

## The Swelling of Cellulosic Networks with Known Amounts of Crosslinks

A. M. RIJKE and W. PRINS, *Cellulose Research Institute, State University College of Forestry, Syracuse, New York*

The objective of the work communicated in this summary of the remarks made by one of us (W. P.) during the Symposium on Chemical Crosslinking of Cellulose, in St. Louis, has been to test the applicability of existing polymer network theories to cellulose and cellulose derivatives. For such a test it is of importance to have at one's disposal networks with exactly known amounts of chemical crosslinks. In particular, one would also want to introduce non-hydrolyzable crosslinks, to be able to study swelling phenomena in aqueous media.

The crosslinking of cellulose and its derivatives in acidic or alkaline aqueous media can be achieved in many ways by making use of the reactivity of the hydroxyl groups on the chain. In none of these cases, however, can suitable analytical procedures for the determination of the number of crosslinks as well as the number of pendant groups, which are invariably introduced, be found.

By working under completely dry conditions, we found that secondary cellulose acetate dissolved in dioxan can be crosslinked with 1,4-dibromobutene-2 to yield ether-type nonhydrolyzable gels, which can be analyzed for crosslinks as well as pendant groups. The pendant groups were counted by analyzing for the Br atom at the end of the pendant group. The sum of crosslinks and pendant groups was obtained by carrying out a double-bond bromination of the gel with a KBr-KBrO<sub>3</sub> solution, keeping the gel sufficiently swollen by employing 70% monochloroacetic acid.<sup>1</sup> Much larger pieces of clear gel could be obtained by employing a different crosslinking agent. For example, cellulose acetate solutions in dry dioxan are readily crosslinked by means of oxalylechloride<sup>1-3</sup> and diisocyanates.<sup>4</sup> Analysis for the oxalyl crosslinks is rather simple<sup>2</sup> but pendant groups in the oxalyl networks elude accurate analysis. If one employs diisocyanates this problem is easily solved.<sup>4</sup> In either case the disadvantage is that ester-type hydrolyzable crosslinks are intro-

duced, thus eliminating the possibility of studying the swelling in aqueous media.

Earlier treatments<sup>5</sup> of the swelling of polymer networks have been chiefly restricted to the statement that maximum swelling will occur if the cohesive energy densities of polymer ( $d_2$ ) and of solvent ( $d_1$ ) are equal. In the case of our ether-type cellulose acetate networks, for example, we found  $d_2 = 9.6$  by measuring the swelling in a series of solvents of known  $d_1$ . This information, however, is not very useful. More recent theories<sup>3</sup> based on the concept of randomly coiled polymer chains in the network show that at least three parameters are needed to predict the swelling of a crosslinked polymer, viz., (1) the number of crosslinks, (2) the degree of swelling at which the chains are unrestrained (to a first approximation this is the same as the reciprocal of the concentration of the polymer solution at which crosslinks are introduced), and (3) the Huggins polymer-solvent interaction parameter. Of these three parameters only the last is related to the cohesive energy density.

If one now measures the swelling of a network over a certain range, by lowering the solvent activity (e.g., by measuring a vapor sorption isotherm or by dissolving increasing amounts of an arbitrary polymer in the solvent phase), it can be shown<sup>3</sup> that at best two of these three parameters can be determined. Relying, then, on an osmometric determination of the Huggins parameter of cellulose acetate solutions before crosslinking we were able to show that cellulose acetate networks behave as rubbery networks as long as the degree of swelling is close to the reciprocal of the concentration at which the crosslinks are introduced. From a more speculative analysis we tentatively concluded that the cellulose acetate chains are not excessively stiff compared with those of other polymers.<sup>3</sup>

Finally, the ether-type networks were deacetylated to yield a regenerated cellulose which contains crosslinks introduced in the *dissolved* state. Some interesting observations of these samples

\* Present address: Laboratory for Physical Chemistry, Technische Hogeschool, Delft, The Netherlands.

could be made. Owing to the presence of crosslinks the degree of x-ray crystallinity in the dry state is extremely low ( $\approx 19\%$ ). The swelling in NaOH solutions is enormously enhanced (3-6 $\times$ ) above the swelling in alkali of normally regenerated cellulose (through the viscose process). The reason for these observations is clear: our samples, especially in the swollen state, are essentially amorphous networks because of the presence of crosslinks that impede crystallization. The increased swelling is of interest because it demonstrates very markedly that crosslinking in itself does not necessarily reduce the swelling, as is often assumed, or desired from a technological point of view. The state at which crosslinks are introduced (e.g., before or after a coagulation step in spinning) plays a decisive role

in determining the swelling, as is also brought out clearly by our experiments with cellulose acetate networks and the three-parameter rubbery-network theory.

### References

1. Rijke, A. M., Dissertation, 1961, Leiden University, the Netherlands.
2. Signer, R., and von Tavel, P., *Helv. Chim. Acta*, **26**, 1972 (1943); von Tavel, P., Dissertation, 1939, Bern, Switzerland.
3. Rijke, A. M., and Prins, W., *J. Polymer Sci.*, 1961 (in press).
4. Mukherjee, B., Cellulose Research Institute, Syracuse, N. Y., unpublished results.
5. Gee, G., *Trans. Inst. Rubber Ind.*, **18**, 266 (1943); Bristow, G. M., and Watson, W. F., *Trans. Faraday Soc.*, **54**, 1731 (1958).

END OF SYMPOSIUM

## POLYMER NEWS

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The first European Plastics and Rubber Conference will be held in Paris from May 18 to May 29, 1961, under the auspices of the International Union of Pure and Applied Chemistry.

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