

# Effects of Low Molecular Weight Aliphatic Diols on the Polyurethane Elastomers Prepared from Hydroxyl-Terminated Polybutadienes\*

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## Synopsis

Hydroxyl-terminated polybutadienes were prepared by using azo initiators such as di(4-hydroxybutyl)-2,2'-azobisisobutyrate and di(3-hydroxybutyl)-2,2'-azobisisobutyrate, one of which contains primary and the other secondary hydroxyl groups. The effects of aliphatic diols and 2,4-toluene diisocyanate (TDI) in the presence of dibutyltindilaurate (DBTDL) as catalyst, on crosslinking of primary and secondary hydroxyl groups, were studied. Polyurethane elastomers from these polymers are prepared by using different ratios of diols, 2,4-toluene diisocyanate and catalyst. Physical properties such as hardness, tensile strength, 100% modulus, and elongation at break of these polymers were studied with a view to compare them with the physical properties of elastomers prepared from ARCO R-45M.

## INTRODUCTION

Polyurethanes based on polyethers and polyesters have, in general, high tensile strength, high tear strength, high abrasion resistance, and resistance to degradation by oils, greases, and solvents.<sup>1,2</sup> Moreover, they can be easily processed by liquid casting techniques which reduce the fabrication equipment costs.<sup>3</sup> Nowadays polyurethanes derived from hydroxyl-terminated polybutadienes are used for a number of different applications such as composite propellants, adhesives, coatings, foams, etc.<sup>4,5</sup>

Hydroxyl-terminated polybutadiene is a castable liquid material. These polymers are extremely interesting since they structurally fulfill the requirement of compatibility and conventional rubber chemicals and can be utilized to produce urethane elastomers using standard urethane technology.

Although many excellent texts and publications have described in detail the chemistry and technology of castable urethane systems based on polyethers, polyesters and castor oils,<sup>6,7</sup> little information is available relating to the use of hydroxyl-terminated polybutadienes as urethane intermediates.<sup>8</sup>

Verdol and co-workers<sup>9,10</sup> have studied the physical properties of urethane elastomers and urea-urethane elastomers prepared from liquid hydroxyl-terminated polybutadiene (ARCO R-45M). Recently, Minoura and co-workers<sup>11,12</sup> have studied the curative effects of aliphatic and aromatic diols on liquid hydroxyl-terminated polybutadiene (ARCO R-45M).

The polyurethane elastomers obtained by the chain extension of terminated hydroxyl groups with diisocyanate have a superior hydrolytic stability arising

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TABLE I

Polymers	$\bar{M}_n$	OH value	Microstructure		
			<i>trans</i> -1 (4%)	<i>cis</i> -1 (4%)	1,2-Vinyl (%)
HTPB <sup>a</sup>	2800	44.0	45.0	29.0	26.0
HTPB <sup>b</sup>	2400	54.0	46.0	30.0	24.0
ARCO R-45M	3400	34.0	55.0	25.0	20.0

<sup>a</sup> Polymer prepared by using di(4-hydroxybutyl)-2,2'-azobisisobutyrate initiator.

<sup>b</sup> Polymer prepared by using di(3-hydroxybutyl)-2,2'-azobisisobutyrate initiator.

from the nonpolar main chain of hydroxyl terminated polybutadiene. The elastomers based on these polymers can be easily compounded with a large amount of filler. Thermoplastic polyurethanes<sup>13</sup> have been prepared from liquid hydroxyl-terminated polybutadiene (ARCO R-45M). Nowadays, the consumption of hydroxyl-terminated polybutadiene as a raw material for polyurethane elastomer is insignificant in comparison with that of polyether polyol and polyester polyol.

The present work describes the crosslinking of hydroxyl-terminated polybutadienes by 2,4-toluene diisocyanate (TDI) and aliphatic diols to give the basic data for the practical use of hydroxyl terminated polybutadiene. It also describes the effect of low molecular weight aliphatic diols on crosslinking of primary and secondary hydroxyl groups. Physical properties such as hardness, tensile strength, 100% modulus, and elongation at break of these polymers are studied and compared with the properties of elastomers prepared from hydroxyl-terminated polybutadiene (ARCO R-45M).

## EXPERIMENTAL

### Materials

Hydroxyl-terminated polybutadienes prepared<sup>14</sup> by using azo initiators such as di(4-hydroxybutyl)-2,2'-azobisisobutyrate and di(3-hydroxybutyl)-2,2'-azobisisobutyrate of the following specifications are used in this investigation. Hydroxyl-terminated liquid polybutadienes were demoisturized before use under reduced pressure (Table I).

Low molecular weight aliphatic diols, such as 1,4-butane diol, 1,3-butane diol, and ethylene glycol obtained from BDH (England), were dried before use over Linde 4A type molecular sieves. They were distilled and dried under reduced pressure.

2,4-Toluene diisocyanate (TDI) 80:20 isomer, obtained from M/S Aldrich Chemical Company (United States), was of reagent grade material and was used without further purification.

Dibutyltindilaurate (DBTDL), obtained from M/S Wilson Laboratories (Bombay), was of reagent grade material and was used as such.

### ELASTOMER PREPARATION

Table II describes various formulations that were used in the preparation of polyurethane elastomers. The procedure for the preparation of these elastomers is described below:

Hydroxyl-terminated polybutadiene (HTPB), low molecular weight diol, and

TABLE II  
Formulations (Equivalent Ratio)

Materials	I	II	III	IV	V
(i) Hydroxyl-terminated polybutadiene (HTPB)	2.00	1.75	1.50	1.25	1.00
(ii) Low mol wt diol	0.00	0.25	0.50	0.75	1.00
(iii) 2,4-toluene diisocyanate	2.00	2.00	2.00	2.00	2.00

catalyst (DBTDL) were mixed homogeneously in a glass tube with heating at about 70°C. Then 2,4-toluene diisocyanate (80:20 isomer) was added to the homogeneous mixture with vigorous stirring. These operations were carried out as fast as possible; otherwise, quick gelation occurs. The viscous reaction mixture was degassed under reduced pressure and cast on a mold (treated with silicone release agent). After some time it was cured at 120°C for 8 h in a mold, with an additional 7-day room-temperature cure.

The quantity of catalyst (DBTDL) used was 0.03 g/100 g HTPB + low mol wt diol.

## MEASUREMENTS

**Hardness.** Hardness was measured by a Shore-A Durometer hardness tester (United States).

**Tensile Properties.** One hundred percent modulus, tensile strength, and elongation at break were measured by a Scott tester. The Specimen was cut from an about 2-mm-thick sheet using an ASTM-standards-type dumbbell.

## RESULTS AND DISCUSSION

Tables III–V describe the details of the physical properties of the polymers prepared by using di(4-hydroxybutyl)-2,2'-azobisisobutyrate, di(3-hydroxybutyl)-2,2'-azobisisobutyrate, and hydrogen peroxide as initiators.

Liquid hydroxyl-terminated polybutadiene prepared by using hydrogen peroxide as initiator (ARCO R-45M) possesses predominantly primary terminal hydroxyl groups of the allylic type, and has very much less pot life. However, in the case of polymers prepared by using azo initiators, the pot life in the primary hydroxyl group containing polymers is less than the pot life of polymers having the secondary hydroxyl group.

Hardness, 100% modulus, tensile strength, and elongation at break of the urethane elastomers based on hydroxyl-terminated polybutadiene prepared by using di(4-hydroxybutyl)-2,2'-azobisisobutyrate, 2,4-toluene diisocyanate, and low molecular weight diols are higher than in case of the hydroxyl-terminated polybutadiene prepared by using di(3-hydroxybutyl)-2,2'-azobisisobutyrate as initiator. In the case of R-45M ARCO the physical properties found are all higher in comparison with the polymers prepared by azo initiators.

Physical properties of the urethane elastomers are enhanced by an increase in the molar ratio of diols/HTPB. No particular trends are observed in physical properties of all the polyurethane elastomers by using different diols.

It can also be seen from Tables III–V that the physical properties of the elastomers are increased by changing the ratio of diol/HTPB. When the amount

TABLE III  
Physical Properties of Polyurethane Elastomers Prepared from HTPB [Using Di(4-Hydroxybutyl)-2,2'-Azobisisobutyrate as Initiator], Different Diols and 2,4-Toluene Diisocyanate (TDI)

Physical properties	Formulations				
	I	II	III	IV	V
			<u>1,4-Butane diol</u>		
Hardness (HsA)	30	35	40	45	45
100% modulus (kg/cm <sup>2</sup> )	6.5	7.5	8.0	10.0	11.0
Tensile strength (kg/cm <sup>2</sup> )	6.5	8.0	10.0	13.0	15.0
Elongation at break (%)	100	120	150	175	200
			<u>1,3-Butane diol</u>		
Hardness (HsA)	30	30	35	40	45
100% modulus (kg/cm <sup>2</sup> )	6.0	7.0	7.5	9.0	10.0
Tensile strength (kg/cm <sup>2</sup> )	6.0	8.0	9.0	12.0	14.0
Elongation at break (%)	100	125	160	180	210
			<u>Ethylene glycol</u>		
Hardness (HsA)	30	35	40	40	45
100% modulus (kg/cm <sup>2</sup> )	8.0	8.0	9.0	10.0	10.0
Tensile strength (kg/cm <sup>2</sup> )	8.0	9.0	11.0	12.0	14.0
Elongation at break (%)	100	125	140	160	175

of HTPB is decreased and the amount of low molecular weight diol is increased, the physical properties are increased.

## CONCLUSIONS

Liquid hydroxyl-terminated polybutadienes of primary and secondary hydroxyl groups were prepared by using azo initiators, such as di(4-hydroxybutyl)-2,2'-azobisisobutyrate and di(3-hydroxybutyl)-2,2'-azobisisobutyrate. The physical properties of the prepared elastomers were compared with the elastomers prepared from R-45M. The curative effects of aliphatic diols on

TABLE IV  
Physical Properties of Polyurethane Elastomers Prepared from HTPB [Using Di(3-Hydroxybutyl)-2,2'-Azobisisobutyrate as Initiator], Different Diols and 2,4-Toluene Diisocyanate (TDI)

Physical properties	Formulations				
	I	II	III	IV	V
			<u>1,4-Butane diol</u>		
Hardness (HsA)	30	35	40	40	45
100% modulus (kg/cm <sup>2</sup> )	5.5	6.5	7.0	8.0	8.5
Tensile strength (kg/cm <sup>2</sup> )	5.5	7.0	8.0	10.0	11.0
Elongation at break (%)	110	110	125	140	170
			<u>1,3-Butane diol</u>		
Hardness (HsA)	35	30	30	35	40
100% modulus (kg/cm <sup>2</sup> )	6.0	6.5	7.0	7.5	9.0
Tensile strength (kg/cm <sup>2</sup> )	6.0	7.0	8.0	9.0	11.0
Elongation at break (%)	100	120	130	150	160
			<u>Ethylene glycol</u>		
Hardness (HsA)	30	35	40	40	45
100% modulus (kg/cm <sup>2</sup> )	6.5	6.5	8.0	9.0	9.5
Tensile strength (kg/cm <sup>2</sup> )	6.5	7.5	9.0	10.0	11.5
Elongation at break (%)	100	125	150	160	180

TABLE V  
Physical Properties of Polyurethane Elastomers Prepared from HTPB (ARCO R-45M) Different Diols and 2,4-Toluene Diisocyanate (TDI)

Physical properties	Formulations				
	I	II	III	IV	V
			<u>1,4-Butane diol</u>		
Hardness (HsA)	30	35	40	45	50
100% modulus (kg/cm <sup>2</sup> )	8.0	8.5	10.0	11.0	13.0
Tensile strength (kg/cm <sup>2</sup> )	11.0	13.0	15.0	17.0	19.0
Elongation at break (%)	150	200	250	275	225
			<u>1,3-Butane diol</u>		
Hardness (HsA)	30	30	35	40	45
100% modulus (kg/cm <sup>2</sup> )	7.0	8.0	10.0	12.0	14.0
Tensile strength (kg/cm <sup>2</sup> )	10.0	12.0	14.0	17.0	20.0
Elongation at break (%)	150	175	200	250	350
			<u>Ethylene glycol</u>		
Hardness (HsA)	30	35	45	50	55
100% modulus (kg/cm <sup>2</sup> )	7.0	9.0	10.0	11.0	12.0
Tensile strength (kg/cm <sup>2</sup> )	12.0	15.0	16.0	18.0	20.0
Elongation at break (%)	220	240	290	270	225

hydroxyl-terminated polybutadienes were also studied. The physical properties of the elastomers were found to increase with increase in the molar ratio of low molecular weight diol to hydroxyl-terminated polybutadiene. The physical properties are higher in the case of R-45M compared with the polymers prepared by using azo initiators. Preparation of thermoplastic polyurethanes from the prepared hydroxyl-terminated polybutadiene is under investigation.

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