Anion Exchanging Polymers from Sodium Cellulose Xanthate and Polyethylenimine

SVEN SONNERSKOG
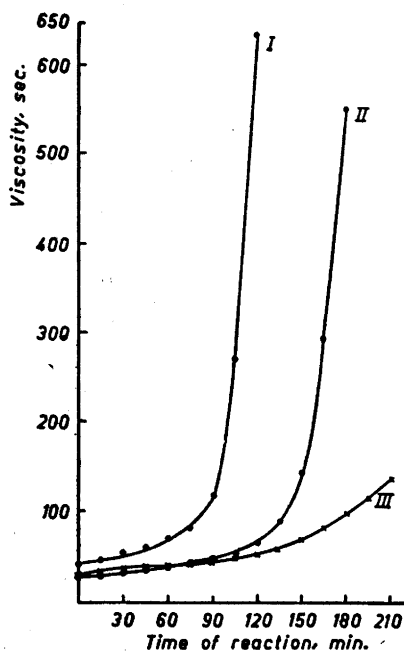
A-B Svenskt Konstsilke, Borås, Sweden

Fig. 1. Diagram, showing the viscosity increments in a Cochius tube at the gelation of technical viscoses, containing an excess (w/w) of polyethylenimine). Weight ratio polyethylenimine / cellulose = 3. Content of polymers in solution = 16 %. Type of Cochius tube: length = 195 mm, diam. = 18 mm, length of air bubble = 20 mm (approx). Temperature of solution 19.0° C.

Curve I: Low degree of ripeness, high salt index. (Index = 21).
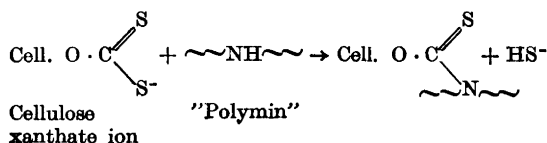
Curve II: Medium degree of ripeness, salt index = 10.

Curve III. High degree of ripeness, low salt index. (Index = 2).

Alkaline solutions of sodium cellulose xanthate react with polyethylenimine at room temperature. If an excess (weight by weight) of the latter polymer is present, solidification gradually takes place, accompanied by a strong syneresis. The final, transparent gel shows all distinctive features of rubber elasticity in a qualitative sense. Another striking change is established at a subsequent purification of the gel in water. The specimen keeps its geometric shape and degree of swelling virtually unchanged. Furthermore, this purified gel is insoluble in cuprammonium solution.

The time required for complete gelation is highly dependent on the composition and physical state of the viscose. At a given salt index a technical grade of viscose reacts faster than a corresponding one, from which anions such as trithiocarbonate have been removed by ion exchange. Such a solution shows a slightly greenish yellow colour even after complete gelation, which would imply that a reformation of trithiocarbonate ions is suppressed. Appreciable amounts of sulphide ions are formed, however, as can be seen by successive tests with standard reagents. It is apparent that a reaction takes place between cellulose xanthate ions and polyethylenimine, carbon disulphide acting as an interlinking agent. As is known, there is always a small amount of free carbon disulphide present in every viscose [1] at equilibrium. In the actual case the *added* polymer acts as an acceptor of CS_2, thus also causing a gradual dexanthation of the cellulose, but this circumstance alone does not explain the observed insolubility in cuprammonium.

The rates of gelation of technical viscoses are shown in Fig. 1. At a high salt index the gel point is reached within two hours, to judge from the viscosity increments in a Cochius tube. At a low salt index gelation is very slow. The change of viscosity during the same time is insignificant, but gelation is complete within 20—24 h. The same statement is valid for all viscoses, purified by anion exchange before the addition of coreactant. Their flow diagrams are not included here due to this circumstance.

Purification of the final crude reaction mixture is simple in principle but tedious in practice. The following description is valid for the specimen obtained in accordance with curve II in Fig. 1. The jelly was cut into chips, soaked in running distilled water for several days, until tests for sulphide ions were negative. This operation was repeated after swelling in dilute sodium hydroxide solution (strength 4 % b.w., temperature 70°C, time of

swelling 60 min.). For complete regeneration the wet chips were immersed in cold 1 N hydrochloric acid for 24 h, followed by washing in distilled water, soaking in sodium hydroxide solution and a final washing with hot distilled water until the excess of inorganic base has been removed.

The highly swollen, transparent chips show

$$\text{Cell. } O \cdot C \underset{S^-}{\overset{S}{\diagup}} + \sim\sim NH\sim\sim \rightarrow \text{Cell. } O \cdot C \overset{S}{\diagup} + HS^-$$
$$\underset{\sim\sim N\sim\sim}{}$$

Cellulose "Polymin"
xanthate ion

an average water content of 92 %. Drying at 70—80°C reduces the volume at least a tenfold. The dry polymer is a brittle, light yellow or amber, transparent resin, which cracks into flakes on rewetting. Polymer, prepared from viscose of medium degree of ripeness, showed a nitrogen content of 13.6 % (Kjeldahl) and a sulphur content of 2.1 % (Grote-Krekeler).
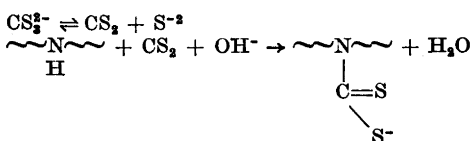
The wet polymer (primary gel or reswollen resin) acts as an anion exchanger. Chloride ions are adsorbed at the regeneration step in hydrochloric acid. This is easily seen at the addition of dilute nitric acid to a washed sample; chloride ions immediately reappear in the aqueous phase, as indicated by silver nitrate. Ion exchange in sodium hydroxide solution operates in an analogous manner and was used for determination of exchange capacity. A direct titration of chloride ions liberated by 1 N sodium hydroxide showed a value of 4.15 mequiv./g dry polymer. An alternative test, carried out by passing the aqueous phase through a hydrogen saturated cation exchanger, followed by alkalimetric titration, showed a capacity of 4.40 mequiv./g dry polymer.

It is apparent that a considerable amount of polyethylenimine has been linked to the cellulose molecules. As the interaction between the two components ends in non-solubility in cuprammonium, the formation of infinite networks by a chemical reaction between the two polymer species seems most probable. The polyelectrolyte (cellulose xanthate), as

well as polyethylenimine possesses abundant degree of functionality for a crosslinking reaction. Available information from analogous cases [2] indicates a reaction scheme as follows:
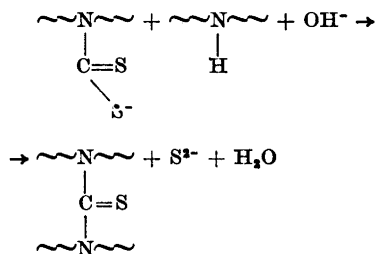
1. Formation of N-substituted thiourethans:

2. Formation of a derivative from dithiocarbamic acid. This may occur at random along chain molecules:

$$CS_3^{2-} \rightleftharpoons CS_2 + S^{-2}$$
$$\sim\sim N\sim\sim + CS_2 + OH^- \rightarrow \sim\sim N\sim\sim + H_2O$$
$$\overset{|}{H} \qquad\qquad\qquad\qquad \overset{|}{\underset{\diagdown}{C}=S}$$
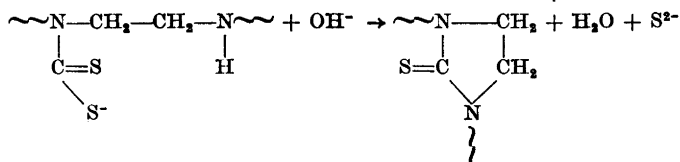$$\qquad\qquad\qquad\qquad\qquad\quad S^-$$

possibly accompanied by a minor formation of thiourea groupings, low enough to prevent insolubilization. (Alkaline solutions of polyethylenimine do not change their solubility characteristics when saturated with carbon disulphide at room temperature):

Interlinking:

$$\sim\sim N\sim\sim + \sim\sim N\sim\sim + OH^- \rightarrow$$
$$\overset{|}{\underset{\diagdown}{C}=S} \qquad \overset{|}{H}$$
$$\qquad\quad S^-$$

$$\rightarrow \sim\sim N\sim\sim + S^{2-} + H_2O$$
$$\overset{|}{C}=S$$
$$\overset{|}{\sim\sim N\sim\sim}$$

Intralinking:

$$\sim\sim N-CH_2-CH_2-N\sim\sim + OH^- \rightarrow \sim\sim N\!-\!\!\!-CH_2 + H_2O + S^{2-}$$
$$\overset{|}{\underset{\diagdown}{C}=S} \qquad\qquad \overset{|}{H} \qquad\qquad\qquad S=C \quad CH_2$$
$$\qquad\quad S^- \qquad\qquad\qquad\qquad\qquad\qquad\qquad \diagdown N \diagup$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$

At the purification of the crude reaction mixture components according to (2) are removed. All essential features of the reaction seem to be satisfactorily explained by the two cases in combination, e. g.

a. The formation of sulphide ions during the reaction.

b. The decreased rate of gelation when trithiocarbonate ions are removed by ion exchanger.

c. The regular formation of trithiocarbonate ions in viscose is suppressed by polyethylenimine.

d. The presence of sulphur and nitrogen in the purified polymer.

The analytical data permit an estimation of an average structural unit of the infinite network. This building unit may be preferably expressed by telling the numbers of anhydroglucose units and ethylenimine units statistically shared to a single interlinking unit:

$$\frac{b \text{ units of ethylenimine}}{a \text{ anhydroglucose units}} \mid \text{interlinking unit } (> C = S)$$
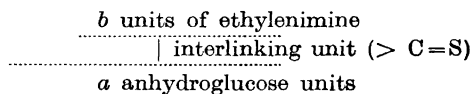
Weight of building unit $= 162a - 1$
$+ 44 + 43b - 1 = 162a + 43b + 42 = M_w$

Two equations are obtained from analytical data:

$14b/M_w = 13.6/100$, $32/M_w = 2.1/100$
with approximative solution (whole numbers) $a = 5$, $b = 15$, $M_w = 1\,500$.

% $N_{calc} = 14.0$, % $S_{calc} = 2.1$

The calculated building unit M_w contains 14 centres where anion exchange is possible. The maximum exchange capacity would thus be $14\,000/1\,500 = 9.3$ mequiv./g dry polymer, which should be compared with 4.4 mequiv./g, found in the actual case. Such a relation seems in no way unreasonable.

1. Hermans, P. H. *Physics and Chemistry of Cellulose Fibres*, Elsevier Publishing Co., Amsterdam 1949, p. 337.
2. Kline, E., in Ott, E. *Cellulose and Cellulose Derivatives*, Interscience Publishing Inc., New York 1943, p. 849.

The Ultraviolet Spectrum of Vitamin A₂

GEORG LAMBERTSEN and OLAF R. BRÆKKAN

Governmental Vitamin Laboratory, Norwegian Fisheries Research Institute, Bergen, Norway

The spetroscopic properties of vitamin A_2 have been investigated by several workers [1-3]. The most complete data up till now have been given by Cama and Morton [3] who made vitamin A_2 by reducing retinene₂ with lithium aluminium hydride. We have previously reported a method for the determination of vitamin A_2 based on a calculation of the data obtained from the ultraviolet absorption curve after careful chromatography of the unsaponifiable matter [4]. The method was extensively compared with the hitherto used method for the determination of vitamin A_2 based

Table 1. Relative extinction values for vitamin A₂-alcohol in abs. ethanol.

Wavelength	E/E_{max}	Wavelength	E/E_{max}
230	0.206	304	0.376
235	0.195	305	0.390
240	0.167	310	0.475
245	0.150	315	0.552
250	0.160	320	0.640
255	0.189	325	0.730
260	0.210	330	0.820
265	0.250	335	0.890
270	0.303	340	0.940
272	0.351	345	0.979
274	0.395	348	0.993
275	0.407	350	0.996
276	0.416	351	1.000
277	0.416	352	0.999
278	0.409	354	0.995
280	0.400	355	0.992
282	0.426	356	0.984
284	0.473	360	0.958
285	0.495	365	0.908
286	0.510	370	0.855
288	0.498	375	0.761
290	0.441	380	0.637
292	0.374	385	0.523
294	0.338	390	0.449
295	0.324	395	0.362
296	0.320	400	0.249
298	0.324	410	0.078
300	0.388	420	0.025
302	0.355		