

Crosslinking Studies of Polyether-Ester-Based Polyurethane Systems

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Synopsis

Ether- and ester-based prepolymeric diols suitable for polyurethane elastomer formation were prepared from polyoxytetramethyleneglycol and polyoxytetramethylene-oxypropyleneglycol with dicarboxylic acids like adipic acid, maleic acid, and phthalic acid. Crosslinked polyurethane elastomers were prepared from these prepolymers using various concentrations of trimethylolpropane as a crosslinker and toluenediisocyanate as the curing agent. Crosslinked polyurethanes were also prepared by a method taking excess toluenediisocyanate other than that of the stoichiometric requirement and curing it at a comparatively higher temperature. The data on mechanical properties of these elastomers show that both methods of crosslinking in polyurethane imparts a similar effect on mechanical properties.

INTRODUCTION

Crosslinking of polyurethanes is of primary importance in the modification of their properties. Attaining a crosslinked polyurethane by the use of tri or polyfunctional alcohol or isocyanate is the well-known and widely applied procedure. Flexible and semiflexible foams, cast elastomers, and most reactive systems are crosslinked polyurethanes. Triols like trimethylolpropane, castor oil, glycerol or polyols like polyvinyl alcohol can be used to introduce crosslinking in polyurethanes. Crosslinking in polyurethane can also be introduced by preparing polyurethanes with higher NCO/OH ratio (R value) as the excess diisocyanate reacts with the urethane groups forming trifunctional allophanate linkages. Crosslinking at higher R value is also reported to proceed through the formation of isocyanurate linkage, which is an isocyanate trimer moiety.¹ The allophanate formation is much slower than that of the basic polyurethane reactions.² Therefore, the allophanate groups are formed mainly during the final curing process and if the overall NCO/OH ratio is higher than unity. Up to 40% of the urethane groups can serve as crosslinking points subject to this condition. This crosslinking process resulted in increase of tensile strength, tear strength, modulus, and a decrease in elongation.³ The

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changes in mechanical properties were more pronounced at lower range of R values (0.9–1.2) and in case of soft elastomers based on polyethers.⁴ Nierzwicki⁵ studied the effect of R value in an ester-based polyurethane on the microphase separation phenomena. The statistical treatment on crosslinking in polyurethane with excess diisocyanate was made by Dusek et al.⁶ Even then a systematic comparative account of crosslinking in polyurethanes by a triol and by higher R values have not been made so far. In the present investigation the crosslinking in polyurethane by trimethylolpropane and higher R values are compared. Polyether-ester-based toluenediisocyanate-cured soft polyurethanes were used in this study, as it is the system where crosslinking is having a pronounced influence on mechanical properties.

EXPERIMENTAL

The prepolymers, polyoxytetramethyleneglycol (POTMG), polyoxytetramethylene adipate (POTMAA), polyoxytetramethylene maleate (POTMMA), polyoxytetramethylene phthalate (POTMPA), polyoxytetramethyleneoxypropyleneglycol (POTMOPG), polyoxytetramethyleneoxypropylene adipate (POTMOPAA), polyoxytetramethyleneoxypropylene maleate (POTMOPMA), and polyoxytetramethyleneoxypropylenephthalate (POTMOPPA) were prepared by the procedure described previously.⁷ Trimethylolpropane (TMP) was dried under vacuum before use. Toluenediisocyanate (TDI, AG Fluka) was used as received.

Polyurethane elastomers in the form of sheet having thickness 3–4 mm was prepared from required amount of prepolymeric diols and TMP (in case needed) with calculated amount of TDI as per the procedure reported before. The curing of polyurethane was carried out at 60°C for 5 days in the case of elastomers prepared with TMP crosslinker, whereas curing was carried out at 75°C for 5 days in case of elastomers prepared with higher R values.

Tensile strength and elongation at break of the cast polyurethane elastomers were measured using an Instron Model 1122 (England) by the standard procedure⁸ at the crosshead speed 20 mm/min. The average of four values was taken.

RESULTS AND DISCUSSIONS

The structure of the prepolymers and TMP is given in Figure 1. All the polymers are structurally different but comparable. Since TDI is the diisocyanate widely employed in the preparation of elastomers, it was chosen as the curing agent. All the elastomers were prepared in a one shot process without chain extender. Hence the resultant polyurethanes were having low tensile values. The crosslinking in polyurethane at higher R values is reported to proceed through the formation of allophanate and isocyanurate linkages. Allophanate groups are formed from the isocyanate and urethane group [eq. (1)] and the isocyanurate group as the result of isomerization of the isocyanate [eq. (2)], which is also called the isocyanate trimer. Allophanate

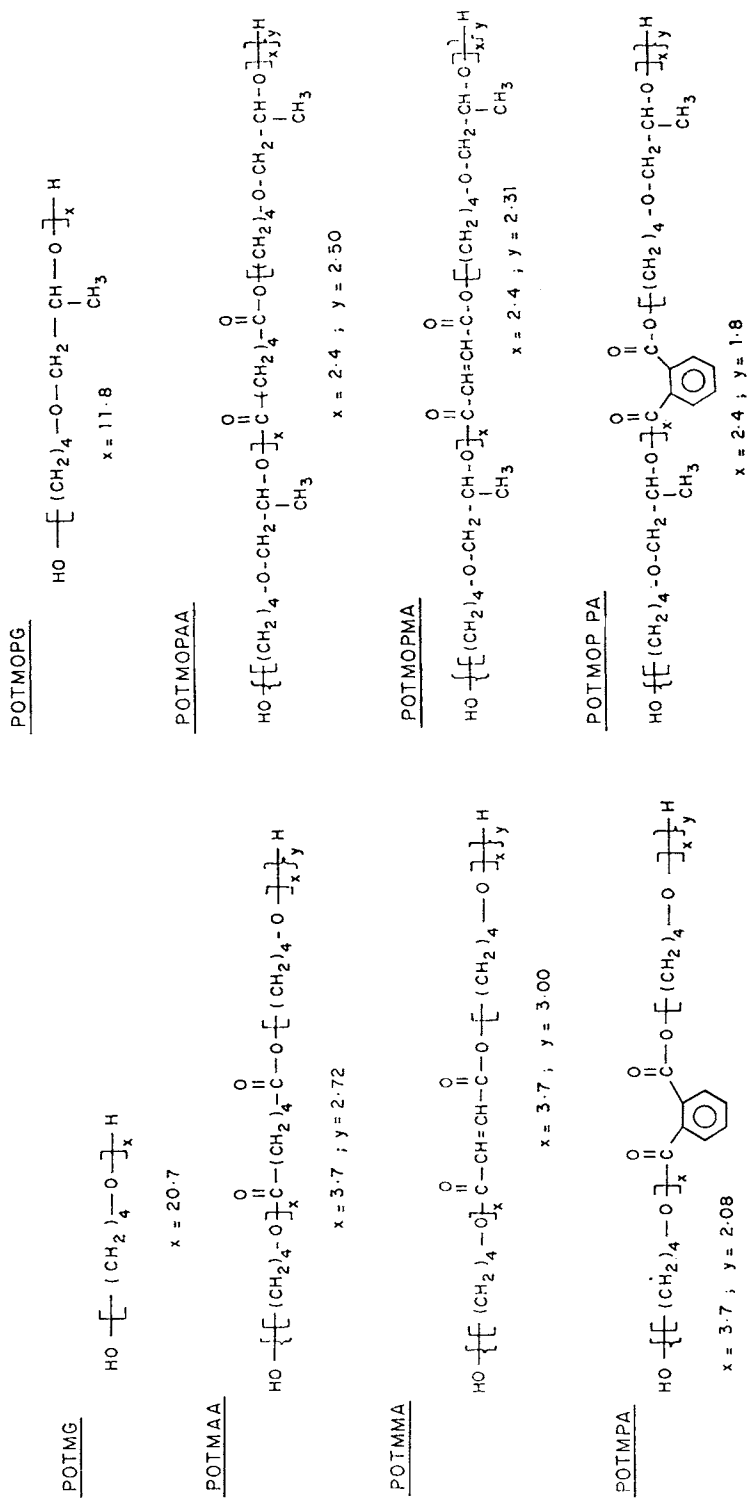
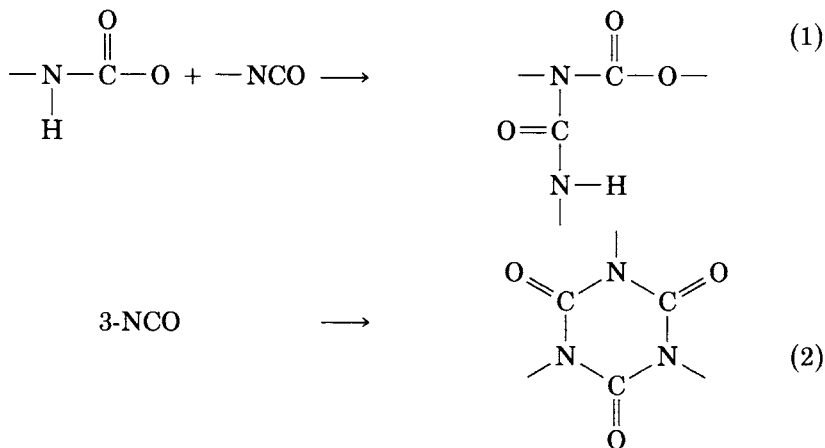


Fig. 1. Structure of prepolymers with average stoichiometry of each segment.

formation is the favorable reaction in the uncatalyzed reaction system. Isocyanurate trimer will be formed preferentially in the urethane reaction catalyzed by the basic catalyst:



Due to the complex behavior of the isocyanate monomer, in addition to these two reactions, depending upon the condition, it may involve other side reactions such as dimerization, biuret formation, etc.⁹

It was observed, in the present investigation, that the tensile strength and hardness increased considerably on an increase of R value (Tables I and II). About three- to fivefold increase in tensile strength and nearly twofold increase in hardness was obtained by increasing the R value from 0.9 to 1.3. Generally the percentage elongation increased steeply by the increase of R value from 0.9 to 1.1, reached a maximum at 1.1, and decreased with further increase in R value (Figs. 2 and 3). In the case of elastomers having very poor tensile value (e.g., POTMOPG-TDI, POTMOPPA-TDI), the elongation maximum was attained at a much higher R value, greater than 1.1 (Fig. 3). In these two polyurethane systems the elastomers prepared at low R values have poor strength, which is not sufficient for tensile tests.

Generally higher elongation is favored by an elastomer with a linear structure having high molecular weight and crosslinking leads to decrease in elongation. Here the R value of 0.9 and 1.0 should result in a linear polyurethane and the R value of 1.0 should result in a polyurethane of maximum molecular weight. Hence these elastomers, from difunctional monomers, may be expected to give a maximum elongation at the R value of unity. But almost all the polyurethanes prepared exhibited a maximum elongation at the R value of 1.1–1.2. There are several reasons for the necessity of using excess diisocyanate other than the theoretical stoichiometric requirement to give the polyurethane of maximum molecular weight.¹⁰ First a small error in the determination of the hydroxyl number of the prepolymer will shift the observed R value. Second the diisocyanate will react with traces of moisture and other impurities present in the system, thus disturbing the stoichiometric balance. But these two corrections are minor. Third, in addition to being highly reactive towards active hydrogen compounds, diisocyanates are also reactive towards themselves, forming well-defined dimers [eq. (3)] and

TABLE I
Effect of TMP Concentration on the Mechanical Properties (Hardness and Tensile Strength)
of POTMG-, POTMAA-, POTMMA- and POTMPA-Based TDI-Cured Polyurethane Elastomers

TMP[OH] prepolymer [OH]	POTMG-TDI polymer		POTMAA-TDI polymer		POTMMA-TDI polymer		POTMPA-TDI polymer	
	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)
0	13	140.2	12	45.1	12	27.5	6	8.8
0.2	14	137.3	12	51.0	12	38.2	6	10.8
0.3	16	159.8	14	59.8	18	43.1	8	12.7
0.4	18	164.7	17	61.8	24	91.2	10	23.5
0.5	21	197.1	20	72.6	26	118.7	11	38.2
0.6	22	205.9	22	79.4	26	159.8	13	50.0

TABLE II
 Effect of TMP Concentration on the Mechanical Properties (Hardness and Tensile Strength)
 of POTMOPG-, POTMOPAA-, POTMOPMA-, POTMOPMA- and POTMOPPA-Based
 TDI-Cured Polyurethane Elastomers

TMP[OH] prepolymer [OH]	POTMOPG-TDI polymer		POTMOPAA-TDI polymer		POTMOPMA-TDI polymer		POTMOPPA-TDI polymer	
	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m ⁻²)
0	—	—	13	42.2	12	31.4	—	—
0.2	10	25.5	16	59.8	12	32.4	—	—
0.3	11	30.4	18	82.4	14	35.3	10	9.80
0.4	13	37.3	18	109.8	16	47.1	11	21.6
0.5	15	43.1	22	170.6	18	82.4	11	33.3
0.6	16	48.0	24	186.3	18	108.8	11	37.3

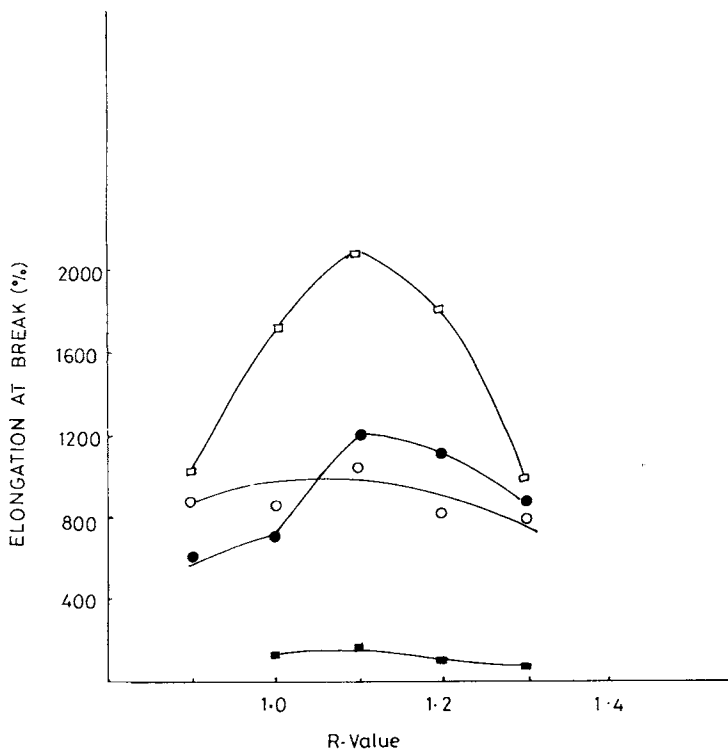
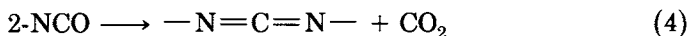
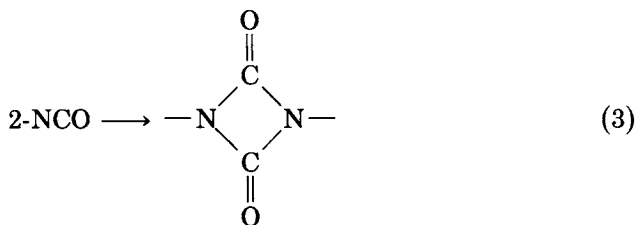


Fig. 2. Effect of R value on elongation at break of TDI-cured Polyurethane elastomers based on prepolymers: (○) POTMG; (●) POTMAA; (□) POTMMA; (■) POTMPA.

carbodiimide [eq. (4)], which is not



susceptible to crosslinking, but affects only the stoichiometric equivalence of the diisocyanate. Fourth, a minimum tensile strength is required to attain a maximum elongation especially in case of soft elastomers. The observation of maximum elongation at R value greater than 1.1 observed in case of POTMOPG- and POTMOPPA-based TDI-cured system is due to the higher crosslinking necessary to have enough tensile value to reach this elongation maximum.

The inherent viscosities of the polyurethanes were measured in DMF at 30°C and these values increased with an increase of R value, evidencing the improvement in molecular weight. Generally beyond the R value of 1.1, these

TABLE III
 Effect of R Value ($[\text{NCO}]/[\text{OH}]$ ratio) on the Mechanical Properties (Hardness and Tensile Strength) of POTMG-, POTMAA-, POTMMA-, and POTMPA-Based TDI-Cured Polyurethane Elastomers

R value	POTMG-TDI polymer			POTMAA-TDI polymer			POTMMA-TDI polymer			POTMPA-TDI polymer		
	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)
0.9	12	79.4	0.212	11	30.4	0.318	11	20.16	0.481	—	—	0.210
1.0	12	140.2	0.316	12	45.1	0.394	12	27.5	—	6.0	8.8	0.298
1.1	15	156.9	0.388	16	59.8	0.510	12	38.2	—	10.0	10.8	0.298
1.2	18	159.8	—	21	70.6	—	18	47.1	—	10.0	31.4	0.389
1.3	22	215.7	—	23	84.3	—	22	88.3	—	11.0	47.1	—

TABLE IV
Effect of R Value ($[\text{NCO}]/[\text{OH}]$ ratio) on Mechanical Properties (Hardness and Tensile Strength) of POTMOPG-, POTMOPAA-, POTMOPMA-, POTMOPMA- and POTMOPPA-Based TDI-Cured Polyurethane Elastomers

R value	POTMOPG-TDI polymer			POTMOPAA-TDI polymer			POTMOPMA-TDI polymer			POTMOPPA-TDI polymer		
	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)	Hardness (Shore A)	Tensile strength $\sigma \times 10^{-4}$ (N m^{-2})	η_{inh} (DMF, 30°C)
0.9	—	—	0.203	10	10.8	0.182	10	11.8	0.310	—	—	0.133
1.0	—	—	0.228	13	42.2	0.191	12	31.4	0.408	—	—	0.139
1.1	11	30.4	0.231	15	58.8	0.189	14	34.3	—	10	10.8	0.146
1.2	12	36.3	—	18	79.4	—	16	39.2	—	11	31.4	—
1.3	14	42.2	—	20	108.8	—	17	60.8	—	11	53.0	—

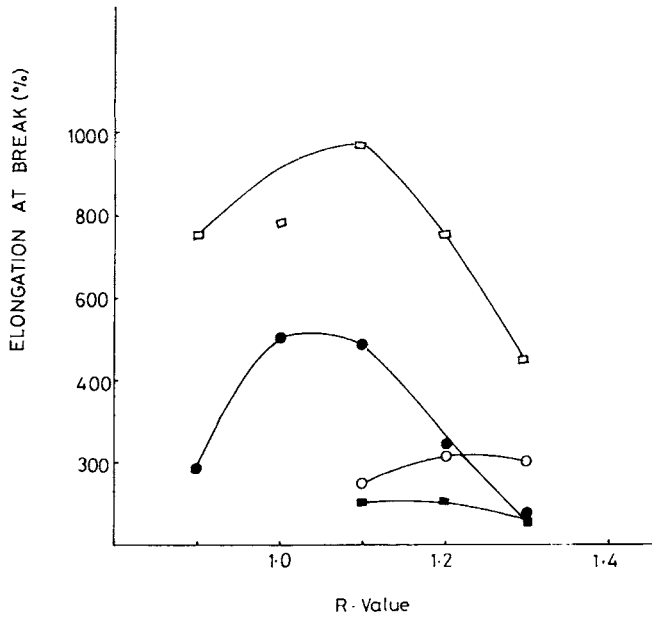


Fig. 3. Effect of R value on elongation at break of TDI-cured polyurethane elastomers based on prepolymers: (○) POTMOPG; (●) POTMOPAA; (□) POTMOPMA; (■) POTMOPPA.

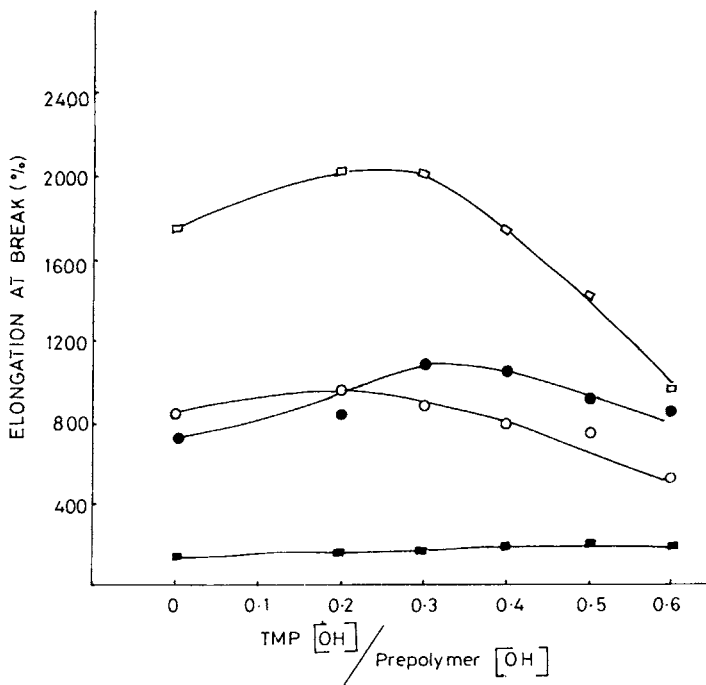


Fig. 4. Effect of TMP concentration on elongation at break of TDI-cured polymethane elastomers based on prepolymers: (○) POTMG; (●) POTMAA; (□) POTMMA; (■) POTMPA.

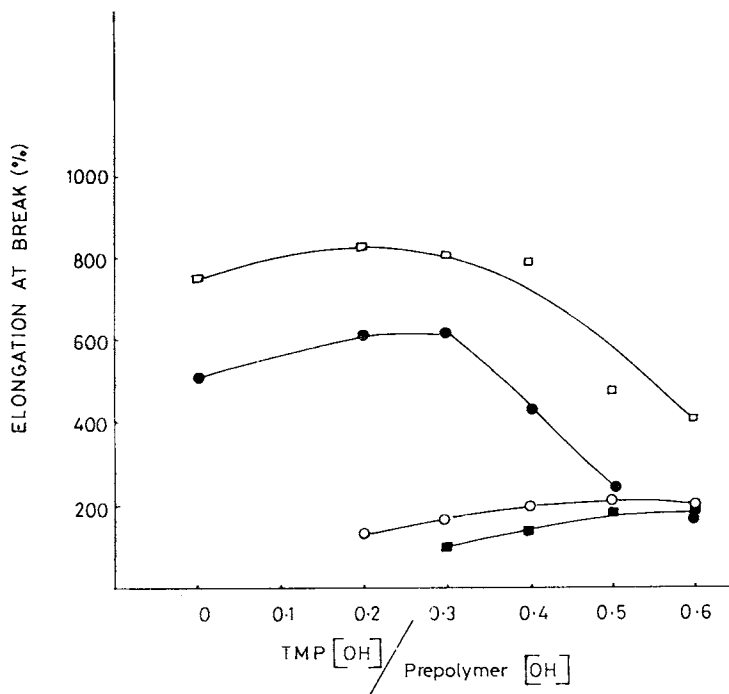


Fig. 5. Effect of TMP concentration on elongation at break of TDI-cured polymethane elastomers based on prepolymers: (○) POTMOPG; (●) POTMOPAA; (□) POTMOPMA; (■) POTMOPPA.

polymers were not soluble in DMF and gelled instead (Tables I and II). As the present systems did not involve any catalyst, the crosslinking that occurred at higher R value might have been due to the allophanate linkage. It is difficult to have a quantitative data on the degree of crosslinking by the allophanate group in competition with the other side reactions at higher R values. But the use of trifunctional hydroxy compounds yields more precise information. The effect of the extent of crosslinking by TMP on mechanical properties was studied by varying the ratio of the hydroxyl group concentration from TMP to that of the prepolymers in the range of 0 to 0.6 (Tables III and IV). In all the cases the hardness and tensile strength increased with increase in amount of TMP. The elongation increased at first, reached a maximum at the ratio of 0.2–0.3, and decreased again (Fig. 4). Even though the ratio of crosslinker required to get a maximum elongation was 0.2–0.4 in many cases, a different value was obtained in a few cases. A higher ratio (0.5–0.6) was required to attain maximum elongation from elastomers like POTMOPG–TDI and POTMOPPA–TDI (Fig. 5). These polymers having very low tensile strength show a similar trend in the case of crosslinking at higher R value also. This confirms that optimum tensile strength for the elongation maximum is observed with a certain percentage of crosslinking only in the case of elastomers having very low tensile strength. Crosslinking by both excess isocyanate (higher R value) and TMP improves the hardness and tensile strength in a comparable manner.

Thus crosslinking by higher R value and by the introduction of TMP increased the hardness and tensile strength, whereas the elongation increased

at first, reached a maximum at a particular crosslinking, and decreased further. A totally new phenomenon has been observed on elongation regarding the effect of crosslinking in a soft polyurethane system having low tensile strength. The crosslinking introduced in polyurethanes by taking excess diisocyanate is as effective as that of a triol crosslinking on modifying the mechanical properties.

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