

## Studies on Disulfide-Crosslinked Nylon. I. Elastic Disulfide-Crosslinked Polycaprolactam Fiber

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### Synopsis

Elastic disulfide-crosslinked polycaprolactams of different sulfur contents (0.4-3.3%) were prepared by the reaction of *N*-methoxymethyl polycaprolactam (D.S., 0.30) with different amounts of thiourea, the hydrolysis with excess potassium hydroxide, and the spinning into aqueous hydrogen peroxide.

The fibers obtained exhibited high elongation at break (500-300%), low initial modulus (13-1 kg/mm<sup>2</sup>), and high elastic recovery. The initial modulus decreased with increased crosslinking. Heat-treatment of the fibers at 140°C lowered the initial modulus remarkably. The effect of the crosslinking and the residual methoxymethyl substitution on the structure and the physical properties of the untreated and heat-treated fibers is discussed.

The residual methoxymethyl groups were removed completely from the fibers by hydrolysis with formic acid. The removal led to marked reduction in the elongation and much increase in the initial modulus.

### INTRODUCTION

Wool, a crosslinked protein fiber, has long served as a challenging model for making new valuable fibers. However, relatively little work has been reported on the production of crosslinked synthetic fibers, and in most of work, crosslinking has been done by the posttreatment of fibers under heterogeneous conditions. The "built-in" structure of the preformed fibers then could profoundly influence the crosslinking both in location and in extent, and the effect of such a treatment on the physical properties should be much complicated.

This paper deals with the direct preparation of disulfide-crosslinked polycaprolactam fibers from *N*-mercaptomethyl polycaprolactams<sup>1</sup> by reaction spinning. Some of the properties of the crosslinked fibers will be also discussed in connection with the crosslinks.

### EXPERIMENTAL

#### Analyses

Methoxy contents were determined by Zeisel's method. Sulfur contents were obtained by the standard oxygen combustion method.

D.S.<sub>M</sub> (degree of substitution of amide hydrogen of polycaprolactam derivatives with methoxymethyl) and D.S.<sub>S</sub> (degree of substitution of amide hydrogen with mercaptomethyl and its disulfide) were calculated from the following equations:

$$D.S._M = \frac{32 \times 113 \times M}{31 \times 32 \times 100 - 32 \times 44 \times M - 31 \times 46 \times S}$$

$$D.S._S = \frac{31 \times 113 \times S}{31 \times 32 \times 100 - 32 \times 44 \times M - 31 \times 46 \times S}$$

where *M* is methoxy content (wt %) and *S* is sulfur content (wt %). D.S.<sub>Total</sub> (degree of total substitution of amide hydrogen) was calculated as follows:

$$D.S._{Total} = D.S._M + D.S._S$$

Mercaptan and disulfide contents were determined by the method of Leach<sup>2</sup> with minor modification.<sup>3</sup> The reaction of samples with methylmercuric iodide in a Sørensen buffer solution (pH, 7.3) containing 8 *M* urea and 0.5 *M* potassium chloride was followed polarographically. The reaction was carried out at 30°C with agitation for more than 3 days for the completion. Mercaptan in the sample was considered equal to the amount of methylmercuric iodide consumed. For the determination of disulfide, samples were allowed to react with methylmercuric iodide in an ammonium chloride-ammonia buffer solution (pH, 9.4) containing 0.2 *M* sodium sulfite, 8 *M* urea and 0.5 *M* potassium chloride at 50°C for more than 6 days. The equilibrium uptake of methylmercuric iodide was taken as the sum of mercaptan and disulfide present in the polymer.

#### Preparation of N-Mercaptomethyl Polycaprolactam<sup>1</sup>

Into 20 ml of 80% aqueous methanol were dissolved 6 g of *N*-methoxymethyl polycaprolactam (D.S.<sub>M</sub>, 0.304; Teikoku Chemical Industries Ltd., Japan) and a given weight (0.3–1.5 g) of thiourea (TU) with stirring at ca. 70°C for 1 hr. After the solution was cooled to 30°C, a methanol solution of hydrogen chloride which was equimolar to TU used (conc. HCl, 0.3–1.5 ml; methanol, 0.8–4.0 ml) was added with vigorous stirring and the mixture was left to react for 3 or 15 min. Then 80% aqueous methanol (2–10 ml) containing twice as much sodium hydroxide as TU used was added. The mixture was kept at room temperature for 6 hr. All procedures were carried out under nitrogen atmosphere.

The resulting solution was used directly for either spinning or casting films.

#### Spinning

The hydrolyzed solution was extruded into a hydrogen peroxide solution by nitrogen pressure through a glass nozzle. The fibers were wound on a bobbin and washed with tap water for 6 hr. To avoid the self-adhesion of

the fibers of low D.S.<sub>s</sub> in subsequent drying, the fibers were rewound on another bobbin in a way that the fibers did not touch each other. The fibers were immersed in 5% hydrogen peroxide for 1 hr for completion of the oxidation and washed again with tap water for 6 hr followed by air-drying.

### Physical Properties

For the determination of the stress-strain curve, a piece of sample (testing length, 2.0 cm) was stretched at a rate of 100%/min. From the curve obtained were calculated the initial modulus, the elongation at break and the breaking strength.

For the determination of the elastic recovery, a piece of sample (testing length, 10.0 cm) was stretched to 100% extension at a rate of 20%/min and released at the same rate. The length at 1 min after completely released was read. The stretching and releasing were repeated. The recovery at  $n$ 'th cycle is expressed by  $(20 - l_n)/l_0 \times 100$  (%) where  $l_n$  is the length after  $n$ 'th releasing and  $l_0$  is the original length.

The relaxation modulus was obtained as follows. A piece of sample (testing length, 10.0 cm) was mounted on relaxation apparatus and was placed in a glass tube containing silicon oil for 2 min, the tube being in a thermostat. The sample was extended to 25% strain in about 1 sec. The stress measured with a strain gauge at 5 sec after the extension was taken for calculating relaxation modulus at 5 sec,  $E_r(5)$ .

The wide angle x-ray diffraction photograph was taken with Rigaku Denki x-ray diffractometer 3D-F with Ni-filtered Cu-K $\alpha$ .

The density was measured at 30°C by use of a density gradient tube made of toluene and carbon tetrachloride.

### Heat-Treatment

Samples were fixed on a wooden frame and placed in an oven of 140°C for 30 min. The samples were removed from the frame and conditioned before the physical measurements.

The effect of the heat-treatment on the properties of the disulfide-crosslinked polycaprolactam fiber was found to depend much on the moisture in the oven during the treatment. The experiments reported in the present paper were done in a day when it was around 60% RH. No attempt was made to control the moisture of the oven.

### Removal of Methoxymethyl Groups from the Crosslinked Polycaprolactam by Hydrolysis

Samples were wound on a glass reel and placed in a beaker filled loosely with glass fibers so that swollen samples did not slip off the reel. A formic acid solution was put into the beaker and the reaction was carried out at 50°C for a given time. The samples swelled much in the hydrolyzing medium. When the hydrolyzed samples were washed with tap water and

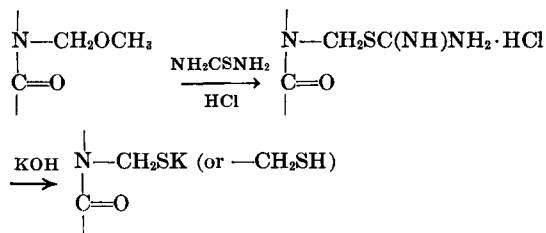
air-dried, the samples contracted to their original length. The physical properties were measured after aging at room temperature for 6 months.

## RESULTS AND DISCUSSION

### Preparation of Disulfide-Crosslinked Polycaprolactam Fiber

Reaction spinning where crosslinking and fiber formation occur simultaneously is expected to produce uniformly crosslinked fibers. It appears that the crosslinking reaction to apply for the reaction spinning is limited. The use of difunctional crosslinking agents seems to be undesirable because stoichiometric control of the crosslinking reaction under spinning conditions is difficult to achieve and branching of the difunctional reagent rather than crosslinking may proceed more. It was considered that backbone polymer should have self-crosslinkable groups and the crosslinking reaction should proceed at a proper rate. Oxidation of mercaptan of the backbone polymer to disulfide was chosen in the present study for the introduction of crosslinks into polycaprolactam fibers.

*N*-Mercaptomethyl polycaprolactams (in the form of potassium mercaptide) of various degrees of sulfur substitution were prepared from *N*-methoxymethyl polycaprolactam (D.S.<sub>M</sub>, 0.30) according to the following sequences:



The reaction conditions used were similar to those reported by Cairns et al.<sup>1</sup> for the preparation of *N*-mercaptomethyl polyhexamethyleneadipamide.

Various degrees of the *N*-mercaptomethyl substitution were attained by using different amounts of thiourea. The solution of *N*-mercaptomethyl polycaprolactam was cast into a film by evaporating solvent. The film was washed thoroughly with water and dried. Sulfur and methoxy contents of the film were determined, and the degrees of substitution with *N*-mercaptomethyl (D.S.<sub>S</sub>) and *N*-methoxymethyl (D.S.<sub>M</sub>) of the original polymer in solution were calculated. The film was partly crosslinked by air-oxidation. The total degree of substitution (D.S.<sub>Total</sub>) was nearly equal to D.S.<sub>M</sub> of *N*-methoxymethyl polycaprolactam which was used as a starting material, when equimolar amounts of hydrogen chloride and thiourea were used. This indicates that the postulated reaction proceeds without any side reaction. The yield of the mercaptomethyl substitution based on the amount of thiourea was between 43 and 62% when the reaction was carried out for 15 min. When twice molar amount of

TABLE I  
Reaction of *N*-Methoxymethyl Polycaprolactam with Thiourea

Reaction conditions <sup>a</sup>				Product				
Thiourea used, g	HCl/thiourea mole ratio	Reaction time, min	Sulfur found, %	Methoxy, %	Yield, <sup>b</sup> %	D.S. <sub>s</sub> <sup>c</sup>	D.S. <sub>M</sub> <sup>c</sup>	D.S. <sub>Total</sub> <sup>c</sup>
0.5	1	3	0.70	6.95	23	0.028	0.284	0.312
0.5	1	15	1.37	6.29	43	0.054	0.257	0.311
0.5	2	15	1.98	5.05	64	0.078	0.205	0.283
1.0	1	3	3.22	4.73	52	0.128	0.194	0.322
1.0	1	15	3.34	4.34	54	0.132	0.178	0.310
1.5	1	15	4.73	3.16	62	0.188	0.130	0.318

<sup>a</sup> *N*-Methoxymethyl polycaprolactam (D.S.<sub>M</sub>, 0.304) was allowed to react with thiourea in the presence of hydrogen chloride.

<sup>b</sup> Based on thiourea used.

<sup>c</sup> D.S.<sub>s</sub>: Degree of substitution of amide hydrogen with mercaptomethyl group. D.S.<sub>M</sub>: Degree of substitution with methoxymethyl group. D.S.<sub>Total</sub>: D.S.<sub>s</sub> + D.S.<sub>M</sub>.

TABLE II  
Reaction Spinning of *N*-Mercaptomethyl Polycaprolactam

Sample designation	Spinning solution <sup>a</sup>			Spinning conditions <sup>b</sup>				Fiber Sulfur found, %
	Thiourea used, g	Reaction time, min	Viscosity CP	Nozzle diameter mm	Extruding pressure atm	Temperature of coagulation bath °C	Winding velocity m/min	
<i>M</i> <sub>1</sub>	0.3	3	330	0.5	1.5	25	13	0.39
<i>M</i> <sub>2</sub>	0.5	15	300	0.5	0.6	25	26	1.23
<i>M</i> <sub>3</sub>	0.75	15	140	0.5	1.0	28	26	1.87
<i>M</i> <sub>4</sub>	1.0	15	280	0.2	1.0	21	13	3.25
<i>M</i> <sub>5</sub>	1.5	15	130		Could not be spun			

<sup>a</sup> Six grams of *N*-methoxymethyl polycaprolactam of D.S. 0.304 was allowed to react with thiourea as described in Experimental, and the reaction solution was used as spinning solution after being aged for 6 hr.

<sup>b</sup> The spinning solution was extruded under nitrogen pressure into 5% aq. H<sub>2</sub>O<sub>2</sub>.

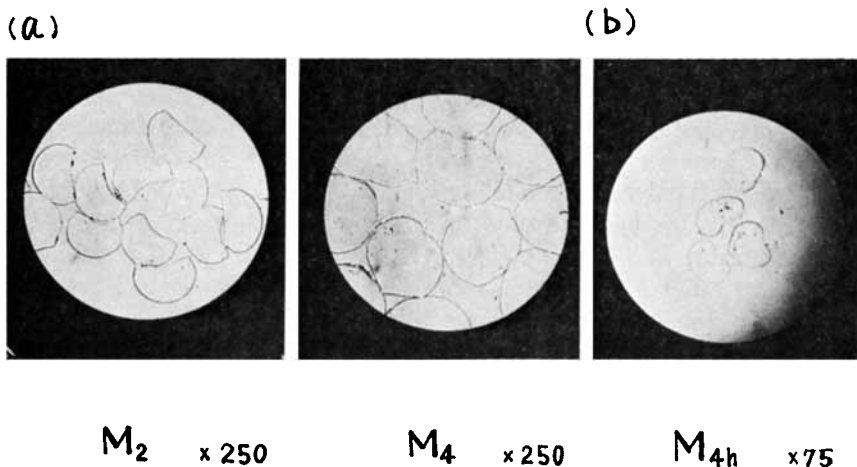


Fig. 1. Cross-sections of disulfide-crosslinked polycaprolactam fibers. (a) Untreated; (b) hydrolyzed.

hydrogen chloride was used, the yield was improved but  $D.S._{Total}$  of the product was lower than that of the starting material. In this case, some of the methoxymethyl groups seems to be lost via hydrolysis. The results are summarized in Table I.

The preparation of the crosslinked polycaprolactam fiber was achieved by spinning the solution of mercaptomethyl polycaprolactam (in the form of potassium mercaptide) into dilute aqueous hydrogen peroxide at room temperature. Mercaptide was preferred rather than free mercaptan because the former was more stable towards air-oxidation than the latter.<sup>1</sup> The preparation and the spinning conditions of mercaptomethyl polycaprolactam are listed in Table II. The amount of hydrogen chloride used was equimolar to thiourea throughout the spinning experiments.

There were two competing effects of the mercaptomethyl substitution on the formation of fibers. The polymer containing mercaptide groups was more hydrophilic, resulting in slower coagulation as the substitution increased. On the other hand, the crosslinking took place faster as the substitution increased, therefore, precipitation of the polymer from a hydrogen peroxide solution occurred faster as  $D.S._s$  increased. Consequently, the samples of low  $D.S._s$  such as  $M_1$  formed fibers slowly even in a very dilute hydrogen peroxide solution by the precipitation mechanism, while the samples of high  $D.S._s$  such as  $M_4$  formed fibers fast in 5% hydrogen peroxide by the insolubilization due to the crosslinking. Fibers of higher  $D.S._s$  than that of  $M_4$  were not obtained. When  $M_5$  in solution was extruded into higher concentration of hydrogen peroxide, the crosslinked polymer separated rapidly, but it was too weak to draw.

Much change in the fiber cross-section is observed microscopically with increasing  $D.S._s$  as shown in Figure 1a. While the cross-section of  $M_2$  was semicircular in shape, that of  $M_4$  was circular. It appeared that the

coagulation of the former in the spinning bath was slow and incomplete, hence, the resulting soft filament became hard slowly in a pressed form (semicircular cross-section) on a winding bobbin. On the other hand, the latter coagulated fast in the bath to form circular cross-section because of the surface tension.

The modified polycaprolactam fibers made in this work were insoluble in either solvents for unsubstituted polyamides or *N*-methoxymethyl polyamides, showing that the crosslinks were formed by the reaction spinning. Bruck<sup>4</sup> converted a polycaprolactam fiber into disulfide-crosslinked one according to the same reaction scheme as employed in the present work under heterogeneous reaction conditions. It was observed that the cross-linked fiber swelled differentially in *m*-cresol, resulting in helical coiling.

TABLE III  
Analyses of Disulfide-Crosslinked Polycaprolactam

Sample	Sulfur found, %	Mercaptan, <sup>a</sup> $\mu$ mole/g	Disulfide, <sup>a</sup> $\mu$ mole/g	Sulfur <sup>b</sup> calc'd, %
<i>M</i> <sub>1</sub>	0.39	11	27	0.21
<i>M</i> <sub>2</sub>	1.23	9	225	1.46
<i>M</i> <sub>3</sub>	1.87	10	289	1.88
<i>M</i> <sub>4</sub>	3.25	12	443	2.87

<sup>a</sup> Determined polarographically.

<sup>b</sup> Calculated from mercaptan and disulfide contents.

This phenomenon was considered to be due to the uneven distribution of the crosslinking density across the fiber axis. The fibers prepared in the present work by the reaction spinning did not undergo crimping in *m*-cresol. This suggests that the crosslinking takes place evenly in a coagulating spinning mixture to form a uniformly crosslinked fiber in the case of the reaction spinning.

The sulfur contents of the fibers determined are given in Table III. The mercaptan and disulfide contents were estimated by Leach's polarographic method<sup>2</sup> with minor modification.<sup>3</sup> The mercaptan content of the fiber was very low, and the most of the sulfur in the fiber was found in the form of disulfide. The sulfur content calculated from the mercaptan and disulfide contents agreed well with the sulfur content found by the sulfur analysis. The analyses of sulfur and methoxy made on one fibrous sample gave D.S.<sub>S</sub> of 0.112 and D.S.<sub>M</sub> of 0.201. Thus, D.S.<sub>Total</sub> (0.313) did not change by the reaction spinning. All these results led to a conclusion that most of the mercaptan converted to disulfide and both the rest of the mercaptan and the residual methoxymethyl remained unchanged throughout the spinning procedure. Earland and Raven<sup>5</sup> reported that hydrogen peroxide did not oxidize disulfide of *N*-mercaptomethyl polyhexamethylencapamide.



### Properties and Structure of Disulfide-Crosslinked Polycaprolactam Fiber

The mechanical properties of the disulfide-crosslinked polycaprolactam fibers are characterized by low initial moduli, high elongations at break and low apparent breaking strengths as shown in Table IV and Figure 2. The

TABLE IV  
Properties of Fresh Disulfide-Crosslinked Polycaprolactam Fibers<sup>a</sup>

Sample	Denier	Breaking strength, g/d	Elongation at break, %	Initial modulus, kg/mm <sup>2</sup>
$M_1$	96	0.28	470	7.0
$M_2$	34	0.30	450	6.5
$M_3$	220	0.30	450	2.1
$M_4$	54	0.45	450	0.2

<sup>a</sup> Measured about one week after preparation.

stress-strain curves resemble that of rubber. In the case of the most cross-linked fiber ( $M_4$ ), the stress increased progressively as the fiber was extended. The mechanical properties of the fibers were found to change on aging at room temperature. In Figure 3 are shown the change in the stress-strain curve of  $M_4$  on aging. The initial modulus increased and the elongation at break decreased on storing the fiber for one month. The stress-strain curve stopped changing further after a few months. The stress-strain curves of the aged samples are illustrated in Figure 4. The comparison of the stress-strain curves in Figure 4 and Figure 2 shows that the stress required for stretching increases on aging, and the yield regions are distinguished more easily for the aged samples except  $M_4$ . The observed change in the stress-strain relationship might arise from the slow formation of secondary bonding which might form restricting structures against

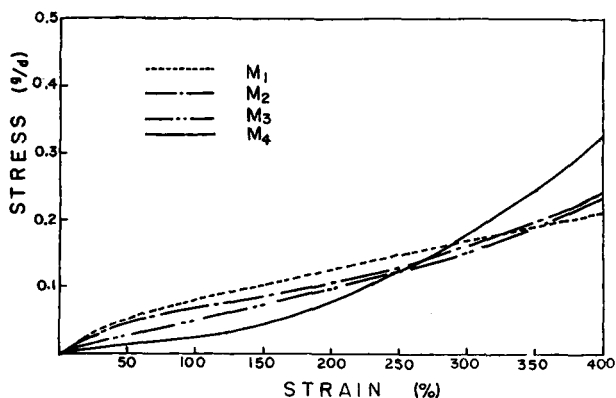


Fig. 2. Stress-strain characteristics of fresh disulfide-crosslinked polycaprolactam fibers.

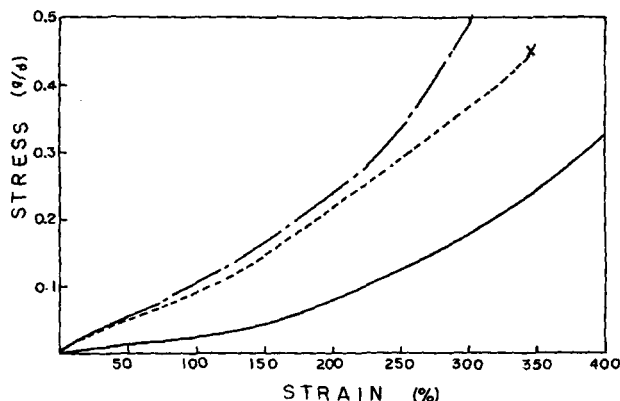


Fig. 3. Effect of aging on the stress-strain relationship of  $M_4$ . A week after preparation, (—); a month after preparation, (---); four months after preparation, (-·-·).

stretching. Both the initial modulus and the stress at the yield point increased with decreased crosslinking. The crosslinking presumably prevents the rearrangement of the polymer chains and the formation of secondary networks. The newly formed structure on aging may be labile in a hydrogen-bond-breaking medium; indeed, the initial phases of the stress-strain curves of the aged samples in water (Fig. 5) were similar to those of the unaged samples measured in the dry atmosphere.

The mechanical properties of the aged fibers are recorded in Table V. The elongations at break of the samples ranged between 300 and 500% and the breaking strengths were between 0.43 and 0.57 g/d. The initial modulus decreased markedly as the crosslinking increased, ranging between 13.0 kg/mm<sup>2</sup> for  $M_1$  and 1.2 kg/mm<sup>2</sup> for  $M_4$ . The elastic recoveries of the samples from stretching were high. All the samples show almost complete recoveries after several stretching-releasing cycles are applied, as shown in

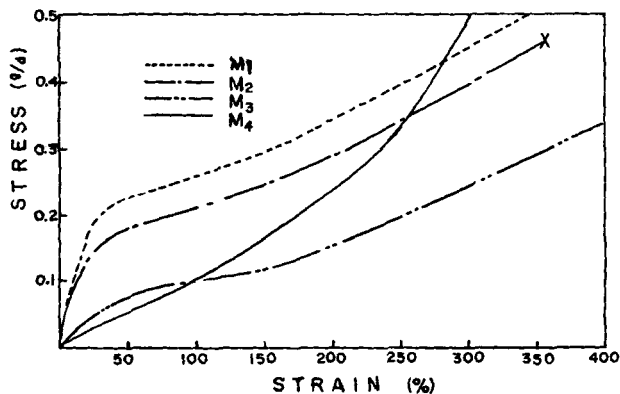


Fig. 4. Stress-strain characteristics of aged disulfide-crosslinked polycaprolactam fibers.

TABLE V  
Properties of Aged Disulfide-Crosslinked Polycaprolactam Fibers<sup>a</sup>

Sample	Denier	Breaking strength, g/d	Elongation at break, %	Initial modulus, kg/mm <sup>2</sup>	Specific gravity, 30°C
<i>M</i> <sub>1</sub>	96	0.57	400	13.0	1.130
<i>M</i> <sub>2</sub>	34	0.47	350	12.0	1.138
<i>M</i> <sub>3</sub>	220	0.43	500	4.3	1.140
<i>M</i> <sub>4</sub>	54	0.50	300	1.2	1.141

<sup>a</sup> Measured about one month after preparation.

TABLE VI  
Repeated Elastic Recoveries from 100% Extension

Sample	Number of stretching-releasing cycle				
	Recovery, %				
	1	2	3	4	5
<i>M</i> <sub>1</sub>	74	67	65	63	62
<i>M</i> <sub>2</sub>	81	76	74	74	74
<i>M</i> <sub>3</sub>	84	81	79	77	75
<i>M</i> <sub>4</sub>	95	92	92	92	92
Spandex (210 denier)	96	96	96	96	96

Table VI. The elastic recovery of a Spandex fiber is also shown in the Table for comparison. Generally speaking, the more crosslinked sample showed better recovery.

It has been well established that the substitution of the amide hydrogen of polyamides with alkyl, alkoxy and other groups lessens hydrogen bonding between the polymer chains and reduces the regularity of the polymer arrangement.<sup>6,7</sup> As a consequence, *N*-methoxymethylated polyhexamethylenedipamide, for instance, exhibits lower melting point, lower crystallinity,

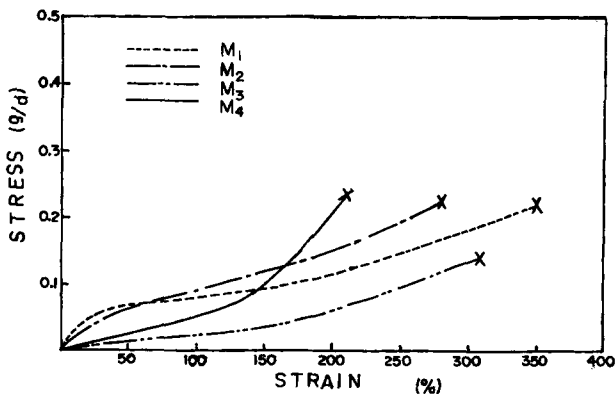


Fig. 5. Stress-strain characteristics of disulfide-crosslinked polycaprolactam fibers (wet).

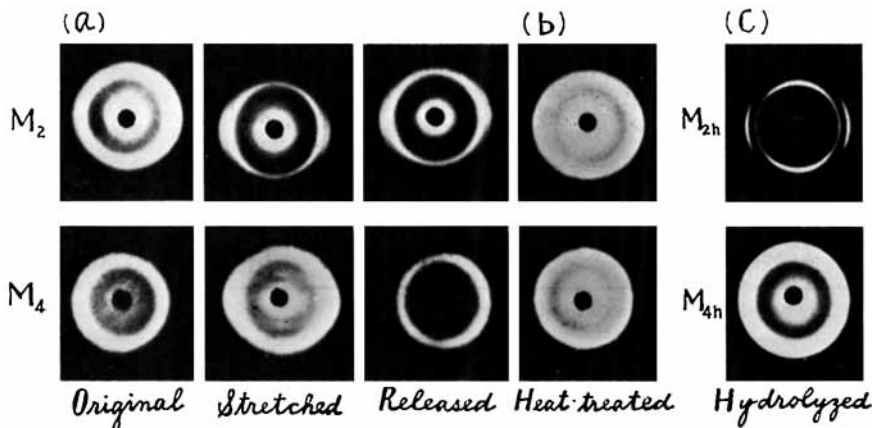


Fig. 6. X-ray diffraction photographs of disulfide-crosslinked polycaprolactam fibers. (a) Aged; (b) heat-treated; (c) hydrolyzed.

and higher reversible extension. In the present work, the amide substitution with both methoxymethyl and the disulfide linkages resulted in the elasticity. The elongation at break did not depend on the density of the crosslink. The elastic recovery of the crosslinked fiber was better than that of comparably substituted *N*-methoxymethyl polyhexamethylene-adipamide.<sup>6</sup>

The x-ray study revealed that the highly crosslinked sample ( $M_4$ ) was amorphous while the less crosslinked sample ( $M_2$ ) was partly crystalline although the diffraction patterns of  $M_2$  were diffuse. Crosslinking apparently disturbed crystallization. When both samples were stretched at 100% extension, the polymer molecules underwent orientation. In addition,

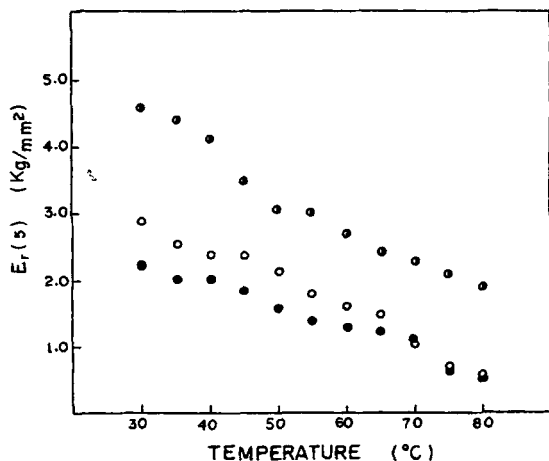


Fig. 7. Relaxation modulus versus temperature in silicon oil. Sulfur contents of samples: 0.93%, (●); 1.92%, (○); 2.90%, (●).

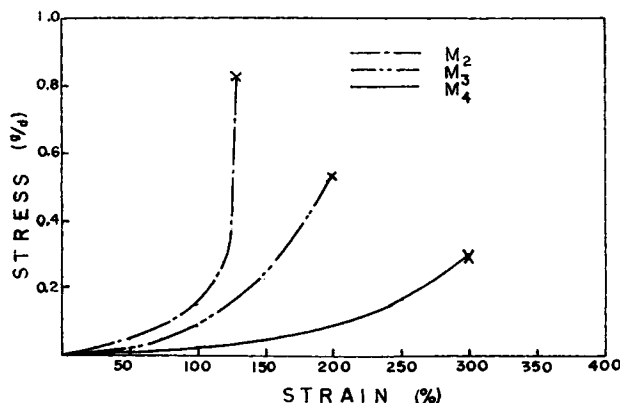


Fig. 8. Stress-strain characteristics of heat-treated disulfide-crosslinked polycaprolactam fibers.

tion, the crystallization accompanied stretching in the case of  $M_4$ . The highly crosslinked fiber ( $M_4$ ) returned to its original unoriented amorphous structure, when the force of the extension was removed. The less crosslinked sample ( $M_2$ ), however, remained oriented when the force was removed. The x-ray photographs for the above discussion are collected in Figure 6a.

The specific gravities of the fibers measured are listed in Table V. The specific gravity increased with increased crosslinking. The amorphous  $M_4$  showed a higher density than the partly crystalline  $M_2$ . The amount of sulfur in the fiber seems to have more pronounced effect on the specific gravity than the crystallinity.

The relaxation moduli of the samples measured in silicon oil are plotted against temperature in Figure 7. The modulus decreased with increasing temperature. The fiber seems to be in a transition region from glassy to rubbery regions at room temperature.

The effect of the heat-treatment on the properties of the crosslinked fibers was studied. The samples were kept at a constant length and heated at 140°C for 30 min. The stress-strain curves and x-ray diffraction photographs of the heat-treated samples are shown in Figure 8 and Figure 6b, respectively. The stress-strain curve of the most crosslinked  $M_4$  became almost identical with that of the fresh  $M_4$  by the heat-treatment. This suggests that the weak secondary-bonded network structure of the aged sample was ruptured during the heat-treatment. The stress-strain curves of  $M_2$  and  $M_3$  became similar to that of  $M_4$  after the heat-treatment. The initial modulus was low and the stress increased progressively without the yield region as the fiber was stretched. The initial moduli of  $M_2$  and  $M_3$  were much lower than those of fresh  $M_2$  and  $M_3$ , respectively. These also indicate the breakdown of the original network structure. The initial modulus increased with decreased crosslinking. This could be explained by the formation of more stable small crystallites during the heat-treatment.

TABLE VII  
Properties of Heat-Treated Disulfide-Crosslinked Polycaprolactam Fibers

Sample	Breaking strength, g/d	Elongation at break, %	Initial modulus, kg/mm <sup>2</sup>
$M_2$	0.80	140	1.4
$M_3$	0.53	200	0.4
$M_4$	0.30	300	0.2

The crystallites could serve as crosslinks in effect. The initial modulus, then, could depend on the net effect of crosslinking and the formation of the crystallites. As was the case on aging, crosslinking might oppose the rearrangement of polymer chains to form the crystallites. Thus, the less crosslinked fiber forms more crystallites during the heat-treatment. An alternative and less probable explanation is the formation of methylene bridges between methoxymethyl groups during the heat-treatment.<sup>7</sup>

The physical properties of the heat-treated fibers are collected in Table VII. The initial moduli of the heat-treated fibers were about one tenth of those of the corresponding aged ones. The elongation at break of the heat-treated  $M_4$  (300%) was equal to that of the aged  $M_4$ , while the elongations of other heat-treated samples were about two fifths of those of the corresponding aged ones. The elongation of the heat-treated fiber in-

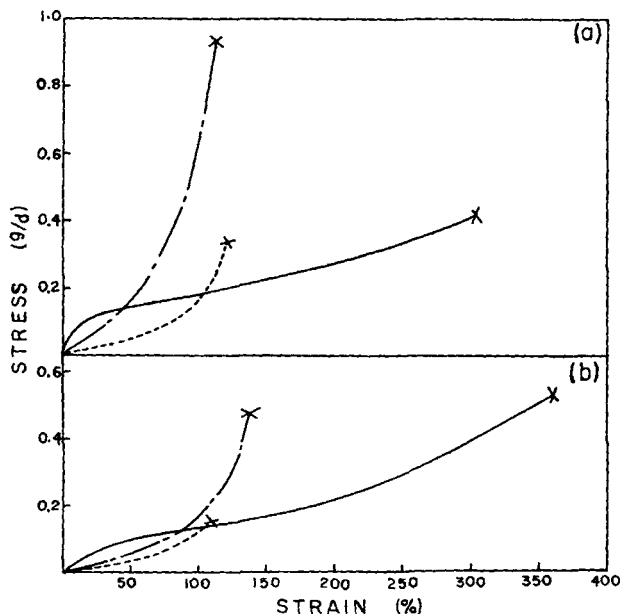


Fig. 9. Comparison of stress-strain curves of heat-treated and untreated samples. S contents of samples: (a) 1.10%; (b) 2.45%. Untreated, dry, (—); heat-treated, dry, (---); heat-treated, wet, (- - -).

creased with decreased crosslinking. The breaking strength increased appreciably by the heat-treatment. The strength increased with increased crosslinking.

In Figure 9 are shown stress-strain curves of the heat-treated samples in water and in the atmosphere along with the curves of the untreated samples. The structure of the heat-treated sample was rather stable towards water as the stress-strain relationship in water was similar to that in the dry atmosphere. The more crosslinked sample was more stable.

It is interesting to note that the change in the stress-strain curves of  $M_4$  was the least. This appears consistent with the following data of heat set. A couple of fibers ( $M_2$  and  $M_4$ ) were kept at 100% extension at 120°C for 1 hr. The sets obtained were 93% for  $M_2$  and 24% for  $M_4$ , respectively. It was also evident that the crosslink opposed flow of the polymer segments in cold water. Samples ( $M_2$  and  $M_4$ ) were kept at 100% extension in water at 25°C for 1 hr. While 68% of the extension was set in the case of  $M_2$ , only 9% was set for  $M_4$ . More detailed work will be described in a following paper on the mechanism of setting in various aqueous media.

#### Removal of Methoxymethyl Groups from the Disulfide-Crosslinked Polycaprolactam

Hydrolytic removal of the residual methoxymethyl from the disulfide-crosslinked fibers was investigated. In a preliminary experiment with film samples, it was shown that the methoxymethyl groups were completely removed from the polymer when the film was treated with 85% formic acid at 50°C for 15 min. Slight loss of sulfur was accompanied when the film was treated longer (see Table VIII). As the less crosslinked polymer dissolved partly in 85% formic acid, it was allowed to react in 20% formic acid for a longer period.

TABLE VIII  
Removal of Methoxymethyl Groups from  
Disulfide-Crosslinked Polycaprolactam Film<sup>a</sup>

Reaction time, min	Methoxymethyl, %	Sulfur, %
0	4.50	3.18
5	trace	3.18
15	0	3.08
60	0	2.57

<sup>a</sup> Samples were hydrolyzed in 85% formic acid at 50°C.

The x-ray diffraction patterns are shown in Figure 6c to indicate that the hydrolyzed samples are more crystalline compared with the untreated ones. Orientation of the polymer chain was also observed. The fibers swelled in the formic acid longitudinally and contracted during washing and air-drying. Orientation of the molecule could occur in the latter stage of the treatment because the samples were not allowed to shrink freely.

TABLE IX  
Disulfide-crosslinked Polycaprolactam Fibers Free from Methoxymethyl Groups

Sample	Conditions of hydrolysis <sup>a</sup>		Properties of hydrolyzed fibers				
	Concentration of formic acid, %	Reaction time, min	Methoxymethyl, %	Sulfur, %	Breaking strength, g/d	Elongation at break, %	Initial modulus, kg/mm <sup>2</sup>
<i>M</i> <sub>2h</sub>	20	60	0	1.10	0.7	120	150
<i>M</i> <sub>3h</sub>	85	15	—	2.08	0.7	120	82
<i>M</i> <sub>4h</sub>	85	15	0	2.79	0.5	60	18

<sup>a</sup> Samples were hydrolyzed in formic acid at 50°C.



The stress-strain curves and the properties of the hydrolyzed fibers after being aged at room temperature for 6 months are recorded in Figure 10 and in Table IX, respectively. It was found that the initial modulus increased about fifteen times by the removal of the methoxymethyl groups. The higher initial modulus of the hydrolyzed fiber seems to be due to increase in crystallinity and crystal orientation. The initial modulus of the hydrolyzed fiber increased with decreased crosslinking and with increased crystallinity and orientation. The elongation at break decreased considerably by the hydrolysis probably also due to higher crystallinity and orientation. Crosslinking itself may reduce the elongation since  $M_{4h}$ , which was

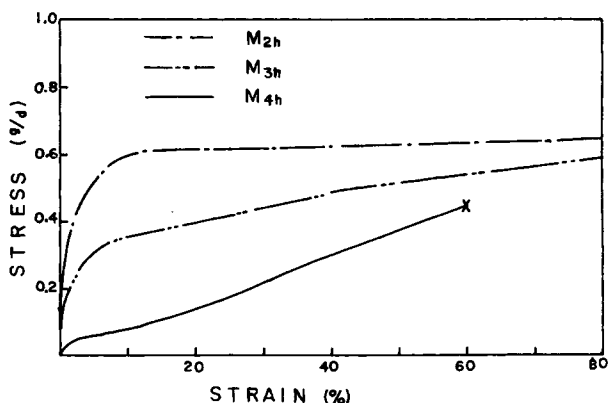


Fig. 10. Stress-strain characteristics of hydrolyzed disulfide-crosslinked polycaprolactam fibers.

the most highly crosslinked and had the lowest crystallinity and orientation, had the lowest elongation. It should be mentioned, however, that the elongation at break and the breaking strength of the hydrolyzed fiber varied much from one sample to another probably due to the irregular damage caused by the treatment. The cross-section of a hydrolyzed sample ( $M_{4h}$ ) is given in Figure 1b to show the damage.

As mentioned in the Experimental, the wet disulfide-crosslinked fibers made by the reaction spinning tended to glue together when being dried. This tendency decreased as the crosslinking increased. The fibers did not stick to each other after being treated with formic acid. Thus the observed self-adhesion of the fibers arose from the residual methoxymethyl groups. It was reported that polycaprolactam fibers treated extensively with formaldehyde glued together.<sup>8</sup>

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