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Study of Polymer Solution by Small-Angle Neutron Scattering in the Intermediate Momentum Range

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In the investigation of polymer solutions by small-angle neutron or X-ray scattering, the intermediate momenutm range corresponds to the distance between the radius of gyration R_G and the statistical subunit length l of the polymer chain. In this range, where the specific polymeric behaviour prevails, it can be shown, using the Debye relation, that the scattering curve presents a q^{-2} singularity, q being the momentum transfer. For real chains in solution this singularity is broadened by different factors: 1 – For a vanishing concentration c, there is a trivial effect due to the finite mass of the polymer [H. Benoit (1953). *J. Polym. Sci.*, **XI** (5), 507–510]. The scattering law is written as

$$S(q) \underset{c \to 0}{=} \frac{kc}{R_G^2 \left(q^2 + \dfrac{M_w}{M_n} R_G^{-2} \right)}$$

where k is constant, M_w and M_n are respectively the weight-average and the number-average molecular weight. 2 – For non-zero concentrations another broadening appears, due to the pair interaction between molecules. The scattering law is now

$$S(q) = \frac{kc}{R_G^2 \left(q^2 + \dfrac{M_w}{M_n} R_G^{-2} + \xi_{(c)}^{-2} \right)}.$$

The pair interaction term $\xi^{-2}(c)$ is linearly dependent on concentration. When the concentration is high enough one expects deviation of this broadening from linearity due to triplet interaction, *etc.* However in the case of a polymer solution a characteristic effect is predicted. Two concentration ranges are defined with respect to a critical concentration C^* at which the distance between chains d equals the radius of gyration R_G. (*A*) For $C > C^*$, but well below the density of bulk material, the chains overlap, and $\xi^{-2}(c)$ represents the pair interaction between *segments*. The inequality $d < R_G$ and the Flory inequality $vN^{1/2} > l^3$, where N is the number of segments per chain, indicate that $R_G^2 \xi^{-2} > 1$. Thus the scattering law reduces to the simple Lorentzian form

$$S(q) = \frac{kc}{R_G^2 (q^2 + \xi_{(c)}^{-2})}$$

where the term $\xi^{-2}(c)$ is interpreted as a screening length and is given by

$$\xi_{(c)}^{-2} = \xi_{sd}^{-2} = Avc$$

where A is a constant independent of molecular mass, and v the excluded volume, for one statistical unit of the chain. Evidence for the 'semi-dilute' range of polymer solutions must be given by the c dependence of ξ^{-2}. This has been done by small-angle neutron scattering [J. P. Cotton, B. Farnoux & G. Jannink (1972). *J. Chem. Phys.* **57**, 290–294] for polystyrene of molecular mass $M_1 = 6 \cdot 5 \times 10^5$ and $M_2 = 2 \cdot 1 \times 10^6$ in solution in deuterated benzene. (*B*) For $C > C^*$ the solution is dilute and the broadening $\xi^{-2}(c)$ takes into account the pair interaction between the *chains*. The chain concentration expansion of the thermodynamical functions yields

$$\xi_{(c)}^{-2} = \xi_d^{-2} = A(u/N^2)c$$

where u is the excluded volume for the coil–coil interaction. Experimental values of A and u indicate that $R_G^2 \xi_d^{-2} > 1$, for concentrations greater than 10^{-3} g cm^{-3} and for polymer molecular masses greater than 10^5. The Lorentzian form was thus again used to interpret the small-angle scattering experiment. The data where taken from a light scattering experiment with polystyrene of molecular mass $M_3 = 7 \cdot 5 \times 10^6$ in solution in benzene [A. Benoit & C. Picot (1966). *Pure Appl. Chem.* **12**, 545–561]. Interpolation of the light scattering and neutron scattering data gives a continuous concentration dependence of ξ^{-2} between 10^{-3} and 10^{-1} g cm^{-3} and shows: (1) ξ^{-2} is linearly dependent upon c above C^* *and* below C^*, (2) around $C^* \xi^{-2}$ deviates from linearity; (3) $\xi_{sd} < \xi_d$, which reflects the inequality $u < N^2 v$. This last inequality is noteworthy as a typical polymer configuration effect. Osmotic pressure concentration dependence agrees also with this interpretation [J. P. Cotton, B. Farnoux, G. Jannink & R. Ober (1973). *J. Phys. A*: *Math. Nucl. Gen.* **6**, 951–957; J. P. Cotton, B. Farnoux, G. Jannink & C. Strazielle (1974). *J. Polym. Sci. C*. In the press].

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