Behavior of Free Linear Chains of Polystyrene in a Network of Methyl Methacrylate in Toluene

Jyotsana Lal,*,† Jacques Bastide,‡ Rama Bansil,§ and François Boué†

LLB, CEN, Saclay, 91191 Gif-Sur-Yvette Cedex, France, ICS (CRM-EAHP), CNRS-ULP, 6 rue Boussingault, 67083 Strasbourg Cedex, France, and Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215

Received December 2, 1992; Revised Manuscript Received July 28, 1993®

ABSTRACT: We have used small-angle neutron scattering (SANS) to study the spatial distribution of free chains of deuterated polystyrene (PSD), in a network of methyl methacrylate (MMA) in toluene, and compared it to PSD chains dispersed in a semidilute solution of PMMA chains of the same PMMA concentration. First, we just studied the gels with no free chains of PSD inside them. Gels show increased scattering compared to the solutions, contrary to the predictions of the classical theories. Second, linear PSD chains were introduced in the system: again increased scattering is observed from chains in the gel compared to the chains in an equivalent semidilute solution. These results imply that when the translational entropy of free PSD chains is weak (especially for the larger ones), they would tend to mix less efficiently with the gel than with the solution. At low q, the scattering increases with molecular weight and progressively tends to a master curve varying as $q^{-2.5}$. We discuss an explanation of this effect in terms of the percolation model of heterogeneities. The larger molecular weight PSD chains define the contour of the large percolation clusters in the gel and thus would reveal them. Only in the case where we remove the solvent does the system show strong segregation effects which override the effects of the heterogeneities of the network.

I. Introduction

We are interested here in the spatial arrangement of linear polymer chains introduced inside a polymer network. In our study a third component is used which is a good solvent for both the linear chains and the network, which, now swollen with a solvent, is a gel. Such ternary systems, apart from being a way to study or probe the network are often encountered in nature and science. Polymer networks and gels are often used to control phase separation processes between two species or used as substrates or for separation of various molecular species (e.g. membranes, filters, electrophoresis, and gel permeation chromatography).

Scattering of different types of radiations allows us to study arrangements of such chains if a contrast in index exists or can be created between the un-cross-linked free chains and the rest of the network system. Using the small-angle neutron scattering (SANS) technique such a contrast can be easily created by labeling (e.g. deuterating) the un-cross-linked free chains, which can be of the same chemical species (same monomeric unit) or be different from the one of the network.

One way of preparing such systems is to introduce the free polymer chains from outside the network by either spreading them on the network[1] (i.e. the whole system is above the glass transition) or by swelling the network in a polymer solution of un-cross-linked free linear chains.[2] Another way is to build the network around the linear chains, adding them prior to gelation instead of introducing them from the outside. In this case the networks have been made formerly either from monomers in the bulk state[3] or from linear polymer chains in semidilute solution.[2]

Light scattering has been used in similar systems, but mainly in the quasi-elastic regime in order to study the dynamics of free chains.[4-7] Bansil et al.[4] have studied the self-diffusion of free chains by dynamic light scattering (DLS) inside a network of methyl methacrylate-*co*-ethylene dimethacrylate (MMA + EDMA) built around the chains by polymerization of MMA monomers in toluene with EDMA as the cross-linker. In this case, they have studied the diffusion of linear chains of polystyrene (PS) chemically different from the MMA gel made in toluene which is an isorefractive solvent with the gel and creates a natural contrast for observing the motion just due to the free chains of PS. The interaction between PS and MMA gel is also made more compatible by use of toluene which is a good solvent for both of them. In a second experiment[7] they used free chains of linear poly(methyl methacrylate) (PMMA) which are chemically identical to the gel. In this case dioxane had to be used instead of isorefractive toluene; the correlation function thus displayed both the collective diffusion of the gel and the self-diffusion motion of free chains. Laplace inversion techniques were used for their separation. Well characterized molecular weights of PS allowed a detailed study in the first case.[4] With increasing molecular weights two distinct scaling regimes were observed. At low molecular weights of PS chains a Stokes-Einstein type scaling of the diffusion constant was observed with a crossover to reptation behavior above a critical molecular weight. An unusual *increase* in the diffusion constant of PS was however encountered with a further *increase* of molecular weight and *decreasing* temperature, inconsistent with the reptation prediction.[8] One reason for this unusual increase in diffusion constant with molecular weight greater than 300 000 was given to be the unfavorable interaction between PS chains and the MMA network. Prompted by previous studies[2] of linear PSD (deuterated) chains in a PSH network as well as by the above unusual behavior, we decided to study the correlation of PS chains inside MMA gels. We made our system very close to the one of Bansil et al.[4] The difference here is that we have to adapt it to SANS by using deuterated chains of PS (PSD). Further, to observe only the distribution of the free PSD chains we prepared MMA gels in a contrast matched mixture of deuterated and hydrogenated toluene.

---

† LLB.
‡ ICS.
§ Boston University.
® Abstract published in *Advance ACS Abstracts*, October 1, 1993.

0024-9297/93/2226-6092$04.00/0

Table I

M_w	Φ^*	Φ_{PSD}	$R_g \approx 1/q$ (Å^{-1}) ($S(q)$ vs $1/q^2$)	R_g ($\Phi < \Phi^*$, Å) (ref 15)	$R_{g,bulk}$[a] (Å)
39 000	4.2%	1.06%	85	68	53
218 000	1.07%	0.19%	193	191	125
351 000	0.73%	0.12%	235	254	159
751 000	0.40%	0.05%	326	400	233

[a] $R_{g,bulk} = 0.275M_w^{0.5}$ for semidilute solutions. See text for further details.

II. Experimental Methods

Preparation of Gels. We first followed the procedure suggested by Polysciences for deinhibiting the MMA monomers by passing them through a column of resin beads. The gels were made by polymerization of MMA monomer with the cross-linker EDMA (ethylene dimethacrylate) in a contrast matched mixture of deuterated (2.7% by volume) and hydrogenated toluene with catalyst ABIN (azobis(isobutyronitrile)). First, the deuterated chains of PSD were dissolved in the contrast matched solution of toluene to which MMA was added (12.5% by volume), and finally, to this we added the cross-linker EDMA (the cross-link ratio is defined as EDMA/(EDMA + MMA) by volume, varying from 4% to 6%). To initiate the polymerization reaction, 20 mg of ABIN/mL of MMA was added to the above solution. This solution was then bubbled with a continuous stream of argon gas for 4 min or more because any remaining oxygen acts as an inhibitor of the polymerization reaction. The sample cells (1-mm quartz cells) were sealed and immersed in a water bath at 55 °C for several days.

Different samples were prepared with increasing molecular weights of PSD chains, whose concentration was consequently decreased, the product of concentration and molecular weight of different lengths of PSD chains being kept constant in order to maintain comparable scattering. This is with reference to the free energy of mixing of linear PSD and PMMA chains for which the mean field theory of Flory–Huggins has ΦM_w as a unique parameter. A similar procedure was also used in the DLS study of Bansil et al.[4] The molecular weights M_w of PSD used in this study are 751 000, 351 000, 218 000 and 39 000 with polydispersity index M_w/M_n = 1.31, 1.30, 1.70, and 1.04, respectively. The molecular weights used are rather monodisperse, except M_w = 218 000. The volume fraction Φ_{PSD} of the PSD chains used for each M_w are listed in Table I. The volume fraction Φ_{PSD} becomes rather small for large M_w (0.05%). The initial concentration of cross-linker corresponding to the gel threshold was about 2.5%.

SANS. The neutron scattering was done at the small-angle neutron spectrometer PACE at LLB. The wavelength of the incident neutron beam used was 10.5 and 15.2 Å. The scattering was performed at a temperature of 22 and 45 °C. The data were collected by annular cells of the detector. The raw data were treated for scattering from an empty cell, incoherent background, sample thickness, and transmission. For each spectrum the scattering was normalized by the spectrum of water which was used as a standard in order to correct for detector efficiency. No direct absolute calibration was done, but instead the above ratio was multiplied by a crosssection of water at the given wavelength $d\Sigma/d\Omega(\lambda_1)$ corresponding to values of Oberthur.[9] Similar treatment was done at the other wavelength λ_2. This leads to the overlap of the data in the two q ranges corresponding to λ_1 and λ_2, the data being now represented in absolute units.

III. Results

Gels with No PS Chains. Some samples were made by polymerization of MMA in deuterated toluene with no free chains of PS inside. The scattering from such samples is that from the gel itself. Figure 1 shows the scattering from gels of different cross-linking ratios on a log $S(q)$ versus log q plot. On the same plot we show scattering from a semidilute solution of PMMA chains (M_w = 463 000) of the same concentration as the MMA gels (12.5% by volume).

One observes that the signal from the gels is higher than that from the semidilute solution. At the high q values all the data seem to fall on a straight line of slope 1.6. At low values of q there is a leveling of intensity as q decreases. The value of $S(q=0)$ increases and the value of q at which the intensity levels off decreases with increasing cross-link ratio.

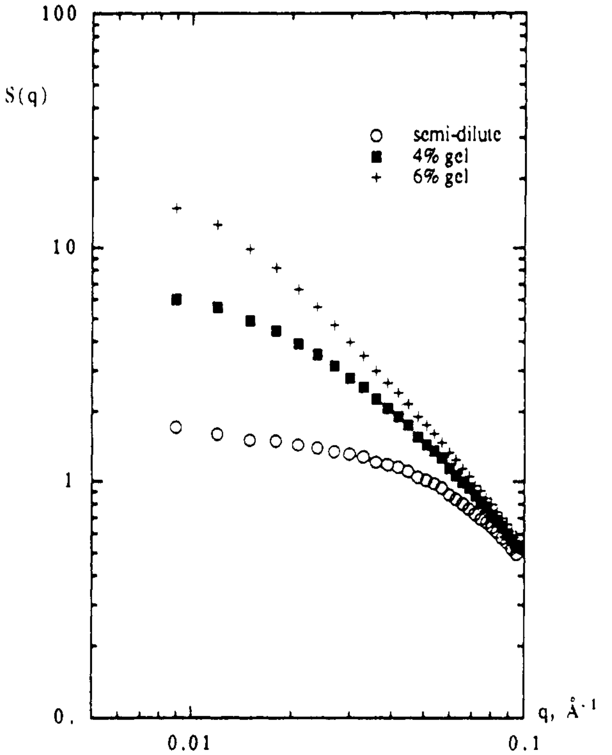

Figure 1. log $S(q)$ (units cm^{-1}) versus log q of MMA gels in deuterated toluene and a semidilute PMMA solution of the same polymer concentration as the gel (12.5% by volume).

Such behavior has already been observed in other gels. In randomly cross-linked polystyrene[10,11] the signal observed might be equal to the one from a semidilute solution but becomes greater than the semidilute solution as the cross-linking ratio is increased beyond a certain value.[2] In certain gels[12,13] a signal larger than the semidilute solution is readily observed. A greater amount of scattering from the gels than from a solution is not predicted by the classical theory of the swelling of gels[14] corresponding to a balance between osmotic pressure and elasticity. The theories rather predict a slightly lower scattering due to reduction of fluctuations by the elastic modulus when a solution forms a gel.

Gels with PS Chains. We recall that the samples used in this study were prepared using a solvent mixture of hydrogenated and deuterated toluene, which contrast matches the MMA chains of the network. Therefore the scattering is due to only the deuterated polystyrene (PSD) chains. A small coherent signal is recorded from the blank sample, i.e. almost a contrast matched gel. One can compare in Figure 6 (Appendix) where we have plotted the spectrum $S(q)$ (not divided by Φ) of the blank and PSD chains in 4% cross-linked gels. The signal from the matched gel is obviously smaller by a factor close to 10 except for the first point at the smallest q where the collimation effects are not well removed. For semidilute solutions such a blank does not give any additional scattering even at the lowest q. The additional scattering may be due to clusters of cross-links which may have a different scattering contrast.

Figure 2 presents the SANS data log $S(q)/\Phi$ versus log q for PSD chains of increasing molecular weight inside MMA gels with a 4% cross-linking ratio at 22 °C. At large

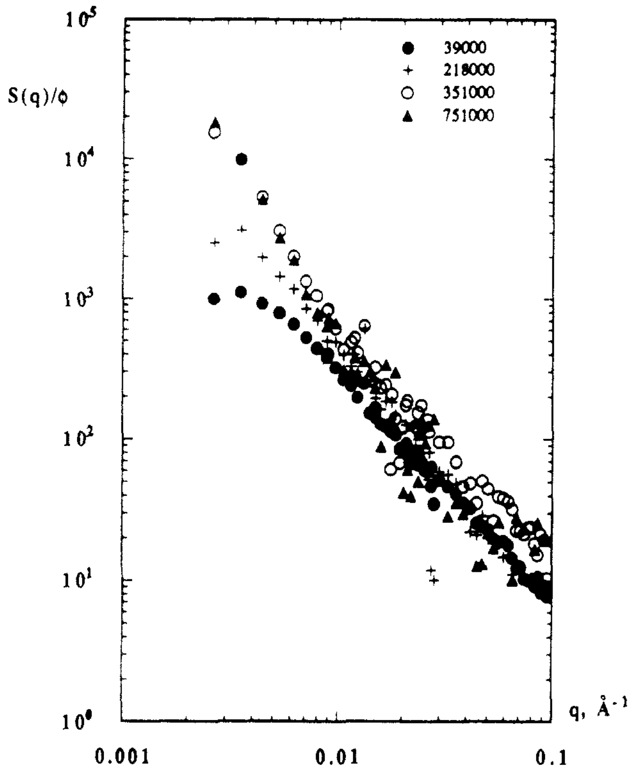

Figure 2. log $S(q)/\Phi$ (units cm^{-1}) versus log q of free PSD chains of increasing molecular weight inside a MMA gel of cross-linking density 4.0% at 22 °C. The concentration of PSD chains Φ_{PSD} = 1.06, 0.19, 0.12, and 0.05% for molecular weights M_w of PSD used in this study 39 000, 218 000, 351 000, and 751 000, respectively.

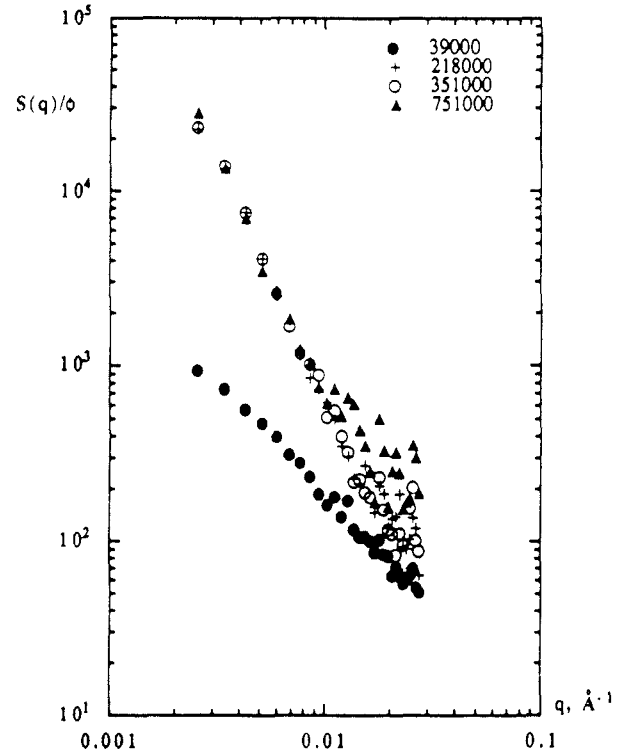

Figure 3. log $S(q)/\Phi$ (units cm^{-1}) versus log q of free PSD chains of increasing molecular weight inside a MMA gel of cross-linking density 5.5% at 45 °C. The concentration of PSD chains Φ_{PSD} = 1.06, 0.19, 0.12, and 0.05% for molecular weights M_w of PSD used in this study 39 000, 218 000, 351 000, and 751 000, respectively.

q, the data are noisy, especially for PSD chains of high molecular weights because their concentration is low. However, within experimental accuracy all the data on the high q side approximately fall on a single curve of slope 1.6.

The behavior at low q deserves more interest: as the molecular weight of the linear PSD chain increases, the scattering intensity at low q also increases. The value of q at which the intensity levels off is lower for M_w = 218 000 than for 39 000. The curves of the two largest molecular weight PSD chains (M_w = 351 000 and 751 000) show no leveling off in intensity in the available q range. For the two high molecular weight PSD chains, the scattering $S(q)/\Phi$, is nearly the same all over the q range, except maybe the lowest q value. The data on the low q side for the two largest molecular weight PSD chains follow a slope of 2.5. The same trends in the scattering from PSD chains in MMA gels were observed for two independent series of gels with cross-linking ratios ranging between 4% and 6%, but at two different temperatures, 22 and 45 °C. However, for the higher cross-linking ratio (5.5%) (Figure 3), even the scattering for PSD chains of M_w = 218 000 is larger than the one for 4% at the same temperature and falls approximately on the curves of M_w = 351 000 and 751 000.

All curves could be attempted to be described by a Ornstein–Zernike law

$$S(q) \approx S(0)/(1 + q^2\xi^2) \qquad (1)$$

but the minimum value of q, q_{min}, must not be too large compared to ξ. A good q range, $q_{min} < 1/\xi$ is signaled by leveling of the intensity at low q on a log–log plot. For chains of $M_w > 218\,000$, neither $S(0)$, the intensity at zero q, nor ξ, the correlation length, can be extracted. If a ξ exists, $\xi > 1/q_{min} > 1/(3 \times 10^{-3})$ Å^{-1}. For chains of lower molecular weights 39 000 and 218 000 the leveling of log $S(q)$ is visible in Figure 2 and we can extract $S(0)$ and ξ from data over a limited range of low q values. By linear fits of $1/S(q)$ versus q^2 we obtain, for chains of M_w = 218 000, $S(0)/\Phi$ = 9025 (cm^{-1}) and ξ = 439 Å and, for chains of M_w = 39 000, $S(0)/\Phi$ = 1728 (cm^{-1}) and ξ = 215 Å. Let us remark here that such a plot of $1/S(q)$ versus q^2 would correspond to the Guinier regime $1/I(q) \approx (1 + q^2(R_g^2/3))$ if $I(q)$ corresponded to the single chain form factor. The R_g that we would obtain would equal $\xi\sqrt{3}$ = 760 Å for chains of M_w = 218 000 and $R_g = \xi\sqrt{3}$ = 372 Å for chains of M_w = 39 000. These values are far too large even if chains were completely expanded under the excluded volume effect. Therefore we conclude that high correlations exist and we extract a correlation length ξ from the data. For a 5.5% sample this could only be done for chains of M_w = 39 000, $S(0)/\Phi$ = 1351 (cm^{-1}), and ξ = 262 Å (apparent $R_g = \xi\sqrt{3}$ = 454 Å).

Scattering from PSD chains in the gel can also be compared to scattering from such chains in an equivalent semidilute solution. Figure 4 is log $S(q)/\Phi$ versus log q plot representing scattering from PSD chains of increasing molecular weight in a semidilute solution of PMMA (M_w = 463 000) of the same concentration as the MMA gel. Using again contrast matching, we observe here also scattering just from the PSD chains. The blank semidilute solution gives a flat contribution of 0.7 cm^{-1}, which seems to verify the contrast matching. Here also the scattering increases with increasing molecular weight at low q like in a MMA gel (Figures 2 and 3), but if we compare scattering at low q of similar molecular weights, the scattering observed here is more than 10 times lower than that from free PSD chains inside MMA gels. At the high q side again the data fall on a single curve of slope 1.6. These two facts, together with the low concentration of chains used, indicate that we have measured here *intra-*

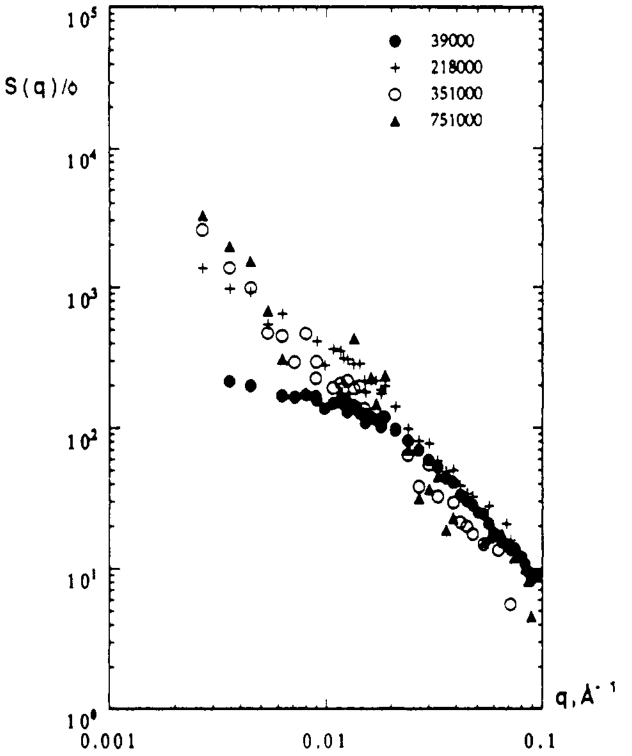

Figure 4. log $S(q)/\Phi$ (units cm^{-1}) versus log q of free PSD chains of increasing molecular weight in a semidilute PMMA solution of the same polymer concentration as the gel. The concentration of PSD chains Φ_{PSD} = 1.06, 0.19, 0.12, and 0.05% for molecular weights M_w of PSD used in this study 39 000, 218 000, 351 000 and 751 000, respectively.

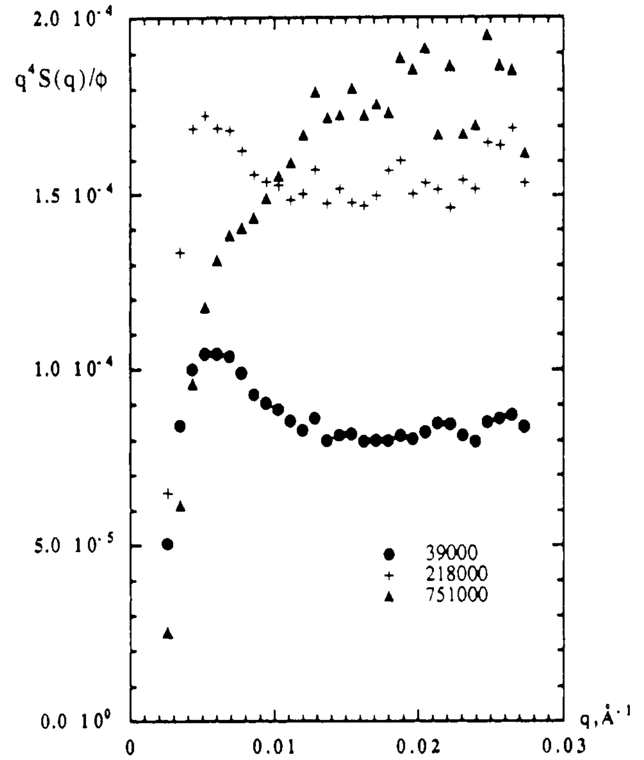

Figure 5. $q^4S(q)/\Phi$ (units cm^{-1}) is plotted as function of q for a dried binary mixture of PSD/PMMA.

chain scattering (form factor) unlike in the case of gels: thus, we have estimated below the overlap concentration Φ^* and the radius of gyration R_g of the species PSD in our system. We compare our data to PS chains in semidilute solution by assuming that PMMA chains are absent; i.e. PSD chains are alone in toluene. We first calculate $\Phi^* = M_w/(^4/_3\pi R_g{}^3\mathcal{N}_{av})$, from the data of PS in toluene: knowing that $R_g \approx 0.12M_w{}^{0.6}$ in a dilute solution[15] gives $\Phi^* \approx 200M_w{}^{-0.8}$. We find that for all molecular weights, $\Phi_{PSD} < \Phi^*$ (cf. Table I). For the different M_w, we can compare the calculated value of R_g from the above formula to the one extracted from a linear plot of $1/S(q)$ vs q^2. We find a good agreement between the calculated and measured R_g (See Table I): the measure of the latter is related to the value of q at which leveling off of intensity occurs, as visible here only for low molecular weights. The difference between measured and calculated R_g varies from 1% to 25%. It should be realized the scattering from the chains is extremely low at high values of q, because the concentration of linear PSD chains is extremely small (Table I) and consequently the statistics is rather poor especially for high M_w PSD chains since the product $M_w\Phi$ = constant.

From the agreement between measured and calculated R_g we thus infer that no strong segregation occurs between PSD and PMMA chains in the case of PSD in PMMA semidilute solution; the toluene, as expected, keeps both chains compatible. We measure thus the form factor of the chains. A more detailed study for semidilute solutions could be done in parallel with the light scattering studies already made by Kent et al.[16]

To summarize, the scattered intensity from labeled chains in a gel is much larger than a semidilute solution of the same polymer concentration. Such a behavior means that the distribution of free chains is not as uniform in the gel as in the semidilute solution. In other words, in the gel, the "form factor of the chains" is modulated by a stronger "interchain correlation" than that in a semidilute solution.

Dried Gels with PS Chains. Dried gels with 5.5% cross-link with PSD chains were prepared by slowly heating them, up to their glass transition temperature T_g and then drying them under vacuum, followed by a final gentle flattening and polishing of the dried pieces above T_g. We further subtracted from the total scattering of these samples a blank measured from a similar dried gel with no chains. In Figure 5, $q^4S(q)/\Phi$ plotted as a function of q approaches a plateau at large q. This means that a strong q^{-4} dependence of scattering is observed from the PSD/PMMA binary mixture (Figure 5), which indicates the presence of sharp interfaces between two regions in space (Porod's law). The scattering given by Porod's law is

$$S(q) = 2\pi K^2 S\varphi/Vq^4 \qquad (2)$$

K (cm^{-2}) is the contrast length density for neutron's and is defined as $(b_{PSD}/v_{PSD} - b_{PMMA}/v_{PMMA})$ where b_{PSD} and b_{PMMA} are the scattering lengths and v_{PSD} and v_{PMMA} are the partial volumes of PSD and PMMA, respectively. Φ is the volume fraction of the PSD chains in the dried sample. For uniform spheres the surface to volume term S/V reduces to $3/R_p$ where R_p is the radius of Porod's sphere. From the level of Porod's plateau, i.e. $S(q)q^4/\Phi$, we can deduce the value of Porod's radius R_p. As seen in Figure 5 the level of Porod's plateau rises; i.e. R_p decreases with increasing molecular weight of PSD chains. R_p is 658, 324, and 282 Å for M_w = 39 000, 218 000, and 751 000, respectively. For M_w = 39 000 and 218 000 PSD chains this characteristic size is much larger than the radius of gyration $R_{g,bulk} = 0.275M_w{}^{1/2}$ of the ideal PSD chains in a PSD bulk, which are 53 and 125 Å, respectively. For PSD chains of M_w = 751 000 R_p happens to be comparable to its radius R_g = 233 Å (Table I). The binary mixture of the MMA network and the free chains appears to be strongly segregated into regions rich in PSD chains and some regions which are poor in PSD chains, and a typical size of such regions is R_p. Such a size for R_p is a priori different from the size R_g of the chains.

At this stage, we could be tempted to describe the scattering by the Debye–Bueche law $S(q) = S(0)/(1 + q^2\xi^2)^2$, where ξ is a simple cutoff related to the volume fraction and the volume/surface ratio ($\xi = 4\Phi(1-\Phi)V/S$). However, in addition to the plateau the curves for chains of M_w = 39 000 and 218 000 also exhibit at least one bump at q_m before reaching Porod's plateau. This bump is not observed for a Debye–Bueche law, which we abandon from hereon. This bump could be due to curvature correction to Porod's q^{-4} law (Kirste–Porod formulation), a positive correction term which appears when the scattering vector is of the same magnitude as the curvature of the interfaces. The position of the bump indicates in this case the characteristic length in a two phase media, and the width is related to the polydispersity of sizes. One possibility is to treat the data as the sum of scattering from individual spheres with no interaction. In this case, $R_m q_m \approx 2.75$ for monodisperse spheres, giving $R_m \approx 2.75 q_m^{-1} \approx 460$ and 550 Å, respectively, for M_w = 39 000 and 218 000, thus very different from R_p. This discrepancy could be explained by polydispersity in the system[17,18] and the real contrast K between the segregated regions (cf. Appendix).

In summary, strong segregation or phase separation takes place between the MMA chains of the network and the free PSD chains, when the solvent toluene which keeps both the chains of the network as well as the free chains compatible is removed. The PSD poor and rich regions created here do not follow the same structure as in the presence of toluene. At variance, also from the solvent case, is the fact that PSD chains of smaller M_w seem to be segregated into larger regions than the chains of larger M_w; this could be due to kinetic reasons. Kinetics here would be strongly related to the self-diffusion coefficient D of the chains which depends on their M_w and concentration.

IV. Discussion

(a) Gels with No PS Chains. We observe here gels in their state of preparation, and the signal is larger than the one of the solution of the same concentration. Such an effect is always observed experimentally between the gels swollen from their state of preparation and the semidilute solution at the same concentration.[11-13] Both effects are in contradiction with the classical theories, for which the motion of the chains in the network is reduced when a gel is made out of a solution: the classical thermodynamics predicts an Ornstein–Zernicke law for scattering with a lower $S(q=0)$ derived by Tanaka et al.[14]

$$S(q=0) \approx \Phi^2/(\kappa_{\text{os-gel}} + {}^4/_3\mu) \qquad (3)$$

where $\kappa_{\text{os-gel}}$ and μ are respectively the osmotic bulk modulus and the shear modulus of the gel. The model of a homogeneous gel would predict only a difference in scattering of a gel and that of a semidilute solution of the same concentration, which obeys eq 3 with $\mu_{\text{sol}} = 0$ and the $\kappa_{\text{os-sol}} = \kappa_{\text{os-gel}} + {}^1/_3\mu$. This corresponds to a moderately lower $S(q=0)$ for a gel in the preparation state than for the equivalent semidilute solution. When the gel is swollen more (overswelling), the scattering is predicted to be even lower than for a semidilute solution. Here the opposite is observed. This could be due to additional heterogeneities of the solvent concentration related to the heterogeneous structure of cross-linking in the network. In the case of a small cross-linking ratio, the scattering of the gel can stay equal to the one from a semidilute solution in the preparation state and the heterogeneities are revealed only by swelling the gel. Therefore the increased scattering was attributed to the heterogeneities of swelling of the gel which are themselves in turn related to heterogeneities of cross-linking.[11]

A simple picture for the appearance of such heterogeneities was proposed[19] for a randomly cross-linked gel made from a solution of long chains. A percolation model is used to describe the clusters of regions more cross-linked than the average above the gel point in a randomly cross-linked gel. In this model when two junctions are located at neighboring lattice sites, a "frozen blob" is formed which is already in an optimal excluded volume conformation. The average size and the spread of the size of clusters of frozen blob increase when the percolation threshold is approached with increasing cross-link densities. For a semidilute solution of long chains, many more cross-links must be introduced to reach the percolation threshold of frozen blobs than to pass the gel point of the chains. There is a progressive unscreening of these clusters on overswelling (on swelling from the preparation state) and stretching in a uniaxial direction because the tightly cross-linked regions are perturbed less than the soft interstitial regions. This establishes a contrast between the two kinds of regions in space, and it leads to greater scattering at low q values.

Following this picture, it is possible that in the preparation state the signal of the gel remains equal to the one of the semidilute solution: indeed, real percolation clusters in the preparation state are screening each other in such a way that neither cluster sizes nor fractal dimension is visible. It is only when the system is diluted that they unscreen themselves progressively. Experimentally identical $S(q)$ are observed for a solution and a gel of not too high cross-linking density especially in the case of randomly cross-linked gels. However, using the same chemistry but a slightly higher cross-link ratio makes the scattering from the gel slightly higher, giving the impression that the scattering progressively tends to the $q^{-1.6}$ law.[2] A proposed explanation is that when the gels are more tightly cross-linked, one can expect that some regions of very high cross-link density will start to expel the solvent. There the heterogeneities will be revealed even in the preparation state. In any case where the scattering is larger than the solution, it would be decomposed into two q ranges.[19,20] For $q > 1/\xi\text{sol}$

$$S(q) \approx q^{-(5/3)} \qquad (4)$$

here ${}^5/_3$ is the excluded volume exponent (self-avoiding random walk) of the chains of the frozen blobs. For $1/\xi_{\text{gel}} < q < 1/\xi_{\text{sol}}$, we observe

$$S(q) \approx q^{-D^{\text{s}}_{\text{f}}(3-\tau)} \approx q^{-(8/5)} \qquad (5)$$

ξ_{gel} being the correlation length of the gel in a pure solvent and ξ_{sol} being in the semidilute solution at the same concentration. D^{s}_{f} is the exponent of swollen percolation clusters, and τ is the exponent which characterizes the distribution of cluster sizes in the percolation model.

The MMA gels in our experiment are observed in the preparation state. These are prepared not by cross-linking of long polymer chains but by polymerization of monomeric and polyfunctional units. This procedure might make them more heterogeneous. The cross-linking ratios used here are closer to the one for the initial gelation (2%). Inspite of it the swelling ratios which are observed are not very large. The gels swell by a factor of 1.5–2 in volume with respect to the volume at the concentration of preparation. Finally, the gels are very brittle. All these factors indicate that the structure of the gels is rather heterogeneous. This might explain why the scattering from the gel is already rather large in the state of preparation and no additional swelling of the gel is needed to reveal the heterogeneities. Also, an apparent collapse of the scattering curves toward a $q^{-1.6}$ law is observed (Figure 1). In principle, for such a case the former model does not readily apply. Thus a priori different methods of preparation of gels lead to surprisingly close behaviors.

In summary, the higher scattering at low q here could be related to a heterogeneous structure, for which we propose a fractal, percolation-like structure. Heterogeneous structure was proposed for the same MMA gels, prepared in the same way based on the static light scattering[21] where an increase in scattering with increasing % EDMA was observed at a growing rate and appears quite large for the 6% cross-link. Brillouin scattering[22] seems also to reveal the heterogeneities from the same MMA gels. The wavevector dependence of the measured phase velocity $v(k)$ changes upon increasing the cross-link content above the gel threshold. More specifically for a high cross-linking concentration a maximum and minimum in $v(k)$ have been observed. The k position of these minima and maxima have been associated with the characteristic size of a more or less cross-linked region. Results from depolarized light scattering[22] also lead us to assume that further clustering of the polymers takes place in this system for high cross-link ratios.

The scattering from the gel could be just due to the thermal fluctuations in the one phase stable region coupled with frozen fluctuations of the gel $S(q=0) = kT/(\partial^2 F/\partial\phi^2)$. The increased scattering from the gel could also be attributed to the approach of phase separation in the system, i.e. $1/S(q=0) \rightarrow 0$. For $S(q=0)$, there are two possibilities: First, $S(q=0) = 1/\kappa_{\text{os-gel}}$ and complete separation should occur when the osmotic pressure is constant, i.e. when the bulk modulus is zero

$$\kappa_{\text{os-gel}} = \kappa_{\text{os-sol}} - \mu = 0 \tag{6a}$$

Second, in principle phase separation for elastic materials characterized by two moduli κ and μ and using the total free energy should occur when[23]

$$\frac{\partial^2 F}{\partial \phi^2} = \frac{1}{S(q=0)} \approx \kappa_{\text{os-gel}} + {}^4/_3\mu = 0 \tag{6b}$$

Following eq 6a the scattering would be slightly higher than in the solution case and the onset of spinodal decomposition would occur slightly earlier whereas using (6b) the scattering will be slightly lower than in the solution case and the onset of decomposition will be slightly delayed. In either case we are definitely not in the limit of strong segregation. In both cases (6a) and (6b), we would, however, expect a stronger exponent for the variation of $S(q)$ with q, and even more dramatic changes when increasing the EDMA ratio, unless such changes are limited by the elastic structure of the network, which is similar to the effect of the additional contribution of the term ${}^4/_3\mu$ in eq 6b for elastic network systems but active only in the second stage of the decomposition after the initial separation. As eqs 6a and 6b are written for homogeneous gels, it still remains unclear how heterogeneities affect the phase transition itself. We expect that domains of shrunken or swollen regions are pinned around regions of high and low cross-link densities of the gel. This goes back to the heterogeneity picture described above.

(b) Gels with Chains. The classical theories for the case of building a network around free chains are very similar to the one for just the network and solvent described above. In Flory–Huggins description, phase separation in a mixture could occur for the following reasons: first, the entropy of mixing of the free chains may be insufficient to balance the elasticity of the network, which could drive the system toward decomposition. This is similar to eq 6a, $\kappa_{\text{os-gel}} = 0$. Second, if the chains are of different species than the network, the χ parameter is usually positive, which shows another trend toward phase separation. On the other hand, this separation could still be slowed or limited in size by the elasticity of the network, which would not accept too large a concentration of linear chains within its own structure. This condition is equivalent to eq 6b.

When the gels are dried, as described above, a strong separation is seen between PSD and PMMA chains more due to a strong positive χ parameter than due to the elasticity of the network. We note that the sizes at which the separation is pinned are much larger than the mesh size of the network. Here the demixing term is probably much stronger than the elasticity term. Therefore, the second effect of the network, i.e. slowing or limiting separation (cf. eq 6b), is effective here only after segregation into larger cluster sizes, for large χ parameters, has taken place. Similar effects are observed for interpenetrating networks (IPN) made of two immiscible polymers. Recently, we introduced inside the dried PMMA network chemically identical free chains of DPMMA. Here we do not observe strong q^4 scattering like in the case of free PSD chains; in fact we have strongly reduced the effect of the demixing term by decreasing the χ parameter.

When the gels are not dried, the signal has a much weaker q dependence ($q^{-2.5}$ instead of q^{-4}). We wish to discuss here this dependence. A possible explanation of a power law between −2 and −4 could be the presence of a diffuse interface between regions of different concentrations, due to incomplete phase separation. The latter could be weak enough to be pinned by the network structure, the toluene acting as a good solvent for both the polymers. Such an interface could be a fractal surface, but we have no simple model to support its existence. It has been calculated that objects with surface undulations of the same order of magnitude as the overall size of the object give rise to such intermediate slopes. Higher values than the exponent −2 (Ornstein–Zernicke), i.e. −2.7 to −3.5, are also seen in the intermediate stages of spinodal decomposition, for $S(q)$'s at $q > q_{\text{m}}$ (q_{m} corresponds to maximum in $S(q)$) which has be pinned by the network, and are similarly seen for the interpenetrating network (IPN) of two immiscible polymers. Such slopes should vary for different molecular weight chains depending on the degree of advancement of the decomposition or on the strength of the separation, at variance with our results where we do not observe a change of slope at small q with the increase in size of the large polymer chains. The absence of very strong scattering at low q by large polymer chains in the gels is reminiscent of the case of gels with no chains discussed above where also the scattering is lower than expected at the approach of phase separation in the system.

On the other hand, we are tempted by the following different picture: due to slight expulsion from the network, the PSD chains trace its heterogeneous structure by preferentially going to less cross-linked regions, i.e. regions of lower elastic free energy. This means that the local concentration of free labeled chains will create a "contrast" that reveals or labels the clusters of high cross-linking densities in the network. As a working assumption, we can postulate, as before, that such regions can be represented as percolation clusters. If the weak segregation occurred *irrespective of the size of clusters*, the labeling by PSD chains would be similar to that by an ordinary deuterated solvent. Thus, for the same (limited) range of q such as $1/\xi_{\text{gel}} < q < 1/\xi_{\text{sol}}$ one would again get eq 5.

In eq 5, $^8/_5 = D^{\text{s}}_{\text{f}}(3 - \tau)$ where $D^{\text{s}}_{\text{f}} = 2$ is the fractal dimension[20,24] of the larger clusters in the (limited) domain of distance scales (ranging from ξ_{sol} to ξ_{gel}) in which the clusters are swollen by excluded volume and $(3 - \tau) = 0.8$.

For $q < 1/\xi_{\text{gel}}$, one should then observe the Ornstein–Zernicke law:

$$S(q) \approx S(0)/(1 + q^2\xi_{\text{gel}}^{\;2}) \tag{7}$$

But *we do not expect long polymer chains* which are free to move inside a network *to behave exactly as an ordinary solvent*. A small molecule can penetrate freely all the holes of clusters of any size. Long polymer chains will probably not. Presumably, they will not go into holes smaller than their average radius of gyration R_{g}: it would cost too much deformation energy. It is easier for them to escape into the relatively larger holes of the larger clusters. In the picture of percolation clusters these holes contain also smaller clusters, but very likely the chains will cross clusters smaller than their R_{g} rather than being effectively constrained by them. Hence the chains and the smaller clusters should intercross each other as in an ideal mixture: these smaller clusters will not be revealed and will remain "invisible" in the scattering.

As a consequence, the screening of correlations between the bigger clusters (regarding the scattering) which was induced by the presence of the small clusters, in the case of a labeled solvent, vanishes. The (scattering) correlation length $\xi_{1\text{c}}$ must now be shifted to larger distances. To lower the confinement energy, these distances should be larger than the radius of gyration of the chains. This means that only clusters of sizes comparable to the R_{g} are revealed by scattering; thus there are no more polydispersity effects and the $(3 - \tau)$ term should also be removed. Note that, in this range of scales, the bigger clusters are not swollen (the excluded volume interactions remain screened off). Their fractal dimension is that of the bulk D^{b}_{f} instead of the swollen one D^{s}_{f}. Therefore, in the case when $R_{\text{g}} \gg \xi_{\text{gel}}$ and in the range of q such as

$$1/\xi_{1\text{c}}\ (\approx 1/R_{\text{g}}) < q < 1/\xi_{\text{gel}}$$

the labeled chains should trace the bulk fractal dimension D^{b}_{f} of the larger clusters only.

Since $D^{\text{b}}_{\text{f}} = {}^5/_2$, one expects

$$S(q) \approx q^{-5/2} \tag{8}$$

Obviously, the intensity should start to saturate and follow an Ornstein–Zernicke law for $q < 1/\xi_{1\text{c}}$.

As seen above, the experimental variation ($q^{-2.5}$) that we observe in the case of the larger chains is approximately in agreement with this dependence.

In the case of smaller chains, R_{g} becomes comparable with ξ_{gel}. This is the first reason why one should observe a dependence weaker than the one given by (7): only a crossover regime can be seen. Such an argument should be valid essentially in the case of the chains with molecular weight 39 000. Note that, in addition, the "segregation" between the more and the less cross-linked regions should be less pronounced for the shorter chains (since the entropy of mixing of the chains is larger). This is valid for chains with molecular weight 39 000 as well, and may explain why, in the case of the 218 000 chains, the $q^{-2.5}$ dependence is attained only in the case of the larger cross-linking density (Figure 3).

According to our picture and in the case of very long chains, one should get, for $1/\xi_{\text{gel}} < q < 1/\xi_{\text{sol}}$, a regime in which one probes the fractal dimension $D^{\text{s}}_{\text{f}} = 2$ of clusters expanded by excluded volume. In practice, ξ_{gel} and ξ_{sol} are too close to each other to allow the observation of anything other than a crossover regime.

Finally, we remark that by our assuming such a weak segregation process, i.e. a modulation of the concentration of the free chains driven by the local cross-linking density, each chain would stay in a nonconfined conformation, intermediate between the ideal and the excluded volume states. The statistics should indeed be Gaussian on length scales larger than ξ_{sol}, due to screening effects resulting from the presence of the network and of the other free chains. Conversely, on length scales smaller than ξ_{sol}, the local statistics of the PSD chains should remain in an unperturbed excluded volume state. Therefore one expects $S(q) \approx q^{-5/3}$ for $q > 1/\xi_{\text{sol}}$, which is in agreement, within the experimental accuracy, with the slope 1.6 that we observe for all the systems of chains trapped in gels, for the larger q values. The conformation of the chains on length scales larger than ξ_{sol} could actually be checked by deuterating only a fraction of the PSD chains and extrapolating to zero ϕ_{D} fraction.

The preferential localization of large chains in regions of lower cross-link density could also account for the increase in the diffusion constant seen by Bansil et al.[4] The regions of lower cross-link density offer less friction to the diffusive motion of the PS chains and thereby could lead to an increase in their observed diffusion constants. Such an explanation ignores the effect of narrow bottlenecks which would slow the single-chain motion as seen in Monte Carlo simulations[25] inside random media. Such an explanation should be refined with further work. In particular we will study the perfectly miscible pair of PMMA gel/DPMMA chains. This system would be closer to the system PS/PVME studied by Rotstein and Lodge.[5]

IV. Summary and Conclusions

(i) In summary, the MMA gels have been observed by SANS using deuterated toluene, and compared to "equivalent" semidilute solutions at the same concentration. Gels show a larger signal than the solutions, contrary to the predictions of classical thermodynamics. As for other gels, this increased scattering can be attributed to heterogeneities of cross-linking. The scattering is very similar to one of randomly cross-linked PS gels, for which percolation clusterlike heterogeneities were proposed to explain the observed $q^{-1.6}$ dependence.

(ii) Linear PSD chains were introduced into similar networks by building the latter around them. Again, a strong increase of scattering is observed in the gel with respect to a semidilute PMMA solution containing the same PSD chains. We believe the linear PSD chains separately lightly from the network chains, mainly because of the elasticity of the network. Only for the dried samples, where the χ parameter is large, is the phase separation strong and leads to the q^{-4} Porod law characteristic of sharp interfaces in a two phase medium. In the presence of toluene which makes the effective χ parameter low, it is more likely that the linear chains invade the soft regions (less cross-linked) of the network. However, except for small chains where a $q^{-1.6}$ law is observed, as for gels swollen by solvent molecules, $q^{-2.5}$ is observed for large chains. An explanation involving similar fractal heterogeneities, but revealed only for the large clusters is given.

Appendix

Assuming a polydisperse system with log normal distribution[16,17] with σ as the index of polydispersity, $R_{\text{m}} =$

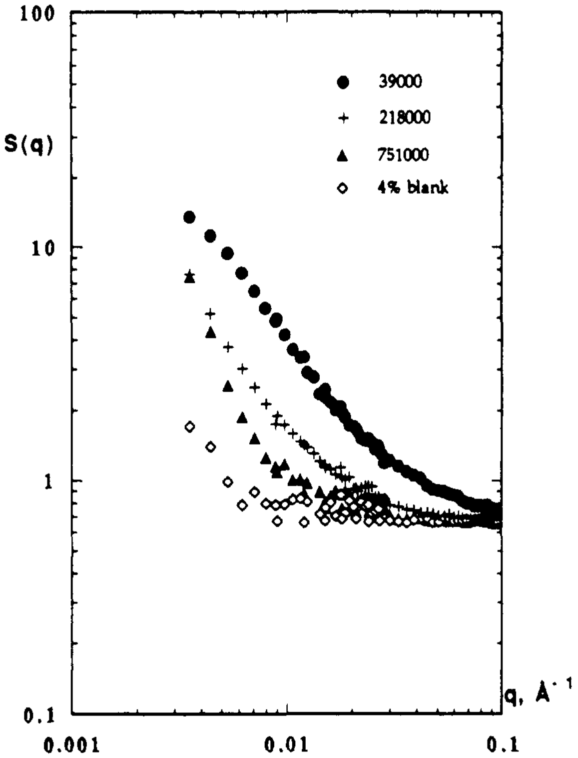

Figure 6. Spectrum $S(q)$ (not divided by Φ) of the blank and the PSD chains inside a MMA gel of cross-linking density 4.0% at 22 °C (units cm^{-1}).

$R_0 \exp(3.4\sigma^2)$ increases with σ meanwhile R_p decreases as the level of Porod's plateau increases.[16] For $M_w = 39\,000$ the difference between the values R_m and R_p ($R_m < R_p$) cannot be explained in terms of polydispersity alone. Let us define the volume fractions Φ_1 of the PSD chains in the PSD rich regions and Φ_2 of the PSD in the PMMA rich regions. Since for the $M_w = 39\,000$ the initial volume fraction Φ_0 is greater, the two phases produced by phase separation are closer in Φ_1 and Φ_2. This makes the actual contrast $K^2_{\text{eff}} = (\Phi_1 - \Phi_2)^2K^2$ lower by a factor easily of order 2. Introducing it in (2) can make the real R_p smaller than R_m. Such an effect would be less important for $M_w = 218\,000$ where one could assume $\Phi_1 = 0$ and $\Phi_2 = \Phi_0$.

References and Notes

(1) Boué, F.; Farnoux, B.; Bastide, J.; Lapp, A.; Herz, J.; Picot, C. *Europhys. Lett.* **1986**, *1*, 637.
(2) Zielinski, F. H.; Buzier, M.; Lartigue, C.; Bastide, J.; Boué, F. To be published in *Prog. Colloid Polym. Sci.*
(3) Briber, R. M.; Bauer, B. J. *Macromolecules* **1991**, *24*, 1899.
(4) Bansil, R.; Pajevic, S.; Konak, C. *Macromolecules* **1990**, *23*, 3380.
(5) Rotstein, N. A.; Lodge, T. P. *Macromolecules* **1992**, *25*, 1316.
(6) Pajevic, S.; Bansil, R.; Konak, C. *Macromolecules*, in press.
(7) Pajevic, S.; Bansil, R.; Konak, C. *J. Non-Cryst. Solids* **1991**, *131–133*, 630.
(8) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(9) Ragnetti, M.; Geiser, D.; Hocker, H.; Oberthur, R. C. *Makromol. Chem.* **1985**, *186*, 1701.
(10) Bastide, J.; Boué, F.; Buzier, M. In *Molecular Basis of Polymer Networks*; Baumgärtner, A., Picot, C., Eds.; Springer Verlag: Berlin, 1989; p 48.
(11) Mendes, E.; Lindner, P.; Buzier, M.; Boué, F.; Bastide, J. *Phys. Rev. Lett.* **1991**, *66*, 1595.
(12) Mallam, S.; Horkay, F.; Hecht, A. M.; Geissler, E. *Macromolecules* **1989**, *22*, 3356.
(13) Falcao, A.; Pedersen, I. S.; Mortensen, K.; Boué, F. Riso National Laboratory Report, 1991.
(14) Tanaka, T.; Hocker, L. O.; Benedek, G. B. *J. Chem. Phys.* **1973**, *59* (9), 5151.
(15) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C. *Macromolecules* **1974**, *7*, 863.
(16) Kent, M. S.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1992**, *25* (20), 5383.
(17) Roman, J. P.; Hoornaert, P.; Faure, D.; Biver, C.; Jacquet, F.; Martin, J. M. *J. Colloid Interface Sci.* **1991**, *144* (2), 324.
(18) Biver, C.; Taupin, C.; Ober, R. Preprint.
(19) Bastide, J.; Leibler, L. *Macromolecules* **1988**, *21*, 2647.
(20) Daoud, M.; Leibler, L. *Macromolecules* **1988**, *21*, 1497.
(21) Mallamace, F.; Micali, N.; Vasi, C.; Bansil, R.; Pajevic, S.; Sciortino, F. *J. Phys. II Fr.* **1992**, 2, 2081.
(22) Mallamace, F.; Micali, N.; Vasi, C.; Bansil, R.; Pajevic, S.; Sciortino, F. *Prog. Colloid Polym. Sci.* **1992**, *89*, 77.
(23) Onuki, A. To be published in *Phase Transition in Polymer Gels*; Dusek, K., Ed.; Advances in Polymer Science: Springer: New York.
(24) Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* **1990**, *23*, 1821.
(25) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989**, *22*, 1941.