

## Diisocyanate-Linked Polymers. III. Relationships Between the Composition and Ultimate Tensile Properties of Some Polyurethane Elastomers\*†

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### I. INTRODUCTION

The tensile strength and elongation at rupture of elastomers vary markedly with the experimental conditions used in measurement. For example, when measured at a fixed rate of extension, the tensile strength may increase by a factor of 100 or more as the temperature is decreased, and the ultimate elongation may increase concomitantly by a factor of 10 or more and then decrease to a few per cent. The ultimate properties also depend on the chemical nature of the network chains, the degree of crosslinking, and on the regularity of spacing of the crosslinking sites. In addition, those elastomers which crystallize during extension (e.g., vulcanized natural rubber) normally exhibit higher tensile strengths and ultimate elongations than those which do not crystallize (e.g., SBR rubbers). In seeking relationships between the structure and the ultimate properties of elastomers, these various factors which affect ultimate properties must be carefully considered.

Previously<sup>1</sup> a study was made of the tensile strength and ultimate elongation of several series of polyether-polyurethane elastomers prepared from polyoxypropylene glycol 2025 (PPG), trimethylolpropane (TMP), and either toluene 2,4-diisocyanate (TDI) or hexamethylene 1,6-diisocyanate (HDI). The structure of these elastomers was characterized by (1) the number of network chains

per unit volume  $\nu$  and (2) the concentration of urethane groups [U]. These parameters could be varied independently over certain ranges by making appropriate changes in the average molecular weight of PPG 2025 through blending it with dipropylene glycol (DPG). The glass temperature  $T_g$  of the elastomers increased linearly with [U], the rate of increase being considerably greater for the TDI-linked than for the HDI-linked elastomers. These elastomers apparently did not crystallize upon extension, and their ultimate properties, measured at a fixed extension rate, were found to depend on both [U] and  $\nu$ . However, when compared in corresponding temperature states, i.e., at equal values of  $T - T_g$ , the ultimate properties over a wide temperature range were found to be independent of [U], or approximately so, when [U] was less than about 1.85 moles/kg. Also, the ultimate elongation was observed to be inversely proportional to  $\nu$ , although the proportionality constant was temperature-dependent. It thus appears that certain elastomers which do not crystallize have ultimate properties which depend not only on  $\nu$  and  $T_g$  but also on the chemical nature of the network chains.

The present study concerned the ultimate properties of some polyurethane elastomers which contained various amounts of plasticizer, different diisocyanates and hydroxy-terminated prepolymers, and different amounts and types of crosslinkers. It is believed that the interchain attractive forces in these elastomers are relatively weak and also that these elastomers do not crystallize upon extension. After the behavior of such elastomers is better understood, it should be easier to understand the ultimate properties of those elastomers which crystallize and those whose properties are affected by specific interchain forces.

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## II. EXPERIMENTAL

### A. Materials

**Polyoxypropylene Glycol 2025.** One lot of Niax diol PPG 2025, obtained from Union Carbide Chemicals Co., was used throughout this study. After degassing, the material contained 0.01% or less of water,  $0.99 \times 10^{-3}$  moles/g. of hydroxyl,  $3.2 \times 10^{-5}$  moles/g. of carbon-carbon double bonds (about 6 mole-%), and  $1.0 \times 10^{-5}$  moles/g. of carbonyl groups. The hydroxyl content corresponds to an average molecular weight of 2020 if all molecules are difunctional, and to an average molecular weight of 1957 if a correction is made for the monofunctional molecules.

**Dipropylene Glycol (DPG).** This material, also obtained from Union Carbide Chemicals Co., was distilled and the center cut was retained for use.

**Polyester 50/50.** This material reportedly was prepared by the copolymerization of  $\epsilon$ -caprolactone and methyl  $\epsilon$ -caprolactone in a 50/50 mole ratio, with ethylene glycol as the initiator; it was used as received from Union Carbide Chemicals Co. The hydroxyl content was  $0.93 \times 10^{-3}$  moles/g., which corresponds to an average molecular weight of 2150.

**Polyester 80/20.** This material, obtained from Union Carbide Chemicals Co., reportedly was similar to polyester 50/50 except that the molar ratio of  $\epsilon$ -caprolactone to methyl  $\epsilon$ -caprolactone was 80:20. The hydroxyl content was  $0.85 \times 10^{-3}$  moles/g., which corresponds to an average molecular weight of 2260.

**Triethylene Glycol (TEG)** This material, obtained from Union Carbide Chemicals Co., was distilled at reduced pressure and a center cut was retained for use.

**Toluene 2,4-Diisocyanate (TDI).** Hylene T (E. I. du Pont de Nemours & Co., Inc.), which is essentially the pure 2,4-isomer, was distilled and then stored in the absence of moisture.

***m*-Phenylene Diisocyanate (PDI).** This solid material was used as received from Mobay Chemical Co., except that it was liquefied by heating at 60°C. immediately before use.

**Naphthalene 1,5-Diisocyanate (NDI).** This diisocyanate, also obtained from Mobay Chemical Co., was used as received, except that it was liquefied by heating before use.

**1,1,1-Trimethylolpropane (TMP).** This material, as received from Matheson, Coleman and Bell, Inc., was ground and stored in a desiccator over  $P_2O_5$ .

**N,N,N',N' -Tetrakis(2 - hydroxypropyl)ethylene-diamine (Quadrol).** Before use, this material, obtained from Wyandotte Chemicals Corp., was degassed for about 2 hr. at 80–90°C. under 1–2 mm. pressure.

**Castor Oil (DB oil).** Castor oil is a triglyceride consisting of 18-carbon fatty acids, mostly ricinoleic acid but also some oleic and linoleic acids. According to the supplier, Baker Castor Oil Co., castor oil may be considered to be 70% glyceryl triricinoleate and 30% of a diricinoleate triglyceride and therefore 70% trifunctional and 30% difunctional. The DB oil is a grade of refined castor oil which has low moisture and acid content; it was used as received except for degassing. The hydroxyl content was  $2.85 \times 10^{-3}$  mole/g., which corresponds to a molecular weight of 945 if the ratio of trifunctional to difunctional molecules is 70/30.

**Glyceryl Ricinoleate (Flexricin 13).** This material is described by the supplier, Baker Castor Oil Co., as a technical grade of glyceryl monoricinoleate, which consists of about 50% monoricinoleate, 40% diricinoleate, and 10% triricinoleate. The material is trifunctional and has both primary and secondary hydroxyl groups. The hydroxyl content was  $6.08 \times 10^{-3}$  moles/g., which corresponds to an average molecular weight of 493.

**Pentaerythritol Tetraricinoleate (Flexricin 19).** This material is technical grade pentaerythritol tetraricinoleate and was used as received from Baker Castor Oil Co. The hydroxyl content was  $2.70 \times 10^{-3}$  moles/g., which corresponds to a molecular weight of 1480.

**Tetronic 904.** This tetrafunctional material, obtained from Wyandotte Chemicals Corp., is prepared by the addition of propylene and ethylene oxide to ethylenediamine. Since the ethylene oxide is added last, the terminal hydroxyl groups probably are predominantly primary. The manufacturer reported a water content of 0.04%, unsaturation in the range 4.0 to  $6.0 \times 10^{-5}$  moles/g., and a pH of 10 for a 2.5% aqueous solution. The hydroxyl content was found to be  $0.53 \times 10^{-3}$  moles/g., which corresponds to an average molecular weight of 7550. This material is a paste at room temperature but melts at slightly above room temperature.

### B. Preparation of Elastomers

The elastomers were prepared by the one-step cast procedure described previously.<sup>1</sup> An isocyanate-to-hydroxyl equivalence ratio of 1.10 was used in preparing all elastomers, because their

mechanical properties have been found to be relatively insensitive to this ratio when a slight excess of isocyanate is used. Again, 2.5 mg. of ferric acetylacetonate per ml. of diisocyanate was used as the curing catalyst, and all elastomers were cured in open trays for 3 days at 60°C. to yield sheets about  $\frac{1}{8}$  in. thick. A brief study showed that the catalyst concentration could be doubled without significantly affecting the mechanical properties of an elastomer.

Theoretical values of  $\nu$  were calculated from the concentration of the crosslinker, which in this work was either a triol or a tetrol. Each triol molecule should produce 1.5 chains in the polymeric network and each tetrol molecule should produce 2 chains. If no inactive or dangling chains are attached to the three-dimensional network and if no sol fraction or plasticizer is present,  $\nu$  equals  $\rho/M_c$ , where  $\rho$  is the density of the elastomer and  $M_c$  is the average molecular weight of chains between junction sites. (In this paper,  $\nu$  represents the number of chains/ml. as calculated from the crosslinker concentration, and  $\nu_e$  represents the number of effective chains/ml., the latter being calculated from measured values of the equilibrium modulus.) Values of  $\nu_e$  were usually found to be less than  $\nu$ , primarily because the PPG contains about 6 mole-% monofunctional molecules which produce dangling chains and a sol fraction in the elastomers. Also, some of the crosslinkers used were mixtures whose exact compositions were unknown. The concentration of urethane groups was calculated from the total amount of diisocyanate used, it being assumed that each diisocyanate molecule formed two urethane groups.

### C. Evaluation of Elastomers

As before,<sup>1</sup> tensile specimens having gage lengths of 2.0 and 1.0 in. were tested, the shorter being used only when the ultimate elongation of an elastomer exceeded 500%. The elongations were calculated from crosshead displacements by assuming that the effective gage lengths of the long and short specimens were 3.2 and 1.8 in., respectively, even though it is known that these values depend somewhat on the extensions, especially when the extensions are greater than a few hundred per cent. The long and short specimens were tested at crosshead speeds of 10 and 5 in./min.; these speeds correspond to strain rates of about 3.1 and 2.8 min.<sup>-1</sup>, respectively.

Values of Young's modulus  $E$  were calculated from the slopes of plots  $\alpha S$  vs.  $\gamma$ , where  $\alpha$  is the

principal extension ratio,  $S$  the stress based on the unstressed cross-sectional area of a specimen, and  $\gamma$  the strain which equals  $\alpha-1$ . Such plots normally gave straight lines for elongations up to about 100%. As the test temperature is increased from some low temperature, the modulus decreases to a minimum and then increases gradually. When the temperature is sufficiently high that the modulus increases with temperature or even is independent of temperature, the modulus is assumed to be an equilibrium or near-equilibrium value. A less sensitive indication of whether equilibrium exists is the slope of a plot of  $\log \alpha S$  vs.  $\log \gamma$ , designated by  $n$ . When this slope is unity, the stress-strain data are often near-equilibrium values.

Equilibrium swelling measurements were made in benzene on some of the elastomers. It was assumed that equilibrium had been reached after a sample had been in the solvent for 4 days. The results are reported as the swelling ratio  $q_m$ , which equals  $V/V_0$ , where  $V$  is the volume of the swollen elastomer and  $V_0$  the volume of the elastomer after the benzene had been removed by heating the swollen sample overnight under vacuum. The difference between  $V_0$  and the initial volume of elastomer equals the volume of sol removed during the swelling. Although it is unlikely that all sol was removed during the swelling experiment (especially when large amounts of sol were present) the values obtained are believed to be sufficiently precise for present needs.

Glass temperatures were measured by an automatic quartz-tube-type dilatometer.<sup>2</sup> In this dilatometer, the change in length of a cylindrical specimen is measured by a linear variable differential transformer and is recorded while the temperature is decreased slowly and automatically from ambient to  $-120^\circ\text{C}$ .; then the temperature is allowed to increase slowly to ambient. Values of  $T_g$  obtained from plots of length against temperature while the temperature is decreased ordinarily agree within a few degrees with the values obtained while the temperature is increased. The average of the two values usually is reported.

### III. RESULTS AND DISCUSSION

The experimental work can be divided into three major parts, each being designed to give information about different factors which affect the ultimate tensile properties. In the first part, two series of elastomers were prepared for which the parameters  $[U]$  and  $\nu$  were held constant, and thus any basic variations among the ultimate properties of these

elastomers should be due to differences in either their molecular structure or interchain forces. The elastomers in both series contained PPG, DPG, and TMP; in one series TDI and 0–20% plasticizer were added, and in the other series four different diisocyanates were used. In the second part of the experimental work, elastomers were prepared from two different polyester-type diols; for these,  $\nu$  was held constant but [U] was varied so that their ultimate properties could be compared with those of similar elastomers prepared previously from PPG. In the third part, three triols and three tetrols were used as crosslinkers in elastomers prepared from PPG, DPG, and TDI; for all these elastomers [U] was the same but the concentration of each crosslinker was varied. This work was designed to show whether or not the ultimate properties depend on the chemical nature of the crosslinker and how the ultimate properties vary with the crosslinker concentration.

#### A. Elastomers Having Identical [U] and $\nu$

Elastomers containing 0, 5, 10, 15, and 20% isodecyl pelargonate as plasticizer were prepared from PPG, DPG, TMP, and TDI. In an attempt to obtain elastomers having the same modulus, the same concentration of TMP was used in each formulation, and the concentration was selected to give theoretically  $1.87 \times 10^{-4}$  chains/ml. Because the previous work<sup>1</sup> showed that the  $T_g$  of elastomers linked by a given diisocyanate increased linearly with [U], the value of [U] was kept constant at 1.42 moles/kg.; this was accomplished by varying the molar ratio of DPG/PPG from 0.109 to 0.479 as the plasticizer concentration was increased from 0 to 20%.

Table I shows that the  $T_g$  of the elastomers is decreased from  $-52.5$  to  $-66.5^\circ\text{C}$ . as the plasticizer concentration is increased from 0 to 20%, even though each elastomer has the same [U]. In contrast, other experiments have shown that when 20% isodecyl pelargonate is added to the unplasticized formulation without changing the molar ratio of the elastomer ingredients,  $T_g$  is decreased from  $-52.5$  to below  $-90^\circ\text{C}$ . For the elastomers having the same [U] values, the progressive decrease of  $T_g$  with increase in plasticizer content can be attributed to the net result of two opposite effects. As the plasticizer content is raised, more urethane groups, or tolylene groups, are included along a chain of a given length. This change in structure increases the chain stiffness<sup>3</sup> and interchain forces, both factors tending to in-

TABLE I  
PPG Elastomers with [U] = 1.42 and  $\nu = 1.87 \times 10^{-4}$ ,  
Plasticized with Isodecyl Pelargonate

IDP, wt.-%	$T_g$ , °C.	Test temp. $T - T_g$ , °C.	$E$ , psi	$\left(\frac{298}{T}\right)^E$	$n$	
0	-52.5	123.5	192	166	1.0	
			101.5	186	172	1.0
			77.5	180	180	0.9
5	-57.5	106.4	172	159	1.0	
			82.5	160	160	0.98
10	-61.5	110.4	163	151	1.0	
			86.5	163	163	0.98
15	-63.5	112.4	150	139	1.0	
			88.5	148	148	1.0
20	-66.5	115.4	150	139	1.0	
			91.5	148	148	1.0

crease  $T_g$ . However, these effects are more than offset by the plasticizer, which separates the chains, decreases their interactions, and increases their mobility.

The tensile properties of the series of plasticized elastomers were measured over a wide temperature range. At the elevated temperatures, the modulus for each elastomer was found to increase with the temperature, as shown by Table I. This temperature dependence indicates that near-equilibrium values were obtained, although after each value is reduced to 298°K. by multiplying by 298/ $T$ , the resulting values decrease somewhat with increasing temperature. The reduced modulus decreases from about 166 to 139 psi as the concentration of plasticizer is increased, even though each elastomer contained the same concentration of TMP. From one viewpoint, the modulus might have been expected to increase with the plasticizer concentration, since the PPG contained about 6 mole-% monofunctional molecules, which form dangling or inactive chains in the network, as well as an inactive sol fraction. Since the PPG/DPG ratio was decreased as the plasticizer concentration was increased, the concentration of monofunctional molecules in the formulations was decreased, and this would tend to increase the modulus. Perhaps, however, as the plasticizer concentration was increased, more cyclic structures formed during the polymerization and the modulus was decreased because of these structures. A theoretical value of the modulus for these elastomers can be calculated from the TMP concentration and the kinetic theory expression  $E = 3\nu RT$ , where  $R$  is the gas constant and  $T$  the absolute temperature. The calculated modulus is about 200 psi, which actually is in fair agreement with the experimental

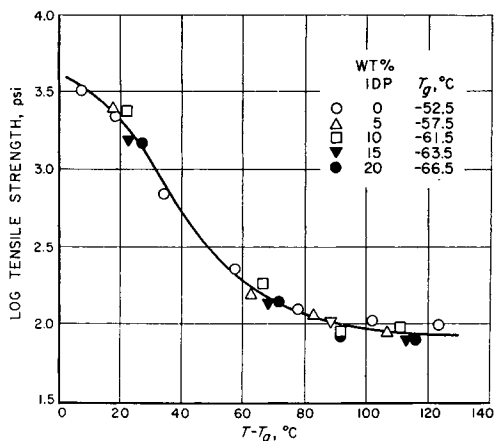


Fig. 1. Tensile strength of plasticized PPG elastomers with  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$ .

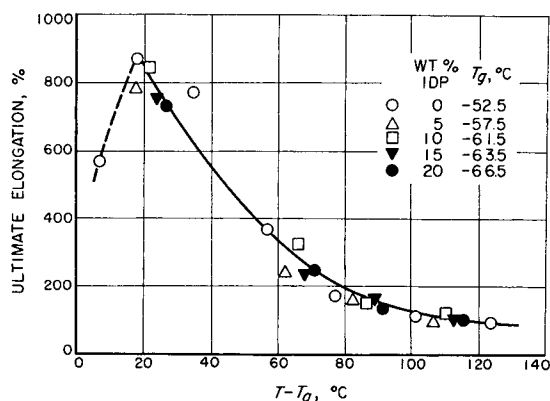


Fig. 2. Ultimate elongation of plasticized PPG elastomers with  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$ .

ones, especially considering the monofunctional material in the PPG.

The ultimate properties of the elastomers are shown plotted against  $T - T_g$  in Figures 1 and 2; all points are seen to lie close to the curves drawn. This result indicates that specific interchain forces have no effect on the ultimate properties, except insofar as they affect  $T_g$ . If interchain forces affected the ultimate properties, the incorporation of 20% plasticizer would undoubtedly reduce the interchain forces sufficiently so that the ultimate properties of the plasticized elastomer would be different from those of the unplasticized elastomer.

Further evidence that interchain forces have no basic effect on the ultimate properties of certain elastomers was obtained by studying elastomers containing PPG, DPG, and TMP and linked with either HDI, TDI, *m*-phenylene diisocyanate (PDI), or naphthalene 1,5-diisocyanate (NDI). Each elastomer had a  $[U]$  of 1.42 moles/kg. and sufficient

TABLE II  
PPG Elastomers with  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$   
Prepared from Different Diisocyanates

Diisocyanate	$T_g, ^\circ\text{C}$ .	Test temp. $T - T_g, ^\circ\text{C}$ .	$E, \text{psi}$	$\left(\frac{298}{T}\right)^E$	$n$
HDI	-67.5	138.5	163	141	1.0
		116.5	160	148	0.99
		92.5	151	151	0.98
TDI	-52.2	123.5	192	166	1.0
		101.5	186	172	1.0
		77.5	180	180	0.99
PDI	-50.5	121.5	150	130	1.0
		99.5	149	138	0.99
		75.5	147	147	0.97
NDI	-17.0	88.0	201	174	0.92
		66.0	203	188	0.91
		42.0	202	202	0.94

TMP to give theoretically  $1.87 \times 10^{-4}$  chains/ml. Tensile data were again measured over a wide temperature range, and the modulus values at elevated temperatures are given in Table II. Except for the NDI-linked elastomers, the modulus is seen to increase with increasing temperature, although the modulus values, after reduction to 298°K., decrease with increasing temperature. The NDI-linked elastomer was somewhat opaque, probably indicating that the NDI had not dissolved completely, and measurements were not made on this elastomer at values of  $T - T_g$  sufficiently large to give a reliable estimate of the equilibrium modulus, as shown by the temperature dependence of the modulus and the exponent  $n$ . However, values of the reduced modulus for the four elastomers range only from about 130 to 174 psi, which can be compared with the theoretical value of 200 psi.

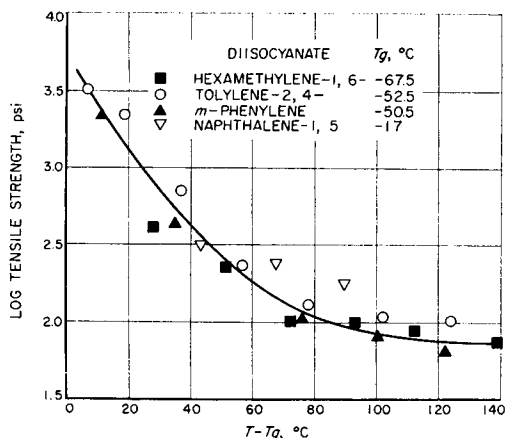


Fig. 3. Tensile strength of PPG elastomers with  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$ , linked by different diisocyanates.

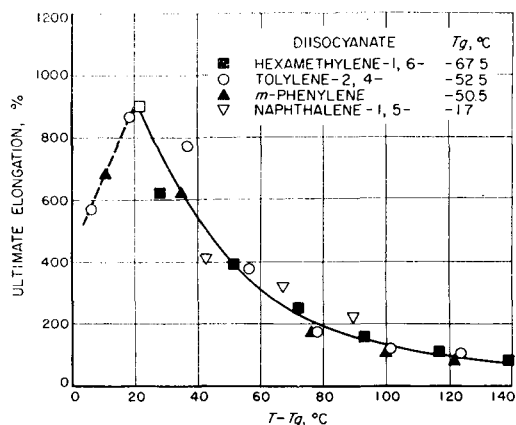


Fig. 4. Ultimate elongation of PPG elastomers with  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$ , linked by different diisocyanates.

The major difference in the HDI, TDI, PDI, and the NDI-linked elastomers is their glass temperatures, which are  $-67.5$ ,  $-52.5$ ,  $-50.5$ , and  $-17^\circ\text{C}$ ., respectively. This range of  $T_g$  probably occurs primarily because of the variation in chain stiffness<sup>3</sup> caused by the interspersion of tolylene, phenylene, and naphthalene groups between the PPG chains. However, no difference is observed in their ultimate properties when they are plotted against  $T - T_g$ , as shown by Figures 3 and 4; all tensile strengths and ultimate elongations are the same at equal values of  $T - T_g$ . Only three values for the ultimate properties of the NDI-linked elastomer are shown and, although these values lie close to the curves, they do seem to be less temperature-sensitive than those of the other elastomers. The data available, however, are too few to show decisively whether or not some small difference exists between the properties of the NDI-linked elastomer and those linked by the other diisocyanates. However, these results on the four elastomers strongly suggest that interchain forces have no significant effect on the ultimate properties and their temperature dependence, except as they affect  $T_g$ . Also, a close comparison of the curves in Figures 3 and 4 with those in Figures 1 and 2 shows that the elastomers in both series have identical ultimate properties.

### B. Elastomers Containing Polyester-Type Diols

The elastomers discussed thus far have had network chains composed largely of PPG, a polyether. To see the effects of others types of chains, elastomers were prepared from two hydroxy-terminated polyesters: polyester 50/50 and polyester 80/20. These polyesters had been prepared from a 50:50

TABLE III  
Polyester Elastomers with  $\nu = 1.87 \times 10^{-4}$

Poly- ester	[U], moles/ kg.	$T_g$ , $^\circ\text{C}$ .	Test temp. $T - T_g$ , $^\circ\text{C}$ .	E			$n$
				psi	$\left(\frac{298}{T}\right)E$		
50/50	1.28	$-50.5$	121.5	306	265	1.0	
			75.5	292	292	0.94	
50/50	1.85	$-43.5$	114.5	386	334	1.0	
			68.5	359	359	0.97	
50/50	2.30	$-40.0$	111.0	400	347	1.0	
			65.0	392	392	0.96	
80/20	1.28	$-50.5^a$	71.0	472	409	1.0	
			25.0	408	408	0.94	
80/20	1.57	$-47.0^a$	71.0	476	412	0.99	
			25.0	424	424	0.97	
80/20	1.85	$-43.5^a$	71.0	506	438	1.0	
			25.0	430	430	0.98	
80/20	2.30	$-40.0^a$	71.0	522	452	1.0	
			25.0	454	454	0.94	

<sup>a</sup> Assumed to be the same as for the elastomers prepared from polyester 50/50.

and an 80:20 molar ratio of  $\epsilon$ -caprolactone and methyl  $\epsilon$ -caprolactone. Elastomers were prepared from the polyesters, triethylene glycol (TEG), TMP, and TDI. The structural parameter  $[U]$  was varied in these formulations, but each contained sufficient TMP to give theoretically  $1.87 \times 10^{-4}$  chains/ml. This variation of the parameter was accomplished by appropriate changes in the molar ratio of TEG to polyester. Because the ratio of primary to secondary hydroxyl groups in the polyesters is considerably greater than in PPG, and because it seemed desirable for both diols to react with TDI at about the same rate, TEG was used in place of DPG as the low molecular weight diol.

The elastomers prepared from polyester 50/50 had  $[U]$  values of 1.28, 1.85, and 2.30 moles/kg. The glass temperatures of these are  $-50.5$ ,  $-43.5$ , and  $-40^\circ\text{C}$ ., which increase linearly with  $[U]$ . Modulus values measured at elevated temperatures are seen, in Table III, to increase with increasing temperature, indicating that they are near-equilibrium values. However, the modulus reduced to  $298^\circ\text{K}$ . increases from 265 to 347 psi with increasing  $[U]$ . Furthermore, for a reason which is not apparent, these values are considerably greater than 200 psi, which is the expected value calculated from the concentration of TMP. The ultimate properties of the three elastomers are identical when plotted against  $T - T_g$ , as shown by Figures 5 and 6, although data were measured at a limited number of temperatures.

Elastomers prepared from polyester 80/20 had

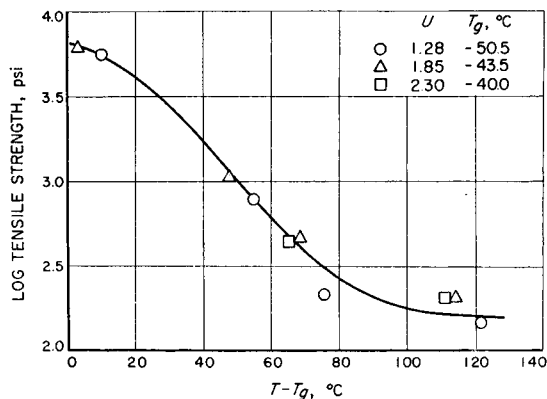


Fig. 5. Tensile strength of polyester 50/50 elastomers with  $\nu = 1.87 \times 10^{-4}$  and different values of  $[U]$ .

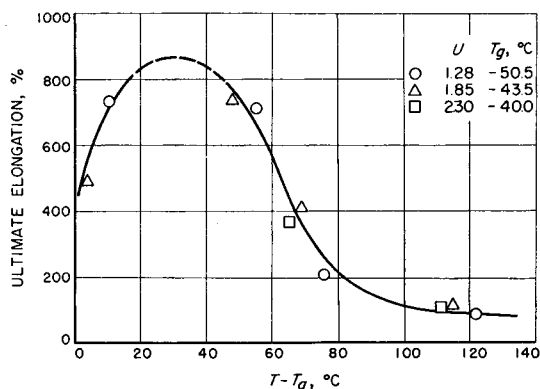


Fig. 6. Ultimate elongation of polyester 50/50 elastomers with  $\nu = 1.87 \times 10^{-4}$  and different values of  $[U]$ .

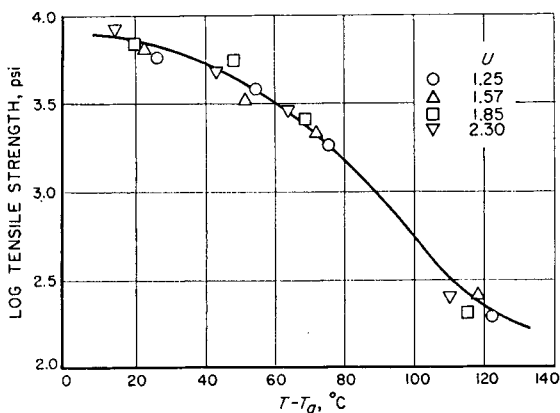


Fig. 7. Tensile strength of polyester 80/20 elastomers with  $\nu = 1.87 \times 10^{-4}$  and different values of  $[U]$ .

$[U]$  values of 1.28, 1.57, 1.85, and 2.30 moles/kg. Glass temperatures of these elastomers were not measured, but they were assumed to be the same as for the similar elastomers prepared from polyester 50/50. The glass temperature for the elas-

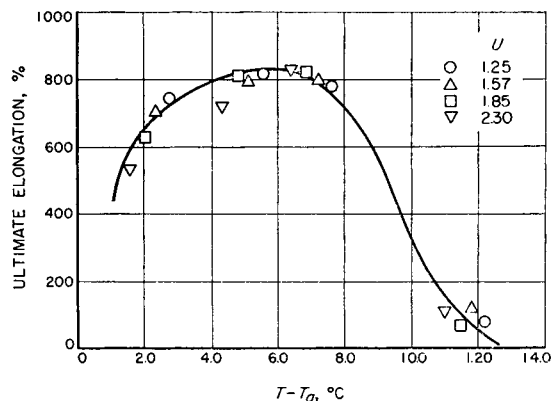


Fig. 8. Ultimate elongation of polyester 80/20 elastomers with  $\nu = 1.87 \times 10^{-4}$  and different values of  $[U]$ .

tomer having a  $[U]$  of 1.57 was estimated by interpolation to be  $-47^\circ\text{C}$ . Table III shows that the modulus values at  $71^\circ\text{C}$ ., when reduced to  $25^\circ\text{C}$ ., are almost identical with values measured at  $25^\circ\text{C}$ .; this close agreement is excellent proof that the reduced moduli represent equilibrium moduli. The reduced modulus, however, increases 10% as  $[U]$  is increased from 1.25 to 2.30, and is about double the expected value of 200 psi. The ultimate properties define single curves when plotted against  $T - T_g$ , as shown in Figures 7 and 8. The shapes of these curves are different from those of the polyester 50/50 elastomers; they seem either to be shifted to the right or to be increasing more rapidly with decreasing temperature than those of the polyester 50/50 elastomers.

A comparison of the properties of the two series of polyester elastomers shows that those containing polyester 80/20 have equilibrium moduli that are 30–50% greater than the moduli of those containing polyester 50/50. Their tensile strengths are roughly the same at the high and low temperatures, but the values for those containing polyester 80/20 increases more rapidly with decreasing temperature than do the values for those containing polyester 50/50. Similar behavior is seen in the variation of ultimate elongation with temperature.

### C. Elastomers Containing Different Types and Amounts of Crosslinkers

Because the only crosslinker investigated thus far has been TMP, elastomers were prepared with the use of three triols and three tetrols, the concentration of each crosslinker being varied in a series of otherwise similar elastomers. In this study, the triols were TMP, a refined castor oil

called DB oil, and glycerol ricinoleate whose trade designation is Flexricin 13. The latter two materials are mixtures of somewhat questionable structure. The tetrols were Quadrol (whose structure is claimed to be *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine), pentaerythritol tetraricinoleate (PETR), and Tetronic 904, which is prepared by the addition of propylene oxide and ethylene oxide to ethylenediamine. A more detailed description of these materials is given in Section II. The glycerol ricinoleate, DB oil, PETR, and Tetronic 904 have apparent molecular weights of 493, 945, 1480, and 7550, respectively; thus, to obtain a given number of chains/ml. in an elastomer, it is necessary to use appreciably larger weight percentages of these crosslinkers than of TMP or even Quadrol. Because the chains in these high molecular weight crosslinkers do not contain ether linkages (with the exception of the Tetronic), it seemed at least possible that the nature of the crosslinker could affect the mechanical properties of the elastomers. The purpose of this study was to see what effect, if any, the nature of the crosslinker has on ultimate properties and how the ultimate properties vary with crosslinker concentration.

All elastomers prepared had a [U] of 1.57, which was achieved in the usual manner by varying the DPG/PPG ratio as the crosslinker type and concentration were changed. The elastomers were characterized by measuring their equilibrium swelling in benzene, their sol fractions, and their tensile properties at four temperatures.

#### Swelling, Sol Fraction, and Modulus Data.

Tables IV to IX give the swelling ratio  $q_m$  achieved in benzene, estimates of the per cent sol obtained concurrently with the swelling data, and the modulus at several temperatures. For each formulation, the tables also give the number of chains/ml. ex-

pected from the crosslinker concentration; it was assumed that each triol molecule should form 1.5 chains and each tetrol molecule should form 2.0 chains. It is seen that most of the elastomers had

TABLE V  
PPG Elastomers with [U] = 1.57, Crosslinked by Castor Oil

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
2.44	10.2	12.5	71	110	0.96
			25	100	0.98
			4.5	104	—
1.87	10.5	18.5	-18	—	—
			71	67	0.89
			25	65	0.93
1.51	12.3	25.1	4.5	69	—
			-18	—	—
			71	36	0.89
1.27	14.6	22.9	25	39	0.83
			4.5	52	—
			-18	—	—
1.05	29.0	48.4	71	27	0.89
			25	39	0.83
			4.5	52	—
1.05	29.0	48.4	-18	—	—
			71	11	0.90
			25	16	0.78

<sup>a</sup> Calculated from composition.

considerable sol, especially those having the smaller crosslinker concentrations. Also, the temperature dependence of the modulus values, as well as the exponent  $n$ , indicates that equilibrium modulus

TABLE VI  
PPG Elastomers with [U] = 1.57, Crosslinked by Flexricin 13

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
2.44	8.7	14.4	71	65	0.97
			25	61	0.91
			4.5	60	—
1.87	17.7	44.0	71	32	0.98
			25	34	0.91
			4.5	42	—
1.51	23.2	50.7	71	17	1.0
			25	23	0.82
			4.5	30	—

<sup>a</sup> Calculated from composition.

values were not obtained, even at the highest temperatures, except for those elastomers having the smaller amounts of sol. In the following discussion, modulus values measured at 71° and reduced to 25° were used in the calculations.

TABLE IV  
PPG Elastomers with [U] = 1.57, Crosslinked by TMP

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
3.12	6.2	9.7	71	157	1.0
			25	145	1.0
2.44	7.7	14.7	71	106	0.99
			25	95	0.96
1.87	9.9	20.2	71	59	1.0
			25	55	0.91
1.51	14.2	27.7	71	29	0.91
			25	27	0.79
1.27	18.5	32.3	71	20	0.89
			25	22	0.78

<sup>a</sup> Calculated from composition.



TABLE VII  
PPG Elastomers with [U] = 1.57, Crosslinked by Quadrol

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
2.44	5.1	4.8	71	196	0.92
			25	182	1.0
			4.5	158	1.0
1.87	6.4	10.2	71	128	1.0
			25	117	1.0
			4.5	114	1.0
1.51	7.1	13.4	71	81	1.0
			25	82	0.93
			4.5	83	0.89
1.20	10.7	19.2	71	46	0.96
			25	40	0.87
			4.5	57	0.82
1.06	17.7	37.6	71	26	0.96
			25	30	0.86
0.79	24.0	43.7	71	20	0.89
			25	24	0.79

<sup>a</sup> Calculated from composition.

TABLE VIII  
PPG Elastomers with [U] = 1.57, Crosslinked by Flexricin 19 (PETR)

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
3.53	4.7	11.4	71	282	1.04
			25	266	1.03
2.44	6.0	14.6	71	192	1.02
			25	176	1.02
1.87	7.3	18.3	71	122	1.01
			25	115	0.99
1.51	7.5	16.1	71	116	1.01
			25	110	0.99
1.27	8.7	19.0	71	92	0.99
			25	89	0.94

<sup>a</sup> Calculated from composition.

TABLE IX  
PPG Elastomers with [U] = 1.57, Crosslinked by Tetronic 904

$10^4 \nu^a$	$q_m$	Sol, wt.-%	Test temp., °C.	$E$ , psi	$n$
1.51	9.3	27.7	71	60	1.0
			25	60	0.94
1.27	8.9	26.5	71	68	0.99
			25	70	0.94
1.06	14.7	35.8	71	38	0.91
			25	24	0.90

<sup>a</sup> Calculated from composition.

The equilibrium modulus and the volume fraction of gel  $v_2$  in a swollen polymer are related by the equation

$$\frac{EV_1}{3gRT} \left( v_2^{1/3} g^{2/3} - \frac{2v_2}{f} \right) + \ln(1 - v_2) + v_2 = -\chi_1 v_2^2 \quad (1)$$

where  $g$  is the gel fraction in the unswollen polymer ( $1 - g$  equals the sol fraction),  $V_1$  the molar volume of the solvent,  $f$  the functionality of the crosslinker, and  $\chi_1$  the polymer-solvent interaction parameter. If  $\chi_1$  is independent of the solvent concentration, or nearly so, a plot of the left-hand side of eq. (1) against  $v_2^2$  should give a straight line which passes through the origin and has a slope equal to  $-\chi_1$ . The data obtained for the elastomers containing the six different crosslinkers were plotted, as shown in Figure 9, to test the applicability of eq. (1) and to determine  $\chi_1$ . It is seen that most of the points lie close to the line whose slope is 0.36, the  $\chi_1$  value. In the previous paper,<sup>1</sup> it was shown that  $\chi_1$  increases linearly with [U] and equals 0.37 for TDI-linked elastomers having a [U] of 1.57; this previous result is thus in close agreement with the present value, which was obtained on elastomers

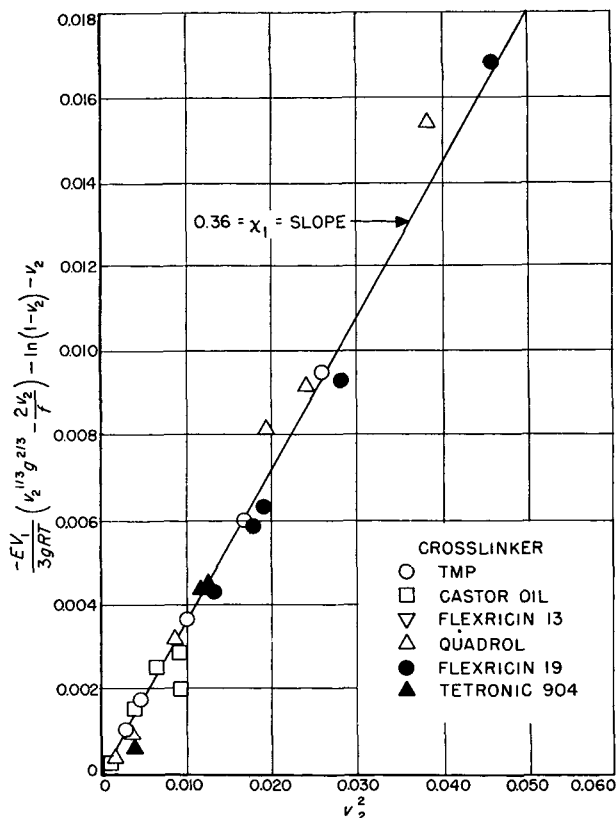


Fig. 9. Determination of  $\chi_1$  from modulus and swelling ratio of PPG elastomers with [U] = 1.57, and different types and concentrations of crosslinkers.

having different crosslinkers and a much wider range of crosslinker concentration than that in the elastomers studied previously.

**Calculated and Observed Values of  $\nu$ .** Tables IV to IX give values of  $\nu$  calculated from the crosslinker concentration and these values are compared in Figure 10 with those calculated from the modulus measured at 71°C. It is seen that the values of  $\nu_e$  obtained from the modulus data are considerably lower than the values of  $\nu$  predicted from the crosslinker concentration, although the differences become less as the concentration of a crosslinker is increased. The observed differences are perhaps not surprising since most of the elastomers contained considerable sol. The sol fraction was formed largely because of the unsaturation in the PPG and, in some elastomers at least, because of side reactions and uncertainties in the stoichiometry.

Other elastomers having  $[U]$  of 1.57 moles/kg. were prepared from DPG, TMP, TDI, and three types of PPG: (1) regular PPG which contained about 6.5 mole-% monofunctional material; (2) PPG which had been stripped by a molecular still until its monofunctional content was 1 mole-%; and (3) a special batch of PPG which contained no monofunctional material, but contained about 5 mole-% trifunctional material. Values of  $\nu$  calculated from the total triol concentration in these

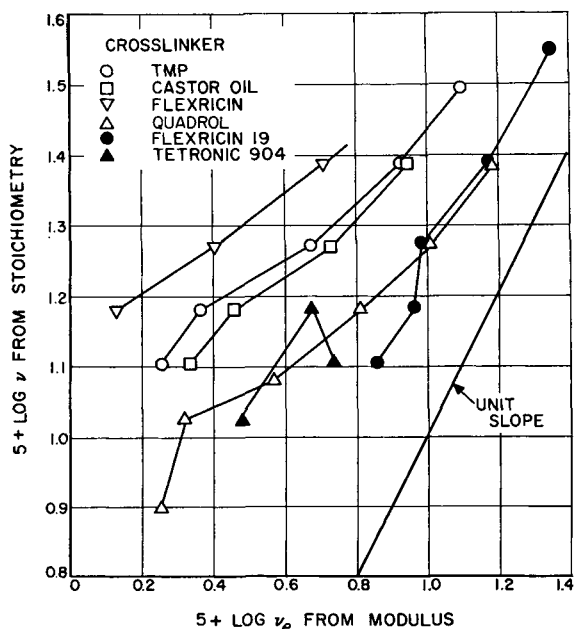


Fig. 10. Comparison of  $\log \nu$  calculated from crosslinker concentration with  $\log \nu_e$  calculated from modulus: elastomers with  $[U] = 1.57$  and different types and concentrations of crosslinkers.

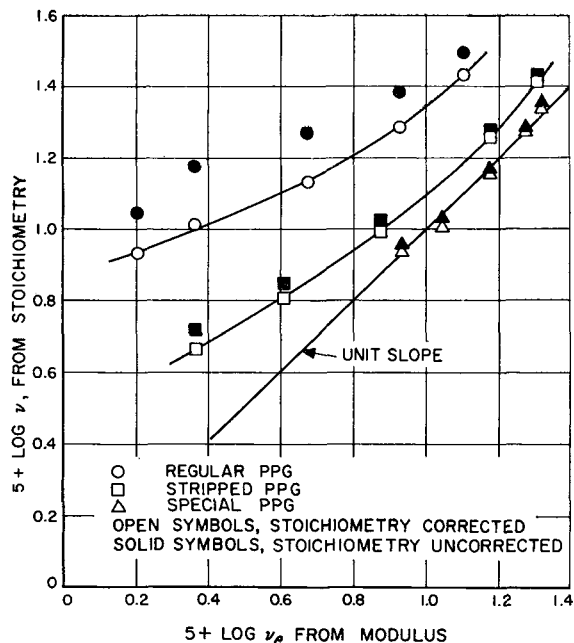


Fig. 11. Comparison of  $\log \nu$  calculated from crosslinker concentration with  $\log \nu_e$  calculated from modulus: elastomers prepared from three types of PPG.

elastomers are compared in Figure 11 with values calculated from the observed modulus. Values of  $\nu$  were calculated from the concentration of TMP in two ways: (1) no correction was made for the monofunctional content of the PPG; and (2) it was assumed that each monofunctional molecule in the PPG converted one TMP molecule into a diol. This method of correcting for the monofunctional content is only a crude approximation, since it is based on the assumption that monofunctional molecules do not cause formation of sol. However, the amount of sol does depend on the monofunctional content; the sol fraction ranged from 5 to 15% in those elastomers prepared from the special PPG, from 9 to 30% in those prepared from the "stripped" PPG, and from 10 to 51% in those prepared from the regular PPG. Furthermore, the sol content in each series of elastomers was directly proportional to the reciprocal of the TMP concentration. However, the important result shown by the data in Figure 11 is that modulus values of elastomers prepared from the special PPG are equal to those predicted from the crosslinker concentration.

**Ultimate Properties.** Ultimate properties measured at a fixed strain rate depend on  $T - T_g$ , the number of effective chains per unit volume  $\nu_e$ , and  $[U]$ . The glass temperatures were measured

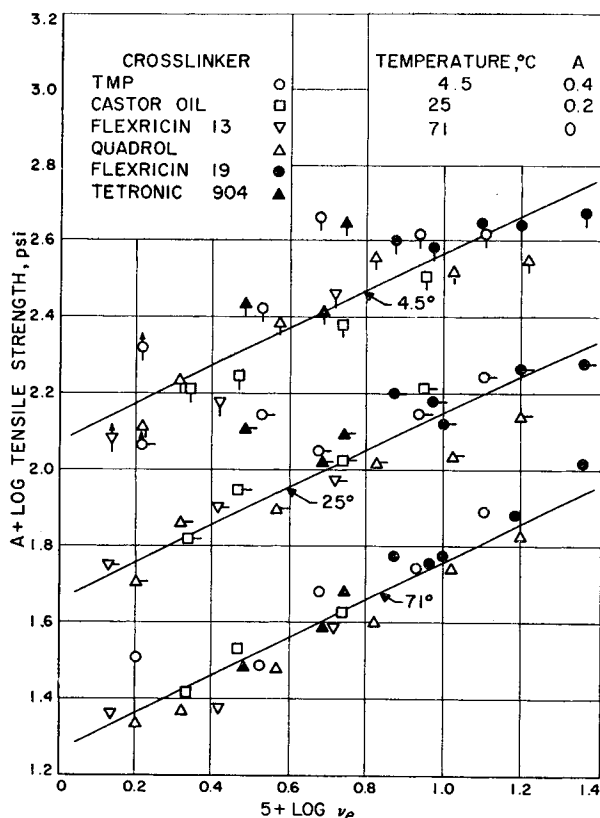


Fig. 12. Variation of log tensile strength at 4.5, 25, and 71°C. with  $\log \nu_e$  for elastomers with different types and concentrations of crosslinkers.

for only a few of the elastomers comprising the six series having different crosslinkers, and the results suggested that  $T_g$  depends somewhat on the sol fraction. However, because few measurements were made, it is necessary to assume that  $T_g$  is the same for each elastomer in the six series. These elastomers have  $[U] = 1.57$ , and the plot of  $T_g$  vs.  $[U]$  given in the previous paper<sup>1</sup> shows that  $T_g$  should be  $-48^\circ\text{C}$ .; this value is consistent with the ones that were measured on the elastomers now being considered.

Figure 12 shows the logarithm of the tensile strength at 71, 25, and  $4.5^\circ\text{C}$ . plotted against  $\log \nu_e$ . (Note that at 4.5 and  $25^\circ$  the points have been shifted upwards for clarity.) These test temperatures correspond to  $T - T_g$  values of 119, 73, and  $52.5^\circ\text{C}$ ., provided  $T_g$  actually equals  $-48^\circ\text{C}$ . Each line in Figure 12 was drawn with a slope of  $1/2$ , and the data fit this relation quite well. An upward-pointing arrow is attached to a few points to indicate that the sample did not break during the tensile test; thus, these points represent only the maximum stress achieved during the test and not

the tensile strength. The log-log plots in Figure 12 show that  $S_b = K_1(T)\nu_e^{1/2}$ , where  $S_b$  is the tensile strength and  $K_1(T)$  is a function only of temperature. The constant  $K_1$  can be considered to equal the tensile strength at temperature  $T$  of a hypothetical elastomer having one mole of effective chains per unit volume.

Tensile strengths at  $-18^\circ\text{C}$ . of elastomers in three series and at  $-23.5^\circ\text{C}$ . of elastomers in the three other series were also measured. However, at these temperatures, many samples did not break within the extension range that could be produced by the testing equipment. However, the data obtained are consistent with  $S_b = K_1(T)\nu_e^{1/2}$ , although they could be fitted equally well, or perhaps better, to a similar equation that contained  $\nu_e$  raised to some power less than  $1/2$ . Actually, the latter type of dependence is probably correct since, from general considerations, it seems quite probable that the tensile strength at low temperatures should be either independent of  $\nu_e$  or vary with some low power of  $\nu_e$ .

The dependence of the ultimate elongation on  $\nu_e$

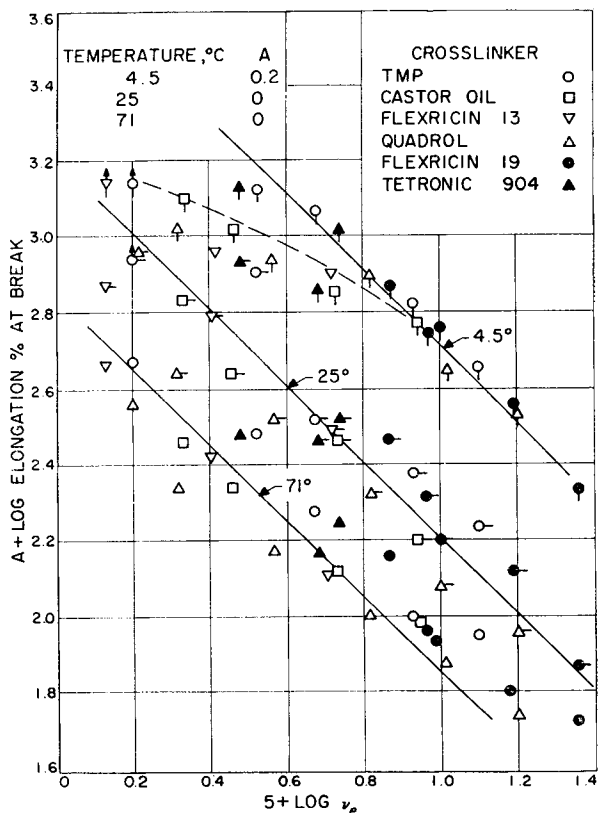


Fig. 13. Variation of log ultimate elongation (%) at 4.5, 25, and  $71^\circ\text{C}$ . with  $\log \nu_e$  for elastomers with different types and concentrations of crosslinkers.

at 71, 25, and 4.5°C. is shown by the log-log plots in Figure 13. (Note that the points at 4.5° have been shifted upwards for clarity.) At each temperature, the lines shown have a slope of  $-1$ , and except for some data at 4.5°C., the points lie reasonably close to the lines. Thus, the per cent ultimate elongation ( $100 \gamma_b$ ) is represented by the equation  $100\gamma_b = K_2(T)\nu_e^{-1}$ , where  $K_2(T)$  is a function only of temperature and represents the ultimate elongation at temperature  $T$  of a hypothetical elastomer having one mole of effective chains per unit volume.

However, Figure 13 shows that this equation represents the data at 4.5°C. only when  $\nu_e$  is greater than about  $6.3 \times 10^{-5}$ ; when  $\nu_e$  is less than this value, the ultimate elongation varies with  $(1/\nu_e)$  raised to some power less than unity. Although the ultimate elongations measured at  $-18$  and  $-23.5^\circ\text{C}$ . are not shown, they were found to vary with  $\nu_e$  in about the same way as the data at 4.5°C. The reason the low-temperature values deviate from the equation  $100\gamma_b = K_2(T)\nu_e^{-1}$  is not known. However, the deviations are observed at temperatures in the range over which plots of ultimate elongation against temperature pass through a maximum. In this temperature range, the ultimate elongation apparently does not depend on  $\nu_e$  as markedly as at higher temperatures. In

fact, such behavior is consistent with the curves shown in the previous paper<sup>1</sup> which compare the temperature dependence of the ultimate elongation of elastomers having different values of  $\nu_e$ . The large increase in elongation with decreasing temperature occurs because the internal viscosity of an elastomer increases, and thus it is not surprising that the ultimate elongation is less dependent on  $\nu_e$  at lower than at higher temperatures.

Figure 14 shows a plot of  $\log K_2(T)$  vs.  $T - T_g$  for the six series of elastomers having  $[U] = 1.57$  and for some series studied previously<sup>1</sup> which had  $[U] = 2.30$  and were prepared from PPG, TMP, and either TDI or HDI. For the elastomers having  $[U] = 1.57$ , the values of  $K_2$  at the three lowest temperatures apply only to those elastomers having  $\nu_e$  greater than  $6.3 \times 10^{-5}$ , as discussed above. Likewise, for the elastomers having  $[U] = 2.30$ , the values of  $K_2$  at the two lowest temperatures apply only to the elastomers having  $\nu_e$  greater than some critical value. (For the elastomers having  $[U] = 2.30$ , the point at  $T - T_g = 120$  was derived from data on HDI elastomers; the other points were derived from data on both TDI and HDI elastomers). Figure 14 shows that the points lie reasonably close to the parallel straight lines and that  $K_2$  does depend on  $[U]$ . Although the previous data suggested that ultimate elongations are independent of  $[U]$ , or nearly so, provided  $[U]$  is less than about 1.85, this observation was based on relatively few data. Also, because of the relatively large experimental error inherent in ultimate property data, it is often difficult to decide whether or not certain apparent trends are real. Although the ultimate elongation does depend on  $[U]$ , at least for large  $[U]$  values, it is probable that  $K_2(T)$  does not increase linearly with  $[U]$ ; thus this dependence may be small when  $[U]$  is less than some critical value.

Figure 14 also shows a plot of  $\log K_1(T)$  vs.  $T - T_g$  for the elastomers having  $[U] = 1.57$ . The points at the lowest temperatures are based on data not presented in this paper, although the other values of  $K_1(T)$  were obtained from lines in Figure 12. The data in the previous paper indicated little or no dependence of the tensile strength on  $\nu_e$ . This behavior may have been observed because  $\nu_e$  did not cover as wide a range as shown in Figure 12. More likely, however, it was observed because the elastomers had  $[U] = 2.30$ , and the tensile strength of such elastomers probably depends to a considerably less extent on  $\nu_e$  than do the tensile strengths of those elastomers having a lower  $[U]$  value.

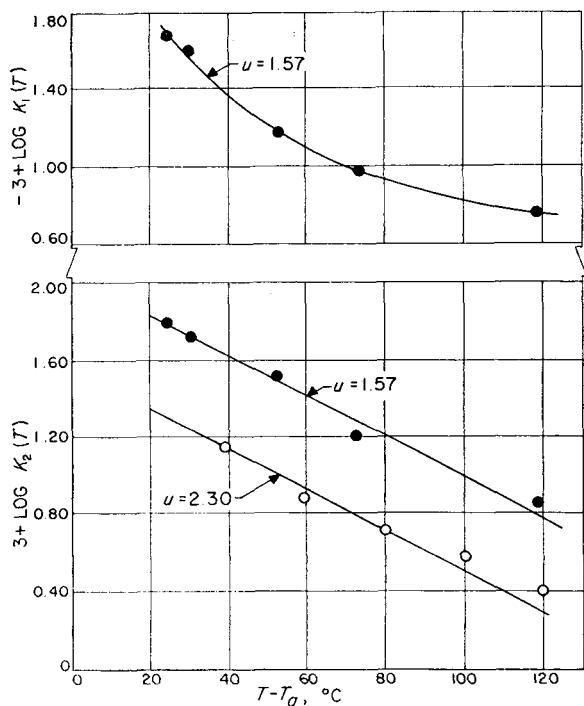


Fig. 14. Variation of  $\log K_1(T)$  and  $\log K_2(T)$  with  $T - T_g$  for various PPG elastomers.

### Correlation of Per Cent Sol with Exponent $n$ .

For strains between 0 and 0.7–1.0, a single stress-strain curve usually follows quite closely the equation  $\alpha S = K\gamma^n$ , where  $n$  and  $K$  are functions of the strain rate and temperature. At high temperatures or sufficiently low strain rates,  $n$  equals unity and  $K$  equals the modulus. However, as the temperature is decreased or the strain rate increased, the viscous forces in an elastomer become significant compared with the elastic retractive forces and the exponent  $n$  decreases. (For a Newtonian liquid,  $n$  equals zero.)

Now, consider a number of elastomers which are similar chemically, have approximately the same  $T_p$ , and have modulus values which decrease as their sol fractions increase. For such a series, the exponent  $n$  can often be correlated semiquantitatively with the sol fraction, provided the stress-strain curves are measured at a correctly selected temperature and strain rate. The temperature and strain rate should be selected such that  $n$  for the elastomer containing the smallest sol fraction is slightly less than unity. Under such experimental conditions, the elastomers will be characterized by  $n$  values which decrease as the sol fraction increases. An explanation for this behavior in terms of viscoelastic theory was given in the previous paper.<sup>1</sup>

To show the semiquantitative relationship between  $n$  and the sol fraction, values of  $n$  at 25° given in Tables IV to IX for the six series of elastomers are shown in Figure 15 plotted logarithmically against the logarithm of the sol fraction. The plot shows that  $n$  is approximately unity when the sol fraction is small but that it decreases with increasing sol fraction. The points do scatter considerably about the line, possibly

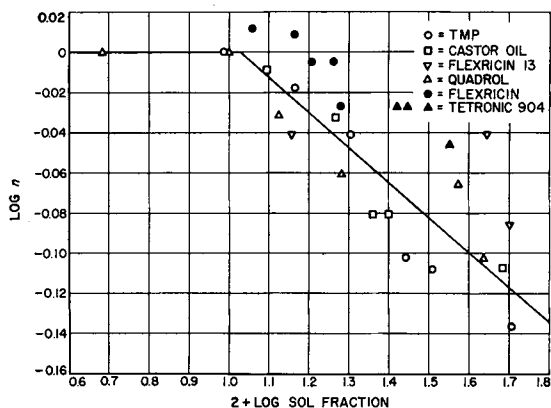


Fig. 15. Log-log plot showing the variation of  $n$  with sol fraction for elastomers with different types and concentrations of crosslinkers.

because neither the sol fractions nor the exponent  $n$  were measured with high precision. In fact, it is known that the values for the sol fractions, which were obtained as part of the equilibrium swelling experiments, tend to be less than the correct values, especially for the elastomers having the larger amounts of sol. However, the plot does show that  $n$  can be used as a semiquantitative index of the relative amounts of sol in certain series of elastomers.

### D. Comparison of Ultimate Properties of Various Elastomers

The previous paper<sup>1</sup> presented the ultimate properties of elastomers prepared from PPG, DPG, and TDI and sufficient TMP to form theoretically  $1.87 \times 10^{-4}$  chains/ml. The parameter  $[U]$  was varied, but those elastomers having  $[U]$  values of 1.42, 1.57, and 1.85 had essentially the same ultimate properties at equal values of  $T - T_p$ . Average values of the ultimate properties of these three elastomers are given by the single curves labeled PPG-TDI in Figures 16 and 17. Here, the curves labeled PPG-HDI represent the ultimate properties of similar elastomers prepared previously by the use of HDI and having  $[U]$  values of 1.42 and 1.85.

Figures 1 and 2 show the ultimate properties of elastomers with  $[U] = 1.42$ ,  $\nu = 1.87 \times 10^{-4}$ , and 0–20% isodecyl pelargonate, and Figures 3 and 4 show the ultimate properties of elastomers which also had  $[U] = 1.42$  and  $\nu = 1.87 \times 10^{-4}$  but were linked by different diisocyanates. The curves from Figures 1–4 are also shown in Figures 16 and 17. These figures show that the four types of polyurethane elastomers have the same ultimate properties at equal values of  $T - T_p$ .

As shown by Figures 16 and 17, the ultimate

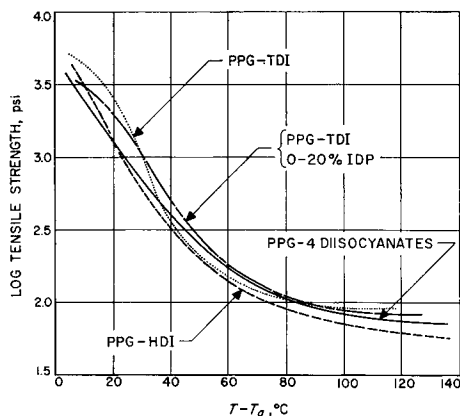


Fig. 16. Comparison of the tensile strengths of four series of PPG elastomers.

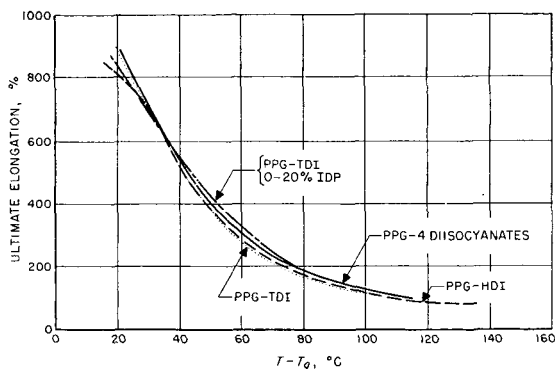


Fig. 17. Comparison of the ultimate elongations of four series of PPG elastomers.

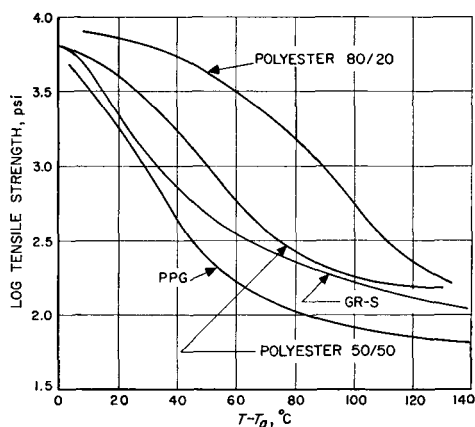


Fig. 18. Comparison of the tensile strengths of three types of polyurethane elastomers and an SBR (GR-S) rubber.

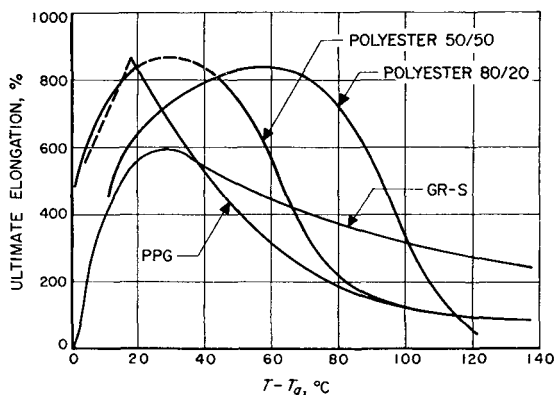


Fig. 19. Comparison of the ultimate elongations of three types of polyurethane elastomers and an SBR (GR-S) rubber.

properties of a large number of elastomers prepared from PPG and a given concentration of TMP can be represented by single curves; these curves are shown in Figures 18 and 19 labeled PPG. For comparison, Figures 18 and 19 also show the curves

from Figures 5-8, which represent the ultimate properties of the elastomers prepared from polyester 50/50 and polyester 80/20. Figures 18 and 19 also show the ultimate properties of an SBR (GR-S) rubber which had about  $1.2 \times 10^{-4}$  chains/ml. and which was extensively studied previously.<sup>4</sup> The ultimate elongations of the SBR rubber are not strictly comparable, primarily at the low temperatures, to those of the polyurethane elastomers, because the ultimate elongations of the polyurethane elastomers were measured on dumbbell-shaped tensile specimens and were calculated from the cross-head displacement by the assumption that the effective gage length remained constant. Because the effective gage length does not remain constant, ultimate elongations that are greater than a few hundred per cent tend to be high. On the other hand, the ultimate elongations of the SBR rubber were measured by testing rings, and thus the elongations are quite reliable. These considerations suggest that the maximum elongations of the polyurethane elastomers may not be as much greater than for the SBR rubber as shown in Figure 19. However, Figure 19 does show that the ultimate elongations for the four different types of elastomers do vary differently with temperature, although the fundamental reasons for these differences are not known.

Figure 18 shows that the tensile strengths for the different types of elastomers vary differently with temperature. However, it appears that the tensile strength for each elastomer type approaches  $6.5-8.0 \times 10^3$  psi ( $4.5-5.5 \times 10^8$  dynes/cm.<sup>2</sup>) at low temperatures.

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## Synopsis

The ultimate tensile properties (tensile strength and elongation at rupture) of various series of polyurethane elastomers which apparently do not crystallize were studied. Elastomers which contained 0-20% isodecyl pelargonate were prepared from polyoxypropylene glycol 2025 (PPG), dipropylene glycol (DPG), trimethylolpropane (TMP), and toluene 2,4-diisocyanate (TDI); the ratios of ingredi-

ents were varied so that all elastomers had approximately the same number of chains per unit volume  $\nu$  and the same concentration of urethane groups [U]. Unplasticized elastomers were also prepared that were similar except that they were linked by hexamethylene 1,6-diisocyanate, TDI, *m*-phenylene diisocyanate, and naphthalene 1,5-diisocyanate. Over a wide temperature range, the ultimate properties of elastomers in both series were identical at equal values of  $T - T_g$ . Series of elastomers were also prepared from TMP, TDI, triethylene glycol, and two polyester diols: a 50/50 and an 80/20 copolymer of  $\epsilon$ -caprolactone and methyl  $\epsilon$ -caprolactone. In these series,  $\nu$  was held constant and [U] was varied. Within each series, the ultimate properties were identical at equal values of  $T - T_g$ , although the ultimate properties depended on the nature of the polyester diol and were different from those of similar elastomers prepared from PPG. To study the effect of the crosslinker type and the concentration, elastomers having a constant [U] were prepared from PPG, DPG, TDI, and six crosslinkers, three being trihydroxy and three being tetrahydroxy materials. At a given temperature, the tensile strength and ultimate elongation appeared to be independent of the crosslinker type and proportional to  $\nu_e^{1/2}$  and  $1/\nu_e$ , respectively, the proportionality constants being temperature-dependent. On these elastomers, equilibrium swelling ratios in benzene and rough values of the per cent sol were also measured and certain relations among these and the mechanical properties were observed.

### Résumé

On a étudié les propriétés de tension limite (force de tension et élongation à la rupture) de différentes séries d'élastomères de polyuréthane qui apparemment ne cristallisent pas. Des élastomères qui renferment 0-20% de pèlargonate d'isodécyle ont été préparés à partir de polyoxypropylène-glycol 2025 (PPG) dipropylène glycol (DPG), triméthylolpropane (TMP) et de toluène 2,4-diisocyanate (TDI). Les rapports de réactifs ont été variés de sorte que tous les élastomères aient à peu près le même nombre de chaînes par unité de volume  $\nu$  et la même concentration de groupes uréthanes [U]. On a préparé de même des élastomères non plastifiés excepté qu'ils ont été pontés par de l'hexaméthylène 1,6-diisocyanate, TDI, le *m*-phénylène diisocyanate, et du naphthalène 1,5-diisocyanate. Dans un grand domaine de température, les propriétés limites de ces élastomères, sont identiques dans les deux séries à valeur  $T - T_g$  égale. Des séries d'élastomères ont aussi été préparées à partir de TMT, TDI, triéthylène glycol, et deux polyesters diols: un copolymère 50/50 et 80/20 de  $\epsilon$ -caprolactone et de méthyl  $\epsilon$ -caprolactone. Dans ces séries,  $\nu$  était gardé constant et [U] était varié. Dans chacune de ces séries, les propriétés limites étaient identiques à égale valeur de  $T - T_g$  bien que ces propriétés dépendent de la nature du polyester diol et étaient différentes de celles

d'élastomères similaires préparés à partir de PPG. Pour étudier l'effet du type de l'agent de pontage et de la concentration, des élastomères ayant un [U] constant ont été préparés à partir de PPG, DPG, TDI, et six "agents de pontage", trois étant de dérivés trihydroxylés et trois autres des tetrahydroxylés. A température donnée, la force de tension et l'élongation limite semblent être indépendantes du type de l'agent de pontage et proportionnelles respectivement à  $\nu_e^{1/2}$  et  $1/\nu_e$  les constantes de proportionnalité étant indépendantes de la température. Sur ces élastomères les rapports de gonflement à l'équilibre dans le benzène et les valeurs approximatives des % de sol ont également été mesurés et on a observé certaines relations entre ces propriétés et les propriétés mécaniques.

### Zusammenfassung

Das Verhalten verschiedener Reihen offenbar nicht kristallisierender Polyurethanelastomere bei Zerreihsversuchen (Zugfestigkeit, Reissdehnung) wurde untersucht. Elastomere mit einem Gehalt an Isodecylpelargonat von 0-20% wurden aus Polyoxypropylenglykol 2025 (PPG), Dipropylenglykol (DPG), Trimethylolpropan (TMP) und Toluyl-2,4-diisocyanat (TDI) dargestellt; das Verhältnis der Bestandteile wurde so variiert, dass alle Elastomeren annähernd die gleiche Kettenzahl pro Einheitsvolumen  $\nu$  und die gleiche Konzentration an Urethangruppen [U] besaßen. Ähnliche nicht weichgemachte Elastomere wurden gleichfalls dargestellt, mit der Ausnahme, dass sie mit Hexamethylen-1,6-diisocyanat, TDI, *m*-Phenylendiisocyanat und Naphthalin-1,5-diisocyanat vernetzt waren. In einem weiten Temperaturbereich waren die Reisseigenschaften der Elastomere beider Serien bei gleichen Werten von  $T - T_g$  identisch. Auch aus TMP, TDI, Triäthylenglykol und zwei Polyesterdiolen, ein 50/50 und ein 80/20 Copolymer von  $\epsilon$ -Caprolacton und Methyl- $\epsilon$ -caprolacton, wurden Elastomerreihen dargestellt. Bei diesen Reihen wurde  $\nu$  konstant gehalten und [U] variiert. Innerhalb jeder Reihe waren die Reisseigenschaften bei gleichen Werten von  $T - T_g$  identisch, hingen jedoch von der Natur des Polyesterdiols ab und unterschieden sich von denjenigen ähnlicher Elastomere aus PPG. Zur Untersuchung des Einflusses des Vernetzertyps und seiner Konzentration wurden Elastomere mit konstantem [U] aus PPG, DPG, TDI und sechs Vernetzern, drei Trihydroxy und drei Tetrahydroxyverbindungen, dargestellt. Bei einer gegebenen Temperatur waren Zugfestigkeit und Reissdehnung offenbar vom Vernetzertyp unabhängig und zu  $\nu_e^{1/2}$  bzw.  $1/\nu_e$  proportional, wobei der Proportionalitätsfaktor temperatureabhängig war. An diesen Elastomeren wurden auch der Gleichgewichtsquellungsgrad in Benzol und ungefähre Werte für die % Sol gemessen sowie gewisse Beziehungen zwischen diesen und den mechanischen Eigenschaften beobachtet.

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