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.

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[1] This work was carried out under ONR Contract N5ori-07654, T. O. 54, NR-330-025.

[2] (a) R. S. Stein and P. M. Doty, THIS JOURNAL, **68**, 159 (1946); (b) R. M. Badger and R. H. Blaker, *J. Phys. Colloid Chem.*, **53**, 1051 (1949).

[3] P. J. Flory and T. G. Fox, THIS JOURNAL, **73**, 1904 (1951).

[4] L. R. G. Treloar, *Proc. Phys. Soc.*, **55**, 345 (1943).

[5] L. Mandelkern and P. J. Flory, THIS JOURNAL, **74**, 2522 (1952); see also, S. Neuman and P. J. Flory, *J. Polymer Sci.*, **10**, 121 (1953).

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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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[1] E. H. Riesenfeld and G. W. Feld, *Z. anorg. allgem. Chem.*, **119**, 225 (1921).

[2] O. von Deines and H. Grassmann, *ibid.*, **220**, 337 (1934).

[3] For a recent review, see: Margot Goehring, "Fortschritte der Chemischen Forschung," Band 2, Heft 3, Springer Verlag, Heidelberg, 1952.

of the labeled reaction partner. These activities were measured on samples of barium sulfate, prepared from S, H_2S and SO_2 by oxidation, and were corrected for self-absorption.[4] The results are given in Table I.

TABLE I

Reactant labeled with S^{35}	Reactant used in excess	Ratio (as %) of specific activities of elementary sulfur and of labeled react. partn.
H_2S	H_2S	61, 64
SO_2	H_2S	34, 32, 34
SO_2	SO_2	31, 28
H_2S	SO_2	71, 70, 67, 66
		68, 74, 74, 70

The conditions in each series of experiments have been varied widely; reactants were sometimes added as solutions, sometimes in gaseous form, either undiluted, or diluted with nitrogen. Occasionally an excess of 0.1 *N* HCl was present, in which case the reactants were added as solutions of their sodium salts.

Lanthanum nitrate was added, sometimes before, sometimes after the reactants were mixed, to precipitate the sulfur. In most cases the elementary sulfur was filtered off within two hours but occasionally it was left in the solution overnight. In all experiments the mixing of the reactants was performed in less than one hour, in order to reduce the effect of reactions between the added compound and the reaction products, like polythionic acids.

Our results indicate that under all circumstances the main portion of the elementary sulfur originates from H_2S and SO_2 in the ratio 2:1. This conclusion is in agreement with all theories on the subject, in which the partial reaction responsible for the sulfur formation does not simultaneously produce other sulfur compounds.[1,5,6,9]

There is also formal agreement with the mechanism proposed by Zil'berman,[7] but only if the primary reaction is supposed to be really termolecular—as it is written by him—which is highly improbable. The reaction-mechanism of von Deines and Grassmann[2] could be made to agree with our results by introduction of several suppositions not explicitly made by these authors. Our observations exclude the mechanism proposed by Heinze.[8]

Another conclusion which may be derived from our results is that no appreciable exchange of sulfur between H_2S and SO_2 occurs within the time required for the formation of sulfur. The absence of such an exchange rules out the rapid formation of an intermediate compound in equilibrium with both reactants, unless the former compound contains sulfur atoms in positions which are not equivalent.

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[4] A. H. W. Aten, Jr., *Nucleonics*, **6**, No. 1, 68 (1950).

[5] F. Foerster and A. Hornig, *Z. anorg. allgem. Chem.*, **125**, 86 (1922).

[6] H. Stamm and M. Goehring, *cf.* the review by the latter, *loc. cit.*

[7] Ya. I. Zil'berman, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1257 (1940).

[8] E. Heinze, *J. Prakt. Chem.*, **99**, 109 (1919).

[9] H. Basset and H. G. Durrant, *J. Chem. Soc.* (London), 1401 (1927).

β-RAY INITIATION OF POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE

Sir:

The effect of β-radiation as an initiator of polymerization of pure styrene, pure methyl methacrylate and an equimolar mixture of these monomers has been studied.

The source of β-particles was an equilibrium mixture of anhydrous $Sr^{90}Cl_2$ and $Y^{90}Cl_3$ (half life of 19.9 years) giving a spectrum of electrons with a maximum energy of 2.24 Mev. The source was placed in a small glass bulb of about 2 mm. diameter. It was held by a rigid stem at the center of the spherical end of a small distilling flask which had a capacity of 8 cc. and which was filled with the monomer to be studied. The total energy of the particles entering the monomers was $5.0 \times 10^{-6} \pm 0.5 \times 10^{-6}$ cal./sec. and was completely absorbed by the surrounding monomer. The range of the 2.24 Mev. β-particles is *ca.* 11.5 mm. (depending upon the density of the material); the inner radius of our monomer-containing bulb was 12.4 mm.

The rates of β-ray induced polymerization of styrene, methyl methacrylate and the equimolar mixture were all measured at 30.5° in the vessels described above. Control experiments were made under identical conditions to measure the purely thermal rate. The results are shown in Table I.

TABLE I

POLYMERIZATION AT 30.5°

% CONVERSION PER HOUR

β-Ray induced	Monomer	Thermal
0.019	Styrene (S)	0.007
.26	Methyl methacrylate (MMA)	.11[a]
.039	Equimolar mixture (S) and (MMA)	.016

[a] This rate is somewhat high due probably to adventitious peroxides remaining after our purification procedure.

Each result given in Table I is the average of at least three runs—the maximum deviation being approximately 10% in the case of the β-ray induced polymerization. Air was found to be a powerful inhibitor of the β-ray induced polymerization and the thermal polymerization.

The composition of the copolymers was determined by C–H analysis and calculation of the % methyl methacrylate. The result of the determination[1] gave a methyl methacrylate content in the copolymer of 50.2% ± 4.0.

Walling, *et al.*,[2] have shown that an equimolar solution of styrene and methyl methacrylate gives a copolymer containing 49% methyl methacrylate

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[1] Clark Microanalytical Laboratory, Urbana, Ill., and Joseph F. Alicino, Metuchen, N. J.

[2] C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950).