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Urethane Elastomers Containing Disulfide and Tetrasulfide Linkages

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The chemorheology of two cross-linked polyurethane elastomers containing (1) disulfide groups and (2) tetrasulfide groups was investigated by stress relaxation experiments. It was found that the tetrasulfide-containing elastomer underwent stress decay at a rate 10 times faster than the disulfide-containing elastomer, showing that the tetrasulfide linkage undergoes bond interchange much more rapidly than the disulfide linkage. Spectroscopic evidence is cited tending to confirm the greater stability of the disulfide linkage. The behavior of a cross-linked polyurethane elastomer without polysulfide linkages is presented for comparison.

Introduction

The chemorheological behavior of thiokol-type polymers has been thoroughly investigated by a number of workers.¹ In the case of cross-linked polymers of this type it has been established by Tobolsky and co-workers that stress relaxation takes place by a mechanism of interchange between polysulfide linkages. This mechanism involves scission of the linkage and recombination to give an unstressed chain. The kinetics of the process have been completely worked out on the basis of this mechanism.¹ On the basis of a proposal of Gee² and of spectroscopic data on low molecular weight polysulfides^{3,4} it would seem that the disulfide linkage should be more stable than the higher polysulfides. In order to test this hypothesis, two "model" compounds were prepared. Both are cross-linked polyurethane elastomers differing only in that one contains disulfide linkages while the other contains tetrasulfide linkages. Such polyurethane elastomers are conveniently prepared in the following manner.

A low molecular weight polyether or polyester, terminated with hydroxyl groups, is treated with excess diisocyanate (usually 2,4-toluene diisocyanate), to form polyurethane chains terminated by isocyanate groups. This material, the prepolymer, can be cured by reaction with hydroxyl-containing substances, and cross links can be introduced by curing with triols. The properties of these polymers have been described elsewhere.⁵⁻⁷ Schonfeld⁸ introduced monosulfide bonds into such a polymer by utilizing the hydroxy-terminated polythioacetal, namely, $\text{HOCH}_2\text{CH}_2(\text{-SCH}_2\text{CHOCHO-$

$\text{CH}_2\text{CH}_2)_n\text{-SCH}_2\text{CH}_2\text{OH}$. However, the physical properties of the polymer were not described.

In the present work, the disulfide linkage was introduced into the polymer by partially replacing the curing agent (1,2,6-hexanetriol) with dithiodiglycol, namely, $\text{HOCH}_2\text{CH}_2\text{-S-S-CH}_2\text{CH}_2\text{OH}$. The tetrasulfide linkage was added in an identical manner except tetrathiodiglycol was used, namely, $\text{HOCH}_2\text{-CH}_2\text{-S-S-S-S-CH}_2\text{CH}_2\text{OH}$. The polyurethane elastomer prepared from 1,2,6-hexanetriol was studied as a basis for comparison.

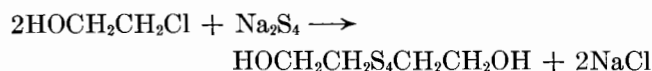
Experimental

Urethane prepolymer, Cyanoprene 4590, was kindly donated by the Cyanamid Corporation. Cyanoprene 4590 is a polyester terminated by isocyanate linkages. The free NCO concentration of cyanoprene 4590 is about 2.75%.

Tetrathiodiglycol was prepared by treating 2 moles

- (1) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley and Sons, Inc., New York, N. Y., 1960, Section IV, pp. 12, 13, and Section V, p. 8.
- (2) F. Fairbrother, G. Gee, and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955).
- (3) J. E. Baer and M. Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).
- (4) J. A. Barltrop, P. M. Hayes, and M. Calvin, *ibid.*, **76**, 4348 (1954).
- (5) J. A. Offenbach and A. V. Tobolsky, *J. Colloid Sci.*, **11**, 39 (1956).
- (6) P. C. Colodny and A. V. Tobolsky, *J. Am. Chem. Soc.*, **79**, 4320 (1957).
- (7) R. J. Athey, *Rubber Age* (N. Y.), **85**, 77 (1959).
- (8) E. Schonfeld, *J. Polymer Sci.*, **49**, 277 (1961).

of 2-chloroethanol with 1 mole of sodium tetrasulfide in an aqueous medium according to the reaction



After adding the 2-chloroethanol over a period of 0.5 hr. (using 0.5 *M* quantities) the temperature had risen from 40 to 75°. The reactants were held at 70–80° for a period of 2 hr. On cooling to room temperature the product was isolated by ether extraction, filtered, and dried by heating for 2 days in a vacuum oven at 50°. The product was a yellow oil and the analysis corresponded very closely to the composition $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_4$.

Dithiodiglycol was obtained commercially from the Wateree Chemical Co.

The cure recipes studied are shown in Table I. The required weight of prepolymer was weighed out and heated to 100° *in vacuo* and the required quantities of curing agents were added. The mixture was stirred well and poured into a mold preheated to 130–135°. The cure mixture became extremely viscous and almost solidified within a few minutes. The sample was

Table I

	Sample number		
	1	2	3
Urethane prepolymer	20 g.	20 g.	20 g.
1,2,3-Hexanetriol ^a	0.29 g.	0.29 g.	0.509 g.
Dithiodiglycol	0.411 g.
Tetrathiodiglycol	...	0.56 ml.	...

^a Acetone solution containing 0.29 g. of 1,2,6-hexanetriol per ml.

then molded at 130° for 30 min. under a pressure of 10,000 p.s.i. Curing was completed by heating in a forced-draught oven at 100° for 24 hr. A Gehman torsion tester⁹ was used to determine the 10-sec. modulus ($3G(10)$) as a function of temperature and the stress relaxation studies were made with a relaxation balance.¹⁰

Results and Discussion

Figure 1 shows the 10-sec. modulus temperature curves for samples 1, 2, and 3 prepared according to the recipes in Table I. Each network chain in sample 1 contains one disulfide linkage and has the structure

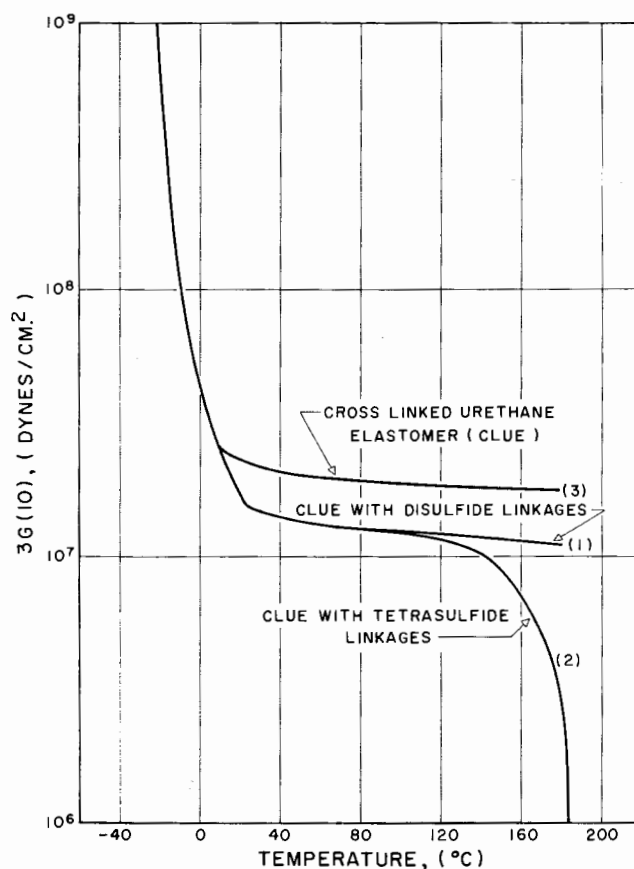
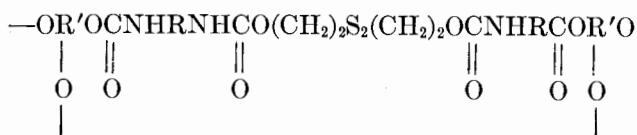


Figure 1. Ten-sec. modulus ($3G(10)$) plotted as a function of temperature for samples 1, 2, and 3.

where R is the urethane prepolymer backbone and R' is $\text{CH}_2\text{C}(\text{C}_2\text{H}_5)\text{CH}_2$. Sample 2 has a structure identical with the above except that S_2 is replaced by S_4 .

Inspection of Fig. 1 shows that, up to 180°, samples 1 and 3 exhibit the characteristic viscoelastic behavior of a cross-linked polymer with the rubbery flow region entirely suppressed. Sample 2 on the other hand has an apparent rubbery flow region starting at just above 100°. Since polymers 1 and 2 are identical in structure with the exception of the polysulfide linkage, it is concluded that the apparent rubbery flow region in sample 2 is due to bond interchange between tetrasulfide groups. The various linkages of sample 3 and these plus the disulfide linkages of sample 1 are "stable" within the 10-sec. measurement interval up to 180°.

Figure 2 shows the relative stress decay of sample 3 at 120°. This is compared with sample 1 at 120° and sample 2 at 100° and it can be seen that stress decay in sample 2 is faster than in the other polymers

(9) ASTM Book of Standards D1043-51, 1958.

(10) Ref. 1, Section IV, p. 1, and Plate IV, p. 1.

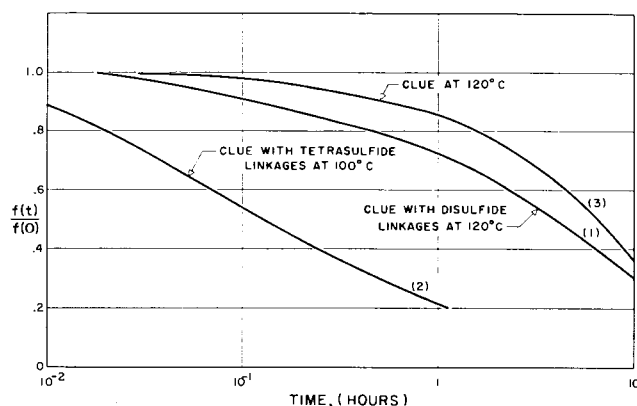


Figure 2. Relative stress at constant extension vs. log time for sample 1 at 120°, for sample 2 at 100°, and for sample 3 at 120°.

though 20° lower in temperature. The chemical relaxation time, τ_{ch} , defined as the time when the ratio of the stress at time t to the initial stress ($f(t)/f(0)$) is equal to $1/e$, is presented in Table II for the three polymers at 120°. This further serves to point out the striking differences among the three samples.

Table II

Sample	Reference	τ_{ch} , sec.
1	This work	26.3×10^3
2	This work	3.5×10^2
3	Sample IV of ref. 6	34.9×10^3

Figure 3 gives a plot of the relative stress decay vs. logarithmic time of sample 2 at several temperatures

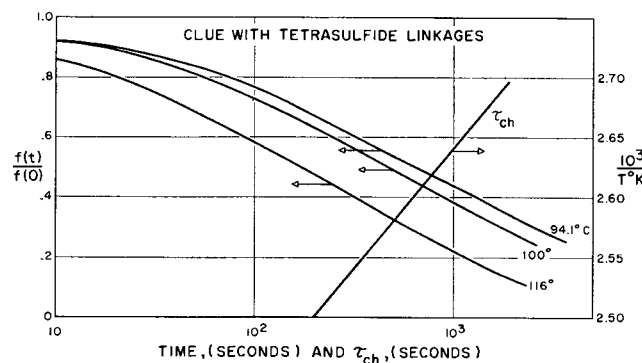


Figure 3. Relative stress at constant extension vs. log time for sample 2 at various temperatures, and also log τ_{ch} vs. $1/T$ for sample 2.

and also includes a plot of log τ_{ch} as a function of $1/T$. The slope of this line gives the activation energy for chemical flow¹ and this has a value of 24.4 kcal. mole⁻¹. The agreement between this value and the value of 25.9 kcal. mole⁻¹ obtained for the activation energy for stress decay by bond interchange in cross-linked polyethylene tetrasulfide¹¹ is reasonably good.

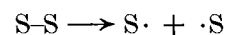
The specific rate constant for the interchange reaction in sample 2 is 1.00×10^{-3} sec.⁻¹ at 100°. For cross-linked polyethylene tetrasulfide,¹¹ the specific rate constant is 1.79×10^{-3} sec.⁻¹ at this temperature. The similarity between the two values tends to show that the mechanism of stress decay in sample 2 is the same as in cross-linked polyethylene tetrasulfide, that is, interchange between tetrasulfide linkages.

The results presented above indicate that the disulfide linkage is much more stable than the tetrasulfide linkage. That this is so can be explained by Gee's analogy² between the bonding in O₂ and that in S₂. He attributes the binding in S₂ to a normal single bond plus two three-electron bonds. Thus in the scission of a tetrasulfide (or higher polysulfide) linkage, the odd electron on each free-radical end will be able to form a three-electron bond with the adjacent sulfur atom as shown.



In the scission of a disulfide linkage, three-electron bond formation is not possible and thus the linkage is more stable than higher polysulfide linkages.

Calvin⁴ and co-workers studied the ultraviolet absorption spectra of cyclic disulfides and attributed the absorption peak found at 2500 Å. to the transition



Baer and Carmack³ observed the ultraviolet spectra of low molecular weight aliphatic disulfides and tetrasulfides and found the absorption peak for the disulfides to be at 2520 Å. corresponding to an energy of 115 kcal. mole⁻¹ and the absorption peak for the tetrasulfides to be at 3000 Å. corresponding to an energy of 95.2 kcal. mole⁻¹.

If the ultraviolet absorption of polysulfides is due to the transition suggested by Calvin, the observations of Baer and Carmack tend to lend further support to the greater stability of the disulfide linkage relative to the tetrasulfide linkage. The disulfide linkage may however show rapid interchange in the presence of ionic catalysts such as mercaptides.

(11) A. V. Tobolsky, R. B. Beevers, and G. D. T. Owen, *J. Colloid Sci.*, **18**, 359 (1963).