Universality for Static Properties of Polystyrenes in Good and Marginal Solvents

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This Letter reports the first experimental evidence that solutions of linear flexible polymers are characterized by a concentration-dependent universal length which is easily scaled to be independent of molecular weight M ($3\times10^5 \leqslant M \leqslant 2.6\times10^7$) and of solvent quality. It is also found that the product of M and the derivative of the osmotic pressure π with respect to concentration c, $M(\partial\pi/\partial c)_T$, is universal and independent of solvent quality or M.

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The discovery of an analogy between magnetism and polymer chain conformation at infinite dilution[1] and its extension to finite concentration[2] have stimulated the study of polymer solutions during the past several years. Although the analogy for finite concentration corresponded only to a particular distribution of chain lengths in a "good" solvent (strong monomer-monomer repulsion), it was successful in predicting the power-law behavior observed for properties such as the static screening length[3] and osmotic pressure[3,4] in the semidilute regime. This regime corresponds to mass concentrations c such that the volume fraction $\varphi \ll 1$, but $c \gtrsim c^* \equiv M/N_A R_G{}^3$. Here, N_A is Avogadro's number, and R_G is the radius of gyration of an isolated polymer coil. (Thus c^* is the internal mass concentration of an isolated coil.) Many of the properties of solutions of such entangled coils in good solvents are molecular-weight independent and vary as some power of c. Similar behavior is observed at a theta point where the second virial coefficient B_2 vanishes, but the exponents are different.[5] Here, B_2 is the coefficient of the linear term in the expansion of $M\pi/cN_A k_B T$ in powers of c.

As recently shown,[6-9] the restrictions inherent in the magnetic analogy can be eliminated by use of conformation-space renormalization-group techniques. Results have been obtained for finite concentrations in good solvent,[9,10] and as a function of solvent quality at vanishing polymer concentration.[7,8] This theoretical progress offers hope for a unified treatment. Comparison[10] with the measured osmotic pressure[11] $\pi(c)$ for the good-solvent case is encouraging, and, in good agreement with the predictions, shows $M\pi/cN_A k_B T$ to be a universal function of c/c^* independent of molecular weight.

For solvents of intermediate quality (marginal solvents), mean-field theory has been used to predict behavior[12] in the semidilute regime which is not intermediate between that manifested in good and theta solvents. In particular, the thermodynamic quantity $(\partial\pi/\partial c)_T$ and the static screening length ξ_ρ are predicted to vary as c^1 and $c^{-0.5}$, respectively, while scaling arguments[3] yield $c^{1.25}$ and $c^{-0.75}$ for good solvents and c^2 and c^{-1} for theta solvents. Here ξ_ρ is the range of the density-density correlation function which has the Ornstein-Zernike form in the semidilute regime.[3,13]

Experimental evidence for marginal behavior is based on both dynamic measurements[12] (quasielastic light scattering) and static measurements[14,15] (x-ray and neutron scattering). Unambiguous interpretation of the dynamic measurements is not currently possible, however, and the static measurements are confined to relatively low-molecular-weight samples at high concentration. A well studied example is offered by polystyrene in methyl ethyl ketone (MEK) which is considered to show almost purely marginal behavior.[12,14]

By obtaining further experimental evidence concerning the effects of solvent quality we have been able to show that both $(\partial\pi/\partial c)_T$ and a characteristic length scale ξ exhibit universal behavior over a wide concentration range, independent of molecular weight or solvent quality. Consequently, a single framework exists within which it may well be possible to interpret both thermodynamic and scattering data for any linear flexible polymer in a nontheta solvent. In the asymptotic regime $c > c^*$, the observed behavior is consistent with scaling results and does not require the marginal-solvent hypothesis.

The experimental data consist of measurements of the intensity and angular distribution of light scattered by the various samples at 25 °C made with apparatus to be described separately.[16] The polystyrenes were purchased from Interchim ($M_w = 2.6\times10^7$, 7.2×10^6; $M_w/M_n < 1.3$), Toyo Soda ($M_w = 3.84\times10^6$, $M_w/M_n \leq 1.04$) and Pressure Chemicals ($M_w = 1.8\times10^6$, $M_w/M_n \leq 1.1$; $M_w = 3\times10^5$, $M_w/M_n \leq 1.06$; $M_w = 1.75\times10^4$, $M_w/M_n \leq 1.04$). Here, M_w and M_n are the weight and number average molecular weights, respectively. Solutions were filtered very slowly with pore sizes ranging from 0.2 to 3.0 μm depending on M_w and c. By measuring the dilute-solution properties of samples which had been repeatedly filtered at semidilute concentrations, it was verified that the filtration employed did not damage the polymers. We also confirmed the quoted values of M_w to within 10%. Concentrations were measured with a differential refractometer.

In general, the scattered intensity $S(q)$, corresponding to the scattering wave vector q, is given by

$$S^{-1}(q) \propto (\partial\pi/\partial c)_T[1 + q^2\xi^2 + O(q^4\xi^4)], \qquad (1)$$

which defines the characteristic length ξ measured in scattering experiments. At low concentration $\xi = R_G/\sqrt{3}$, where R_G is the radius of gyration of an isolated coil, and, as the concentration is increased, ξ crosses over smoothly to ξ_p in the semidilute regime where $S^{-1}(q) \propto (\partial\pi/\partial c)_T(1 + q^2\xi_p^2)$.

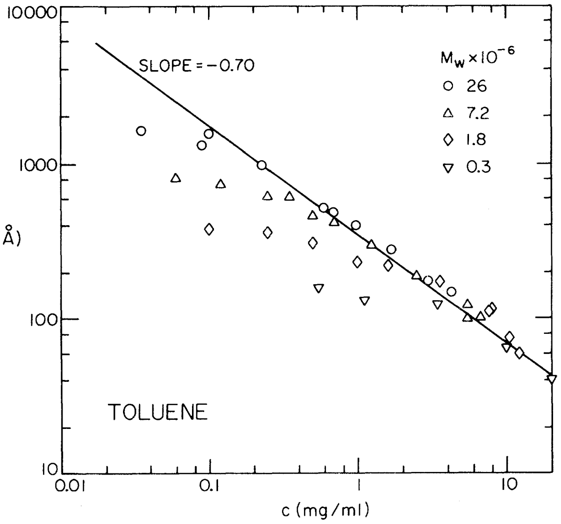

FIG. 1. The generalized length scale ξ as a function of concentration for various molecular-weight polystyrenes in the good solvent toluene.

Figure 1 shows the results for the generalized length scale ξ, defined above, as a function of polymer mass concentration in toluene. As expected, ξ becomes molecular-weight independent at high concentration, with lower-molecular-weight samples requiring higher concentrations to reach the limiting behavior. A fit to the portion we judged to be linear yielded $\xi_p \sim c^{-z}$ with $z = 0.70 \pm 0.03$. This confirms the results of Daoud *et al.* ($z = 0.72 \pm 0.06$) for polystyrene in carbon disulfide[3] and extends the observed concentration range downward more than a decade.

Figure 2 is a similar plot for the solvent MEK, but, in this case, we feel that there is no unambiguous evidence for a linear regime, presumably because of the poor solvent quality of MEK. However, in seeking a unified interpretation of the data presented above, we were able to show that the data sets for both toluene and MEK are identical in a fundamental way. This is illustrated in Fig. 3 which shows the reduced length ξ/R_G versus the reduced concentration X for all of the data. Here R_G is the measured value (as $c \rightarrow 0$) for each molecular weight and solvent, and X, which is directly proportional[10] to c/c^*, was determined from our measurements of the second virial coefficient B_2 as described below. Figure 3 shows not only that ξ/R_G is a universal function of c/c^* over the entire concentration range and not merely for $c \gg c^*$, but that surprisingly the dependence of this function on solvent quality is so weak as to yield the same function to within experimental accuracy for two very dissimilar solvents. The straight line in the figure has a slope of 0.75 and shows that both data

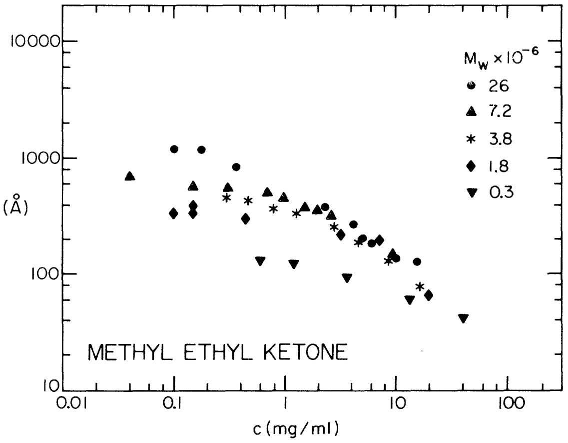

FIG. 2. The generalized length scale ξ as a function of concentration for various molecular-weight polystyrenes in the rather poor solvent MEK.

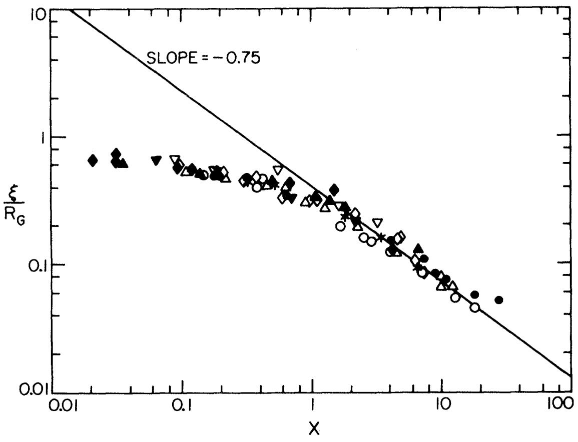

FIG. 3. The reduced length ξ/R_G as a function of the reduced concentration X for various molecular-weight polystyrenes in both toluene (open symbols) and MEK (solid symbols). Symbols are the same as for Figs. 1 and 2. Note that $\xi/R_G \to 1/\sqrt{3}$ as $X \to 0$.

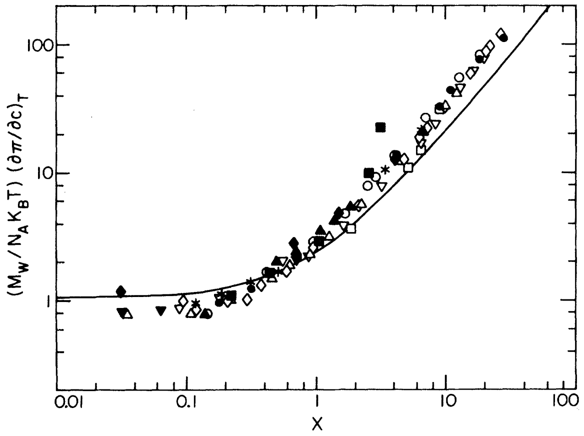

FIG. 4. $M_w(\partial\pi/\partial c)_T/N_A k_B T$ as a function of X for various molecular-weight polystyrenes in toluene and MEK. Symbols are as in Figs. 1 and 2, with the additional data for $M_w = 17\,500$ being represented by open and closed squares for toluene and MEK, respectively. The solid curve is Eq. (2) with no adjustable parameters.

sets are consistent with scaling predictions. Apparently, scaling both ξ and c in terms of the *measured* quantities R_G and B_2 removes sample dependence adequately to make this clear. To our knowledge, Fig. 3 represents the first experimental evidence of a universal length scale for solutions of linear flexible polymers.

In addition to the length scale ξ, we also measured the thermodynamic quantity $(\partial\pi/\partial c)_T$. In this case, a direct comparison with theory is possible because the concentration dependence of π in the good-solvent limit has been calculated by Ohta and Oono.[10] From their Eq. (8) with $M_w/M_n = 1.0$, we obtain

$$\frac{M_w}{N_A k_B T}\left(\frac{\partial\pi}{\partial c}\right)_T = 1 + \frac{1}{8}\left[9X - 2 + \frac{2\ln(1+X)}{X}\right]\exp\left\{\frac{1}{4}\left[\frac{1}{X} + \left(1 - \frac{1}{X^2}\right)\ln(1+X)\right]\right\}, \tag{2}$$

where $X = \alpha(c/c^*)$ with α a constant.

The experimental results for $M_w(\partial\pi/\partial c)_T/N_A k_B T$ vs X are shown in Fig. 4 for various molecular weights in both solvents. Again, we find that all of the results correspond to one universal curve. The variable X is related to the second virial coefficient B_2 by

$$X\left[\tfrac{9}{16} - \ln(M_w/M_n)/8\right] = B_2 c \tag{3}$$

as may be obtained by expanding Eq. (8) of Ref. 10 to first order in X. In relating B_2 and X, we used $B_2 c = \frac{9}{16}X$ which differs from Eq. (3) by less than 6% for $M_w/M_n \leq 1.3$. The solid curve in Fig. 4 is Eq. (2) with no adjustable parameters. We consider the agreement excellent, since Eq. (2) is the result of a first-order ϵ expansion. The deviations at small X are within the errors introduced by the concentration measurements.

Independently of our experimental work, we learned that both Freed[17] and Schäfer[18] have extended the theory to include dependence on solvent quality at finite concentration, and the results presented here are in qualitative accord with their findings. In particular, they both find that ξ/R_G is strongly dependent on X and only weakly dependent on solvent quality. Clearly, studies of the approach to the theta point and the relation between static and dynamic properties in the semidilute regime are needed.

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