MOLECULAR DIMENSIONS OF CELLULOSE DERIVATIVES[1]

Sir:

Although it has been widely believed that the molecules of cellulose derivatives are considerably more extended than typical vinyl polymers, the direct evidence supporting this is principally that of early light scattering measurements,[2] the accuracy of which might be in doubt due to the colloidal contaminants which are difficult to remove. We report here current work on the angular distribution of scattered light from sodium carboxymethyl cellulose (unfractionated, 1.15 acid groups per glucose), NaCMC, and cellulose trinitrate (fractionated), CN, which define more precisely the extent of coiling in these derivatives and demonstrate the inapplicability of the Flory–Fox[3] relation to cellulose derivatives of low and moderate molecular weight.

The customary interpretation of Zimm plots of the scattering data for NaCMC showed its weight average molecular weight to be 173,000 and its z-average end-to-end length to be 2410, 2590 and 3100 Å. in 0.5, 0.05 and 0.01 N NaCl solutions respectively. The corresponding intrinsic viscosities were 7.03, 10.1 and 15.9. These sizes are to be compared with the contour length which is estimated to be 5280 Å. on the assumption that the z-average molecular weight is 1.5 times the weight average one. Hence the mean length of these chains is about half their contour length. Since the Gaussian distribution of segments is no longer a good approximation for chains with valence angle near 110° when the mean length is more than one-third the contour length,[4] we are clearly dealing with non-Gaussian chains.

This fact has implications in both light scattering and intrinsic viscosity interpretations. In the former it means that the radius of gyration and not the mean length should be evaluated from the data since it is only the radius that can unambiguously be determined. The mean length is equal to $\sqrt{6}$ times the radius for Gaussian coils but the proportionality constant increases to $\sqrt{12}$ as a rod-like configuration is approached. Consequently, the sizes listed above are the radii of gyration divided by $\sqrt{6}$. It is of interest to note that the reciprocal intensity *versus* $\sin^2 \theta/2$ plot has a pronounced downward curvature as would be expected for chains deviating from Gaussian behavior. Consequently, the use of dissymmetry measurements leads to dimensions that are too small.

With respect to intrinsic viscosity, it is clear that non-Gaussian chains of this type cannot possibly satisfy the premise of the Flory–Fox relation, that is that the effective hydrodynamic volume of the polymer molecule is spherical and can be characterized by a radius that varies directly with a linear parameter of the Gaussian distribution. This is borne out by the constant Φ of the Flory–Fox relation calculated from the mean lengths and intrinsic viscosities given above and the z-average molecular weight. It is found to have values of about 0.15×10^{21} in contrast to 2.1×10^{21} for Gaussian coiled polymers. The use of the latter value implies that the unusually large temperature dependence of the viscosity observed in cellulose derivatives results solely from changes in dimensions. When the chains are non-Gaussian, however, the temperature dependence of Φ tends to mask these dimensional changes. Consequently, the dimensions of cellulose derivatives cannot be determined from viscosity measurements except within the region of high molecular weight or high temperature where the configurations are Gaussian. The neglect of these considerations has led to the erroneous conclusion that cellulose derivatives at ordinary temperatures are as flexible as typical vinyl polymers.[5]

As an example of Gaussian behavior possible in cellulose derivatives of high molecular weight, we report measurements on one CN fraction in acetone which was found to have a molecular weight of 3.9 million and a mean length of 4070 Å. The ratio of this to the contour length is 1:16.7. Assuming that the mean end-to-end length is proportional to the molecular weight, we find that the transition from Gaussian to non-Gaussian character occurs at a molecular weight of about 150,000 for CN. Of course, the transition occurs at a higher molecular weight for NaCMC since it is somewhat more extended. In the CN fraction mentioned the intrinsic viscosity calculated from the Flory–Fox relation is 35.5, which compares favorably with 31.5 obtained from extrapolating measured values to zero gradient.

GIBBS LABORATORY
DEPARTMENT OF CHEMISTRY PAUL DOTY
HARVARD UNIVERSITY NATHANIEL S. SCHNEIDER
CAMBRIDGE, MASSACHUSETTS ALFRED HOLTZER

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TRACER STUDIES ON THE FORMATION OF SULFUR FROM HYDROGEN SULFIDE AND SULFUR DIOXIDE IN AQUEOUS SOLUTIONS

Sir:

The reaction of hydrogen sulfide and sulfur dioxide in water leads almost quantitatively to sulfur if H_2S is present in sufficient excess[1,2]

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

If sulfur dioxide is used in excess elementary sulfur is formed together with a number of sulfur compounds in solution, mainly polythionic acids (Wackenroder liquid). The composition of this mixture varies strongly with the experimental procedure.[3]

We have investigated the origin of the elementary sulfur using hydrogen sulfide and sulfur dioxide, alternatively labeled with S^{35}, and comparing the specific activity of the sulfur obtained with that

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