

## Light Scattering Studies on the Ripening of Viscose Solution

KALYAN K. GHOSH, *Department of Chemistry, Shaw University, Raleigh,  
North Carolina 27602*

### Synopsis

Investigations were made on cellulose xanthate molecular weights by light scattering during the ripening of the solutions of (a) viscose-containing colored thio salts and (b) pure cellulose xanthate separated from viscose. Though an apparent reduction in molecular weight was recorded with time of ripening for the viscose solution, no such fall was observed with pure cellulose xanthate. The apparent fall of molecular weight in the case of viscose has been shown to be due to the increasing absorption of the incident beam and to the change in the value of  $dn/dc$  with progressive color formation. Reproducible results can be obtained for cellulose xanthate solutions freed from color. Intrinsic viscosity of the viscoses and the degree of polymerization (D.P.) of the regenerated cellulose from viscoses during ripening were also measured and found to be constant. The results indicate that no degradation of cellulose molecule takes place during the ripening process, irrespective of the state of degradation of alkali cellulose from which the viscose is made.

### INTRODUCTION

Physicochemical processes accompanying the "ripening" of viscose solutions are complex, and despite several attempts, very little is known regarding the state of cellulose molecules at this stage of the viscose process. Early investigations<sup>1-7</sup> were made by viscosity measurements of commercial viscoses. Application of light scattering to determine the molecular and interaction parameters of viscose has been made recently,<sup>8-12</sup> but because of the nonideal solution compositions, the results of such experiments and interpretation of data may suffer from uncertainties.

In an attempt to examine the suitability of light scattering techniques to study viscose solutions, Onyon<sup>9</sup> used two model viscoses of different CS<sub>2</sub> content and observed that the molecular weight of cellulose xanthate gradually decreases with the time of ripening, thus indicating the degradation of cellulose molecules. This observation is contradictory to previous understanding<sup>13</sup> that, although there would be considerable degradation during the "aging" of alkali cellulose, there is very little if any degradation during the ripening of the viscose solution.

The present work reports the results of further investigations on the state of cellulose molecule during the "ripening" of viscose solution by light

scattering and viscosity measurements. Special effort has particularly been made to study the solutions of pure cellulose xanthate separated from all the by-products of the viscose reaction, to avoid interference in the light scattering measurements.

## EXPERIMENTAL

### Samples

Viscose solutions were prepared in the laboratory from cotton cellulose (D. P. 1200) using a simulated industrial process. Cellulose was steeped into 18% sodium hydroxide solution at 25°C for 30 min, and then filtered and pressed on glass filters to a press-weight ratio of 1:3.5. Alkali cellulose thus obtained was "aged" at 25°C for different lengths of time (0 to 72 hr) before xanthation. Xanthation was carried out by injecting measured volumes of CS<sub>2</sub> in small increments to alkali cellulose over a period of 3 hr. The orange-yellow crumbs of sodium cellulose xanthate were dissolved in 2.5*N* NaOH solution to a cellulose concentration of 6%. The stock solutions of viscose were stored at -5°C before use. The sample designations and descriptions are given in Table I.

TABLE I  
Designation and Description of Viscose and Pure Cellulose Xanthates

Sample designation		Age of alkali Cellulose, hr	CS <sub>2</sub> , % (on basis of dry cellulose)
Viscose	Cellulose xanthate		
V-1	P-X-1	0	72
V-2	P-X-2	24	72
V-3	P-X-3	48	72
V-4	P-X-4	72	72

Pure cellulose xanthate solutions were prepared from the aliquots of viscose solutions as follows: Cellulose xanthate was precipitated completely from the viscose by slowly adding excess of methanol to the viscose solution maintained at 0°C. The light-yellow precipitate of sodium cellulose xanthate was then quickly filtered and washed several times with methanol to free it from colored thio salts. Excess methanol was removed by washing with ether, and the vacuum-dried product was redissolved in 2.5*N* sodium hydroxide. The concentration was adjusted to 6% cellulose. This solution was similarly stored at -5°C before use.

### Ripening

Stock solutions of both viscose and cellulose xanthate were diluted five-fold with 2.5*N* sodium hydroxide and then placed in a bath maintained at 30° ± 0.1°C. Aliquots were withdrawn at definite intervals for physical and chemical measurements.

### Light Scattering

The usual procedures and precautions were taken to obtain optically clear solutions free from extraneous dust and microgel particles. A Brice-Phoenix Universal Light Scattering Photometer, Series 1999-10, was employed. The wavelength used was 546  $m\mu$  for both the solutions. Scattering intensities were measured at 45°, 90°, and 135°C using semioctagonal dissymmetry cells. Molecular weights were calculated using the Debye equation<sup>14</sup>

$$Hc/\tau = 1/M_w + 2Bc$$

where  $\tau$  is turbidity in  $\text{cm}^{-1}$ ,  $c$  is concentration in  $\text{g}/\text{cm}^3$ ,  $B$  is the second virial coefficient, and  $H$  is a constant relating refractive index of solvent,  $dn/dc$ , Avagadro number, and the wavelength of light.

For highly colored solutions, absorption correction according to the method of Brice et al.<sup>15</sup> was applied. Intrinsic dissymmetry  $[Z]$  was determined from a plot of  $1/(Z-1)$  versus  $c$ ,<sup>16,17</sup> and the values were used to evaluate the  $P(\theta)$  for interference effects.

### Refractive Index Increment

Refractive index increment,  $dn/dc$ , for cellulose xanthate was determined using a Brice-Phoenix Differential Refractometer. A value of 0.185 ml/g was obtained. The determination of  $dn/dc$  for viscose solutions is difficult

TABLE II  
Refractive Index Increment,  $dn/dc$ , for Viscose and Cellulose Xanthate Solutions

Sample	$dn/dc$ , ml/g	Reference
Viscose	0.21	Tait et al. <sup>8</sup>
Viscose	0.23	Claesson and Brunn <sup>18</sup>
Viscose	0.20, 0.19	Onyon <sup>9</sup>
Cellulose xanthate	0.185	Present work

because of its deep orange color. The value also depends upon the amount and distribution of xanthate groups. The values obtained by previous workers are reported in Table II. Since the viscoses made in this study are similar to those used by Onyon,<sup>9</sup> his value of 0.20 ml/g was used.

### Viscosity

Viscosity measurements were made with a standard Ostwald viscometer at a temperature of  $30^\circ \pm 0.1^\circ\text{C}$ . The efflux time for 10 ml of water at this temperature was 130 sec. No kinetic energy corrections were made, and the intrinsic viscosity,  $[\eta]$ , was determined from the plot of  $(\eta_{sp}/c) = [\eta]$ .

### Degree of Polymerization

At definite time intervals during the ripening, cellulose was regenerated by treating aliquots of the viscose with a solution of the following composition<sup>19</sup>: H<sub>2</sub>SO<sub>4</sub>, 8.0 g; glucose, 10.0 g; ZnSO<sub>4</sub>, 1.0 g; Na<sub>2</sub>SO<sub>4</sub>, 12.0 g; and water, 69.0 g.

The regenerated cellulose was first freed from acid by water and then from colloidal sulfur by repeated washing with 2% Na<sub>2</sub>S solution at 50°C. Finally, the purified cellulose was dried at 50°C.

The degree of polymerization of the regenerated cellulose was determined following the method of nitration of Alexander and Mitchell.<sup>20</sup> The cellulose trinitrate thus prepared was dissolved in ethyl acetate, and the viscosity for a solution of 0.07% cellulose nitrate was measured at 30°C. The degree of polymerization was calculated from the following equations:

$$D. P. = K[\eta] = \frac{\eta_{sp}/c}{1 + k'\eta_{sp}}$$

where  $K = 75$  and  $k' = 0.35$  for ethyl acetate.

## RESULTS AND DISCUSSION

### Light Scattering

Throughout the discussion the term "viscose" will refer to the solution of sodium cellulose xanthate containing all the by-product colored salts, and "pure cellulose xanthate" to the same solution freed from colored salts.

The results of light scattering measurements with viscose solutions indicate that the molecular weight decreases gradually with the time of ripening. Plots of  $c/\tau$  versus  $c$  for a representative viscose as a function of time are shown in Figure 1. The molecular weights for sample V-3, calculated after correction for particle scattering factor have been found to decrease from  $7.69 \times 10^5$  at 0 hr to  $1.26 \times 10^5$  at 96 hr, showing a fivefold decrease. This observation, although similar to that made by Onyon<sup>9</sup> and to the viscosity measurements of Signer and Meyer<sup>6</sup> does not agree with the findings made earlier<sup>1,7</sup> with commercial viscoses. Viscosity measurements made in this work also indicated no change in the intrinsic viscosity values during ripening.

The discrepancy arises from the faulty observations of scattering intensity in the presence of the colored thio salts, which formed even in more quantities with time of ripening. A measurement of the transmission showed a decrease from 89% for freshly prepared viscose to 60% after ripening for 96 hr, when the solution becomes deep orange in color. The decrease in molecular weight with the time of ripening appears to be more apparent than real.

A second contributing factor influencing the light scattering observation is a change in  $dn/dc$ , which can occur with a change in degree of xanthation and its distribution. The progressive formation of colored thio salts

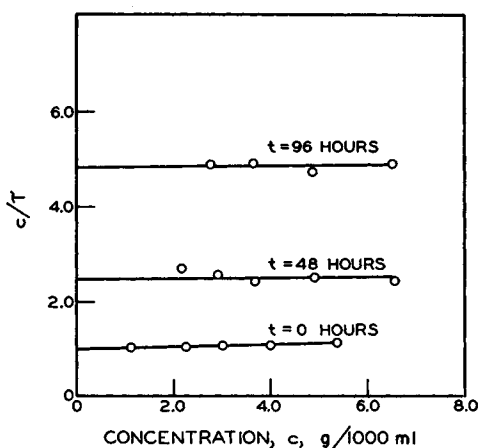


Fig. 1. Plot of  $c/\tau$  vs.  $c$  for the viscose solution at different hours of ripening. "Age" of alkali cellulose, 0 hr.

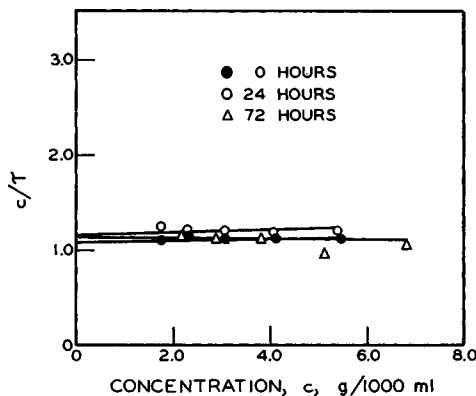


Fig. 2. Plot of  $c/\tau$  vs.  $c$  for pure cellulose xanthate solutions at different hours of ripening. "Age" of alkali cellulose, 72 hr.

changes the composition of the solution, also affecting the value of  $dn/dc$ . Therefore, the measurements of molecular weight by light scattering in such a complex and variable system is unlikely to produce reliable results.

To avoid these difficulties, a series of experiments were also made with pure cellulose xanthate solutions. The  $c/\tau$  versus  $c$  plot as a function of time of ripening for sample P-X-4 is shown in Figure 2. No degradation up to 72 hr of ripening for such a sample was observed. Although the ripening of pure cellulose xanthate solutions was conducted up to 120 hr, no appreciable color development was noticed. To determine if the initial chain degradation during the aging of alkali cellulose has any influence on further chain degradation during the ripening stage, similar measurements were made with viscoses prepared from alkali celluloses which were either undegraded or degraded for an insufficient length of time. However, in each

TABLE III  
Molecular Weights of Cellulose Xanthates and Viscose in 2.5*N* NaOH  
Solutions at Different Times of Ripening at 30°C

Sample	$M_w \times 10^{-5}$ , at ripening hour					
	0 hr	24 hr	48 hr	72 hr	96 hr	120 hr
P-X-1	12.99	12.82	12.82	13.33	13.33	—
P-X-3	—	—	7.35	7.63	7.35	8.27
P-X-4	5.71	5.71	—	5.97	—	—
V-3	7.69	—	2.31	—	1.26	—

case the molecular weight of cellulose xanthate remained steady for the whole period of ripening. The data are summarized in Table III. It should be noted that the molecular weight data presented should not be considered as absolute because of several uncertain factors. However, their relative values are significant.

### Viscosity

It has been observed that the viscosity of undiluted viscose solutions decreases during the ripening period, passes through a minimum, and then increases on further aging. In the case of ripening of diluted (1% cellulose or less) viscose, however, no such change in viscosity is observed. Ghosh et al.<sup>21</sup> demonstrated that in the case of concentrated solutions, the decrease is due to a further increase in dispersion of the cellulose xanthate molecules, not to chemical degradation. Since the intrinsic viscosity of viscose is influenced by factors such as cellulose D. P., degree of xanthation and xanthate substitution, strength of alkali, etc., all the preparative and solution conditions were maintained constant to obtain time-dependent viscosity values during solution aging. Time-dependent intrinsic viscosity values for the four viscose solutions are shown in Table IV. Within the limits of experimental error, the data show a steady intrinsic viscosity for all the viscose solutions studied over a ripening period of 168 hr. These observations support the results obtained by light scattering experiments with cellulose xanthate and demonstrate that no degradation of cellulose occurs at this stage of viscose process.

TABLE IV  
Intrinsic Viscosities of Viscose Solutions in 2.5*N* NaOH  
Solutions at Different Times of Ripening at 30°C

Sample	$[\eta]$ , at ripening hour							
	0 hr	24 hr	48 hr	72 hr	96 hr	120 hr	144 hr	168 hr
V-1	2.075	2.075	2.000	2.150	—	2.075	2.100	—
V-2	1.750	1.650	1.700	1.700	1.730	—	—	—
V-3	1.430	1.430	—	1.350	1.420	1.350	—	—
V-4	1.330	1.330	1.270	1.420	—	1.420	—	1.300

### Degree of Polymerization of Regenerated Cellulose

The effect of ripening on the D. P. of cellulose was also studied by regenerating the cellulose from viscose solutions and determining its D. P. by nitration and viscosity measurement in ethyl acetate solution. The D. P. of four samples of a viscose sampled at 0, 9, 20, and 70 hr of ripening are shown in Figure 3. The D. P. remained fairly constant over the period studied, supporting the light scattering observations and viscosity measurements.

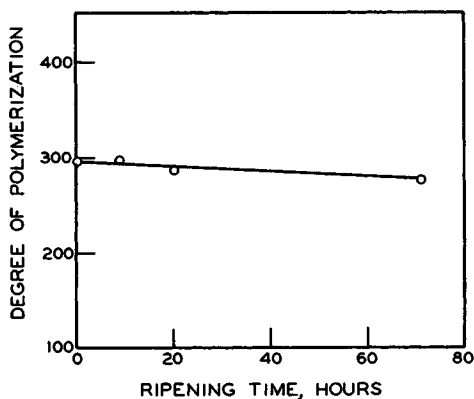


Fig. 3. Degree of polymerization of regenerated cellulose at different hours of ripening.

### CONCLUSIONS

Determination of molecular weight of pure cellulose xanthate along with the intrinsic viscosity and D. P. measurements of viscose have confirmed earlier observations<sup>1,7</sup> that no degradation of cellulose molecules occurs during the ripening, irrespective of the state of degradation of alkali cellulose used for its preparation.

Secondly, the study has also shown the possible sources of error in the results of light scattering measurements with viscose solution. The gradual decomposition of the xanthate group and the reaction of freed  $\text{CS}_2$  with NaOH lead to the progressive formation of highly colored thio salts. Measurements of scattering intensities in such solutions would introduce additional complexities due to consumptive absorptions by colorants yielding erroneous informations about the polymer component of viscose.

Such difficulties, however, may be avoided either by separating the cellulose xanthate from viscose by the method described in this paper or by removing the colored ions by an ion exchange method as shown by Samuelson and Gartner.<sup>22</sup>

Further, the cellulose xanthate molecules in viscose are anisotropic, which is attributable to the gradual distribution and decomposition of xanthate groups along the cellulose chain. Absolute data on the molecular param-

eters of cellulose xanthate cannot be obtained unless proper compensation is made for such anisotropy which also changes with time of "aging."

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Received January 20, 1970

Revised November 19, 1970