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Abstract

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ON THE RELATION BETWEEN MOLECULAR WEIGHT, THE SECOND VIRIAL COEFFICIENT, AND THE DIMENSIONS OF POLYMER COILS IN A GOOD SOLVENT

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Existing thermodynamic theories of solutions of linear coil-like macromolecules establish a relation between the molecular weight M, the second virial coefficient A_2, the coil dimensions in solution $\overline{(h^2)}^{1/2}$, and their swelling coefficient α. The correctness of the assumptions underlying one or another of these theories, and the validity of the relations obtained in it, can be checked by the simultaneous experimental determination of the quantities M, A_2, $\overline{(h^2)}^{1/2}$, and α. Up to the present time, however, the literature has contained practically no experimental data suitable for such a check. The experiment that ensures the simultaneous and direct determination of the four quantities indicated above is the measurement of light scattering by dilute polymer solutions. The difficulties that arise in this case are associated with the desirability of carrying out the corresponding measurements with polymers of very high molecular weight.

The theory of Flory—Orofino (^{1}) leads to the relation

$$A_2 = \frac{2^{1/2}\pi^{3/2}N_A}{3^{3/2}}\frac{\overline{(h^2)}^{3/2}}{M^2}\Psi(\alpha), \tag{1}$$

where N_A is Avogadro' s number; $\Psi(\alpha)$ is a function of the swelling coefficient α:

$$\Psi(\alpha) = \frac{4}{3^{3/2}}\ln\left[1 + \frac{\pi^{1/2}}{2}(\alpha^2 - 1)\right]. \tag{2}$$

A refinement of the Flory—Orofino theory, undertaken by Casassa and Markovitz (^{2}) by taking account of the connectivity of the segments in the chain, and then by Ptitsyn and Eisner (^{3}) by taking account of the influence of excluded-volume effects, led to a different form of the function $\Psi(\alpha)$. Figure 1 shows the course of the function $\Psi(\alpha)$ according to the three theories indicated. It is evident from the figure that measurements should preferably be carried out in the range of values $\alpha > 1.5$, where the discrepancy between the values of $\Psi(\alpha)$ predicted by the different theories becomes significant and exceeds the errors in the experimental determination of M and $\overline{(h^2)}^{1/2}$. However, large values of the coil swelling coefficients ($\alpha \simeq 1.5$—2.0) are attained only at sufficiently high molecular weights of the polymers ($M \simeq 10^7$).

The difficulties here consist in the fact that, for polymers with sufficiently large coil dimensions, the scattering indicatrix in good solvents is distorted by the influence of excluded-volume effects ([4,5]). To obtain the true value of the coil dimensions $\overline{(h^2)}^{1/2}$, measurements carried out by the method of double extrapolation ([6]) must be interpreted on the basis of a theory that takes excluded-volume effects into account ([7]). In addition, as established in ([8]), for a number of polymer—solvent systems there is an apparent dependence of A_2 on the scattering angle. Therefore, in relation (1) one must use the true value of A_2, obtained by extrapolation to zero scattering angle. The considerations indicated make the overwhelming majority of the data available in the literature on $\overline{(h^2)}^{1/2}$, A_2, and α of little use for checking relation (2). Let us note that until recently, for apro-

calibration of thermodynamic theories, the quantities $\overline{(h^2)}^{1/2}$ and α, calculated from the intrinsic viscosities $[\eta]$ in a good solvent and $[\eta]_\theta$ in an ideal solvent, were used, which is unacceptable in view of the theoretically and experimentally established fact that the coefficient Φ in the well-known Flory-Fox relation

$$[\eta] = \Phi \frac{\overline{(h^2)}^{3/2}}{M}$$

depends on the quality of the solvent ([9]).

We have already reported light-scattering measurements of poly-2,5-dichlorostyrene in an ideal solvent ([10]). Later we measured the light scattering of a number of fractions of this polymer with molecular weights from $3.5 \cdot 10^6$ to $19.6 \cdot 10^6$ in a good solvent—dioxane—which enabled us, along with M, $\overline{(h^2)}^{1/2}$, and A_2, to determine for these fractions the value of the swelling coefficients α.

Fig. 1. Dependence of the function $\Psi(\alpha)$ on α according to the theories: 1 —Flory-Orofino, 2 —Ptitsyn-Eizner, 3 —Casassa-Markovitz, and experimental points for poly-2,5-dichlorostyrene in dioxane (a) and polystyrene in toluene (b)

The measurement was carried out by the method of double extrapolation on a photoelectric nephelometer ([11]). In determining the dimensions of the coils $\overline{(h^2)}^{1/2}$, the influence of excluded-volume effects was taken into account ([7]). As a result of the measurements, values of $\Psi(\alpha)$ were calculated for various fractions on the basis of relation (1), which has the general form:

$$\Psi(\alpha) = \frac{3^{3/2}}{2^{1/2}\pi^{3/2}N_A}\,\frac{A_2M^2}{(\overline{h^2})^{3/2}}. \tag{1'}$$

These experimental values of $\Psi(\alpha)$ are plotted in Fig. 1. It turns out that in the range of α values from 1.5 to 1.8 the points lie considerably below the Flory-Orofino curve (relation (2)) and are grouped near the Casassa-Markovitz curve. On the same graph is plotted the value of $\Psi(\alpha)$ corresponding to our light-scattering measurements of a fraction $M = 20 \cdot 10^6$ of polystyrene in toluene and cyclohexane (^{7}) with $\alpha = 2.4$*. This point lies somewhat above the group of points referring to poly-2,5-dichlorostyrene, but also considerably below the Flory-Orofino curve.

Thus, our measurements for fractions of poly-2,5-dichlorostyrene of high molecular weight reveal a noticeable deviation of the relation between the second virial coefficient, the molecular weight, and the dimensions of the coils of the fractions from that predicted by the well-known Flory-Orofino theory.

It should be noted that the existing theories of polymer solutions are still far from taking detailed account of the specific interaction of a polymer with a solvent of a given chemical composition. One of the principal theoretical assumptions is the assertion that the unperturbed dimensions of polymer coils in an ideal ($A_2 = 0$) solvent $\overline{(h_0^2)}^{1/2}$ do not depend on the nature of this solvent (at a given temperature). Meanwhile, experimental facts (^{12}) are in contradiction with this assertion. Apparently, the very concept of the swelling coefficient α requires in some refinement. In this case the course of the function $\Psi(\alpha)$ may change, and $\Psi(\alpha)$ itself may lose its universal character.

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* This point corresponds to $\Psi(\alpha) = 0.30$, and not 0.35, as was erroneously indicated in paper (^{3}).

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Note: Figure translations are in progress. See original paper for figures.