

Crosslinking and Mechanical Property of Liquid Rubber. I. Curative Effect of Aliphatic Diols

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Synopsis


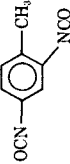


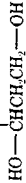
The structure-property relationships of polyurethane elastomer derived from liquid hydroxyl-terminated polybutadiene/low molecular weight aliphatic diol/diisocyanate system were studied. The effects of the amount of low molecular weight diol on the mechanical properties of elastomer were discussed on the basis of the results of the stress-strain curve, swelling, dynamic viscoelasticity, x-ray diffraction, and others. It was found that some particular combinations of low molecular weight diol and diisocyanate specifically affect the properties of elastomers. When the mechanical properties of the elastomers were plotted against the number of methylene carbons in low molecular weight diol, the characteristic zigzag patterns were obtained. These patterns were explained by the difference in the packing and the dependence of the ability of intermolecular hydrogen bonding on whether the number of the methylene carbons was even or odd. This assumption was confirmed by x-ray diffraction.


INTRODUCTION

As is widely recognized, polyurethane elastomers have superior mechanical properties such as high tensile strength, tear strength, abrasion resistance, and oil resistance. Further, the most important feature of the polyurethane elastomer is its castability in the liquid state, which makes the process very simple. These superior characteristics were pointed out in numerous studies¹⁻⁴ in the field of synthetic chemistry and the mechanical properties which have been discussed by Bayer and his coworkers.⁵

In the urethane elastomer industry, liquid hydroxyl-terminated polybutadiene (HT-BD) has been developed as a new field.^{6,7} HT-BD is a castable liquid material. The urethane elastomers obtained by the chain extension of terminated OH groups with diisocyanates have a superior hydrolytic stability arising from the nonpolar main chain of HT-BD. Further, being different from other general polyurethane elastomers, these elastomers based on HT-BD can be compounded with a large amount of filler. As HT-BD has several characteristics as mentioned above, it is expected that the use of HT-BD will expand into a variety of industrial fields.

TABLE I
Materials

Materials (designation)	Structure	Notes	Source
Base polyol Liq. hydroxyl-terminated polybutadiene (HT-BD)	<i>trans</i> -1,4 60%, <i>cis</i> -1,4 20%, Vinyl-1,2 20%	OH val 0.85 meq/g	Idemitsu Petrochemical Co., Ltd. (Poly bd R-45HT)
Diisocyanate 4,4'-Diphenylmethane diisocyanate (MDI)		mp 38°C	Sumitomo Bayer Urethane Co., Ltd.
2,4-Tolylene diisocyanate (TDI)		mp 19.5-21.5°C	Nippon Polyurethane Co., Ltd.
1,6-Hexamethylene diisocyanate (HMDI)	$\text{OCN}-(\text{CH}_2)_6-\text{NCO}$	bp 140°-142°C/20 mm Hg	Sumitomo Bayer Urethane Co., Ltd.
Low molecular weight diol Ethylene glycol (EG)	$\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$	bp 197.6°C	Reagent grade
1,2-Propanediol (1,2-PD)		bp 97°C/20 mm Hg	Reagent grade
1,3-Propanediol (1,3-PD)		bp 210°-212°C	Reagent grade
1,3-Butanediol (1,3-BD)		bp 115°-120°C/21 mm Hg	Dicel Ltd.

Neopentyl glycol (NPG)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HO}-\text{CH}_2\text{CCH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$	mp 127°C	Mitsubishi Gas Chemical Co., Ltd.
1,4-Butanediol (1,4-BD)	HO-CH ₂ CH ₂ CH ₂ CH ₂ -OH	bp 127°C/20 mm Hg	Reagent grade
1,4-Butenediol (1,4-Bute.D)	HO-CH ₂ CH=CHCH ₂ OH	mp 25°C	Toyo Soda Manufacturing Co., Ltd.
1,5-Pentanediol (1,5-PD)	HO-(CH ₂) ₅ -OH	bp 124°C/7 mm Hg	Reagent grade
1,6-Hexanediol (1,6-HD)	HO-(CH ₂) ₆ -OH	bp 144°C/4 mm Hg mp 42.8°C	Ube Industries, Ltd.
Catalyst Dibutyltin dilaurate (DBTDL)	[CH ₃ (CH ₂) ₃] ₂ Sn[OCO(CH ₂) ₁₀ CH ₃] ₂	mp 10°C	Reagent grade
Solvent Dimethyl sulfoxide (DMSO)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{S}-\text{CH}_3 \\ \\ \text{O} \end{array}$	bp 189°C	Reagent grade
Benzene		bp 80.1°C	Reagent grade

But nowadays, the consumption of HT-BD as raw material for polyurethane elastomer is insignificant in comparison with that of polyether polyol and polyester polyol. Taking into account the present circumstances, it would be necessary to improve the method of processing, reinforcing, and crosslinking for future development of HT-BD.

This paper describes the crosslinking of HT-BD by diisocyanates and several aliphatic diols to give basic data for the practical use of HT-BD. While several low molecular weight diols have been investigated as chain extenders for polyurethane elastomer, there have been no systematic studies comparing diols with each other.

In this paper, the effects of the amount of low molecular weight diol, the length of methylene sequences, and side chain of the diol on the mechanical properties of the elastomer are examined. To interpret the mechanical properties, it is necessary to consider the concentrations of polar groups, the crosslinking density, and the orientation of polymer segments. The relationship between the structure and the property of the elastomer derived from HT-BD is discussed on the basis of the results of the stress-strain curve, swelling, dynamic viscoelasticity, x-ray diffraction, and others.

EXPERIMENTAL

Elastomer Preparation

Chemical characterization of the materials used in this study is presented in Table I. HT-BD and low molecular weight diols were demoiatured under reduced pressure before use. Diisocyanates and dibutyltin dilaurate (DBTDL) as catalyst were used without further purification. According to the formulations shown in Table II, polyurethane elastomers having various structures were made. Synthetic procedures for the preparation of these elastomers are described below.

HT-BD, low molecular weight diol, and catalyst were mixed homogeneously in a beaker with heating. Then diisocyanate (molten at 70°C in the case of MDI or at room temperature in other cases) was added to the homogeneous mixture with vigorous stirring. These operations must be carried out as fast 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 silicone release agent) heated to a fixed cure temperature. The mixture was cured at 120°C for 5 hr in a press mold, with an additional seven-day room-temperature cure.

In the case of TDI and HMDI system, DBTDL/(HT-BD + low molecular weight diol) = 0.02/100 or 0.03/100 (wt/wt) was used as catalyst, respectively.

TABLE II
Formulation (Equivalent Ratio)

	1	2	3	4	5	6	7
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 (DBTDL)				varied			

Measurements

As the infrared absorption band at 2250 cm^{-1} assigned to NCO groups disappeared one week after sample preparation, 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 K 6301.

Tensile Properties. 100% Modulus, tensile strength, and elongation at break were measured by an Autograph IS-5000 (Shimazu Seisakusho Ltd.) according to JIS K 6301. Specimens were cut from compression-molded slabs which had a thickness of about 2 mm using a JIS #3-type dumbbell. The rate of strain was 500 mm/min.

Tear Strength. Tear strength was measured by an Autograph IS-5000. Specimen was cut from about 2-mm thick sheet using a JIS B-type dumbbell. The rate of strain was 500 mm/min.

Compression Set. According to JIS K 6301, the test specimen was deformed 25% for 22 hr at 70°C .

Specific Gravity. Specific gravity was calculated by the displacement method in water.

Mooney-Rivlin Plot. Relationship between stress and strain was measured by an Autograph IS-5000 with a strain rate of 100 mm/min. Ring-shaped specimens (inner diameter 45.0 mm, thickness 4.0 mm, width 5.0 mm) were used.

Swelling and Sol Fraction. The equilibrium degree of swelling of each elastomer was determined by immersing a small sample ($20\text{ mm} \times 20\text{ mm} \times 2\text{ mm}$) in 100 ml solvent (benzene or DMSO) for seven days at room temperature and reweighing after rapid surface drying. The equilibrium degree of swelling and sol fraction were calculated using the relations

$$\frac{1}{V_R} = \frac{v_R + v_S}{v_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{W_S}{W_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{W_{S+R} - W_R}{W_R}$$

$$\text{sol (\%)} = \frac{W_0 - W_R}{W_0} \times 100$$

where $1/V_R$ = equilibrium degree of swelling, sol (%) = sol fraction, v_R = volume fraction of rubber component in swollen sample, v_S = volume fraction of solvent in swollen sample, W_R = weight of dry sample after swelling, W_S = weight of solvent contained within swollen sample, W_{S+R} = weight of swollen sample, W_0 = original weight of sample before swelling, ρ_R = density of dry sample after swelling, and ρ_S = density of solvent (0.87865 for benzene and 1.1014 for DMSO at 20°C , respectively).

Soxhlet Extraction. In addition to measurement of the sol fraction, Soxhlet extraction was carried out. A sample, about 2 mm cube, placed in glass filter was extracted with benzene under reflux for 8 hr.

Dynamic Viscoelasticity. Dynamic mechanical measurement was performed on compression-molded film which had a thickness of 0.2 to 0.4 mm, using a Rheovibron Model DDV-II (Toyo Measuring Instruments Co., Ltd.) at a frequency of 110 Hz, ranging in temperature from -130° to 200°C at a rate of about $1^\circ\text{C}/\text{min}$.

Stress Relaxation. Measurement was made on the ring-shaped specimen, the same shape as was used for the Mooney-Rivlin plot calculation. The spec-

imen was strained to 50% using an Autograph IS-5000 with a strain rate of 100 mm/min. The strained specimen was allowed to stand for 36 sec, followed by determining the initial stress. The stress was recorded at specific time intervals.

Differential Scanning Calorimetry (DSC). DSC traces were obtained on a differential scanning calorimeter 8001 (Rigaku Denki Co., Ltd.). Measurement was performed over the range of room temperature to 300°C at a heating rate of 10°C/min.

X-Ray Diffraction Intensity. Relative intensity of the diffraction peak was obtained using nickel-filtered Cu K_{α} irradiation generated by an x-ray diffraction Geigerflex 2042 (Rigaku Denki Co., Ltd.) at 15 mA, 30 kV.

X-Ray Diffraction Pattern. Diffraction pattern was obtained using nickel-filtered Cu K_{α} irradiation for 1.5 hr from an x-ray diffractometer Type GX 2 (Shimazu Seisakusho Ltd.).

RESULTS AND DISCUSSION

All samples in Tables I and II were investigated. However, only cases which show typical effects of compositions are discussed below.

Effect of Low Molecular Weight Diol in HT-BD on Properties of Polyurethane Elastomers

Mechanical Properties

Hardness, 100% modulus, tensile strength, elongation at break, and tear strength of the urethane elastomers, based on HT-BD, diisocyanate (MDI, TDI, or HMDI), and ethylene glycol (EG) as low molecular weight diol, are shown in Figures 1–5. These were plotted versus the molar ratio R of [OH] in diol/[OH] in HT-BD. For each polymer, OH/NCO was fixed at 1.0. In all the cases of other low molecular weight diols being used, a tendency similar to that of EG was observed. That is to say, hardness, 100% modulus, tensile strength, and tear strength of urethane elastomers are enhanced by an increase in the molar ratio

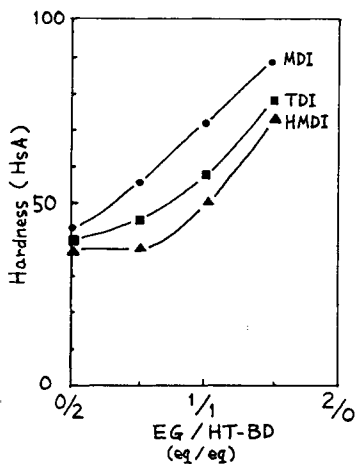


Fig. 1. Effect of diol ratio on hardness.

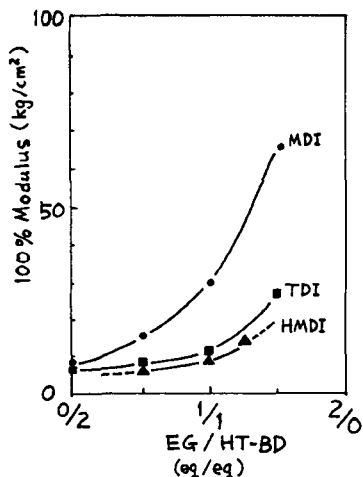


Fig. 2. Effect of diol ratio on 100% modulus.

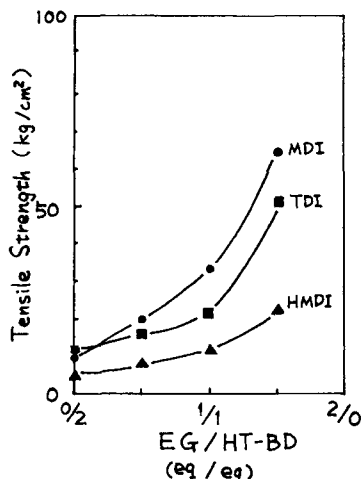


Fig. 3. Effect of diol ratio on tensile strength.

R of EG/HT-BD. The curve of elongation at break has a maximum with increasing molar ratio *R*.

Relationships between the molar ratio *R* and the structural parameters of the elastomers are shown in Table III. The concentrations of urethane groups and diphenylmethane groups are evaluated as follows: On the assumption that the reaction proceeds stoichiometrically, all isocyanate groups are consumed for the formation of urethane groups because the OH/NCO ratio is 1.0. Namely, 1 mole of urethane groups are formed from 1 mole equivalent of isocyanate groups, and the concentration of urethane groups is calculated from the equation

$$\begin{aligned}
 &[\text{concentration of urethane groups}] \\
 &= \frac{[\text{weight of MDI}]/[\text{isocyanate equivalent of MDI}]}{[\text{weight of (HT-BD + EG + MDI)}]} \\
 &\qquad\qquad\qquad \times \text{density} \quad (\text{moles/cc})
 \end{aligned}$$

As the amount of diphenylmethane groups is half of the urethane groups, the

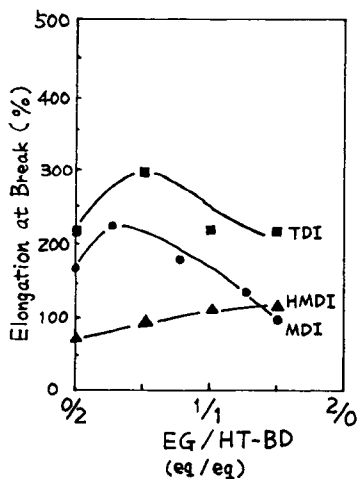


Fig. 4. Effect of diol ratio on elongation at break.

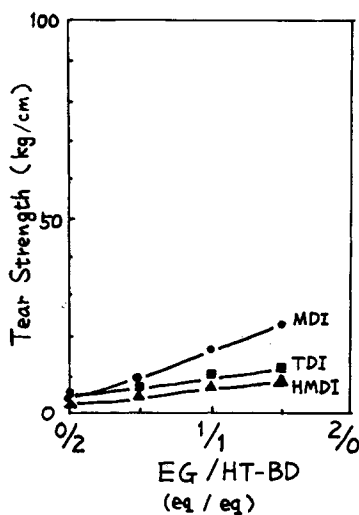


Fig. 5. Effect of diol ratio on tear strength.

TABLE III
Relationship Between EG Content and Concentration of Polar Groups, Average Molecular Weight Between the Crosslinks

HT-BD	2.0	1.5	1.0	0.5	0
EG	0	0.5	1.0	1.5	2.0
MDI	2.0	2.0	2.0	2.0	2.0
Mw between crosslinks	6975	9820	15510	18630	∞
Concentration of urethane groups, (moles/cc) × 10 ⁴	7.21	9.24	13.2	22.9	
Concentration of diphenylmethane groups, (moles/cc) × 10 ⁴	3.60	4.64	6.62	11.5	

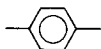
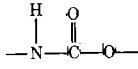
concentration of diphenylmethane groups is evaluated by the following equation:

$$[\text{concentration of diphenylmethane groups}] = [\text{concentration of urethane groups}] \times 0.5 \text{ (moles/cc)}$$

As shown in Table III, the concentrations of urethane groups and diphenylmethane groups increase with increase in the molar ratio R . These polar groups, which have high cohesive forces (see Table IV), participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, resulting in less flexible elastomers. Relationships between the concentration of polar groups and physical properties are plotted in Figures 6 and 7. From these figures it is evident that the mechanical properties of the elastomers are enhanced with increase in the molar ratio R . This result may be due to an increase in polar groups. Further, as described later in the sections on dynamic viscoelasticity, DSC, and x-ray diffraction, the crystallinity of the elastomers increases with increase in the molar ratio R . From these facts, it is considered that the mechanical properties of the elastomers are also affected by the crystallinity.

Relationships between the molar ratio R and the average molecular weight between the crosslinks are also shown in Table III. The average molecular weight between the crosslinks is calculated as follows: Since 1 mole of trifunctional molecules are contained in every 5 moles of HT-BD because the average functionality of HT-BD is 2.2, in the case of the composition HT-BD/EG/MDI = 1/1/2 (eq), for example, the segment structure model should be indicated as in Figure 8. With increase in the molar ratio R , the average molecular weight between the crosslinks increases, i.e., the crosslink density decreases. This effect may cause an increase in elongation at break. On the other hand, with increasing molar ratio R , the concentrations of urethane groups and diphenylmethane groups, which act as constituents of the secondary interchain bondings, increase.

TABLE IV
Cohesive Energy Density of Polar Groups⁸

		
Cohesive energy, kcal/mole	3.90	8.50

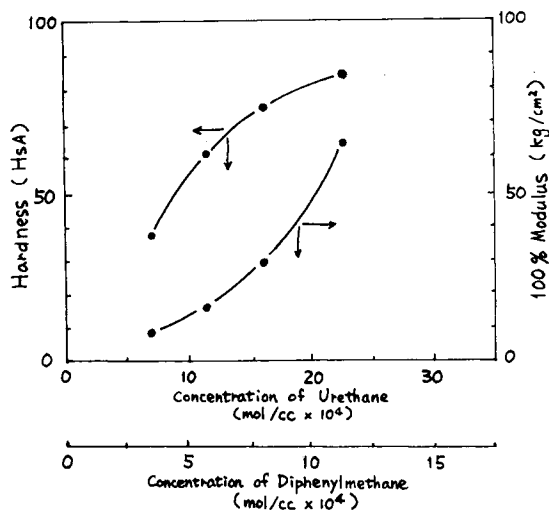


Fig. 6. Relationship between concentrations of polar groups and mechanical properties (HT-BD/EG/MDI system).

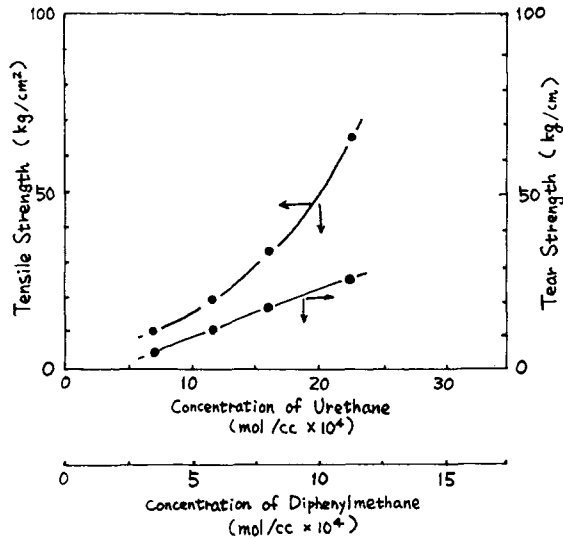


Fig. 7. Relationship between concentrations of polar groups and mechanical properties (HT-BD/EG/MDI system).

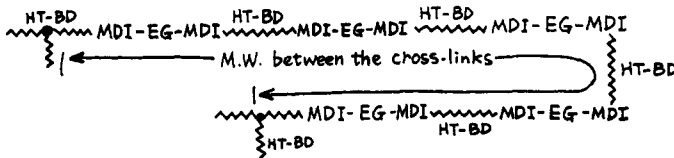


Fig. 8. Structural model of elastomer.

This effect results in a decrease in elongation at break. The maximum in the relationship of the elongation at break versus the molar ratio R can be explained by the balanced effect of these two factors.

Compression Set

With increase in the molar ratio R , the compression set increases (see Fig. 9). This effect probably results from the influence of polymer network and hydrogen bonding. A decrease in crosslink density, which is caused by an increase in molar ratio R , makes the elastomers more plastic, and the compression set consequently becomes greater. Further, when molecular chains are strained with a compressive force, hydrogen bondings may dislocate, and some of them still remain as permanent deformation even after the stress is removed, as indicated schematically in Figure 10.

Mooney-Rivlin Plot

In most cases the stress-strain curve in simple extensions of elastomers is better described by the Mooney-Rivlin equations,

$$f = (C_1 + C_2\alpha^{-1})(\alpha - \alpha^{-2})$$

where f is the stress, α is the extension ratio, and C_1 and C_2 are constants. The

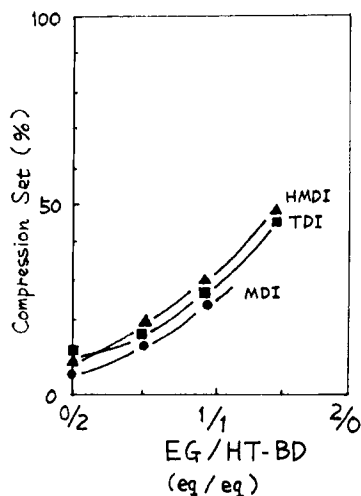


Fig. 9. Effect of diol ratio on compression set.

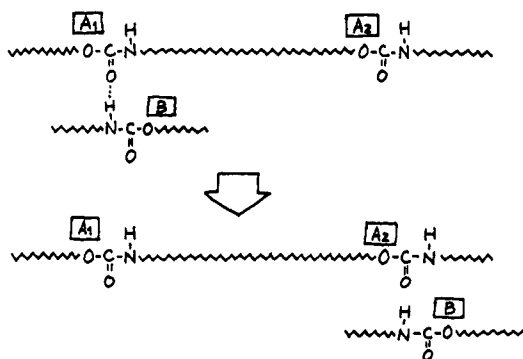


Fig. 10. Model of dislocation arrangements.

C_2 term represents the deviation from the ideal rubber behavior. Some authors^{9,10} have suggested that the C_2 term is associated with a slow stress relaxation process and arises from a failure to achieve equilibrium. Others¹¹⁻¹⁴ have preferred to regard the C_2 term as representing a real equilibrium deviation arising from deficiencies in the Gaussian approximation, and several theoretical modifications have been developed.

In each diisocyanate-cured system, the inclination C_2 becomes greater with increase in the molar ratio R . Figure 11 shows the relationship between the C_2 values and the concentrations of polar groups varying with the molar ratio R . It is considered that the effect of the urethane groups, the diphenylmethane groups, and the crystalline regions prevents the ideal behavior predicted by the rubber elasticity theory. The C_2 term of the MDI-cured and HMDI-cured systems is greater than that of TDI-cured system (see Table V).

In the TDI-cured system, the orientation of the polymer segments is hindered sterically. On the other hand, in the MDI- and HMDI-cured systems, the polymer segments orient and crystallize easier. The difference among the C_2 terms may arise from these effects.

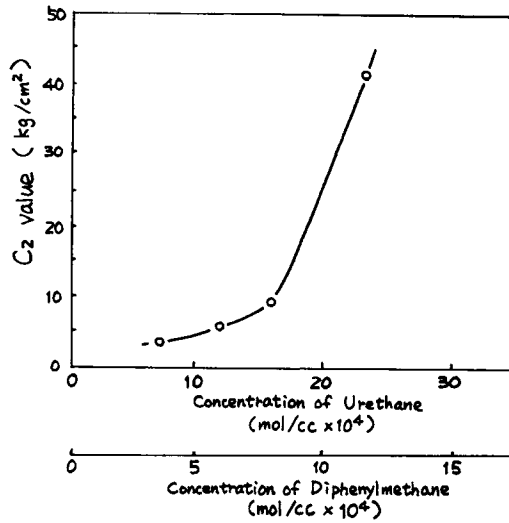


Fig. 11. Relationship between C_2 value and concentrations of polar groups (HT-BD/EG/MDI system).

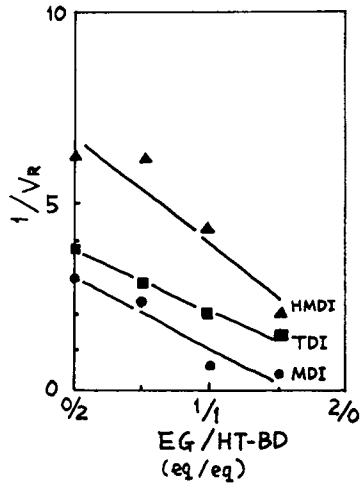


Fig. 12. Effect of diol ratio on degree of swelling (solvent: benzene).

TABLE V
 C_1 and C_2 Values of Mooney-Rivlin Equation^a

	C_1 , kg/cm ²	C_2 , kg/cm ²
MDI system	6.2	44.8
TDI system	2.1	11.2
HMDI system	3.0	38.2

^a HT-BD/EG/diisocyanate = 0.5/1.5/2.0 (eq. ratio).

Swelling

Figures 12 and 13 show the relationship between the molar ratio R and the degree of swelling. In Figure 12, in each diisocyanate system the degree of

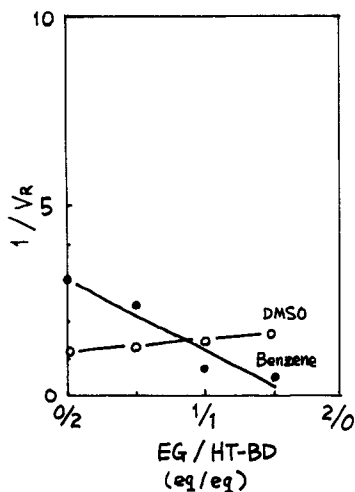


Fig. 13. Effect of diol ratio on degree of swelling (solvent: DMSO, benzene; HT-BD/EG/MDI system).

swelling decreases with increase in the molar ratio R . This may be ascribed to an increase in the concentrations of the polar groups which act as pseudocrosslinking in spite of the decrease in the crosslink density, as tabulated in Table III. Contrary to the result when benzene was used, the degree of swelling increases with increase in the molar ratio R when DMSO was used as a swelling solvent, as shown in Figure 13. It may be considered that not only the soft segments but also the hard segments swell because of the high polarity of DMSO. In this case the degree of swelling is affected mainly by the crosslink density.

Sol Fraction and Soxhlet Extraction

Figures 14 and 15 show the result of sol fractions and Soxhlet extractions of elastomers, respectively. The sol fractions and Soxhlet extractions of the elastomers decrease with increase in the molar ratio R .

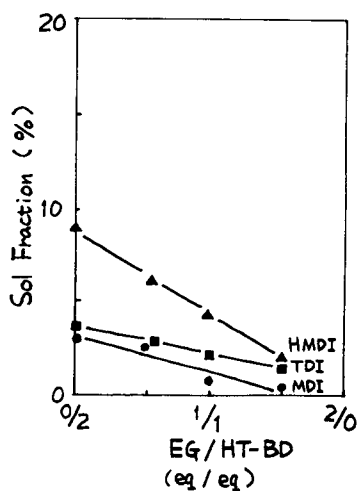


Fig. 14. Effect of diol ratio on sol fraction (solvent: benzene).

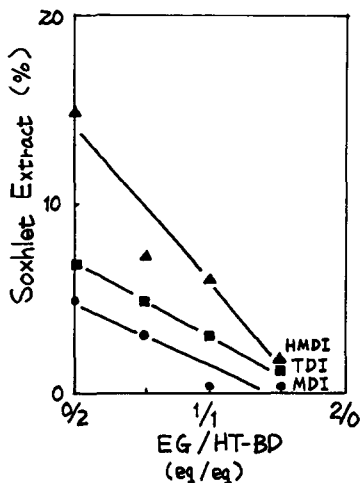


Fig. 15. Effect of diol ratio on Soxhlet extraction (solvent: benzene).

Effect of Molar Ratio of Low Molecular Weight Diol on Dynamic Mechanical Properties

The effects of the molar ratio R on the dynamic mechanical properties of the elastomers were investigated in the polyurethane based on HT-BD/EG/HMDI. Dynamic modulus increases with increase in the molar ratio R . This is ascribed to the effect of an increase in the concentration of urethane groups as described above. With increase in the molar ratio R , the loss tangent peak at about -60°C , which may be ascribed to the polybutadiene blocks, becomes weaker, and another new loss tangent peak appears at about 100°C . This new loss tangent peak may be due to the influence of an increase in crystalline domains (see Fig. 16).

Figure 17 shows the effect of diisocyanates on the dynamic mechanical properties. Loss tangent peaks are observed for all MDI-, TDI-, and HMDI-cured systems at about 60°C . But the strength of the loss tangent is different, that is, for MDI- and TDI-cured systems it appears as shoulder, and for HMDI-cured

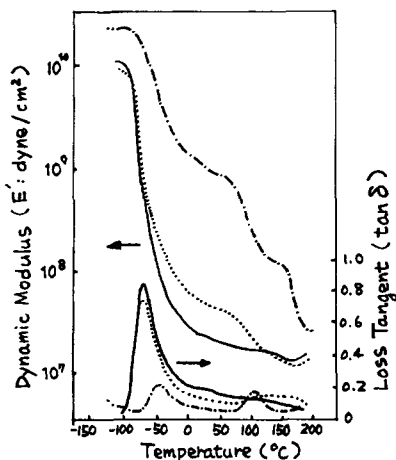


Fig. 16. Effect of diol ratio on dynamic mechanical property (HT-BD/EG/HMDI system): (—) 2.0/0/2.0; (---) 1.0/1.0/2.0; (-·-·-) 0.5/1.5/2.0 (eq. ratio).

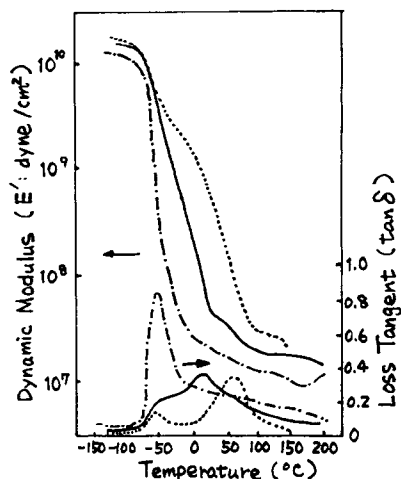


Fig. 17. Effect of diisocyanate on dynamic mechanical property (HT-BD/1,4-BD/diisocyanate system): (—) MDI; (---) TDI; (···) HMDI.

system it appears rather strong. The decreasing order of dynamic modulus is HMDI-cured > MDI-cured > TDI-cured. From the viewpoint of chemical structures, it is expected that MDI- and TDI-cured systems have high dynamic moduli, because they contain benzene rings which have high cohesive energy and bulkiness. This anomalous behavior may indicate that the methylene sequences of HMDI together with that of low molecular weight diol form tight crystalline structures. In the MDI-cured system, there is a very broad loss tangent peak centering around about 10°C. Such a behavior, as if of a single component, suggests good compatibility of the components. In conformity with this, the total energy function (TEF) value indicates a tough mechanical strength of MDI-cured elastomer as shown in Table VI.

Effect of Molar Ratio of Low Molecular Weight Diol on DSC

Figure 18 shows the DSC chart of HT-BD/1,6-HD/HMDI systems. The DSC chart of the elastomer shows a broad endothermic peak from 70° to 150°C and a sharp endothermic peak at 156°C (designated as 1 in Fig. 18). The endothermic peak at 156°C is attributable to the melting point of hard segment domains in the polymer matrix, for this peak is in fair agreement with that of the elastomer synthesized with 1,6-HD/HMDI = 1.0/1.0 (designated as 2 in Fig. 18).

TABLE VI
Total Energy Function (TEF) of Elastomers

	TEF value ^a
MDI system	6.96
TDI system	3.52
HMDI system	1.38

^a Total energy function is calculated from (tensile strength × elongation at break) × 10⁻³.

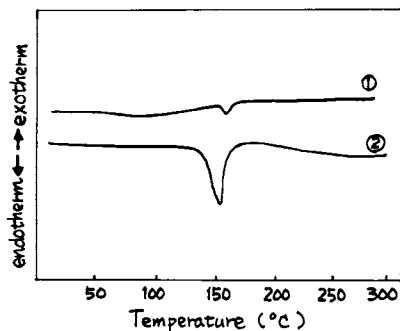


Fig. 18. DSC chart (HT-BD/1,6-HD/HMDI system): (1) 0.5/1.5/2.0; (2) 0/2.0/2.0 (eq. ratio). Sample 2 was synthesized in DMF and purified with methanol in the usual manner.

Effect of Molar Ratio of Low Molecular Weight Diol on X-Ray Diffraction

Figure 19 shows the wide-angle x-ray diffraction intensity of urethane elastomers with varying molar ratio R in the HT-BD/1,6-HD/HMDI system. There is an increase in the crystalline region, that is, an increase in the diffraction intensity of the elastomers, with increase in R . Figure 20 shows the wide-angle x-ray diffraction intensities of the elastomers with changing diisocyanate (MDI, TDI, or HMDI, respectively) in HT-BD/1,6-HD/diisocyanate systems.

The diffraction intensity of the TDI-cured system is weaker than those of the MDI- and HMDI-cured systems. This is interpreted as follows. In the TDI system, the spatial order of polymer segments is restricted sterically, but in the MDI and HMDI systems crystallinity is easily induced because of facility in the orientation of the polymer segments.

Figure 21 shows the x-ray diffraction pattern of HT-BD/1,6-HD/HMDI elastomer system. Debye-Scherrer rings which suggest the existence of crystalline regions can be observed at $2\theta = 19.0^\circ$, 21.7° , and 24.3° (i.e., $d = 4.67 \text{ \AA}$, 4.10 \AA , and 3.66 \AA , respectively). It is therefore concluded that the enhanced mechanical properties of urethane elastomers derived from HT-BD with increase in molar ratio R can be ascribed not only to an increase in the concentration of

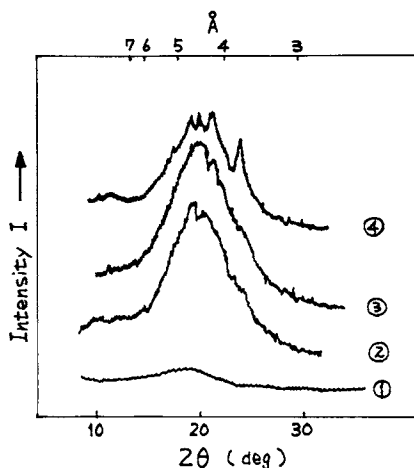


Fig. 19. Effect of diol ratio on wide-angle x-ray diffraction intensity (HT-BD/1,6-HD/HMDI system): (1) 2.0/0/2.0; (2) 1.5/0.5/2.0; (3) 1.0/1.0/2.0; (4) 0.5/1.5/2.0 (eq. ratio).

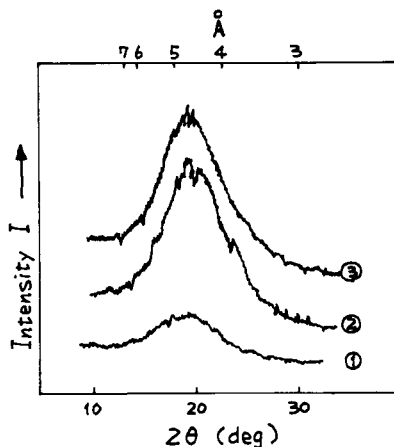


Fig. 20. Effect of diisocyanate on wide-angle x-ray diffraction intensity (HT-BD/1,6-HD/diisocyanate system, 1.0/1.0/2.0 eq. ratio): (1) TDI; (2) MDI; (3) HMDI.

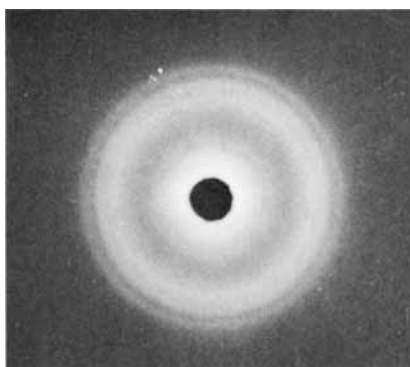


Fig. 21. X-Ray diffraction pattern (HT-BD/1,6-HD/HMDI system, 0.5/1.5/2.0 eq. ratio).

polar groups but also to an increase in the crystalline region in the polymer matrix.

Effect of Length of Methylene Groups in Low Molecular Weight Diol on Properties of Elastomers

Effect of Methylene Groups on Mechanical Properties

The mechanical properties of elastomers are plotted against the number of carbon atoms in the backbone methylene groups of diols in Figures 22–26. The characteristic zigzag curves can be observed. The difference in hard-segment structures between polyurethanes obtained from diols with an even number of methylene groups and those with an odd number of methylene groups is shown schematically in Figure 27, as well as polyamide.

With the even-numbered methylene sequences, bulky benzene rings occupy both sides of the methylene sequences. On the other hand, in the case of odd-numbered methylene groups, they occupy one side. Consequently, more dense crystal structures are formed; further, two hydrogen bondings can be formed per structural unit in the case of an even number, while only one hydrogen bonding

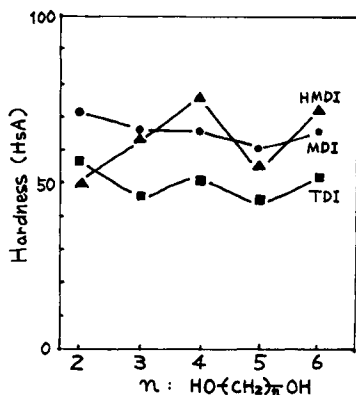


Fig. 22. Effect of number of methylene carbons on hardness (HT-BD/diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio).

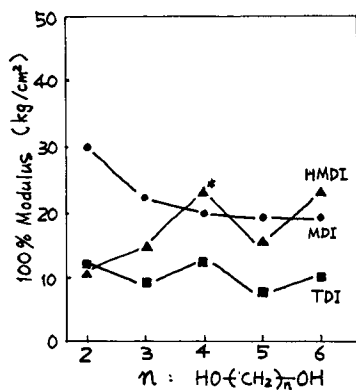


Fig. 23. Effect of number of methylene carbons on 100% modulus (HT-BD/diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio).

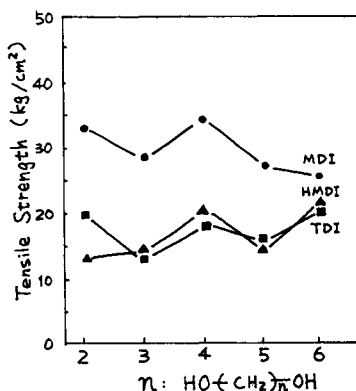


Fig. 24. Effect of number of methylene carbons on tensile strength (HT-BD/diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio).

is formed in the case of an odd number. It is well known that this phenomenon can also be observed in polyamides.¹⁵ As compared with polyamides, consisting of simple repeating units, it is interesting to note that the mechanical properties of polyurethanes, which are complexed ternary systems and consist of soft segments mostly, are affected by the hard-segment structures.

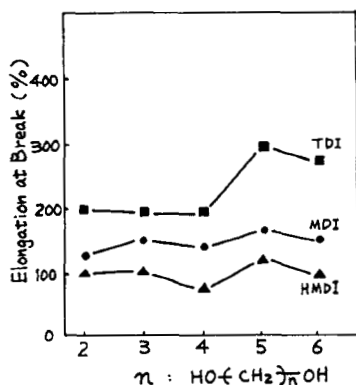


Fig. 25. Effect of number of methylene carbons on elongation a break (HT-BD/diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio).

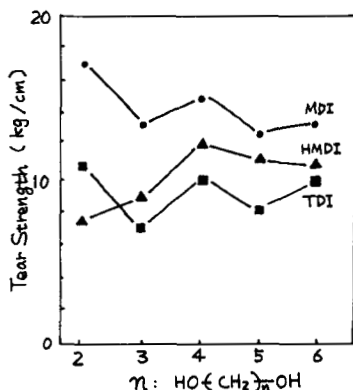


Fig. 26. Effect of number of methylene carbons on tear strength (HT-BD/diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio).

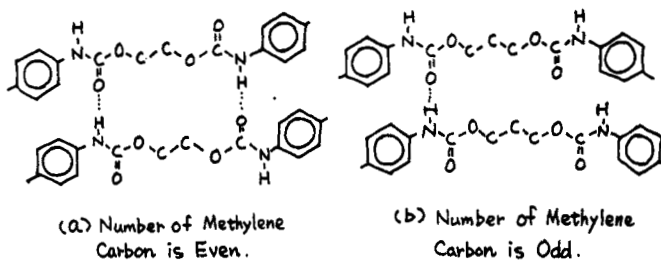


Fig. 27. Hard-segment structure (hydrogen bonding).

The curves of mechanical property such as hardness, 100% modulus, and others show zigzag patterns with variation in the number of methylene groups. On the whole, with an increase in the number of methylene groups, mechanical properties decrease when MDI or TDI is used but increase when HMDI is used. The relationship between the number of methylene groups and the concentration of urethane groups, diphenylmethane groups, and phenyl groups in elastomers is shown in Table VII.

The decrease in mechanical properties with increasing number of methylene groups when MDI or TDI is used is probably due to the decrease in the concen-

TABLE VII
Relationship Between Number of Methylene Groups and Concentration of Polar Groups^a

Diol n in HO—(CH ₂) _{n} — OH		Polar group concentration, (moles/cc) $\times 10^4$				
		EG	1,3-PD	1,4-BD	1,5-PD	1,6-HD
		2	3	4	5	6
MDI cured	urethane	13.3	13.3	13.2	13.1	13.0
	diphenylmethane	6.7	6.7	6.6	6.6	6.5
TDI cured	urethane	13.9	13.8	13.7	13.6	13.5
	diphenylmethane	7.0	6.9	6.9	6.8	6.7
HMDI cured	urethane	13.7	13.7	13.6	13.5	13.4

^a HT-BD/diol/diisocyanate = 1.0/1.0/2.0 (eq. ratio).

tration of urethane groups, diphenylmethane groups, and phenyl groups in the elastomer. When HMDI is used, in spite of the decrease in the concentration of urethane groups, mechanical properties increase with increasing number of methylene groups of low molecular weight diol. This effect can be ascribed to the crystallinity of methylene sequences in hard segments. It is considered that the methylene sequences of diols, as they become longer, crystallize easily with the sequence of HMDI. This increase in crystallinity compensates the decrease in the concentration of urethane groups and makes the elastomer stiff. In addition, there might be some crystallinity in the stock, judging from its opaque appearance. This crystallinity is discussed in the following sections.

When HMDI is used, the mechanical properties of the elastomers are sharply affected by the number of methylene groups of diol, and the zigzag undulation of the curve becomes greater. In the case of the HMDI system, no aromatic ring which has a high cohesive force exists. The mechanical properties of the HMDI system greatly depend on the intermolecular hydrogen bonding and the crystallinity of the methylene sequences, which are affected by the number of methylene carbon atoms of the diol. The effects of the number of methylene carbon atoms of the diol on the mechanical properties of elastomers are also confirmed by varying the HT-BD/diol/diisocyanate ratio. Figure 28 shows the result of the variation in molar ratio of HT-BD/diol/HMDI systems.

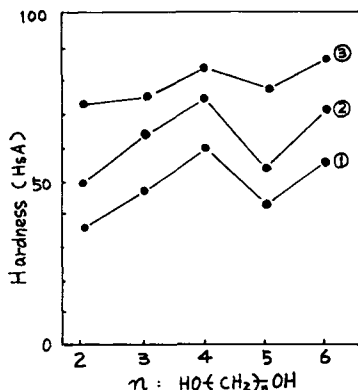


Fig. 28. Effect of number of methylene carbon on hardness (HT-BD/diol/HMDI system): (1) 1.5/0.5/2.0; (2) 1.0/1.0/2.0; (3) 0.5/1.5/2.0 (eq. ratio).

Effect of Number of Methylene Carbon Atoms on Mooney-Rivlin Plot

The C_2 values which are obtained from the Mooney-Rivlin plots of the elastomers varying the methylene carbon atoms of diols are plotted versus the number of methylene carbon atoms of diols in Figure 29. The zigzag patterns are also observed here as in Figures 22–26 and in Figure 28. From this result, here, it appears that the orientation and the crystallinity depend on the number of methylene carbon atoms.

In Figure 29, the C_2 value of the HT-BD/1,6-HD/HMDI system is remarkably high. This implies the high crystallinity of this system. The contributions of the secondary bondings and the crystallinity are expected to decrease at elevated temperatures. Table VIII shows the temperature dependence of the Mooney-Rivlin plots. The C_2 value decreases with increase in temperature and approaches zero at 120°C.

Table IX shows the Mooney-Rivlin plot obtained from the extension of prestrained samples; α_p is the fixed prestrain ratio. The C_2 value of the prestrained sample, which is subjected to stress softening, approaches zero in agreement with the result of Tanaka et al.¹⁶ It can be seen that the mechanical

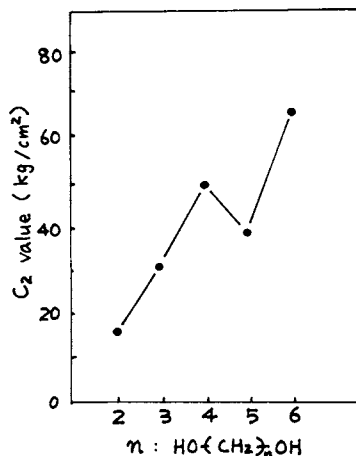


Fig. 29. Effect of number of methylene carbon on C_2 value of Mooney-Rivlin equation (HT-BD/diol/HMDI system, 1.0/1.0/2.0 eq. ratio).

TABLE VIII
Relationship Between Temperature and C_2 Value of Mooney-Rivlin Equation^a

Temperature, °C	R.T.	70	100	120
C_2 , kg/cm ²	67	21	3.7	2.5

^a Formulation HT-BD/1,6-HD/HMDI = 1/1/2 (eq. ratio).

TABLE IX
Relationship Between Prestrain Ratio and C_2 Value of Mooney-Rivlin Equation^a

Prestrain ratio α_p	0	1.5	2.0
C_2 , kg/cm ²	67.0	-3.7	-8.6

^a Formulation HT-BD/1,6-HD/HMDI = 1/1/2 (eq. ratio).

properties of the HMDI system are greatly affected by the secondary bondings. The decrease in the C_2 value may be interpreted by the cleavage of the secondary bondings such as intermolecular hydrogen bonding and crystalline region by prestraining.

Stress Relaxation

Figure 30 shows the stress relaxation behavior with changing temperature. At first, drastic relaxation occurs, and then it gradually moderates. The first relaxation may be ascribed to the viscous flow and diffusion in the noncrystalline region and the crystallization of the noncrystalline region; and the subsequent relaxation can be attributed to the rearrangement of the crystalline region and release from molecular distortion (Fig. 31).

Effect of Number of Methylene Carbons on Dynamic Viscoelasticity

Figure 32 shows the result of the dynamic viscoelasticity measurements on the elastomers obtained using EG, 1,3-PD, and 1,4-BD, having methylene carbons numbering 2, 3, and 4, respectively. In the case of the EG-cured system, a strong loss tangent peak is observed at -65°C . In the cases of 1,3-PD and 1,4-BD, weak loss tangent peaks are observed at -65°C . Further, in the case of 1,3-PD the loss tangent appears as a shoulder and in the case of 1,4-BD, as a

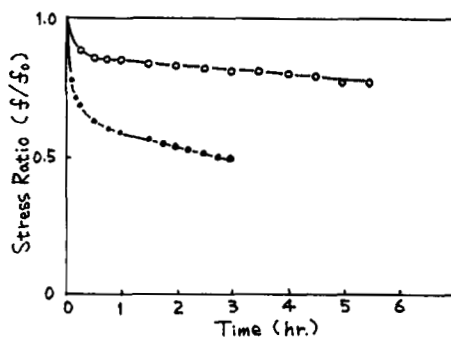


Fig. 30. Stress relaxation (HT-BD/1,6-HD/HMDI system, 1.0/1.0/2.0 eq. ratio): (○) 70°C ; (●) 120°C .

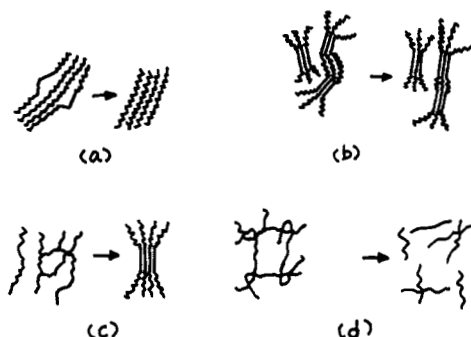


Fig. 31. Mechanism of stress relaxation and change in molecular structure¹⁷: (a) release from molecular distortion; (b) rearrangement of crystalline region; (c) crystallization of the noncrystalline region; (d) viscous flow or diffusion.

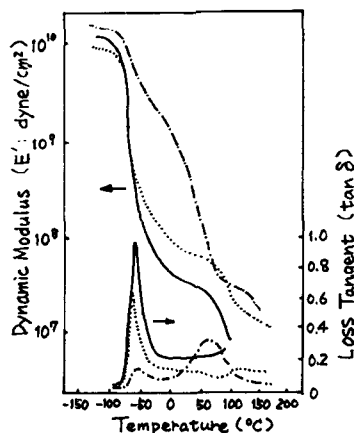


Fig. 32. Effect of diol on dynamic mechanical property (HT-BD/diol/HMDI system, 1.5/0.5/2.0 eq. ratio): (—) EG; (---) 1,3-PD; (-·-·-) 1,4-BD.

strong peak; loss tangent peaks are observed at 70°C. Peaks at 70°C in the cases of 1,3-PD and 1,4-BD can be ascribed to the melting of the crystalline region of methylene sequences.

Peaks at about -65°C may be ascribed to the polybutadiene blocks. The strong peak of EG can be explained as follows. The mobility of the polybutadiene blocks as soft segments is not restricted because of the loose segregation of the hard segments of EG. On the other hand, the weak peak in the cases of 1,3-PD and 1,4-BD is interpreted by the restricted mobility of the polybutadiene blocks under the influence of stiff, hard segments. The decreasing order of dynamic modulus is 1,4-BD-cured > 1,3-PD-cured > EG-cured. This order is in agreement with that of the mechanical strength mentioned before.

Effect of Low Molecular Weight Diol on Wide-Angle X-Ray Diffraction

Figure 33 shows the wide-angle x-ray diffraction intensity of urethane elastomers with diols of varying number of carbon atoms in HT-BD/diol/HMDI systems. The diffraction intensity varies with the diol. An elastomer of high mechanical strength, high C_2 value in the Mooney-Rivlin equation, and high dynamic modulus shows strong diffraction. Therefore, the characteristic zigzag effect of some properties of the systems investigated in this study can be ascribed to the influences of the orientation and the crystallinity of hard segments.

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

Effect of Methyl Side Groups

Tables X and XI show the effects of the side groups of diols on the properties of the elastomers. Comparisons are made fixing the number of methylene groups at 2 in Table X and at 3 in Table XI. The mechanical properties of the elastomers from 1,2-PD and 1,3-BD, which have a methyl side group, are poor in comparison with those from EG and 1,3-PD, which have no side group. It is considered that 1,2-PD and 1,3-BD, which have a secondary OH group, are less

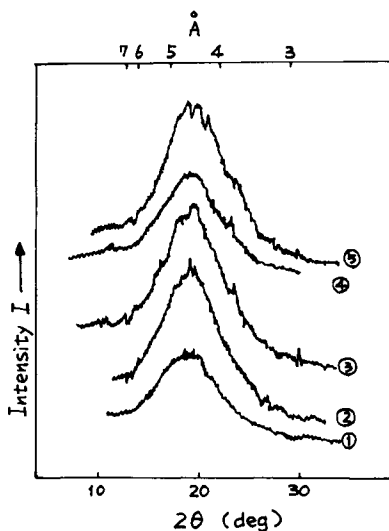


Fig. 33. Effect of diol on wide-angle x-ray diffraction intensity (HT-BD/diol/HMDI system, 1.0/cal property (HT-BD/Diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio): (1) 1,4-BD; (2) 1,4-Bute.D.

TABLE X
Effect of Steric Structure of Low Molecular Weight Diols on Properties of Elastomers^a

Diol Diisocyanate	EG			1,2-PD		
	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness HsA	71	55	50	64	54	47
100 Modulus, kg/cm ²	29	12	11	21	11	7
Tensile strength, kg/cm ²	33	20	13	31	17	9
Elongation at break, %	125	225	120	180	275	125
Tear strength, kg/cm	17	13	7	14	10	5
Benzene extract, %		/5	2.5	6.5	1.0	4.0
10.0						

^a Formulation HT-BD/diol/diisocyanate = 1/1/2 (eq. ratio).

TABLE XI
Effect of Steric Structure of Low Molecular Weight Diols on Properties of Elastomers^a

Diol Diisocyanate	1,3-PD			1,3-BD			NPG		
	MDI	TDI	HMDI	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness HsA	65	47	55	59	38	35	62	45	52
100% Modulus, kg/cm ²	23	9	14	16	5	4	21	9	13
Tensile strength, kg/cm ²	36	24	14	29	20	6	32	22	13
Elongation at break, %	150	200	100	225	350	150	200	300	100
Tear strength, kg/cm	15	13	9	14	8	6	14	11	7
Benzene extract, %	2.0	5.5	10.5	1.5	6.0	20.5	1.0	3.5	7.5

^a Formulation HT-BD/diol/diisocyanate = 1/1/2 (eq. ratio).

reactive than EG and 1,3-PD, which have a primary OH group. This assumption is confirmed by the result of Soxhlet extraction shown in Tables X and XI. Therefore, this inferiority in mechanical properties is attributable to the incompleteness of the chain extension. Further, it is also probable that secondary bonding and crystallinity are restricted by the effect of the methyl side groups.

This is consistent with the result of the poorer mechanical properties of the elastomer from NPG, which has more methyl side groups than that from 1,3-PD, in spite of the fact that both have primary OH groups.

Effect of Alkane Diol and Alkene Diol on Properties of Elastomers

The effect of alkane and alkene diols on the properties of elastomers are examined using the systems incorporating 1,4-BD and 1,4-Bute.D (Table XII). In every diisocyanate cured system, the mechanical properties of elastomers from 1,4-Bute.D are poorer than those from 1,4-BD, particularly in HMDI-cured system.

As described before, it is considered that the mechanical properties of the elastomers cured by HMDI are influenced largely by secondary bondings such as intermolecular hydrogen bonding and crystallinity, but that in the system HMDI/1,4-Bute.D the secondary bondings are disturbed by the steric configuration of 1,4-Bute.D.

Figure 34 shows the result of dynamic viscoelastic measurements of the elastomers from 1,4-BD and 1,4-Bute.D. In the 1,4-BD-cured system, a strong loss tangent peak at 60°C and a weak peak at -60°C are observed. In the 1,4-Bute.D-cured system, a medium peak shifted to 100°C, higher than that of 1,4-BD, a strong peak at -60°C, and an additional weak peak at -100°C are observed.

TABLE XII
Effect of Steric Structure of Low Molecular Weight Diols on Properties of Elastomers^a

Diol Diisocyanate	1,4-BD			1,4-Bute.D		
	MDI	TDI	HMDI	MDI	TDI	HMDI
Hardness HsA	65	52	75	62	42	54
100% Modulus, kg/cm ²	20	13	23	19	7	13
Tensile strength, kg/cm ²	35	19	21	30	10	13
Elongation at break, %	175	225	75	200	180	100
Tear strength, k/cm	15	10	12	14	6	13

^a Formulation HT-BD/diol/diisocyanate = 1/1/1/ (eq. ratio).

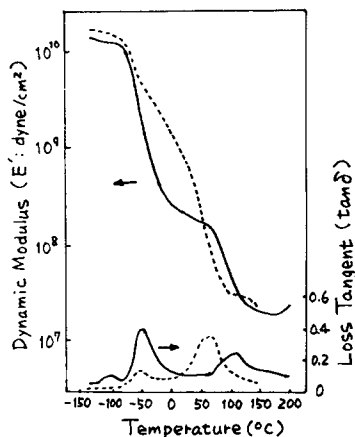


Fig. 34. Effect of diol on dynamic mechanical property (HT-BD/Diol/diisocyanate system, 1.0/1.0/2.0 eq. ratio): (1) 1,4-BD; (2) 1,4-Bute.D.

Dynamic modulus of the cured systems decrease in the order 1,4-BD > 1,4-Bute.D below 60°C and 1,4-Bute.D > 1,4-BD above 60°C. The shift in peak to a higher temperature and the high dynamic modulus when 1,4-Bute.D is used could be ascribed to the hindered rotation of polymer chains because of the double bond in 1,4-Bute. D. In the 1,4-BD-cured system, the higher modulus in the low-temperature region could be due to the crystallinity of the methylene sequences and the restricted mobility of polybutadiene blocks influenced by the crystallinity. In the 1,4-Bute.D-cured system, the lower modulus in the low-temperature region could be ascribed to the low crystallinity and high entropy of the segments from 1,4-Bute.D.

The low crystallinity of the elastomer from 1,4-Bute.D is also confirmed by the x-ray diffraction result shown in Figure 35.

CONCLUSIONS

In order to elucidate the relationship between the properties and the structure of urethane elastomers derived from HT-BD, several low molecular weight diols and diisocyanates were investigated. The mechanical properties of the elastomers increase with increase in the molar ratio of low molecular weight diol to HT-BD. These enhanced properties are ascribed to an increase in crystallinity and polar groups which act as hard segments. The crystallinity was confirmed by the result of dynamic viscoelasticity, DSC, and x-ray diffraction studies.

The elongation-at-break curve has a maximum with increasing molar ratio *R*. This phenomenon can be explained by the balanced effect of the primary and secondary bondings.

Compression set increases with increase in molar ratio *R*. This is interpreted to mean that the decrease in the primary bondings makes the elastomer more plastic and the increase in the secondary bondings fixes the deformation as compression set. The effect of the primary and the secondary bondings, changing inversely to each other, was confirmed by the swelling measurements with different solvents.

Some particular combinations of low molecular weight diol and diisocyanate affect specifically the properties of the elastomers. When the mechanical

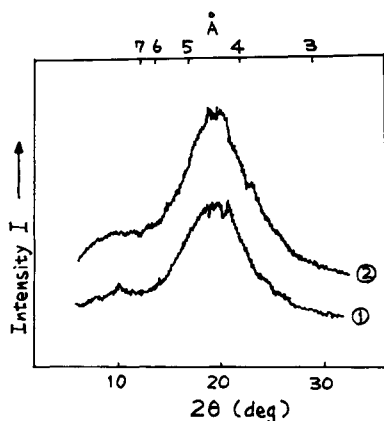


Fig. 35. Effect of diol on wide-angle x-ray diffraction intensity (HT-BD/diol/HMDI system, 1.0/1.0/2.0 eq. ratio): (1) 1,4-Bute.D and (2) 1,4-BD.

properties of the elastomers were plotted against the number of methylene carbons in low molecular weight diol, the characteristic zigzag patterns were observed. These patterns can be explained by the difference in the packing and the ability of intermolecular hydrogen bondings depending on whether the number of the methylene carbons is even or odd.

In spite of a decrease in the concentration of urethane groups with increasing number of the methylene carbons, the mechanical properties of the elastomers derived from HMDI are enhanced. This can be explained on the assumption of the crystallinity of the methylene sequences. The contribution of the crystallinity to mechanical properties is also confirmed by the extraordinary high value of C_2 in the Mooney-Rivlin equation and by the decrease in the C_2 value at elevated temperature or by deformation hysteresis. This assumption, which is supported by the loss tangent peak at about 50°–70°C in dynamic viscoelasticity results, is confirmed by x-ray diffraction.

This paper was presented at the First Meeting of the Research Group of Polymer Chemistry and Technology, Japan on October 3rd, 1975, presided by Mr. S. Miyazaki, president of Hirono Chemical Industry Co., Ltd.

Thus, the mechanical properties of urethane elastomers are affected not only by the urethane groups and aromatic rings but also greatly by the crystallinity. The mechanical properties of the elastomers derived from the diols which have methyl side groups or double bonds are poor because of the disturbance in orientation.

This paper was presented at the First Meeting of the Research Group of Polymer Chemistry and Technology in Japan on October 3, 1975, presided by S. Miyazaki, president of Hirono Chemical Industry Co., Ltd.

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