

Conductometric Determination of Sulfhydryl Groups in Swollen Polycaprolactam Fibers Having Disulfide and Alkylene Sulfide Crosslinks

Stephen D. Bruck and Sylvia M. Bailey

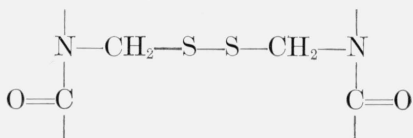
(December 6, 1961)

A simple conductometric titration method is discussed for the determination of sulfhydryl groups in nonionic polymer networks, such as disulfide and alkylene sulfide crosslinked polycaprolactam fibers. The diffusion of the titrant into the crosslinked polymer is accomplished by swelling the network structure, thereby eliminating the necessity of destroying the crosslinks and/or breaking the polymer chains.

1. Introduction

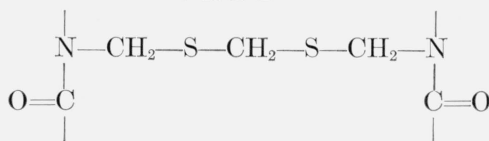
In current communications [1, 2, 3]¹ a method is discussed for producing macroscopic deformations (such as crimping and coiling) in polycaprolactam fibers by crosslinking. The disulfide and alkylene sulfide crosslinks used were introduced into the oriented, swollen, *N*-methylmethoxylated fibers (swelling agent: methyl alcohol) and consisted primarily of the following structures:

Fiber A



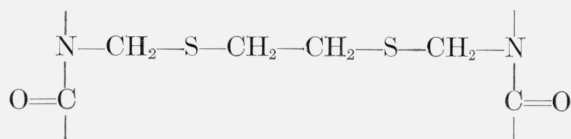
(1)

Fiber B



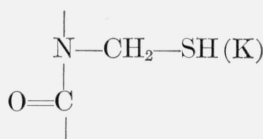
(2)

Fiber C



(3)

In addition to the above crosslinks, various amounts of unreacted sulfhydryl or potassium mercaptide groups having the following structure may also be present:



(4)

A knowledge of the number of sulfhydryl groups in the crosslinked fibers is valuable because one can then estimate the number of crosslinks from the total sulfur content and the number of sulfhydryl groups.

2. Discussion

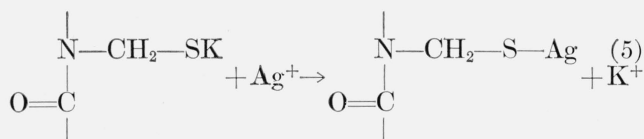
There are numerous methods for the determination of sulfhydryl groups in organic compounds [4, 5]. These include visual titrimetric [6], potentiometric [7], and amperometric [8] techniques, as well as oxidation methods [9, 10]. Similarly, various methods exist for the determination of disulfides and sulfides [4, 5, 11, 12]. There are difficulties, however, when both sulfhydryl groups and disulfide groups (or other sulfur-containing functional groups) are present in the same molecule. In such a case, in order to determine the number of disulfide groups, one must first remove or analyze the sulfhydryl groups (for example, by potentiometric titration with Ag^+), then quantitatively reduce the disulfides to sulfhydryls, followed by analysis of the resulting sulfhydryl groups. Apart from the complexity of this approach, a further difficulty arises if all excess silver ions are not removed from the system after the initial analysis of sulfhydryl groups; any excess Ag^+ will combine with those sulfhydryls that are produced from the reduction of disulfides, thus making an accurate analysis impossible.

In the systems discussed here the unmodified polyamides are essentially nonionic, and the sulfhydryls and crosslinks were introduced into the swollen *N*-methylmethoxylated fibers in the presence of methyl alcohol as swelling agent. It should be possible then to reach the free sulfhydryl (or potassium mercaptide) groups with a specific reagent, provided that the system is in the swollen state. Thus, conductometric titration methods with Ag^+ offer a promising approach. Diffusion of the titrant into the crosslinked polymer is accomplished by swelling the network structure, thereby eliminating the necessity of destroying the crosslinks or breaking the polymer chains. Conductometric techniques are not ordinarily used in sulfhydryl

¹ Figures in brackets indicate the literature references at the end of this paper.

analyses partly because of the interfering effect of electrolytes that do not take part in the analytical reaction. However, in the present work, the unmodified polymer is nonionic and because it is not dissolved, it should not contribute significantly to the total conductance of the solution. Consequently the titration of the sulfhydryl groups with Ag^+ should be free of disturbances provided that the swelling agent is also a suitable medium for the conductance of silver ions.

To ascertain the applicability of such a procedure the effect of increased swelling periods on the diffusion of the titrant into the polymer must be assessed, and evidence must be obtained that the observed end-points are truly indicative of sulfhydryl groups. The first parameter can be checked by carrying out titrations on the system after it has been swollen for different periods in a swelling agent; the second parameter can be ascertained by analyzing the titrated samples for silver. One equivalent of silver corresponds to one equivalent of mercaptide (or sulfhydryl) groups, according to the reaction:



The following experimental procedure was thus adopted.

3. Experimental Details

Samples of crosslinked polycaprolactam fibers were cut to lengths of approximately 1 to 2 mm and swollen in 100 ml of methyl alcohol for periods of 15 min, 2 hr, and 4 hr, respectively, in 250 ml beakers. Such small, cut filaments are subject to a relatively rapid rate of swelling as has already been shown [13,14]. The suspended and swollen filaments were stirred with a magnetic stirrer. The titrant, a solution of 0.0014 *N* AgNO_3 in methanol-distilled water (99:1 by volume), was added in approximately 0.1 ml amounts at 2-min intervals to allow diffusion into the fiber. A Serfass conductometric bridge and platinum electrodes ($\frac{1}{4}$ cm^2 , 1 in. apart) were used, and the titrations were carried out at room temperature. The use of other swelling agents, such as benzyl alcohol, *m*-cresol, or mixtures of these gave poor titration curves due probably to insufficient conductance of Ag^+ in these media. Figure 1, curve A shows a typical conductometric titration curve for the uncrosslinked (control) sample after 2 hr of swelling. Curve B is a typical plot for the crosslinked fibers that contain both disulfide and alkylene sulfide crosslinks, after 2 hr of swelling. Similar plots were also obtained for fibers that had been swollen for 4 hr in methanol. No satisfactory end-points were obtained for those crosslinked samples that had been swollen for only 15 min.

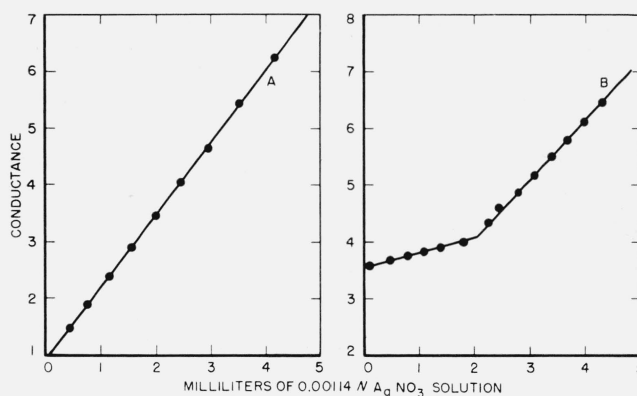


FIGURE 1. Typical conductometric titration curves for an uncrosslinked polycaprolactam fiber (curve A), and a sulfhydryl containing disulfide crosslinked polycaprolactam fiber (curve B).

After the titrations were completed (carried sufficiently past the end-point), the swollen polymer samples were immediately filtered with suction on medium-porosity sintered glass filters, thoroughly washed with ethanol, and dried. Care was exercised to avoid prolonged standing of the samples in light, as the excess silver ions present in the solution from additions past the end-point could be reduced to free silver thus becoming part of the samples after filtration. Each titrated sample was then analyzed for silver. Table 1 gives the equivalents of sulfhydryl groups per 10^6 g of polymer calculated from the titration curves and silver analyses, respectively.

TABLE 1. Equivalents of sulfhydryl groups per 10^6 g of polymer calculated from conductometric titrations and silver analyses

Experiment	Swelling time prior to titration	Sample wt used in titration	Equivalents of sulfhydryls per 10^6 g of polymer	
			Titration	Ag analysis
1	hr	g		
2	2	0.0314	54	51
3	2	.0283	47	51
4	2	.0479	51	
5	2	.0348	46	47
6	4	.0581	44	
	4	.0502	44	46

There is good agreement between the equivalents of sulfhydryl groups obtained from titration curves and from corresponding silver analyses. The fact that the number of equivalents of sulfhydryls did not show significant changes for the samples that had been swollen for 2 and 4 hrs, respectively, indicates that the polymer network was sufficiently swollen after only 2 hrs for the diffusion of silver ions and for their subsequent reaction with the sulfhydryl groups. Cross sections of the titrated fibers indicated that the penetration of the Ag^+ was not restricted to the surface of the fiber, inasmuch as greying of the entire section was observed, instead of a so-called surface "ring." Furthermore, if any untitrated sulfhydryl groups remained in the

polymer, some of these would have reacted with the excess silver ions present in the solution from additions past the end point. In this case the silver analyses would have been higher in contrast to the results in table 1.

It can be concluded, therefore, that it is feasible to determine sulfhydryl groups in a swollen disulfide or alkylene sulfide crosslinked polyamide by conductometric titration with AgNO_3 . The accuracy of the method compares favorably with usual end-group analyses in polymers, and suggests its possible wider applicability.

The authors thank R. A. Paulson, Applied Analytical Research Section, National Bureau of Standards, for the silver analyses.

4. References

- [1] S. D. Bruck, J. Research NBS **65A** (Phys. and Chem.), No. 6, 489 (Nov.-Dec. 1961).
- [2] Structural modification of synthetic fibers, NBS Tech. News Bull. **45**, 152 (1961); Cross-links crimp and coil nylon-6 fiber, Chem. Engr. News pp. 50-51 (Oct. 23, 1961).

- [3] S. D. Bruck, J. Research NBS **66A** (Phys. and Chem.), No. 1, 77 (Jan.-Feb. 1962).
- [4] S. Dal Nogare, Organic Analysis, Vol. I, p. 329 (Interscience Publishers, Inc., New York, 1953).
- [5] S. Siggia, Quantitative Organic Analysis Via Functional Groups (John Wiley & Sons, Inc., New York, 1949).
- [6] W. M. Malisoff and C. E. Anding, Jr., Ind. Eng. Chem. Anal. Ed. **7**, 86 (1935).
- [7] E. R. H. Davies and J. W. Armstrong, J. Inst. Petroleum **29**, 323 (1943).
- [8] I. M. Kolthoff and W. E. Harris, Ind. Eng. Chem. Anal. Ed. **18**, 161 (1946).
- [9] J. R. Sampey and E. E. Reid, J. Am. Chem. Soc. **54**, 3404 (1932).
- [10] I. M. Kolthoff and W. Stricks, Anal. Chem. **23**, 763 (1951).
- [11] I. M. Kolthoff, D. R. May, P. Morgan, H. A. Laitinen, and A. S. O'Brien, Ind. Eng. Chem. Anal. Ed. **18**, 442 (1946).
- [12] R. L. Hubbard, W. E. Haines, and J. S. Ball, Anal. Chem. **30**, 91 (1958).
- [13] S. D. Bruck, J. Polymer Sci. **55**, S 29 (1961).
- [14] S. D. Bruck, J. Research NBS **65A** (Phys. and Chem.) No. 6, 485 (Nov.-Dec. 1961).

(Paper 66A2-151)