

Studies on Disulfide-Crosslinked Nylon. II. Stress Relaxation of Disulfide-Crosslinked Polycaprolactam Fibers in Water

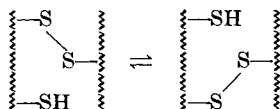
SHIN'NOSUKE MIYAUCHI, MUNENORI SAKAMOTO, and
HIROAKI TONAMI, *Tokyo Institute of Technology,*
Meguro-ku, Tokyo, Japan

Synopsis

The stress relaxation at 100% elongation in water was investigated for disulfide-crosslinked polycaprolactam (DSPC) fibers prepared from N-mercaptomethyl polycaprolactam. The stress decreased faster with increasing temperature and with increasing mercaptan content of the fiber. Little stress decay took place when the fiber was treated with a mercaptan-blocking reagent. It was concluded that the controlling mechanism of the stress relaxation was the mercaptan/disulfide (SH/SS) interchange reaction. The remanent stress observed for the stress relaxation was fairly high and increased with decreasing mercaptan content of the fiber. The stress decay curve was not Maxwellian. It has been suggested that the concentration of mercaptan that could not participate in the interchange with stressed disulfide bonds increased with increasing cycles of the interchange reaction. A kinetic equation is presented and the activation energy of the SH/SS interchange reaction was evaluated as 22.3-23.9 kcal/mole. The stress relaxation of DSPC fibers in dilute β -mercaptoethanol was also studied. The stress decreased more rapidly to almost zero and the decay curve was Maxwellian. The activation energy of the reaction was 17.1 kcal/mole. These results were compared with the stress relaxation of wool fibers.

INTRODUCTION

Considerable attention has been paid to the role of the mercaptan/disulfide (SH/SS) interchange reaction in supercontraction,¹⁻³ set and release of set,⁴⁻⁷ and stress relaxation^{6,8} of wool fibers since Burley^{9,10} showed in 1955 that the ease of creep and degree of supercontraction of wool fibers depend much on the amount of cysteine residues and explained the results by the SH/SS interchange mechanism:



Observations on the physical behavior of wool fibers are often equivocal in discussing the role of cysteine residues because the structure of wool fibers is very complex.

Elastic disulfide-crosslinked polycaprolactam (DSPC) fibers were prepared from N-mercaptomethyl polycaprolactam.¹¹ It was found that DSPC fibers contained not only disulfide crosslinks but also some amount of mercaptan. Therefore, DSPC fibers can serve as a simple wool model in the study of the SH/SS interchange reaction in wool. In this report, the stress relaxation of DSPC fibers in water is discussed in connection with that of wool.

EXPERIMENTAL

Samples

DSPC fibers (S_1 , S_2 , S_3 , S_4) were prepared according to the procedure described in a previous paper¹¹ and used after being aged for one month. S_{4h} was prepared from the same dope used for the preparation of S_4 , but the usual hydrogen peroxide aftertreatment was omitted.

Analyses

Sulfur contents were determined by the standard oxygen combustion method.

Mercaptan contents were found by the polarographic method, utilizing the reaction of mercaptan with methylmercuric iodide.¹¹

Stress-Strain Curves

A piece of sample (testing length, 2.0 cm) was mounted on a tensile tester in an ordinary manner and placed in a slack state for 10 min in distilled water maintained at a desired temperature in a thermally controlled tube. The fiber was stretched at a rate of 100%/min.

Relaxation Moduli in Water

A piece of sample (testing length, 10.0 cm) was mounted on relaxation apparatus and was placed in a slack state in a glass tube containing distilled water for 10 min, the tube itself being in a thermostat. The sample was extended to 25% strain in about 1 sec. The forces measured with a strain gauge at 5 sec after the extension were taken for calculating the relaxation modulus at 5 sec, $E_r(5)$. Cross-sectional area of the dry fiber was used for the calculation of $E_r(5)$ instead of that of the wet swollen sample.

Stress Relaxation

A piece of sample (testing length, 5.0 cm) was mounted on relaxation apparatus and was placed in a slack state in a glass tube containing distilled water at a desired temperature for a given time (usually 10 min). The sample was stretched to a given strain level (usually 100%) in about 1 sec and kept extended. The forces were continuously recorded with a strain gauge. Unless otherwise stated, the stress relaxation was measured by this continuous method.

For the determination of the stress relaxation in $0.01M$ β -mercaptoethanol, a piece of sample was preimmersed in distilled water for 10 min at a desired temperature, then, placed in $0.01M$ β -mercaptoethanol in a slack state at this temperature, for 5 sec, and stretched to 100% strain in about 1 sec and the forces were measured continuously. For the calculation of the relative stress $f(t)/f(0)$, $f(0)$ was substituted by $f(5)$ of the fiber in water measured at the same temperature. Time zero for $f(t)$ was the time when the fiber was put into the aqueous β -mercaptoethanol.

The stress relaxation (intermittent) was observed as follows: The sample was placed in a slack state in distilled water at $90^{\circ}C$ for 10 min. Then the fiber was stretched to 100% strain in about 1 sec, kept stretched, and the forces at 5 sec after being stretched were recorded. The fiber was relaxed immediately. The stretching was repeated occasionally.

RESULTS AND DISCUSSION

Mechanical Properties in Water

It has been demonstrated that the mechanical properties of DSPC fibers are much influenced not only by the crosslinks but also by secondary bonds; and the formation of secondary bonds, in turn, depends upon the degree of crosslinking.¹¹ The effect of secondary bonds appeared to be reduced in water.

Stress-strain curves of DSPC fibers of various sulfur contents measured in water at 25° and $70^{\circ}C$ are recorded in Figure 1. The sulfur content

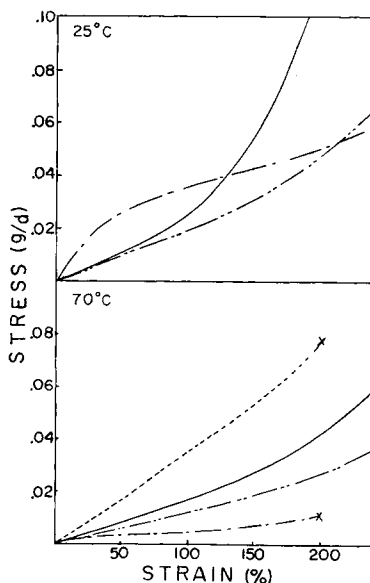


Fig. 1. Stress-strain curves of various samples in water at 25° and $70^{\circ}C$: (---), S_1 ; (-·-·-), S_2 ; (—), S_3 ; (·····), S_4 .

TABLE I
Sulfur Contents of Samples Used

S content (%)	Sample				
	S ₁	S ₂	S ₃	S ₄	S _{4b}
	0.93	1.93	2.45	2.90	2.90

and the degree of crosslinking increased in the order S₁, S₂, S₃, S₄ (see Table I). At 25°C, the least crosslinked sample (S₁) showed a distinct yield point, while a highly crosslinked sample (S₃) showed no yield point. The yield phenomenon is considered to be due to secondary bonds of short relaxation times. The above results indicate that few secondary bonds are involved in highly crosslinked fibers. The stress at 100% strain decreased in the order S₁, S₃, S₂. The least crosslinked sample showed the effect of secondary bonds the most. The stress-strain curve of S₃ did not change much when it was measured at 70°C. On the other hand, the stress-strain curve of S₁ at 70°C was dissimilar to that measured at 25°C. The yield point became indistinguishable and the stress decreased remarkably at 70°C. The secondary bonds probably disappear as the temperature increases. The stress at 100% strain measured at 70°C increased with increased crosslinking. The effect of secondary bonds virtually disappeared at this temperature.

Relaxation moduli at 5 sec, $E_r(5)$, of the samples are plotted against temperatures between 25° and 80°C in Figure 2. S₁ had the highest $E_r(5)$ at low temperatures. The modulus of S₁ decreased rapidly to a value which is expected for an amorphous crosslinked polymer as the temperature was raised. The modulus of S₂ was the lowest at low temperatures and decreased slightly to reach to a constant value at about 40°C. On the other hand, moduli of S₃ and S₄ remained constant when the temperature was raised. These results confirm the discussion on the stress-strain curves.

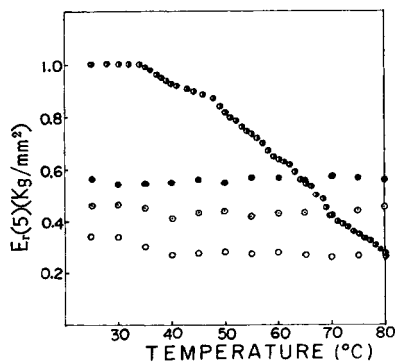


Fig. 2. Relaxation moduli versus temperature for various samples in water: (●), S₁; (○), S₂; (○), S₃; (●), S₄.

Stress Relaxation

It was found that the highly crosslinked DSPC fibers were amorphous without any secondary bonds in water at a wide range of temperatures. In the study of the stress relaxation in water, two highly crosslinked samples, S_4 and S_{4h} , were used. S_4 was prepared according to the usual conditions with the hydrogen peroxide aftertreatment,¹¹ while S_{4h} was prepared from the same dope used for the preparation of S_4 but without the peroxide aftertreatment. As shown in Table II, S_{4h} contains more free mercaptan than S_4 . The difference between the degrees of crosslinking of S_4 and S_{4h} is negligible.

TABLE II
Remanent Stress Observed in Water at 90°C

Sample	SH content, $\mu\text{moles/g}$	Remanent stress, %
S_4	14	28.6
S_{4h}	39	18.1

The stress relaxation was measured at 100% strain level. The effect of the strain level will be discussed later. The fiber was strained in 1 sec and the stress after 5 sec was taken as $f(0)$. Rapid initial decay of stress was not encountered in any case.

The effect of the preimmersion time was examined. Figure 3 shows the stress relaxation curves measured at 90°C after the samples were immersed for 10 and 60 min. Both curves agree well with each other. This suggests that the preimmersion time of 10 min is adequate for wetting and that hydrolysis of DSPC fibers does not take place appreciably in 60 min at 90°C. In the following experiments, samples were preimmersed for 10 min before stretching.

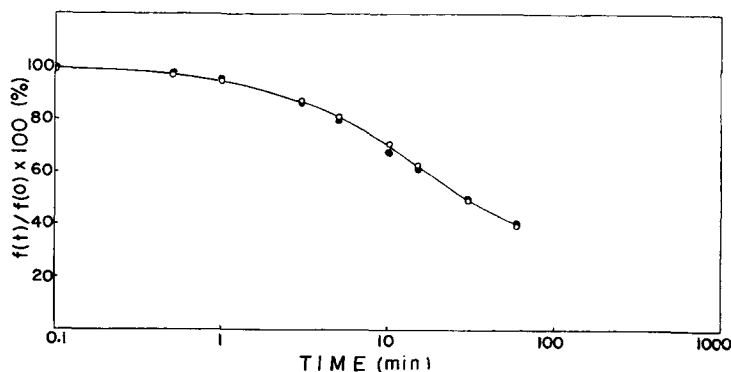


Fig. 3. Effect of preimmersion on stress relaxation of S_4 in water at 90°C: elongation, 100%; preimmersion time: (—○—), 10 min; (—●—), 60 min.

The stress relaxation curves of S_4 measured in distilled water at temperatures between 20° and 90°C are illustrated in Figure 4. The relaxation was very slow at low temperatures. The larger relaxation was observed with increasing temperature. The stress decreased fairly rapidly at 90°C until about 60 min and then seemed to reach a leveling-off value (remanent stress). In order to see whether this stress relaxation is due to the rupture of crosslinks, S_4 was immersed in a relaxed state in water at 90°C and oc-

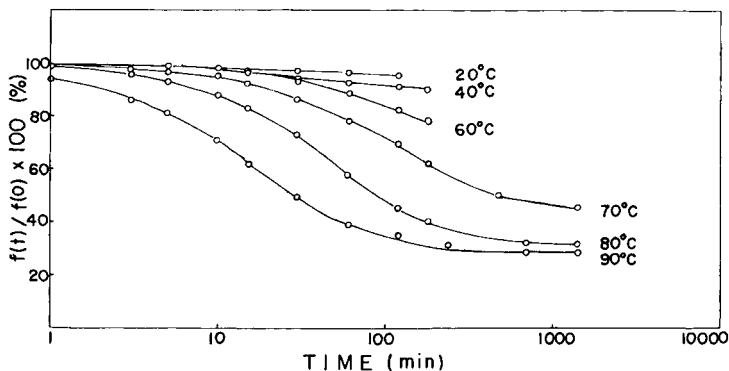


Fig. 4. Stress relaxation of S_4 in water at different temperatures: preimmersion time, 10 min; elongation, 100%.

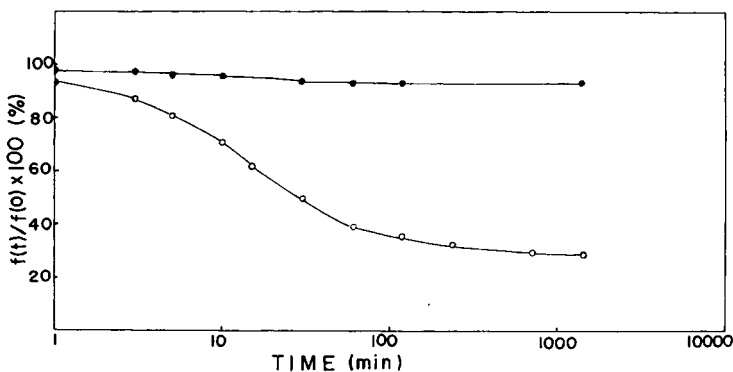


Fig. 5. Stress relaxation of S_4 in water at 90°C: preimmersion time, 10 min; elongation, 100%; (-O-), continuous method; (-●-), intermittent method.

asionally extended to 100% to measure $f(5)$. After each $f(5)$ determination, the sample was relaxed again. The results (intermittent stress relaxation) are shown in Figure 5. The stress was reduced to 93% at most. This indicates that no appreciable change in the amount of disulfide crosslinks occurs during heating in water. The continuous stress relaxation curves of S_{4h} measured at temperatures between 60° and 90°C are recorded in Figure 6. The stress relaxation of S_{4h} was faster and larger than S_4 . This indicates that mercaptan facilitates the stress relaxation in water.

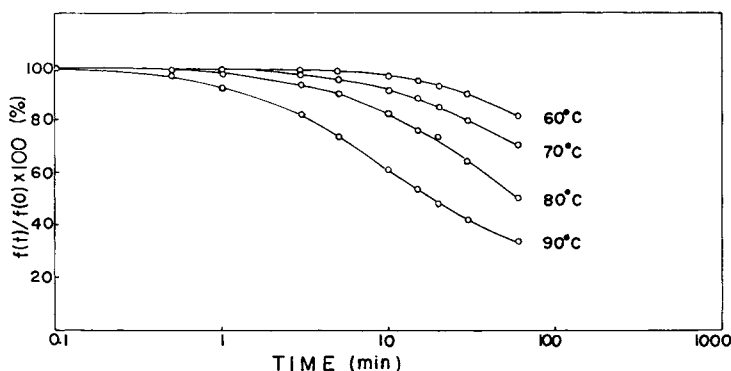


Fig. 6. Stress relaxation of S_{4h} in water at different temperatures: preimmersion time, 10 min; elongation, 100%.

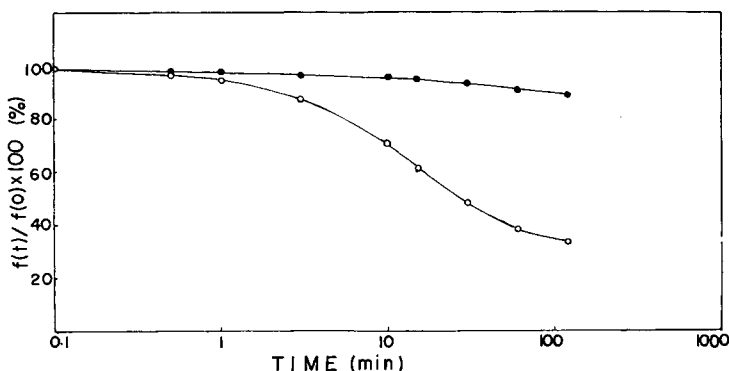


Fig. 7. Effect of 2,4-dinitrofluorobenzene (DNFB) blocking on stress relaxation of S_4 in water at 90°C: preimmersion time, 10 min; elongation, 100%; (-O-), control; (-●-), treated with 1M DNFB methanol solution at 20°C for 24 hr.

S_4 was treated with 2,4-dinitrofluorobenzene (DNFB) to obtain a mercaptan-free sample. The stress relaxation scarcely occurred when the mercaptan-free sample was extended in water at 90°C (see Fig. 7). Polarographic analysis of mercaptan contents of S_{4h} before and after heating in water at 90°C for 1 hr revealed that the mercaptan content of the sample changed little (39 to 40 μ moles/g) by the treatment. From these experiments it may be concluded that the stress relaxation phenomenon of the highly crosslinked DSPC fiber in water is due to the SH/SS interchange reaction, as is the case of polysulfide rubber at elevated temperatures.¹²⁻¹⁴

Kinetics of Stress Relaxation

According to the theory of elasticity of ideal rubber, the stress at time zero, $f(0)$, is given by

$$f(0) = 2N(0)RT(\alpha - \alpha^{-2}) \quad (1)$$

and the stress at time t is given by

$$f(t) = 2N(t)RT(\alpha - \alpha^{-2}) \quad (2)$$

where $N(0)$ and $N(t)$ are the concentrations of crosslinks (moles/cm³) at time zero and t , respectively. R is the gas constant, T is temperature (°K), and α is the extension ratio. The original cross-sectional area is used for the calculation of $f(t)$. The interchange reaction is expressed by

$$-\frac{dN(t)}{dt} = k_1 n(t) N(t) \quad (3)$$

where k_1 is a rate constant and $n(t)$ is the concentration of mercaptan (moles/cm³) at time t which can undergo the SH/SS interchange reaction.

In earlier kinetic studies on the chemical stress relaxation due to the SH/SS interchange reaction, $n(t)$ was assumed to be equal to the concentration of total SH present (n), and therefore a constant for a given sample. A Maxwell expression was derived from this assumption¹⁵:

$$f(t)/f(0) = \exp(-kt). \quad (4)$$

The above equation cannot explain that DSPC fibers apparently showed remanent stress. The assumption that $n(t)$ is equal to n means that any newly formed mercaptan by the interchange reaction can react further with another stressed disulfide bond. However, the newly formed mercaptan may not always be able to come close to the next stressed disulfide bond due to steric arrangement. This consideration leads to the following assumption:

$$-\frac{dn(t)}{dt} = k_2 n(t). \quad (5)$$

Integration of eq. (5) gives

$$n(t) = n(0) \exp(-k_2 t) \quad (6)$$

where $n(0)$ is the concentration of mercaptan at time zero which can undergo the interchange reaction. From eqs. (3) and (6) we obtain

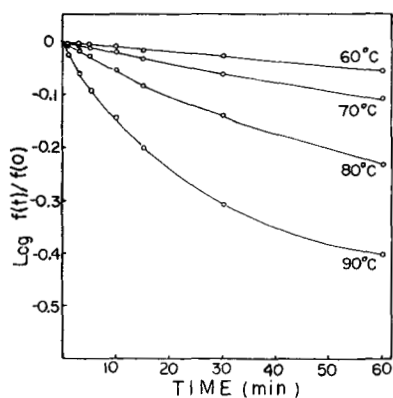
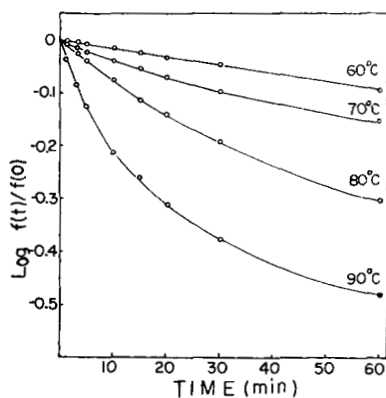
$$\ln N(t)/N(0) = -\frac{k_1 n(0)}{k_2} \{1 - \exp(-k_2 t)\}. \quad (7)$$

From eqs. (1), (2), and (7) we get

$$\ln f(t)/f(0) = -\frac{k_1 n(0)}{k_2} \{1 - \exp(-k_2 t)\}. \quad (8)$$

Equation (8) gives

$$\ln f(\infty)/f(0) = -\frac{k_1 n(0)}{k_2}. \quad (9)$$

Fig. 8. $\text{Log } f(t)/f(0)$ versus time for S_4 .Fig. 9. $\text{Log } f(t)/f(0)$ versus time for S_{4h} .

As $f(\infty) < f(0)$, the relative remanent stress, $f(\infty)/f(0)$, is to increase with decreasing $n(0)$. This equation explains qualitatively the remanent stress values of S_4 and S_{4h} given in Table II.

When $k_2t \ll 1$, eq. (8) is approximated by

$$\ln f(t)/f(0) = -k_1n(0)t. \quad (10)$$

$\text{Log } f(t)/f(0)$ of S_4 and S_{4h} are plotted against time in Figures 8 and 9, respectively. The slopes of the curves at time zero give $k_1n(0)$.

Temperature dependence of k_1 is expressed by

$$k_1 = A \exp(-E_1/RT). \quad (11)$$

The chemical relaxation time (τ) is defined as $1/k_1n(0)$; then

$$\log \tau = E_1/RT + A' \quad (12)$$

where E_1 is the activation energy of the SH/SS interchange reaction.

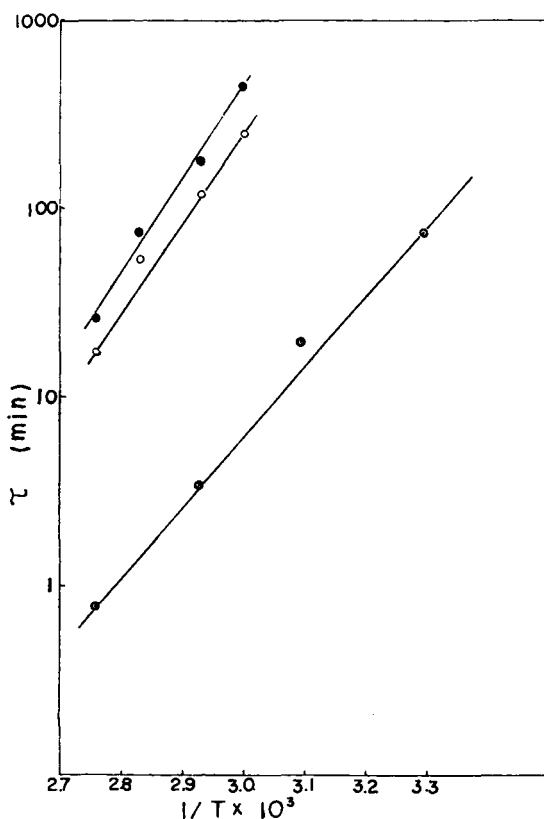


Fig. 10. Arrhenius plots of chemical relaxation times: (●), S_4 in water; (○), S_{4h} in water; (○-), S_4 in 0.01M β -mercaptoethanol.

Figure 10 shows the plots of $\log \tau$ against $1/T$. The activation energy obtained was 22.3 and 23.9 kcal/mole for S_4 and S_{4h} , respectively. These values are nearly equal to 24 kcal/mole observed for the activation energy of the SH/SS interchange reaction in polysulfide rubber at elevated temperatures.^{16,17}

Equation (8) is based on the assumption that the reactivity of mercaptan attached to polymer chains is limited by a steric factor. It is interesting to study the stress relaxation of DSPC fibers in the presence of excess low molecular weight mercaptan. Low molecular weight mercaptan is supposed to be able to move freely in the polymer network and react with any strained disulfide linkage. In this case, k_2 in eq. (8) is zero, in other words, $n(t)$ is equal to n . Therefore eq. (4) can be applied for this system. Figure 11 shows the stress relaxation of S_4 in 0.01M β -mercaptoethanol at different temperatures. A rapid decay to zero stress was observed. Figure 12 shows the plots of $\log f(t)/f(0)$ against time. The linearity of the plots exists in a wider region. Apparently the rate of the reaction is not diffusion controlled. The departure from linearity occurs only when the

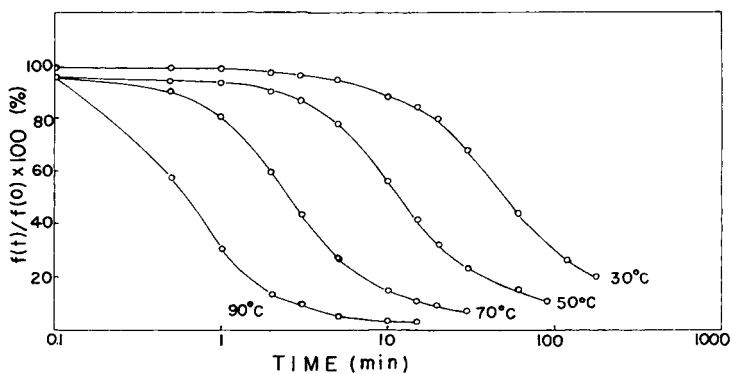


Fig. 11. Stress relaxation of S_4 in 0.01M β -mercaptoethanol at different temperatures: elongation, 100%.

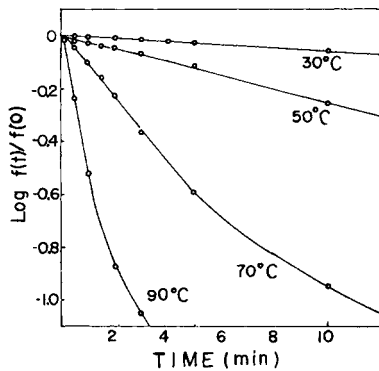


Fig. 12. $\text{Log } f(t)/f(0)$ versus time for S_4 in 0.01M β -mercaptoethanol.

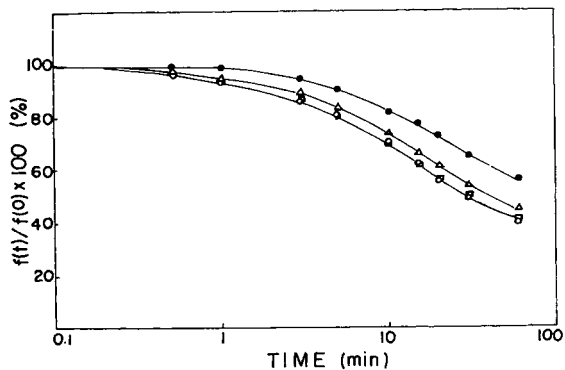


Fig. 13. Effect of elongation on stress relaxation of S_4 in water at 90°C: preimmersion time, 10 min; elongation: (-O-), 100%; (-□-), 80%; (-Δ-), 50%; (-●-), 25%.

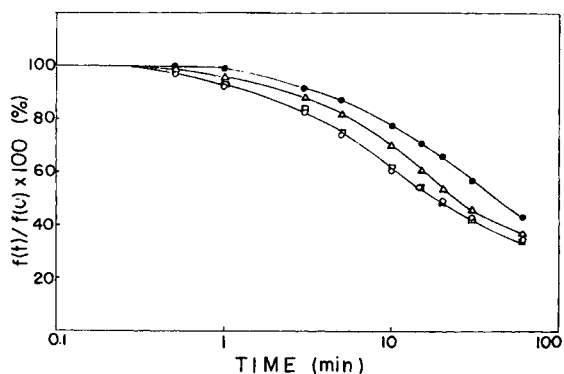


Fig. 14. Effect of elongation on stress relaxation of S_{4h} in water at 90°C : preimmersion time, 10 min; elongation: (○), 100%; (□), 80%; (△), 50%; (●), 25%.

stress decreases to about 25%. The deviation may be due to orientation and crystallization which accompany with cleavage of disulfide crosslinks. The activation energy for the reaction of DPSC fiber was calculated as 17.1 kcal/mole (see Fig. 10).

The effect of the strain level on the stress relaxation was examined. According to Treloar,¹⁸ the equation of rubber elasticity can be applied to strains up to 50%. Tobolsky reported that the relaxation proceeds more rapidly at larger deformations.¹⁹ Figures 13 and 14 show the stress relaxation curves of S_4 and S_{4h} in water at 90°C at different strain levels between 25 and 100%. It was found that the relaxation did not depend on the strain levels between 80 and 100%. However, at lower elongations the relaxation proceeded much slower as the strain level became lower. This unexpected result may be due to the dependence of the equilibrium of the SH/SS interchange reaction on the strain level. The interchange reaction between mercaptan and strained disulfide to form unstrained new disulfide is not reversible when the extension ratio is high enough, but the reverse reaction cannot be neglected when the ratio is low. This would account for the apparent lower rate of the stress decay when the strain level is low.

Comparison of Stress Relaxation Phenomena on Wool and DPSC Fibers

The stress relaxation of wool fibers in aqueous media has been studied in connection with sets of wool fibers. Speakman²⁰ showed that the stress relaxation process can be divided into two stages. According to Wood,²¹ the first, rapid stage involves the breakdown of secondary bonds such as hydrogen bonds, salt linkages, and van der Waals interactions. The activation energy of this process was reported to be 4 to 7 kcal/mole by Rigby.²²

The second, slow stage of the stress relaxation was proposed to be due to the SH/SS interchange reaction.⁶ Weigmann, Rebenfeld, and Dansizer⁸ studied the kinetics of the second stage of relaxation. They divided stress in water at time t , $f(t)$, by stress observed in the presence of an SH-blocking reagent (N-ethylmaleimide) at 1.2 sec, $f_{\text{NEMI}}(1.2)$, as a substitute for $f(0)$ for the SH-controlled stress relaxation. The elimination of SH groups apparently stops the interchange reaction but does not interfere with the first stage of the stress relaxation controlled by the breakdown of secondary bonds. Chemical relaxation times are given as times when $f(t)/f_{\text{NEMI}}(1.2)$ was equal to $1/e$, with assumptions that the decay curve should be Maxwellian and that the remanent stress was negligible. From the relaxation times, activation energies were obtained as 23.6 ± 1.0 kcal/mole for 20% extension and 21.8 ± 0.4 kcal/mole for 40% extension of untreated fibers and 21.3 ± 1.4 kcal/mole for 20% extension of reduced fibers.

Being different from the behavior of wool fibers, amorphous DSPC fibers did not show the initial rapid decay of stress due to the breakdown of secondary bonds when being extended. This is advantageous for studying the SH/SS interchange reaction by the stress relaxation technique. The Weigmann-Rebenfeld-Dansizer treatment may involve additional experimental error due to fiber-to-fiber variation since two different sets of fibers were used for the determination of the relative stress, one in the absence and another in the presence of N-ethylmaleimide.

The rate of the stress relaxation of DSPC fibers in water was much slower than that of wool fibers (second stage), and the remanent stress of DSPC fibers was higher than that of wool fibers. The remanent stress of wool fibers is often considered to be due to crystalline regions stable under the experimental conditions. It is proposed in this paper that the remanent stress of DSPC fibers is due to the steric limitation of reactivity of mercaptan attached to polymer chains.

The activation energies of the SH/SS interchange reaction of wool and DSPC fibers in water agree well with each other. The activation energy of the reduction of DSPC fiber with β -mercaptoethanol is lower than that for the interchange reaction. Kubu and Montgomery²³ studied the reduction of wool with cysteine by stress relaxation measurements and obtained an activation energy of the reaction (18.2 kcal/mole) which was also lower than that of the SH/SS interchange reaction.

Unexpected dependence of the rate of the stress relaxation of DSPC fibers on the strain levels below 80% was observed. The data of Weigmann, Rebenfeld, and Dansizer⁸ on wool also indicated that the stress decreased faster at a higher strain level (40%) than at a lower strain level (20%). Human and Lindley²⁴ reported briefly that when wool was stretched, the reaction of cystine residues with thioglycolate took place faster. More work should be done to reason out these behaviors.

We would like to thank Miss N. Ojima for the sulfur analyses.

References

1. W. G. Crewther and L. M. Dowling, *Text. Res. J.*, **31**, 31 (1961).
2. W. G. Crewther and L. M. Dowling, *Text. Res. J.*, **32**, 834 (1962).
3. W. G. Crewther, *J. Polym. Sci., A*, **2**, 131 (1964).
4. J. B. Caldwell, S. J. Leach, A. Meschers, and B. Milligan, *Text. Res. J.*, **34**, 627 (1964).
5. J. B. Caldwell, S. J. Leach, and B. Milligan, *Text. Res. J.*, **35**, 245 (1965).
6. L. Rebenfeld, *Amer. Dyestuff Repr.*, **54**, 469 (1965).
7. W. G. Crewther, *J. Soc. Dyers Colour.*, **82**, 54 (1966).
8. H.-D. Weigmann, L. Rebenfeld, and C. Dansizer, *Text. Res. J.*, **36**, 535 (1966).
9. R. W. Burley, *Proc. Int. Wool Textile Res. Conf.*, Australia, **1955 D**, p. 88.
10. R. W. Burley, *Nature*, **175**, 510 (1955).
11. H. Tonami, S. Miyauchi, and M. Sakamoto, *J. Appl. Polym. Sci.*, in press.
12. M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 94 (1946).
13. M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).
14. F. R. Bertozzi, F. O. Davis, and E. M. Fettes, *J. Polym. Sci.*, **19**, 17 (1956).
15. A. V. Tobolsky, *Properties and Structure of Polymers*, Chapter IV, Sect. 12, Wiley, New York, 1964.
16. A. V. Tobolsky, *Properties and Structure of Polymers*, Chapter V, Sect. 8, Wiley, New York, 1964.
17. A. V. Tobolsky, W. J. MacKnight, and M. Takahashi, *J. Phys. Chem.*, **68**, 787 (1964).
18. L. R. G. Treloar, *Trans. Faraday Soc.*, **40**, 59 (1944).
19. A. V. Tobolsky, *Properties and Structure of Polymers*, Chapter V, Sect. 1, Wiley, New York, 1964.
20. J. B. Speakman, *Proc. Roy. Soc.*, **103 B**, 377 (1928).
21. G. C. Wood, *J. Text. Inst., Trans.*, **45**, 462 (1954).
22. B. J. Rigby, *Aust. J. Phys.*, **8**, 176 (1955).
23. E. T. Kubu and D. J. Montgomery, *Text. Res. J.*, **22**, 778 (1952).
24. J. P. E. Human and H. Lindley, *Text. Res. J.*, **27**, 917 (1957).

Received April 23, 1969