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STATIC CORRELATIONS IN SEMIDILUTE POLYMER SOLUTIONS*

by

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Introduction

Static correlations in polymer solutions may be conveniently characterized using small angle x-ray scattering (SAXS). In this work, we report SAXS measurements of the concentration dependence of the correlation range, ξ , in semidilute solutions of polystyrene in butanone, a marginal solvent. The purpose of the work is to verify that ξ scales with concentration $C(\xi \sim C^{-x})$ and to compare the static scaling exponent x with the dynamic scaling exponent measured by light scattering methods.

Static correlations in polymer solutions are represented schematically in Figure 1, which shows the concentration dependence of a "characteristic length" associated with monomer-monomer correlations. In dilute solution, the polymer chains are widely separated so monomer spatial correlations extend for distances comparable to the radius of gyration R_G of the individual chains. At a critical concentration C^* , however, the chains begin to entangle and the correlation range becomes concentration dependent. In this semidilute regime(1) correlations within a polymer chain are "screened out" due to the presence of other chains. A considerable body of evidence (1,2,3) indicates that ξ scales with concentration ($\xi \sim C^{-x}$). In very concentrated or bulk systems the screening length becomes comparable to the monomer dimension L and the scaling concept breaks down.

More detailed analysis shows that an exponential spatial correlation function is expected in the semidilute regime(1). That is, if $\delta C(\underline{r})$ the fluctuation in monomer concentration at point \underline{r} , then

$$\langle \delta C(\underline{r}) \delta C(0) \rangle \sim \exp[-r/\xi] \quad (1)$$

The static structure factor $S(K)$ measured by SAXS is the Fourier transform of Eq.(1):

$$S(K) \sim \frac{1}{K^2 + \xi^{-2}} \quad \text{MASTER} \quad (2)$$

where K is related to the scattering angle θ and incident wavelength λ ($K = 2\pi\theta/\lambda$).

The experiments were performed in long slit geometry on a Kratky camera with a one-dimensional position sensitive detector(4). Using weighting function theory(5) the slit-smearred intensity $J(K)$ for this system becomes:

$$J(K) = \frac{A}{(K^2 + \xi^{-2})^{\frac{1}{2}}} \quad (3)$$

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where A is an apparatus constant. Therefore, ξ can be obtained from the slope and intercept of J^{-2} vs. K^2 .

Results

Figure 2 shows J^{-2} vs. K^2 for a typical sample. Although the signal to noise is poor, it is clear that Eq.(3) is obeyed within error. The data in Figure 2 have been corrected for sensitivity of the position sensitive detector and a background due to solvent scattering has been subtracted. Points near $K = 0$ have been dropped because of large errors due to detection of the incident beam. A weighting function of J^{-2} was used in the least-squares straight line fit shown. Data similar to Figure 2 were obtained at five concentrations and two molecular weights. The measured screening length obtained from the data is shown in Figure 3. Within error the data are consistent with the scaling assumption $\xi \sim C^{-x}$ and ξ is independent of molecular weight M. The scaling exponent is obtained from the slope of the data in Figure 3 with the result $x = .5 \pm .1$.

Discussion

The SAXS results are consistent with dynamical scaling behavior observed by light scattering on the same system.(2) In both cases, M independence and scaling behavior are consistent with the model developed by Daoud, et al.(1). In addition, the static and dynamic exponents are equal within error. The magnitude x, however, is not consistent with measurements(1) in good solvents ($x \cong .75$) or with the predictions of scaling theory ($.75(x < 1)$).

The model of entangled polymers developed by Daoud, et al.(1) follows directly from the observed properties of the data (scaling, M independence) and the crossover concept embodied in Figure 1. If ξ is to scale with concentration ($\xi \sim C^{-x}$) and become equal to R_G at the entanglement concentration C^* , ξ must be of the form $\xi \sim R_G (C/C^*)^{-x}$. The scaling exponent $x = \nu / (3\nu - 1)$ follows immediately from the known M dependence of R_G , C^* and $\xi (R_G \sim M^\nu, C^* \sim M^{1-3\nu}, \xi \sim M^0)$ where ν is the excluded volume exponent $\nu = \partial \ln R_G / \partial \ln M$. Taking the Flory value for $\nu = .6$, the predicted scaling exponent is $x = .75$. This result assumes that the chain displays excluded volume behavior ($\nu = .6$) for distances small compared to ξ . While this assumption is valid to very low M in good solvents, excluded volume behavior is observed only at very high M in marginal solvents such as butanone. In fact, a temperature dependent crossover molecular weight M_T can be defined(6) such that excluded volume behavior is observed for $M \gg M_T$ while ideal chain statistics ($\nu = .5$) are observed for $M \ll M_T$.

The crossover molecular weight can be estimated by application of the dilute solution theory of Benmouna and Akcasu(7) to the diffusion data of Gabler, et al.(8) to yield $M_T = 6 \times 10^4$. A single chain then can be visualized as consisting of M/M_T "renormalized" monomers. The renormalized chain would be expected to show excluded volume statistics for $M/M_T \gg 10$ (limiting statistical behavior is expected for a self-avoiding random walk of more than ten steps). It is reasonable to expect, therefore, that in semidilute solution limiting scaling behavior will be observed only for $M \gg 10M_T$ or $M \gg 6 \times 10^5$.

Although the concept of monomer renormalization provides a satisfactory explanation for the observation of different scaling exponents in marginal and good solvents, the magnitude of scaling exponents is still in question since direct application of single chain renormalization along with scaling assumptions leads to the prediction $x > .75$ in marginal solvents. In view of the fact that the observed exponent disagrees with

this prediction, it is clear that contemporary understanding of polymer entanglement in marginal solvents lags that in good solvents.

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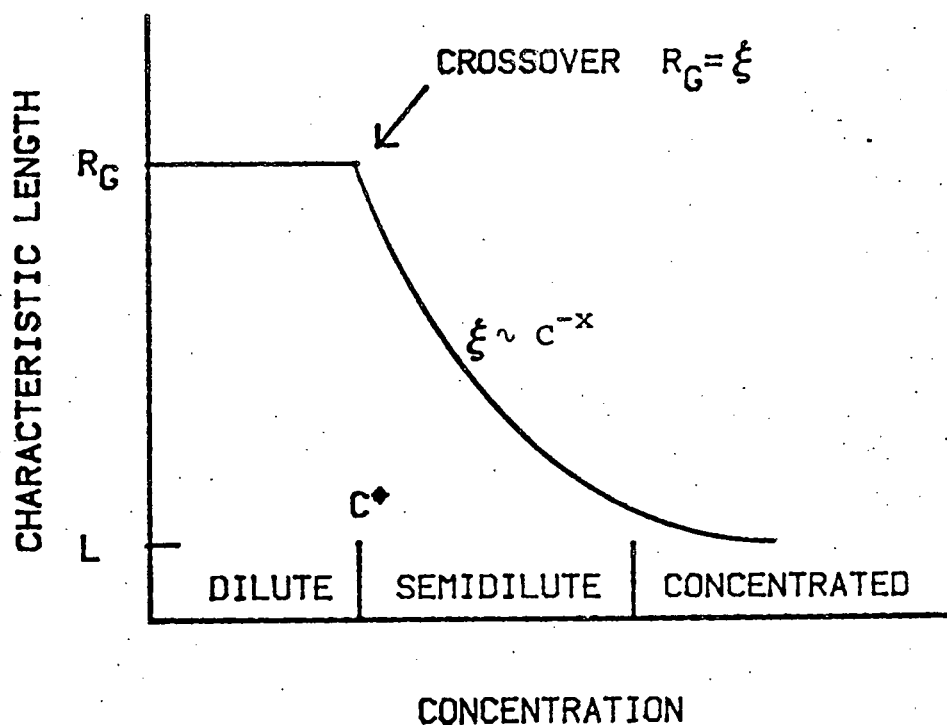


Fig. 1 - Characteristic lengths measured by SAXS of polymer solutions.

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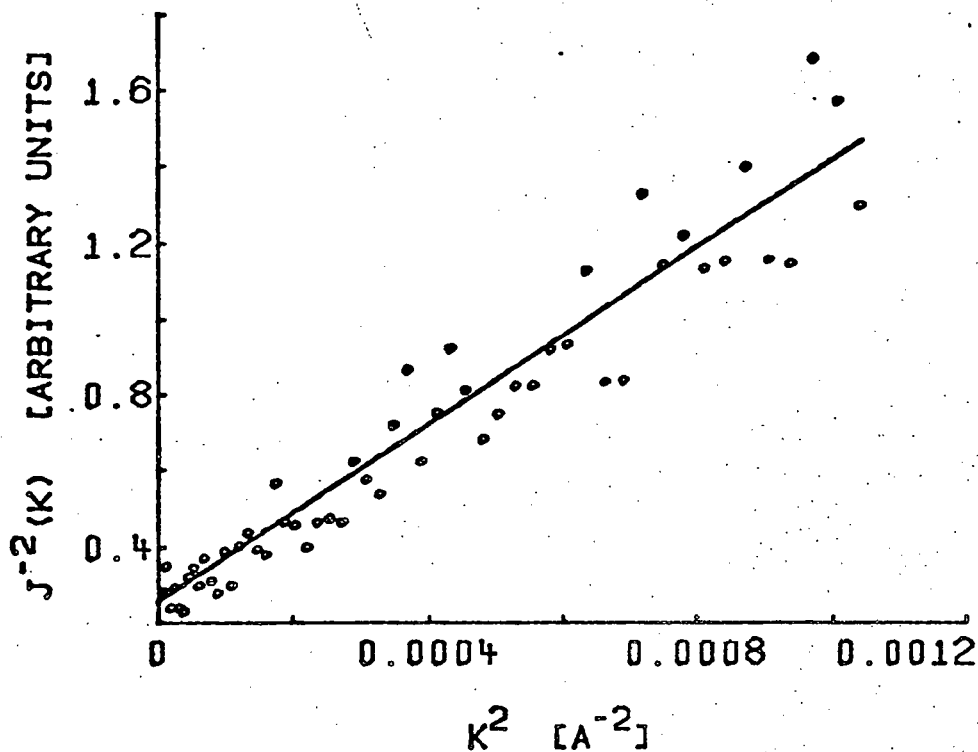


Fig. 2 - Slit-smear scattered intensity for a polystyrene in butanone at 23°C. $M = 390,000$, $C = 4.9$ gm/100 ml.

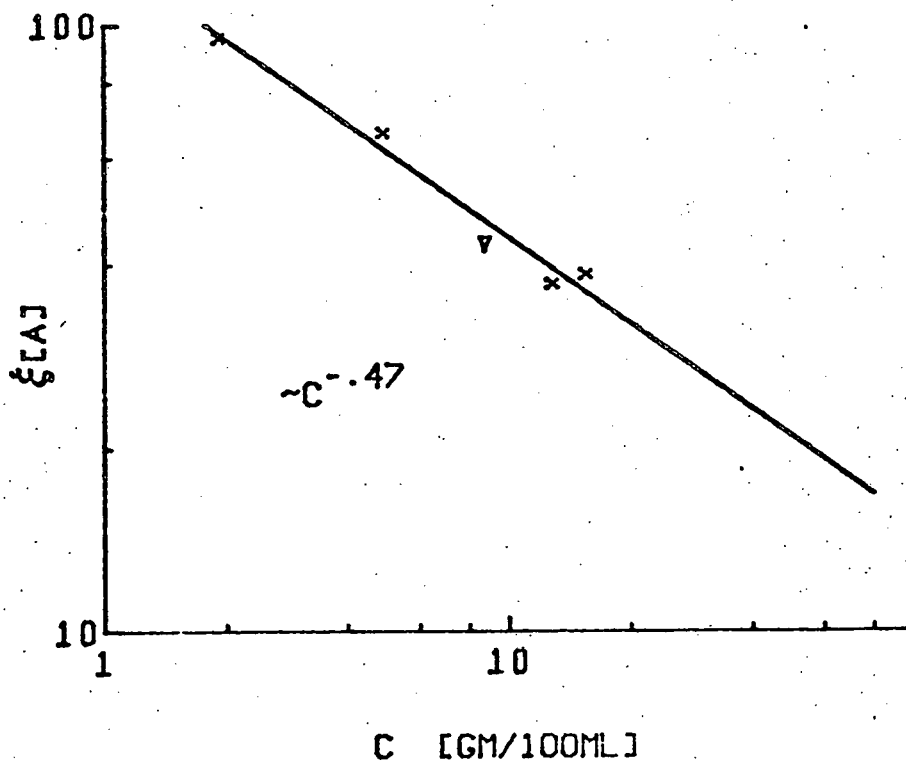


Fig. 3 - Concentration dependence of the static screening length. $M = 390,000x$; $M = 230,000v$; $T = 23^\circ\text{C}$.

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