded to the rubbery state.

The use of aromatic diols led to stiff elastomers because of their bulkiness, inflexibility, and high cohesive force. But they had a processing problem because of their high melting point. The use of aromatic diols involved additional problems, i.e., prolonged curing time, high compression set, and benzene extract for their low reactivity.

References

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4. H. Sugimoto, R. Miura, and M. Takayanagi, *Polym. Prepr., Soc. Polym. Sci. Jpn.*, **23**(1), 167 (1974).

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