Only terms of the type

$$\int \psi_T{}^\dagger \psi_B V \psi_T \psi_B{}^\dagger \mathrm{d}\tau_T \mathrm{d}\tau_B$$

are considered important. That is, the permanent moments, like

$$e\int \psi_T \Sigma x_T \psi_T \mathrm{d}\tau_T$$

are taken as zero. The first-order energy correction for the ground state is therefore zero. The correct wave functions for the degenerate manifold are

$$\psi_\pm = 2^{-1/2}(\psi_T{}^\dagger \psi_B \pm \psi_T \psi_B{}^\dagger)$$

The expectation value of V for these functions does not involve the term

$$-2\Sigma z_T z_B$$

because the transition moments for the monomeric component species are in-plane. What is left is actually the dot product of the respective transition moments, each referred to its own coördinate frame

$$W_\pm = \pm \overrightarrow{m_T} \cdot \overrightarrow{m_B}/R^3$$

where the x component, say, of $\overrightarrow{m_T}$ is

$$(m_T)_x = e\int \psi_T \Sigma x_T \psi_T{}^\dagger \mathrm{d}\tau_T$$

The transition moment for the dimer absorption is

$$\overrightarrow{m_\pm} = \mathrm{e}\int \psi_T \psi_B [\overrightarrow{\mathrm{i}}(\Sigma x_T + \Sigma x_B) + \overrightarrow{\mathrm{j}}(\Sigma y_T + \Sigma y_B)]\, 2^{-1/2}(\psi_T{}^\dagger \psi_B \pm \psi_T \psi_B{}^\dagger)\mathrm{d}\tau_T \mathrm{d}\tau_B = 2^{-1/2}(\overrightarrow{m_T} \pm \overrightarrow{m_B})$$

To illustrate the use of these formulas, let us now assume that the nitrogen atoms in the molecules are in fact oriented as shown in Fig. 7. We would then have

$$\overrightarrow{m_T} = -\overrightarrow{m_B}$$

Substituting in the formula for the energy we find that the lower energy state is W_+

$$+ m_T \cdot (-m_T)/R^3$$

with the corresponding wave function ψ_+. The transition moment from the ground state (long wave length component of the doublet) is

$$2^{-1/2}(m_T + (-m_T)) = 0$$

The transition moment to the state with wave function ψ_-, and energy

$$W_- = + m_T{}^2/R^3$$

is $2^{-1/2}\, \overrightarrow{m_T}$, leading to an intensity proportional to the square, $2\,m_T{}^2$ which is twice the intensity for a single molecule.

Even if the orientations had been switched so as to put the nitrogen atoms directly on top of one another, giving

$$\overrightarrow{m_T} = \overrightarrow{m_B}$$

the same physical result would have been obtained, although the phases in the wave functions would be reversed. The physical result depends on having the transition moments parallel. The fact that experimentally the long wave length component (species Y in Fig. 3) is much the weaker tells us that if a sandwich configuration is correct then the transition moments of the individual dye cations must indeed be virtually parallel.

The dimer split is, of course, $W_- - W_+$ or

$$2\,|m_T|^2/R^3$$

From this we may obtain R by using $|m_T|$ from Table I and the observed splittings for iodide and perchlorate, respectively, 2300 and 4800 cm.$^{-1}$. This gives for the iodide R = 5.8 Å., and for the perchlorate R = 4.5 Å.

The dipole approximation introduces some error (It would give a calculated split which is too high by *ca.* $^1/_3$. Thus we should use $\sim ^4/_3$ the observed splits, which would reduce the calculated R by 10%.) Also, taking the splitting as the energy difference between the peaks results in uncertainty. Even so the values obtained are certainly reasonable. The usual distance between centers for un-charged aromatic systems on top of each other is 3.4 Å. Considering the fact that the dye cations are charged and that this charge cannot be neutralized perfectly by the anions, it seems as if the cations in the perchlorate dimer are virtually in contact. In the iodide it appears that the dye cations actually are separated to a degree by the iodide ions entering as "filling" to the sandwich. If the iodide ions were completely inside the sandwich, R would be 7.7 Å., based on an iodide ion diameter of 4.3 Å.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Chemorheological Study of Polyurethan Elastomers[1]

BY P. C. COLODNY[2] AND A. V. TOBOLSKY

RECEIVED APRIL 26, 1957

Two series of polyurethan elastomers were prepared which contained (a) predominantly urethan linkages and (b) equal numbers of urethan and substituted urea or biuret groups. The chemorheology of these samples was investigated by stress relaxation experiments. It was found that the urethan linkages underwent scission at a rate one-tenth that of the combined rate of the substituted urea and biuret groups.

Introduction

The chemorheology of polyurethan elastomers based on polyester and polyether chains has recently been investigated by Offenbach and Tobolsky.[3] Polyester rubbers cured with benzoyl peroxide had been studied previously.[4] From these works it was concluded that neither the scission of

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(1) This article is based upon a dissertation submitted by Paul C. Colodny in partial fullfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

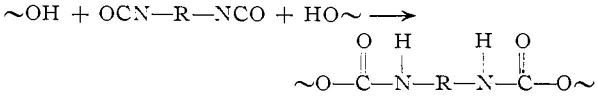
(2) Thiokol Chemical Corporation Fellow 1955-1957.

(3) J. A. Offenbach and A. V. Tobolsky, *J. Colloid Sci.*, **11**, 39 (1956).

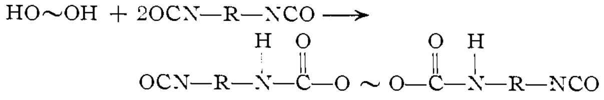
(4) R. D. Andrews, Ph.D. Thesis, Princeton University, 1948.

the ester nor the ether links along the chain contributed appreciably to the stress relaxation of the Vulcollan type rubbers or du Pont Adiprene B at elevated temperatures. The cause of the stress decay at constant elongation was attributed to the scission of urethan, substituted urea and biuret linkages with the urea and biuret groups being thought chiefly responsible.

In this paper clear evidence is presented that shows the relative stability of the urethan groups compared to the substituted urea linkages and the biuret linkages. The basis of this evidence rests with stress relaxation data of rubber samples so prepared from the same linear polyester that one class of specimens contains nearly all urethan links and the other class contains half urethan and the other half both substituted urea and biuret groups. The samples containing principally urethan linkages were prepared first by the direct reaction of the polyester with stoichiometric amounts of isocyanate. Sample I was prepared by the reaction of this polyester, an 80–20 mole % ethylene–propylene adipate, with an equivalent amount of 2,4-toluene diisocyanate. This gave a linear product that flowed at elevated temperature. Sample II was prepared by the reaction of the polyester with methyl triphenyl triisocyanate. Samples III and IV discussed below were prepared as follows. An isocyanate terminated polyester (A), commonly referred to as "prepolymer,"[5] was prepared by the addition of excess diisocyanate to the polyester. Sample III was formed by curing this prepolymer with 1,4-butanediol. A linear material similar to I was obtained which indicates that little or no cross-linking was introduced by allophanate formation. Sample IV was prepared by treating this same prepolymer with 1,2,6-hexanetriol. Sample V was prepared from prepolymer A by the addition of water to form a network containing substituted urea linkages and biuret cross linkages, the sum of these being equal to the number of urethan linkages.



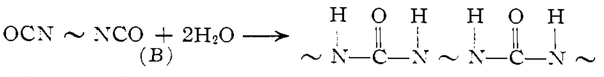
$$\sim OH + OCN{-}R{-}NCO + HO\sim \longrightarrow \sim O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O\sim$$



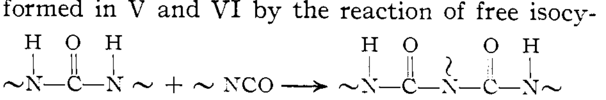
$$HO\sim OH + 2OCN{-}R{-}NCO \longrightarrow OCN{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O \sim O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}NCO$$

(A)

Another prepolymer (B) was prepared using another polyester, Thiokol ZL-219, and the same diisocyanate. Sample VI was prepared by curing this prepolymer with excess water. A substantial number of trisubstituted biuret linkages were also formed in V and VI by the reaction of free isocyanate with the urea hydrogen atoms as indicated by the network structure of the elastomer. The purpose of this duplication was to minimize the possibility of erroneous results due to catalytic effects from trace impurities.



$$\underset{(B)}{OCN \sim NCO} + 2H_2O \longrightarrow \sim \overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}} \sim \overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}} \sim$$



$$\sim\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}} \sim + \sim NCO \longrightarrow \sim\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{\wr}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}\sim$$

(VI)

Experimental

Material.—The polyester used was the Thiokol ZL-219 and an 80-20 mole % ethylene–propylene adipate. The Thiokol polyester had an acid no. of 2.4 and an isocyanate equiv. wt. of 1170 while the ethylene–propylene adipate had an acid no. of 3 and an isocyanate equiv. wt. of 1580. These were dried by heating for 4 hours at 120–130° while a stream of nitrogen was bubbled through the material. The triisocyanate used was Mobay Mondur TM consisting of a 20% solution of methyl triphenyl triisocyanate in CH_2Cl_2. The diisocyanate was du Pont Hylene T which analyzed for 95% 2,4-toluene diisocyanate. The diol and triol were highly purified 1,4-butanediol and 1,2,6-hexanetriol.

Preparation of Elastomers with Predominantly Urethan Linkages.—Sample I was prepared by the reaction of 50.0 g. (0.0316 isocyanate equiv. wt.) of the ethylene–propylene adipate with 2.75 g. (0.0316 equiv.) of 2,4-toluene diisocyanate in a mold at 70° for 4 hours. 131 g. (0.0826 isocyanate equiv. wt.) of the polyester was treated with 10.1 g. (0.0826 equiv.) of methyl triphenyl triisocyanate in CH_2Cl_2 solution for the preparation of II. The reaction was carried out in a sample mold placed in a vacuum oven at 75°. As the sample contained numerous bubbles due to the evaporation of the solvent it was passed through a rubber mill and pressed out at 150° for 30 min. at 20,000 p.s.i.

The prepolymer for III, IV and V was prepared by the addition of 49.5 g. (0.284 mole) of 2,4-toluene diisocyanate, a 10% excess, to 409.9 g. (0.258 isocyanate equiv. wt.) of ethylene–propylene adipate at room temperature and under an atmosphere of nitrogen. The mixture was allowed to react for 48 hours to give a prepolymer with an equiv. wt. of 1760. III was prepared by the reaction of 52.3 g. (0.0298 equiv.) of this prepolymer with 1.34 g. (0.0298 equiv.) of 1,4-butanediol while IV was formed from 51.5 g. (0.0294 equiv.) of prepolymer and 1.31 g. (0.0294 equiv.) of 1,2,6-hexanetriol. The conditions were the same as for I.

Preparation of Samples with Substituted Urea and Biuret Linkages.—Sample V was prepared by the reaction of 50.0 g. (0.0285 equiv.) of this same prepolymer and 1 g., fourfold excess, of water. A prepolymer prepared from 2400 g. (2.03 isocyanate equiv. wt.) of Thiokol Polyester ZL-219 and 394 g. (2.23 moles), a 10% excess, 2,4 toluene diisocyanate gave an equiv. wt. of 1230. 50.0 g. (0.0406 equiv.) of this was mixed with 1 g., also a fourfold excess, of water to give VI. These reactions were carried out at 75° and required 72 hours for completion.

Stress Relaxation Measurements.—All measurements were made on Firestone relaxometers[6] which had been modified for strip samples.[7] All samples were post cured for 1 week at 100° prior to physical study to ensure complete cure.

Results and Discussion

Stress relaxation studies were performed on these samples over a temperature range from 100 to 140° at 20% elongation. The data have been plotted as relative stress, f/f_0, as a function of logarithmic time. As it had been shown in previous studies that such relaxation curves are independent of elongation up to fairly large strains, elongation was not investigated as a variable. The reference stress, f_0, was determined by graphical interpolation for the time 0.01 hour. Duplicate determinations were completely superimposable.

The data for the cure of the ethylene–propylene adipate polyester with the triisocyanate are presented in Fig. 1. Figure 2 contains a comparison of the stress decay curves at 120°. It is apparent

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(5) (a) E. Muller, *et al.*, *Rubber Chem. and Technol.*, **26**, 493 (1953); (b) O. Bayer, *et al.*, *ibid.*, **23**, 812 (1950).

(6) A. V. Tobolsky, I. B. Prettyman and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).

(7) J. A. Offenbach, Ph.D. Thesis, Princeton University, 1955.

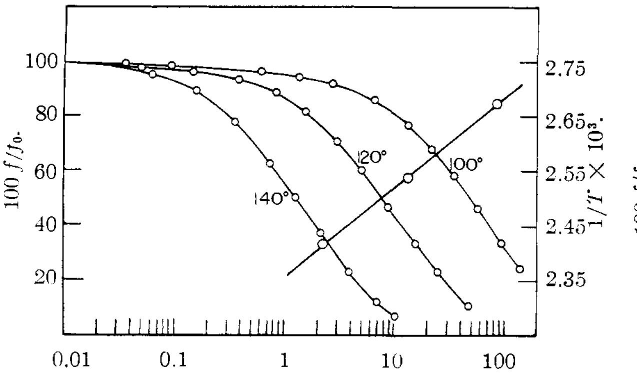


Fig. 1.—Stress relaxation of II.

that all samples approached zero stress asymptotically and underwent a major portion of decay within two decades of logarithmic time. Similar behavior had been observed for the polysulfide,[8] natural and silicone[9] rubbers and other polyurethans.[3] The cause for the stress decay in these materials has been attributed to chemical scission of network chains. Decay due to molecular flow has been shown to extend not over two but over many cycles of logarithmic time.

The stress at a time, t, is related to the number of effective network chains[10] by the equation

$$f = NkT\left(\alpha - \frac{1}{\alpha^2}\right)$$

where f is the stress based on the original cross section at relative length α and N is the number of network chains per cubic centimeter which have never been cut. The stress decay at constant strain and elevated temperature of these rubbers has been found to obey approximately the equation $f/f_0 = e - t/\tau$, where τ is the relaxation time of the sample at the specified temperature. The relaxation time, τ, is equal to the time required for the stress to decay to $1/e$ or 36.8% of its reference value. As τ may be considered to be the reciprocal of a chemical rate constant, it is possible to calculate an activation energy for the process from the slope of a plot of log τ *vs.* $1/T$. The relaxation times in hours and activation energies are listed in Table I. The values for samples I and III were approximately zero.

Table I

Stress-Relaxation Time (Hours)

Sample	τ100°	τ120°	τ140°	$E‡$(kcal./mole)
II	87	14	2.3	27.7 ± 1.5
IV	66	9.7	1.6	28.4 ± 1.5
V	12.7	1.6	0.28	29.2 ± 1.0
VI	14	1.65	0.25	30.8 ± 2.0

Structure of Polymers.—Samples I, II, III and IV contain, besides the polyester backbone, predominantly urethan linkages prepared by the reaction of the hydroxyl terminals with isocyanate

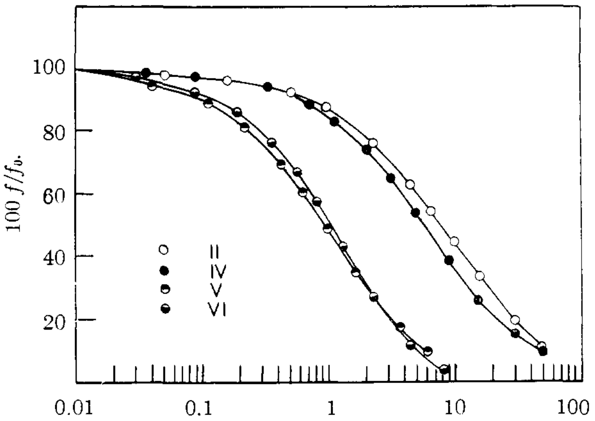
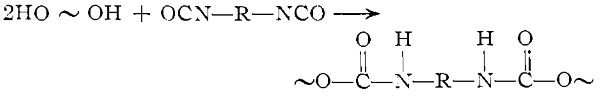
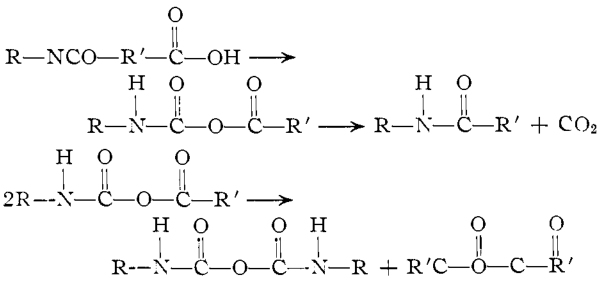


Fig. 2.—Stress relaxation at 120°.



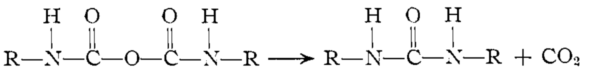
$$2\mathrm{HO}\sim\mathrm{OH} + \mathrm{OCN{-}R{-}NCO} \longrightarrow \sim\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\mathrm{R}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}\sim$$

Small amounts of amide and substituted urea groups also are present due to the reaction of terminal carboxyl groups[11] with isocyanates resulting with the formation of a mixed anhydride which is followed by the loss of carbon dioxide. The mixed anhydride can also undergo a disproportionation into anhydrides of carboxylic and carbamic acids



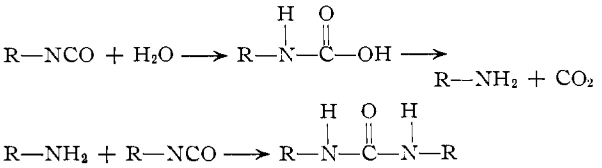
$$\mathrm{R{-}NCO{-}R'{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OH} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'} + \mathrm{CO_2}$$

$$2\mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}\mathrm{{-}R} + \mathrm{R'}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'}$$



$$\mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{O}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}\mathrm{{-}R} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}\mathrm{{-}R} + \mathrm{CO_2}$$

from which a disubstituted urea is formed upon the loss of carbon dioxide. More substituted urea linkages are formed by the reaction of isocyanate groups with traces of water.[12] Despite the anhydrous conditions of the preparation procedures it is likely that this reaction occurred to a small degree.



$$\mathrm{R{-}NCO} + \mathrm{H_2O} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OH} \longrightarrow \mathrm{R{-}NH_2} + \mathrm{CO_2}$$

$$\mathrm{R{-}NH_2} + \mathrm{R{-}NCO} \longrightarrow \mathrm{R{-}}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}\mathrm{{-}R}$$

From the zero relaxation time of sample I and III it can be concluded that the urethan hydrogen atom reacted with free isocyanate to a negligible

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[8] (a) M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946); (b) M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).

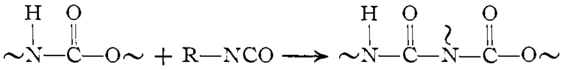
[9] D. H. Johnson, J. R. McLoughlin and A. V. Tobolsky, *J. Phys. Chem.*, **58**, 1073 (1954).

[10] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1950, pp. 348-357.

[11] C. Naegeli, *et al.*, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935); **21**, 1100, 1127 (1938).

[12] S. Petersen, *Ann.*, **562**, 205 (1949).

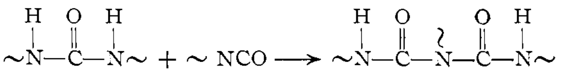
extent to form the allophanate.[13,14] This is particularly evident in III which contained a 10% excess of the diisocyanate in the preparation of the prepolymer. Even if this reaction occurred only



$$\sim\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O\sim + R-NCO \longrightarrow \sim\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\wr}{N}-\overset{\overset{O}{\|}}{C}-O\sim$$

partially the material would have had a loose network structure with a measurable relaxation time instead of undergoing complete flow at the temperature of the relaxation studies. Such behavior is indicative of a linear polymer containing little or no crosslinking.

Samples V and VI were prepared by the addition of water to a prepolymer containing excess diisocyanate. In addition to the formation of disubstituted urea linkages a substantial amount of crosslinking occurred by the reaction of free isocyanate with the urea hydrogen atoms to form trisubstituted biuret groups. This is evidenced by



$$\sim\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}\sim + \sim NCO \longrightarrow \sim\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\wr}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}\sim$$

the stress relaxation data for these samples which indicate that the materials possess a network structure. Also, it has been found by chemical methods that this reaction proceeds at a rate comparable to that of water and isocyanate.[15] The structures of these samples are summarized in Table II.

TABLE II

ELASTOMER STRUCTURE

Sample	Linkages
I	Ester, urethan, no cross-linkages
II	Ester, urethan, triisocyanate cross-linkages
III	Ester, urethan, no cross-linkages
IV	Ester, urethan, triol cross-linkages
V	Ester, urethan, urea, biuret cross-linkages
VI	Ester, urethan, urea, biuret cross-linkages

Possible Sites of Chain Cleavage.—The possibility of ester–ester interchange may be ruled out as a major factor contributing to the stress decay on the basis of previous work involving benzoyl peroxide vulcanizates of the Paraplex type and succinic acid–propylene glycol[4] type originating from the Bell Telephone Laboratories. The relaxation times of these materials were at least ten times longer than those of the samples involved in this investigation. Also, polyurethans having polyester backbones gave comparable relaxation times to polyurethans having polyether backbones which also indicates that neither the ether nor the ester groups were responsible for the stress decay.

The thermal instability of urethans has long been known.[16] It has been shown that aromatic urethans dissociate[12] to isocyanates around 180°. More recently quantitative studies have been made of the kinetics of urethan dissociation[17] in a series of solvents. As the reaction rate was greatly affected by the solvent, little correlation can be made with the present investigation.

It is also well known that substituted ureas dissociate[16] to isocyanates and amines between 170–180°.[12] Kinetic studies[18] of these decompositions in several solvents indicate that the reaction proceeds at an appreciable rate at 150°.

It is obvious from Table I that the samples with predominantly urethane linkages, II and IV, have relaxation times five times greater than those with 50% urethan and 50% substituted urea and biuret groups, V and VI. If this is the effect on the relaxation rate of replacing one half the urethan groups with biurets and ureas, a sample containing all urea and biuret linkages would decay at a rate ten times that of II and IV. Since the relaxation time is inversely proportional to the rate constant for the chain scission reaction it appears that the rate constant for the dissociation of the urethan group is less than one-tenth that for the combined effect of the substituted urea and biuret groups under these experimental conditions. A more quantitative statement differentiating between the substituted urea linkages and the biuret cross linkages is not possible at this time.

Acknowledgment.—The authors wish to express their gratitude to the Thiokol Chemical Corporation for the coöperation extended to us which made this research possible.

PRINCETON, N. J.

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[13] H. Lakra and F. B. Dains, THIS JOURNAL, **51**, 2220 (1929).

[14] J. C. Kogan, presented at the September 1956 meeting of the Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, N. J., September 15–21, 1956.

[15] M. Morton and M. A. Deisz, presented at the September, 1956, meeting of the Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, Sept. 15–21, 1956.

[16] A. W. Hofmann, *Ber.*, **3**, 653 (1870).

[17] T. Mukaijama and Y. Hoshino, THIS JOURNAL, **78**, 1946 (1956).

[18] T. Hoshino, T. M. Mukaijama and H. Hoshino, *ibid.*, **74**, 3097 (1952).