(10) Bershtein, V. A.; Ryzhov, V. A.; Ganicheva, S. I.; Ginzburg, L. T. *Polym. Sci. USSR (Engl. Transl.)* **1983**, *25*, 1597.
(11) Gotlib, Yu. Ya.; Darinsky, A. A.; Klushin, L. I.; Neelov, I. M. *Acta Polym.* **1984**, *35*, 124.
(12) Bershtein, V. A.; Ryzhov, V. A. *Sov. Phys. Solid State (Engl. Transl.)* **1982**, *24*, 90.
(13) Nemoto, N.; Schrag, J. L.; Ferry, J. D.; Fulton, R. W. *Biopolymers* **1975**, *14*, 409.
(14) Kalus, J.; Hoffmann, H.; Reizlein, K.; Ulbricht, W.; Ibel, K. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 37.
(15) Rehage, H.; Hoffman, H. *Faraday Discuss. Chem. Soc.* **1983**, *76*, 363.

Determination of Correlation Lengths in Swollen Polymer Networks by Small-Angle Neutron Scattering

Neil S. Davidson,[†§] Randal W. Richards,*[†] and Ann Maconnachie[‡]

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K., and Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, U.K. *Received May 9, 1985*

ABSTRACT: The analogy between semidilute polymer solutions and swollen polymer networks is reviewed and some implications of current theories are considered. Small-angle neutron scattering has been used to measure a characteristic correlation length in randomly cross-linked polystyrene gels at swelling equilibrium in cyclohexane over the range 308–333 K and in toluene at ambient temperature. The equilibrium polymer volume fraction ranged from ca. 0.01 to 0.3, depending on the cross-link density and the solvent used. These results, together with those from earlier quasi-elastic light scattering measurements, were compared with reported scaling laws for polymer solutions. Although similar behavior was noted, the presence of permanent cross-links restricts the region wherein strong excluded volume effects are evident.

Introduction

Considerable insight into the understanding of highly swollen polymer networks, gels, has been obtained from an analogy with semidilute polymer solutions.[1] In a gel the macromolecules are connected by permanent junctions, the chemical cross-links, while in solutions only transient junctions occur, i.e., entanglements or other constraining interactions. In the spirit of this analogy, it is anticipated that it will only be in the very low-frequency properties that polymer solutions will display a different behavior to gels, that is, when the probing frequency is smaller than the reciprocal lifetime of the transient junctions in the solution. Consequently, the recent advances in polymer solution behavior theory should, in principle, be applicable to gels.

Contemporary theories of semidilute/concentrated solutions express the properties in terms of a fundamental length, ξ, being the radius of a volume inside which intramolecular effects are dominant and beyond which intermolecular effects prevail.[1-12] Static properties and equilibrium thermodynamics are discussed in terms of a static correlation length, ξ_c, while dynamic properties (e.g., as measured by quasi-elastic light scattering (QELS)) are characterized by a hydrodynamic screening length, ξ_h; these two parameters have been assumed to be identical with or at least directly proportional to each other. The detailed relation between the two parameters has been discussed by Muthukumar and Edwards.[51]

For a high degree of polymerization the short-range structure of the macromolecule is relatively insignificant, and universal laws that are a function of temperature, concentration, and interaction parameter can be derived for the global properties of the solution or gel and the characteristic length scales of the macromolecules (ξ or R_g, where R_g is the radius of gyration). Characteristic lengths may be measured directly or extracted by some model-dependent analysis of observable properties. Scattering experiments using light, X-rays, or neutrons are particularly useful since between them they cover a wide range of spatial and temporal resolution. The static scattering law, $S(\mathbf{Q})$, analyzed as a function of scattering vector $\mathbf{Q}$ can provide mean equilibrium dimensions while the first cumulant of the dynamic scattering law, $S(\mathbf{Q},t)$, may provide a cooperative diffusion coefficient that is subsequently interpretable in terms of ξ_h.

We describe here the results of measurement of ξ_c by small-angle neutron scattering (SANS) for randomly cross-linked polystyrene networks at equilibrium swelling at different thermodynamic conditions. Comparisons are made with available data for polymer solutions and our previously reported values for ξ_h obtained by QELS. The results are discussed in the framework of existing ideas on the correlation length, ξ, a précis of which is given in the next section, and the applicability of scaling laws to swollen polystyrene networks is examined.

Theoretical Background

The formulation of a comprehensive theory of polymer solutions and gels requires a thorough theoretical and experimental understanding of ξ. We attempt this here by providing an overview, in précis form, of current ideas on the nature of ξ, and we start with an isolated unperturbed macromolecule. The conformation of such a molecule is exactly describable by rotational isomeric state theory[13] and to all practical purposes is a random walk. In solution, the conformation is expanded by repulsive interactions between topologically remote segments of the chain (with respect to the contour length) that become spatially proximate. The molecule now adopts a self-avoiding walk,[14,15] wherein different segments cannot coincidentally occupy the same volume element of the solution, the well-known excluded volume effect. The theory and description of such self-avoiding walks and the interplay between temperature and solvent in influencing polymer conformation in dilute solutions are at a high level of development.[14]

In the discussion of the conformation of an individual molecule in more concentrated solutions, there have been two main approaches. Edwards uses a self-consistent field

[†] University of Strathclyde.
[‡] Imperial College.
[§] Present address: Exxon Research and Engineering Co., Annandale, NJ 08801.

0024-9297/86/2219-0434$01.50/0

approach for both infinitely dilute solutions[23] and concentrated solutions,[2] wherein the excluded volume effect is introduced as a perturbation of random walk statistics. For concentrated solutions where volumes of occupation overlap with each other, the effect is to screen the long-range intramolecular excluded volume interactions with a consequent alteration of the molecular conformation toward that of an unperturbed random walk. The characteristic length introduced is ξ_E, a screening length analogous to the Debye–Hückel screening length in electrolyte theory, and is defined as

$$\xi_E = (12c\nu N l^{-2})^{-1/2} \quad (1)$$

where c is the polymer concentration, l the statistical step length, ν a parameter characterizing excluded volume interactions, and N the degree of polymerization. Essentially, this theory views the molecule as expanded by excluded volume effects over distances shorter than ξ_E, while for greater distances repulsive interactions are screened and the conformation is that of a random walk.

The second approach to the theory of concentrated polymer solutions has arisen from an analogy between self-avoiding walks and critical phenomena in magnetic materials.[1,4-6,17,18] In particular, the results of the renormalization group techniques developed by Wilson[19] for magnetic spin systems combined with scaling theory have been applied to such solutions. A correlation length also results from this treatment but with a slightly different concentration dependence from that defined by Edwards. The macromolecule is conceived as a series of "blobs" of diameter ξ.[20,21] If we use n as a running bond index that measures the *contour distance* along the chain between individual segments, then the blob concept assumes there is a value of n (n_τ) below which Gaussian statistics prevail and the chain has an unperturbed random walk. The diameter of this thermal blob is ξ_τ, and

$$\xi_\tau^2 = n_\tau a^2 \quad (2)$$

where a is the length of a chain segment. For values of n greater than n_τ excluded volume effects are apparent and the chain statistics are that of a self-avoiding walk; the end-to-end distance of the chain is obtainable from

$$R^2 = (N/n_\tau)^{6/5}\xi_\tau^2 \quad (3)$$

When the concentration of polymer is such that molecules overlap, there exists another value of the monomer index n,n_c, whereat the conformational statistics for $n > n_c$ are those of an unperturbed Gaussian chain due to the interactions responsible for excluded volume effects becoming screened by the intervening chains. Inside such a "concentration blob" the chain statistics are those of a self-avoiding walk and the diameter, ξ_c, is given by

$$\xi_c^2 = n_c^{6/5}a^2 \quad (4)$$

The pair correlation function for a Gaussian arrangement of segments was derived by Debye,[22] and for $1 < r < R$ then

$$g(r) \sim r^{-1} \quad (5)$$

while for self-avoiding walks

$$g(r) \sim r^{-4/3}$$

Fourier transforming these pair correlation functions gives the single-chain scattering law, $P(\mathbf{Q})$, which for a Gaussian coil is

$$P(\mathbf{Q}) \sim \mathbf{Q}^{-2} \quad (6)$$

and for a self-avoiding coil

$$P(\mathbf{Q}) \sim \mathbf{Q}^{-5/3} \quad (7)$$

Hence it would appear possible to obtain a value of ξ_c from the value of the scattering vector, $\mathbf{Q}^{**}$, where the scattering law displays a crossover from Gaussian behavior to excluded volume statistics.

For times less than the characteristic disentanglement time, a solution ($c \geq$ semidilute) will behave as a network with a mesh size, i.e., distance between entanglements of ξ_2.[1,7-10] This mean mesh size is equated to ξ_c or ξ_E since both are proportional to the separation of binary interactions. Scaling law theories have produced a dependence of ξ_c on polymer concentration, c, which is strictly true only for conditions of strong excluded volume and infinite molecular weight.

$$\xi_c \sim c^{-3/4} \quad (8)$$

The differences between scaling-law relations and Edwards original mean field theory arises from the assumption in Edwards theory that the occupation of the neighboring sites to any particular site is uncorrelated with the occupation of that site. Improvements to the original theory have been made,[23,26] yet still retaining the self-consistent field approach. Extrapolation formulas have been obtained from the improved theories that describe polymer solutions from infinitely dilute to the bulk density;[3] moreover these formulas provide the proportionality factors as well as the concentration equipment. The relationships obtained are

$$\xi_E = (^9/_{16}\pi\alpha^{1/3})^{3/4}\omega^{-1/4}l^{-1}c^{-3/4} \quad (9)$$

in the limit $\omega \to \infty$ or $c \to 0$, and

$$\xi_E = (6\omega c)^{-1/2} \quad (10)$$

in the limit $\omega \to 0$ or $c \to \rho$, where α is a numerical factor, ω an interaction parameter, and ρ the bulk density. Evidently, eq 9 reproduces scaling-law data, while eq 10 is the original Edwards' prediction.

Schaefer[11,12] has proposed an alternative source to reconcile the scaling law and mean field results. The main feature of his theory is that the stiffness of real macromolecules counteracts the assumption of free rotation implicit in scaling laws. Due to this rigidity, moderate polymer solution concentrations are required before the size of the thermal blob, ξ_τ, approaches that of the concentration blob, ξ_c. When this condition is obtained, the excluded volume effect is strongly screened and weak, conformational properties are then best analyzed by perturbation methods.

This crossover is at a concentration, c, greater than the overlap concentration, c^*, defined by scaling law theories. A further crossover point, at a concentration $c^\dagger$, is predicted by Schaefer[11,12] where the chain becomes an unperturbed random walk at all length scales. In common with the original scaling-law analysis of Daoud and Jannink,[4] Schaefer[12] has also constructed a "phase" diagram of polymer solution behavior in the plane of a reduced temperature $\tau = (T - \Theta)/\Theta$, where Θ is the Flory temperature of the solution, and solution concentration. These diagrams purport to describe the behavior of polymer solutions with temperature, solvent quality, and concentration, and to some extent some of the predictions have been verified. Due to the finite molecular weight, Θ-solution behavior is displayed over a finite region of τ and c, and it can be shown by scaling-law analysis that in this region $\xi_c \sim c^{-1}$. Rigorously, it is incorrect to describe ξ_c as a screening length in this region, since there are no pairwise excluded volume effects to be screened.[1,9,10] Schaefer identifies ξ_c in this region with a mean distance between

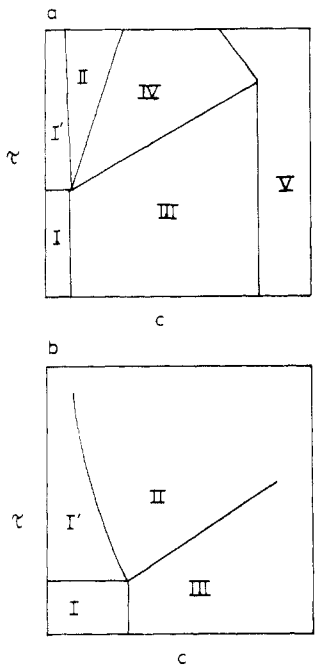

Figure 1. Proposed "phase diagrams" for polymer solutions by (a) Schaefer and (b) Daoud and Jannink. τ is the reduced temperature $(T - \Theta)/\Theta$ and c is the polymer concentration. The diagrams are not to scale and qualitative only. The regions represent the following environments for the chains: (I) dilute Θ; (I') dilute good solvent; (II) semidilute good solvent; (III) semidilute/semiconcentrated Θ; (IV) semiconcentrated marginal; (V) concentrated.

Table I
Predicted Scaling Laws between Correlation Length (ξ_c), Concentration (c), and Interaction Parameter ω

region	solvent type	scaling relation
II	good	$\xi_c \sim c^{-3/4}\omega^{-1/4}$
III	Θ	$\xi_c \sim c^{-1}\omega^{-1/2}$
IV	marginal	$\xi_c \sim c^{-1/2}\omega^{-1/2}$

ternary contacts. At concentrations approaching bulk polymer density, the segments are no longer completely surrounded by solvent, and the characteristic length scale is expected to be the statistical step length. Table I sets out the relationships for ξ_c in each of the regions of the phase diagrams.

The discussion thus far has centered on the pair correlation function for an individual selected chain. We may also obtain the pair correlation function between all segments in the solution.[1] For distances less than ξ_c the total pair correlation function is dominated by segments from the same chain whereon we have chosen our reference segment. For a distance $r > \xi_c$ the segment density of any one chain becomes less than the average density due to the other macromolecules being present. The segments become uncorrelated, dying out in a length ξ_c. The form of the total pair correlation function has been calculated by Edwards[2] for $r > \xi_c$, and the Fourier transform yields a Lorentzian type scattering law.[27,28]

$$S(\mathbf{Q}) = f(T,c)/(\mathbf{Q}^2 + \xi_c^{-2}) \qquad (11)$$

This equation may be utilized in two ways to obtain the correlation length ξ_c: by observation of a crossover in $\mathbf{Q}$ behavior from $\mathbf{Q}^2$ to $\mathbf{Q}^{5/3}$ as the chain statistics take on excluded volume behavior for $r < \xi_c$ (the value of $\mathbf{Q}$ where this is noted is written as $\mathbf{Q}^*$), and from the Lorentzian broadening in the region of $\mathbf{Q}$ where $\mathbf{Q}\xi_c \leq 1$.

For polymer gels, the link with scaling laws is obtained via the c^* theorem,[1] where c^* is the concentration at which chains begin to overlap. When a macromolecular permanent network is swollen to equilibrium by an excess of a thermodynamically favorable solvent, the equilibrium concentration, c_e, is proportional to c^*. Hence, apart from proportionality factors, polymer gels should display a correlation length, ξ_c, and furthermore this parameter should display the same concentration and interaction parameter (temperature) dependence as the equivalent un-cross-linked solution as set out in Table I. It cannot be said that ξ_c in gels is the "permanent" mesh size, i.e., the distance between cross-links, because transient interactions, entanglements, etc. also play a role in determining ξ_c. This is especially true when the gel is in the Θ state.

Over the past 10 years a number of measurements of ξ_c have been reported for semidilute solutions using SANS or SAXS. SANS has been the preferred technique because of the superior contrast available when using a suitable combination of deuterated and hydrogenous solution components. The majority of experiments have utilized the total correlation function, and in particular ξ_c has usually been determined from the Lorentzian broadening. Observation of the position in $\mathbf{Q}$ space of the crossover between scattering laws has been difficult, especially so where the single-chain correlation function is used for the case of a few deuterated molecules dispersed in the solution. It should be noted that although values of the correlation length obtained by the three methods (Lorentzian broadening and crossover point in scattering laws for labeled and unlabeled chains) differ in their absolute values, they display the same c,T behavior.

Scaling-law theory has been supported by data obtained for the concentration dependence of ξ_c for polystyrene in benzene,[27] in toluene,[50] in carbon disulfide,[5,20] and in cyclohexane above the Θ temperature.[29,30] In the latter case the authors showed the temperature dependence of ξ_c followed the scaling-law prediction, but other workers[31] have shown these data to be also consistent with a mean field interpretation. Mean field or marginal solvent behavior has been supported by results obtained for the temperature dependence of ξ_c for polystyrene in cyclopentane,[32] methyl ethyl ketone,[33] and cyclohexane.[29,33] The semidilute Θ concentration dependence of ξ_c may be inferred from data taken from ref 29 and 30.

As far as we are aware, there have only been two reports of attempts to measure ξ_c for swollen gels. Geissler et al.[34] extracted ξ_c from SANS of polyacrylamide–water gels. The results were compatible with scaling analysis predicted behavior for good solvent conditions and with results obtained from intensity measurements of dynamically scattered light using the same gels. Two other points of interest that were reported in this study were a decrease in ξ_c with increasing cross-link density at fixed concentration and perturbation of the SANS signal at low angles, which was attributed to inhomogeneities in the gel structure. Bastide[35] has reported that the SANS signal from a fully deuterated polystyrene network randomly cross-linked in cyclohexane solution using irradiation and then swollen to equilibrium in carbon disulfide was dominated by a large excess of scattering also attributed to static inhomogeneitites and ξ_c could not be determined.

There have been many investigations of quasi-elastic light scattering from both gels and semidilute solutions reported in the literature. Briefly, the results have given substantial support for an analogy between gels and solutions. As discussed above for static measurements, these experiments have produced evidence in favor of both asymptotic scaling laws and mean field theories. Many of these studies have recently been reviewed for solutions by

Roots and Nystrom[36,37] and for gels by Vaughan[38] and by Nossal.[39]

Experimental Section

Network Preparation. Randomly cross-linked networks were prepared by ^{60}Co γ-irradiation of linear atactic polystyrene[40] of molecular weight (M_w) ca. 10^5. The polystyrene was compression-molded into disks of 13-mm diameter and 1-mm thickness which were sealed into evacuated glass ampules prior to irradiation. A range of networks was prepared with total radiation doses between 2 and 10 MGy, thereby having a range of cross-link densities. The sol fraction in each network was removed by exhaustive extraction with toluene.

Solvents and Temperature Range. Networks were investigated when swollen to equilibrium in toluene at 293 K and in cyclohexane over the temperature range 308–333 K. The equilibrium degree of swelling under each solvent condition was determined by a weighing method.[41,42] For SANS experiments, network samples were swollen to equilibrium in deuterated solvents, toluene-d_8 (Aldrich, 99+ atom % d) and cyclohexane-d_{12} (Aldrich, 99.5 atom % d). These solvents were used as received, and it was assumed that the volumetric swelling of the gels was identical with that in the hydrogenous solvents.

Small-Angle Neutron Scattering. SANS measurements on equilibrium swollen networks were made with the D17 diffractometer at the Institute Laue-Langevin, Grenoble, France, and the SAS instrument at AERE Harwell; both instruments are very similar, the major differences being the $\mathbf{Q}$ range available. For D17 a neutron wavelength of 12 Å was used, and sample–detector distances were chosen to give $0.013 \leq \mathbf{Q}/\text{Å}^{-1} \leq 0.097$. On the SAS a wavelength of 6 Å was used and the $\mathbf{Q}$ range obtained was $0.023 \leq \mathbf{Q}/\text{Å}^{-1} \leq 0.16$. Swollen gels were enclosed in quartz cells with an excess of solvent and generally had a path length of ca. 2 mm. Temperature equilibration was ±1 K of the set temperature, and the duration of each measurement varied from ca. 30 min (D17) to 6 h (SAS).

All SANS data from the gels were normalized to the scattering from water obtained under the same conditions. For such normalized scattering, the scattered intensity as a function of $\mathbf{Q}$ can be written as[43]

$$I(\mathbf{Q}) = D_s T_s [d\Sigma_{coh}(\mathbf{Q})/d\Omega + \Sigma_{inc}/4\pi]$$

where Σ_{inc} is the macroscopic incoherent scattering cross section, $d\Sigma_{coh}(\mathbf{Q})/d\Omega$ is the differential macroscopic coherent scattering cross section, D_s is the path length in the sample, and T_s is the transmission of neutrons through the sample. The incoherent scattering constitutes a background signal that must be subtracted to leave the coherent scattering containing the structural information. In view of the aforementioned difficulties of Bastide et al.[35] in obtaining a value of ξ_c for gels, great care has been taken to account accurately for the background. Ideally, a background signal would be obtained from a mixture of polymer segments and solvent without the correlations existing in polymer segments due to short-range and long-range effects. As a closest approach to this situation, mixtures of benzene in cyclohexane-d_{12} and toluene in toluene-d_8 have been used. The neutron transmission and average normalized SANS intensity for a range of such mixtures are shown in Figure 2; these data were found to be relatively independent of temperature, and consequently the data at 308 K for benzene–cyclohexane-d_{12} mixtures have been utilized for the gels over the complete range of temperatures. The intensity data in Figure 2 were used in the following manner. Total macroscopic scattering cross sections were calculated for the swollen gels, and it was assumed that the correct background intensity to be subtracted corresponded to the solvent mixture of the same total scattering cross section, this intensity being interpolated from the intensity–volume fraction plots of Figure 2. After subtraction of this background, suitably corrected for any differences in path length and neutron transmission, we obtained the differential coherent scattering cross section

$$d\Sigma_{coh}(\mathbf{Q})/d\Omega = (\rho_p - \rho_s)^2 S(\mathbf{Q}) \quad (12)$$

where ρ_p and ρ_s are the coherent neutron scattering length densities of the polymer and solvent,[43] respectively. For our measurements with the hydrogenous polymer in deuterated solvents,

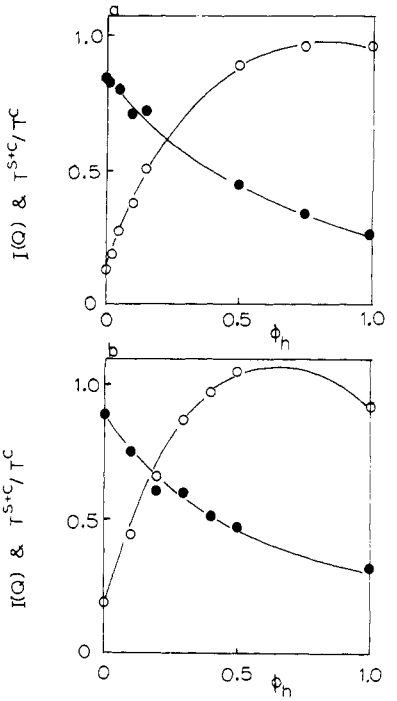

Figure 2. Average water-normalized SANS intensity (○) and transmission (●) for (a) C_7D_8/C_7H_8 toluene and (b) C_6D_{12} benzene/cyclohexane solvent mixture as a function of the volume fraction of hydrogenous component. The sample path length was 2 mm, and the peak wavelength of the incident neutron radiation was 1.2 nm.

we are measuring the total correlation function; hence the corrected neutron scattering intensity, $I_c(\mathbf{Q})$, is given by[44]

$$d\Sigma_{coh}(\mathbf{Q})/d\Omega = I_c(\mathbf{Q}) = (\rho_p - \rho_s)^2 S(\mathbf{Q}) = (\rho_p - \rho_s)^2 f(T,c)/(\mathbf{Q}^2 + \xi_c^{-2}) \quad (13)$$

Data were therefore analyzed by plotting the reciprocal scattered intensity as a function of $\mathbf{Q}^2$, with ξ_c values being obtained from the ratio of the slope to the intercept, at $\mathbf{Q} = 0$, of a linear least-squares fit to the data over the range $\mathbf{Q} \leq \mathbf{Q}^*$.

Results and Discussion

Typical plots of $I(\mathbf{Q})^{-1}$ as a function of $\mathbf{Q}^2$ for three networks of different cross-link density at swelling equilibrium in toluene are given in Figure 3a. Enlargements of the data in the lower range of $\mathbf{Q}$ are shown in Figure 3b. At larger values of $\mathbf{Q}$, a departure from the form of eq 13 is evident for gels with $\phi_e < 0.073$ and is attributed to the crossover in the scattering law due to excluded volume chain statistics inside the diameter of the concentration blob. Although values of ξ_c are extractable in principle from the relation

$$\mathbf{Q}^* = 2\pi\xi_c^{-1} \quad (14)$$

in practice it is difficult to locate this value of $\mathbf{Q}^*$ with any accuracy, even for polymer volume fractions where a crossover was noticed in the $\mathbf{Q}$ range; consequently we have not attempted to utilize eq 14. Another feature of many scattering envelopes of the gels was an appreciable increase in scattered neutron intensity at the lowest values of $\mathbf{Q}$ used. Similar observations have been made by other workers,[34,35] and this increased scattering is attributable to long-range static inhomogeneities in the gels. By contrast, the data for networks swollen in cyclohexane-d_{12} displayed no strong evidence for a crossover in scattering law, as Figure 4 shows for the two extreme temperatures used, i.e., 308 (Θ temperature) and 333 K. Values of ξ_c were therefore only extracted from the Lorentzian broadening analysis.

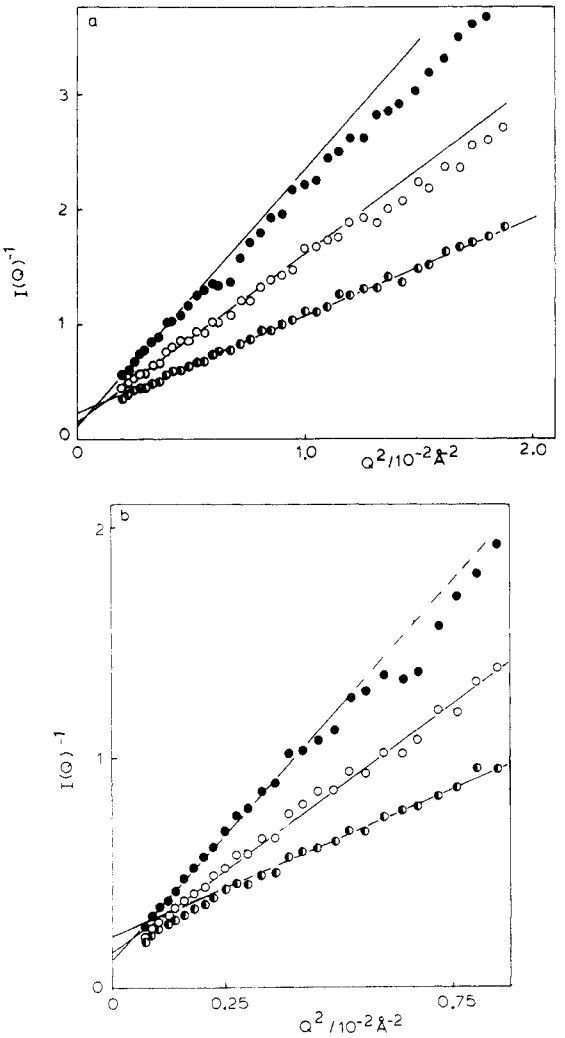

Figure 3. Reciprocal intensity, $I(\mathbf{Q})^{-1}$, against $\mathbf{Q}^2$ over the intermediate range of scattering vector for hydrogenous polystyrene gels at swelling equilibrium in toluene-d_8 at 293 K: (●) $\phi_e = 0.022$; (○) $\phi_e = 0.032$; (◐) $\phi_e = 0.073$.

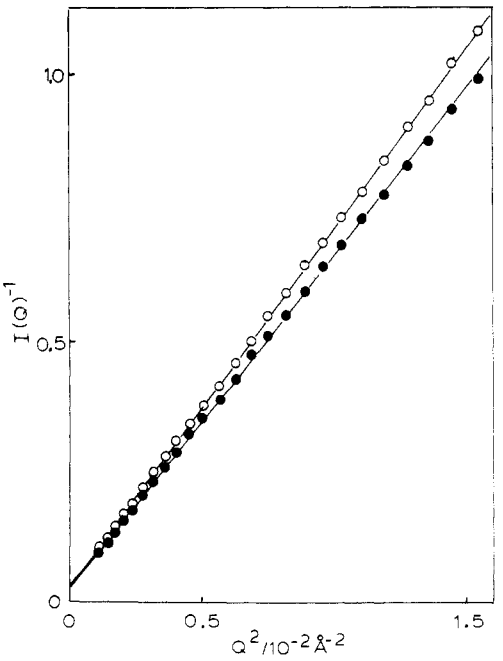

Figure 4. Reciprocal intensity, $I(\mathbf{Q})^{-1}$, against $\mathbf{Q}^2$ over the intermediate range of scattering vector for a hydrogenous polystyrene gel at swelling equilibrium in cyclohexane-d_{12}: (○) at 308 K, $\phi_e = 0.116$; (●) at 333 K, $\phi_e = 0.058$.

Table II
Comparison of Values of the Correlation Length (ξ_c) for Gels at Swelling Equilibrium in Toluene at 293 K Obtained with D17[a] and SAS, Harwell, Diffractometers

code	ϕ_p	ξ_c/nm D17	ξ_c/nm SAS
N3.H200	0.010	7.3	6.7
N2.H300	0.022	4.7	4.4
N2.H400	0.032	4.3	3.1
N2.H600	0.055	2.2	2.0
N2.H700	0.081	2.2	3.2
N3.H1000	0.128	1.7	1.7

[a] Sample–detector distance of 2.8 m.

Table III
Comparison of Values of the Correlation Length (ξ_c), for Gels at Swelling Equilibrium in Cyclohexane Obtained with Sample–Detector Distances of 1.4 and 2.8 m on D17

	308 K			333 K		
		ξ_c/nm			ξ_c/nm	
code	ϕ_p	1.4 m	2.8 m	ϕ_p	1.4 m	2.8 m
N3.H200	0.063	10.6	10.7	0.026	7.5	8.7
N2.H300	0.116	4.7	5.1	0.058	4.4	3.9
N2.H400	0.148	5.2	4.4	0.090	4.2	3.5
N2.H600	0.195	3.7	3.4	0.125	3.2	3.1
N2.H800	0.234	3.2	2.8	0.159	2.8	2.8

The major source of error in the evaluation of ξ_c is the estimation of the volume fraction of polymer in the swollen gel. To minimize this error, gel samples were swollen to equilibrium over a period of 4 weeks under each solvent condition used. After being weighed in the swollen state, each gel was carefully deswollen before drying under vacuum at ca. 373 K to constant weight. By this means the reproducibility of the equilibrium swelling, obtained by comparing identically cross-linked networks, was determined as 10%. This uncertainty in the gel concentration influences the background intensity to be subtracted and could therefore produce artifacts in the values of ξ_c obtained. While such a variation in volume fraction can remove any crossover effects in the scattering and thus preclude observation of $\mathbf{Q}^*$, it was found that it has negligible influence on the value of ξ_c obtained from the Lorentzian broadening analysis. Although the statistical uncertainty in ξ_c obtained from the least-squares fit to the data was ≤2%, this is a somewhat optimistic estimate of the error. A better estimate of the reproducibility of ξ_c is obtained from the comparison of values obtained by SANS on the same gels. Typical results are quoted in Tables II and III, and on average these values agree to within 5% of each other.

A double-logarithmic plot of correlation length, ξ_c, as a function of polymer volume fraction is shown in Figure 5 for gels swollen in toluene. Included in this figure are data for solutions of polystyrene in good solvents,[5,27,50] where strong excluded volume effects prevail. For solutions, the predicted scaling law ($\xi_c \sim c^{-3/4}$) is followed over the whole concentration range utilized, whereas for gels it is only followed up to $\phi_p \leq 0.06$; furthermore, in this region of ϕ_p, the absolute magnitudes of ξ_c for solutions and gels were equivalent to each other. Thus it appears that in this range of polymer concentration the only influence of the permanent cross-links is to limit the degree of equilibrium swelling. The departure from scaling-law analysis at higher volume fractions does not follow a power-law dependence for a marginal regime, as proposed by Schaefer.[12] A smooth curve drawn, by eye, through our experimental points does, however, extrapolate to a value of 14 Å at bulk polymer concentration ($\phi_p = 1$), a value commensurate

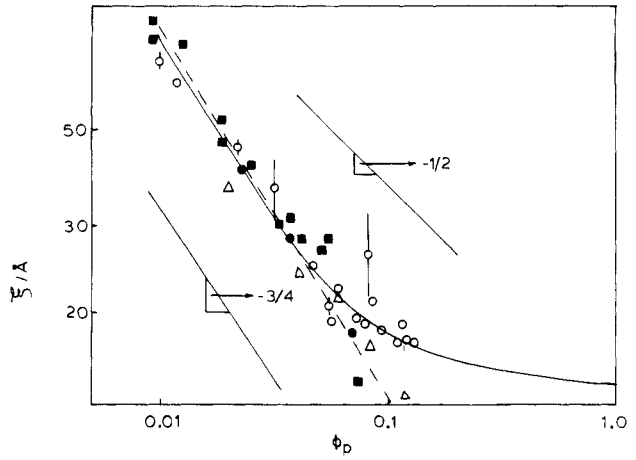

Figure 5. Static correlation length, ξ, against polymer volume fraction, ϕ_p: (○) polystyrene gels at swelling equilibrium in toluene-d_8; (●) polystyrene solutions in carbon disulfide, data from ref 5; (■) polystyrene solutions in benzene, data from ref 27; (△) polystyrene solutions in toluene, data from ref 50.

with the Kuhn effective step length[45] for polystyrene. Increasing polymer volume fraction is accompanied by increasing cross-link density in the equilibrium swollen gels, and therefore it is difficult to associate this departure with one or the other aspect of the gels. However, departures do not appear for the available solution data, and it is tempting to attribute the deviations for gels to the existence of permanent cross-links. Although the segment density in the vicinity of a cross-link will be higher than the average throughout the gel and the existence of junctions will restrict the number of available conformations, the cross-link densities are not so high as to make these factors significant. Furthermore, if the segment densities near junction points are significantly higher than the average, they would lead to greatly increased scattering intensity, probably with a maximum in some region of **Q** since the gel would correspond to a "macrofluid", where the cross-links are the fluid components with the intervening gel acting in the role of a potential energy function. No evidence for such a maximum has been observed, and hence there does not appear to be any correlated long-range density fluctuations of any magnitude. In view of the sparsity of ξ_c data for solutions in good solvents and $\phi_p \geq 0.1$, further discussion on the deviation from scaling laws would be speculative in the extreme.

The correlation lengths for gels at swelling equilibrium in cyclohexane at 308 and 333 K as a function of polymer volume fraction are shown on the double-logarithmic plot in Figure 6. Again, for comparative purposes, data for polystyrene solutions, taken from the literature[29,30] and measured by ourselves, are shown too. In these solutions ξ_c followed the predicted power-law dependence on concentration for the Θ solvent at 308 K and for strong excluded volume conditions at 333 K over the range of polymer volume fraction covered, $0.05 < \phi_p < 0.40$. Furthermore, data in the literature for polystyrene–cyclohexane solutions show a rapid change for the concentration dependence of ξ_c from the Θ to the strong excluded volume prediction with increasing temperature above the Θ temperature. In cyclohexane the magnitude of ξ_c in the gels is again in satisfactory agreement with the values for equivalent solutions. More particularly, agreement is best at low concentrations and at the Θ temperature, while at higher concentration and temperature the values of ξ_c in gels tend to exceed those in solution. In the polystyrene–cyclohexane gel system the effects of temperature and polymer concentration are bound together in terms

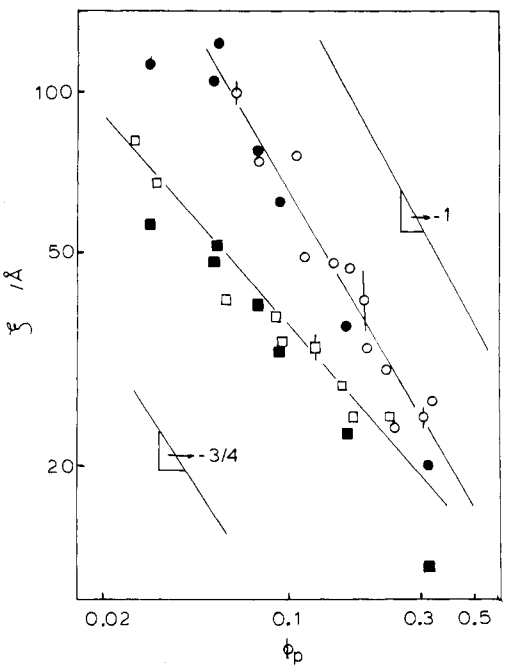

Figure 6. Static correlation length, ξ, against polymer volume fraction, ϕ_p: (○) polystyrene gels at swelling equilibrium in cyclohexane-d_{12} at 308 K; (●) polystyrene solutions in cyclohexane-d_{12} at 308 K; (□) polystyrene gels at swelling equilibrium in cyclohexane-d_{12} at 333 K; (■) polystyrene solutions in cyclohexane-d_{12} at 333 K. Solution data from ref 30 and 31 and this work.

of the macroscopic swelling (i.e., as the temperature increases, the solvent quality improves, the gel swells, and the concentration decreases) and these factors are predicted to have opposing influence on the range of the pair correlation. The equations, obtained by linear regression on the experimental points, for the concentration dependence of ξ_c in the gels swollen in cyclohexane are (where cc is the coefficient of correlation in the least-squares fit)

T/K	ξ_c/Å	cc
308	$0.97(\mp0.05)\phi_p^{-0.85\mp0.06}$	0.965
313	$0.83(\mp0.06)\phi_p^{-0.88\mp0.06}$	0.988
318	$0.96(\mp0.07)\phi_p^{-0.67\mp0.07}$	0.970
333	$1(\mp0.05)\phi_p^{-0.56\mp0.05}$	0.968

At the Θ temperature the power-law exponent was only slightly lower than the predicted value of unity found for solutions. The concentration dependence weakened as the temperature increased and the solvent quality improved. At 333 K, the highest temperature investigated, the value of the power-law exponent was 0.5, the value predicted for solvents giving rise to weak excluded volume effects. This is consistent with the macroscopic swelling of the gels in cyclohexane at 333 K, which is greater than at the Θ temperature but much less than in toluene at ambient temperature. This suggests the solvent quality is poorer than the good solvent limit and the weak excluded volume effect is more suited to a perturbation treatment. This is in contrast to the behavior observed for solutions, which is indicative of a strong excluded volume interaction. It seems as if the permanent cross-links have introduced restrictions on the excluded volume effect compared to linear polymer solutions. Over the range of concentration investigated, there was no firm evidence of a breakdown in simple power-law behavior similar to the results for gels in toluene. On the other hand, it could be argued that since the degree of swelling in cyclohexane was less than in toluene, more emphasis was placed on the higher con-

Table IV
Comparison of the Correlation Length (ξ/nm) for Gels at Swelling Equilibrium in Cyclohexane Obtained by SANS and by Dynamic Light Scattering

code	ϕ_p	ξ(SANS)	ξM_{os}	ξD_c
		T = 308 K		
N3.H200	0.063	9.7	7.1	28.4
N2.H300	0.116	5.8	4.7	22.0
N2.H400	0.171	4.1	3.1	11.0
N4.04D400	0.209	3.5	2.8	8.7
N4.04D600	0.276	2.8	1.8	6.0
N2.H1000	0.323	2.4	1.5	4.0
		T = 318 K		
N3.H200	0.038	8.2	10.0	10.9
N2.H300	0.078	5.1	5.6	11.5
N2.H400	0.128	3.7	4.0	8.1
N4.04D400	0.166	3.1	3.3	7.4
N4.04D600	0.225	2.5	2.2	4.4
N2.H100	0.279	2.2	1.5	4.1
		T = 333 K		
N3.H200	0.026	7.8	13.5	7.8
N2.H300	0.058	5.0	6.2	7.3
N4.04D400	0.134	3.1	3.6	5.2
N4.04D600	0.187	2.6	2.2	3.6
N2.H1000	0.242	2.2	1.9	3.3

Table V
Values of the Exponents γ_M and γ_D for the Concentration Dependence of the Osmotic Modulus (M_{os}[a]) and Cooperative Diffusion Coefficient (D_c[b]) for Gels at Swelling Equilibrium in Cyclohexane and the Implied Exponent, γ_ξ, for the Concentration Dependence of ξ[c]

T/K	γ_M	$\gamma\xi$ from variation of M_{os} with c	γ_D	$\gamma\xi$ from variation of D_c with c
308	2.94 ± 0.17	−(0.98 ± 0.06)	1.17 ± 0.09	−(1.17 ± 0.09)
318	2.62 ± 0.17	−(0.87 ± 0.06)	0.67 ± 0.09	−(0.67 ± 0.09)
333	2.62 ± 0.11	−(0.87 ± 0.04)	0.46 ± 0.12	−(0.46 ± 0.12)

[a] $M_{os} \sim c^{\gamma M}$. [b] $D_c \sim c^{\gamma D}$. [c] $\xi \sim c^{\gamma \xi}$.

centration range and semidilute solution good solvent behavior was not clearly displayed. The apparent value of the exponent of 0.5 might be ascribed to the slope over a limited concentration range of a curve similar to that suggested for the gels in toluene, and indeed experimental data for the latter case over the same higher concentration range might also approximate to such a power law.

At this juncture it is germane to compare values of ξ_c with the mean values of the correlation length obtained from our quasi-elastic light scattering measurements of ref 46 for gels at swelling equilibrium in cyclohexane. These are reported in Table IV along with values interpolated from the above curves for the SANS measurements. The values extracted from the intensity of the dynamically scattered light (M_{os}) are of the same magnitude as the SANS measurements at all three temperatures, whereas the values obtained from the mean decay rate of the photocount correlation function (D_c) exceed the SANS values considerably at the Θ temperature, but the agreement improves with increasing temperature. The experimentally measured power-law exponents of M_{os} and D_c and the implied exponents of ξ from scaling-law analysis[1,7,8] are presented in Table V. The scaling exponents for ξ obtained by the three methods are in reasonable concurrence at the Θ condition, but at higher temperatures only the scaling form of the diffusion coefficient is consistent with the SANS results. At 333 K the behavior is compatible with the predictions for ξ given by theories that treat excluded volume interactions as a perturbation to an otherwise essentially ideal system. The values of apparent scaling exponents at intermediate temperatures could be regarded as reflecting a broad transition region from Θ-solvent to so-called marginal solvent behavior. It is not critical that $\xi(D_c)$ values do not agree with the SANS values despite having the same concentration dependence, since the blob model does not require that the dynamic and static screening lengths are equal, only that they are proportional. It seems that the correlation range of the hydrodynamic interactions is larger than that for static correlations of density fluctuations in the Θ state, but as the temperature and/or solvent quality improves, the screening of hydrodynamic forces becomes more efficient and the static and dynamic correlation ranges coincide. By way of comparison, however, in dilute solutions with good or Θ solvents the hydrodynamic radius is smaller than the radius of gyration.[47] Alternatively, the use of the pure-solvent viscosity in the analysis of quasi-elastic light scattering data may be criticized on the grounds that the concentration of the gels is outside the semidilute regime. The local viscosity may be expected to increase with increasing polymer concentration due to a reduction in free volume. This argument has been used to account for a maximum in the concentration dependence of D_c for polymer solutions.[48] In addition, the gels may be very congested, particularly in the vicinity of cross-links, and segment friction may no longer be totally dominated by the solvent. This concurs with the observation that agreement with the SANS results improves as the temperature is raised and the system approaches the semidilute regime. If this is the case, however, the consistency between the power-law exponents for the concentration dependence of ξ(SANS) and $\xi(D_c)$ must be purely fortuitous. Another hypothesis for disagreement between static and dynamic measurements is that different statistical averages are involved.[37,49] Dynamic measurements are related to $1/r$, whereas static experiments measure $\langle r^2 \rangle$, r being the separation of correlated segments. Static measurements are, therefore, more sensitive to the wings of the correlation function and dynamic measurements more sensitive to short-distance statistics. The conclusion of this analysis is that true scaling behavior in dynamic experiments can only be observed with very high molecular weight polymers and low but semidilute concentration.

Unfortunately none of these arguments can account for the discrepancy between the correlation length $\xi(M_{os})$ from the light scattering intensity measurements and ξ(SANS) or $\xi(D_c)$.

Conclusions

The results reported here, covering a variety of thermodynamic environments, for the concentration dependence of ξ_c in gels at swelling equilibrium provide some support for the analogy between entangled solutions and highly swollen networks. Power laws previously reported for solutions of linear polymers were reproduced in some cases, but differences were also evident. Behavior compatible with predictions for semidilute solutions in good, marginal, and Θ solvents was observed, but the concentration crossovers between these regimes, as indicated in Figure 1, were not strictly evident. It appears the semidilute region over which strong excluded volume effects are present is restricted for the gels compared to the solutions. The mechanism by which permanent junctions may lead to violation of the assumption that the system is semidilute remains to be resolved.

Acknowledgment. N.S.D. thanks the Science and Engineering Research Council for a maintenance grant during this research. The provision of neutron scattering facilities by the same body at AERE Harwell and ILL,

Grenoble, is also gratefully acknowledged. The assistance of the technical establishments at AERE and ILL during the course of this work was invaluable.

Registry No. Polystyrene, 9003-53-6; neutron, 12586-31-1.

References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265.
(3) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(4) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(5) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(6) de Gennes, P.-G. *Isr. J. Chem.* **1975**, *14*, 154.
(7) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(8) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(9) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(10) Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1983**, *44*, 39.
(11) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(12) Schaefer, D. W. *Polymer* **1984**, *25*, 387.
(13) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley: New York, 1969.
(14) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(15) Whittington, S. G. *Adv. Chem. Phys.* **1982**, *51*, 1.
(16) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(17) de Gennes, P.-G. *Phys. Lett. A* **1972**, *38A*, 339.
(18) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 281.
(19) Wilson, K.; Kogut, J. *Phys. Rep.* **1974**, *12C*, 77.
(20) Farnoux, B.; Boue, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1978**, *39*, 77.
(21) Chu, B. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems" Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(22) Debye, P. *J. Phys. Colloid Chem.* **1947**, *57*, 18.
(23) Edwards, S. F. *Proc. Phys. Soc., London* **1965**, *85*, 613.
(24) Edwards, S. F. *J. Phys. A: Math. Gen.* **1975**, *8*, 1670.
(25) Edwards, S. F.; Jeffers, E. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1020.
(26) Edwards, S. F.; Singh, P. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1001.
(27) Cotton, J. P.; Farnoux, B.; Jannink, G. *J. Chem. Phys.* **1972**, *57*, 290.
(28) Cotton, J. P.; Farnoux, B.; Jannink, G.; Ober, R. *J. Appl. Crystallogr.* **1974**, *7*, 189.
(29) Richards, R. W.; Maconnachie, A.; Allen, G. *Polymer* **1981**, *22*, 189.
(30) Cotton, J. P.; Nierlich, M.; Boue, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(31) Okono, K.; Wada, E.; Kunita, K.; Himatsu, H.; Fukuro, H. *J. Phys., Lett.* **1979**, *40*, L171.
(32) Schaefer, D. W.; Lin, J. S. *Macromolecules* **1983**, *16*, 1017.
(33) Okono, K.; Wada, E.; Kunita, K.; Fukuro, H. *J. Appl. Crystallogr.* **1978**, *11*, 134.
(34) Geissler, E.; Hecht, A. M.; Dupplessix, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 225.
(35) Candau, S.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 30.
(36) Nystrom, B.; Roots, J. *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C19*, 35.
(37) Nystrom, B.; Roots, J. *Prog. Polym. Sci.* **1982**, *8*, 333.
(38) Vaughan, J. M. In "Static and Dynamic Properties of the Polymeric Solid State"; Pethrick, R. A., Richards, R. W., Eds.; Reidel: Dordrecht, 1982.
(39) Nossal, R. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems"; Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(40) Parkinson, W. W.; Keyser, In "The Radiation Chemistry of Macromolecules"; Dole, M., Ed.; Academic Press: New York, 1973; Vol II.
(41) Weiss, P.; Herz, J.; Hild, G.; Rempp, P. *Makromol. Chem.* **1970**, *135*, 249.
(42) Davidson, N. S. Ph. D. Thesis, University of Strathclyde, Glasgow, UK, 1984.
(43) Kostorz, G. In *Treatise Mater. Sci. Technol.* **1979**, *15*.
(44) Farnoux, B.; Jannink, G. In "Scattering Techniques Applied to Supramolecular and Non-equilibrium Systems"; Chen, S.-H., Chu, B., Nossal, R., Eds.; Plenum: New York, 1981.
(45) Kuhn, W. *Kolloid Z.* **1939**, *87*, 3.
(46) Davidson, N. S.; Geissler, E.; Richards, R. W., submitted to *Polymer*.
(47) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(48) Patterson, G. D.; Jarry, J. P.; Lindsey, C. P. *Macromolecules* **1980**, *13*, 668.
(49) Daoud, M.; Jannink, G. *J. Phys., Lett.* **1980**, *41*, 217.
(50) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(51) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.

Intermolecular Correlation Functions from Förster Energy-Transfer Experiments

Glenn H. Fredrickson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received April 26, 1985*

ABSTRACT: Fluorescence experiments that probe the transfer of electronic excitations between donor and trap chromophores are investigated as a means of studying intermolecular correlations in macromolecules. Expression for the observables in such experiments are derived, and specific applications are discussed. The theory may allow fluorescence experiments to be used to study the correlation hole in polymer melts and in bulk samples, spatial correlations in the dilute–semidilute regime of solutions, the structure of block copolymers, segment distributions away from surfaces or interfaces, and the time evolution of density fluctuations in spinodally decomposing mixtures. A variety of other applications are possible.

I. Introduction

Illumination of a chromophore or dye molecule with a source of radiation can lead to the absorption of photons and the creation of a singlet electronic excited state. When an ensemble of such chromophores in a condensed medium at room temperature is illuminated, the resulting excited states or *excitations* are effectively localized on the individual chromophores. These excitations can decay through the familiar process of fluorescence but can also be transferred nonradiatively to nearby unexcited chromophores. This latter process is referred to as electronic excitation transport (EET).[1] An expression for the rate at which an excitation is transferred from an excited chromophore (the donor) to an unexcited chromophore (the acceptor) a distance r away was first derived by Förster.[2] If the energy of the excited acceptor molecules

0024-9297/86/2219-0441$01.50/0