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Small-Angle X-ray and Neutron Scattering from Bulk and Oriented Triblock Copolymer Gels

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ABSTRACT: Gels of polystyrene-*block*-rubber-*block*-polystyrene were investigated by small-angle X-ray (SAXS) and neutron (SANS) scattering. The rubber midblock was either poly(ethylene/propylene) (PS–PEP–PS) or poly(ethylene/butylene) (PS–PEB–PS). The gels of these thermoplasts have similar superstructures consisting of domains of associated polystyrene (PS) blocks, connected by the midblocks which are dissolved in an extender oil. The microphase separation is more pronounced in the PS–PEP–PS gels and results in clear interdomain scattering maxima and form factor oscillations. The ordering of the PS domains is a function of block copolymer concentration, molar mass, end block/midblock ratio, deformation, and temperature. Deformations up to 150% extension are reversible at room temperature. The scattering patterns of the unstretched samples were fitted with two different models: a hard-sphere liquid model and a model of a disordered solid with local coordination.

Introduction

Triblock copolymer gels are unique isotropic systems combining softness and elasticity in a wide temperature range. They are hydrophobic and can be processed as thermoplastic materials at high temperatures.[1,2] They are prepared by processing PS–rubber–PS triblock copolymers with an extender oil which is a mixture of saturated aliphatic and alicyclic hydrocarbons. The rubber midblock is either poly(ethylene/butylene) (PEB) or poly(ethylene/propylene) (PEP). Phase separation of the insoluble PS end blocks produces an assembly of PS domains connected by the midblocks into a three-dimensional spatial network in a matrix of solvent and dissolved middle blocks. The properties of this network determine those of the gels.

Previously, we reported[3] that the superstructure of an ABA triblock copolymer PS–PEB–PS (Kraton) gel gives rise to a well-defined low-angle scattering pattern consisting of a sharp maximum and a second one which is more or less pronounced depending on the polymer concentration. The angular position of these maxima also depends on the polymer concentration. At higher angles, but still in the small-angle region, a broad maximum is also observed. Due to a poor signal-to-noise ratio in the tail of the scattering curve, this maximum could not be measured accurately on a conventional Kratky-type camera.

The two low-angle peaks were attributed to interdomain interference, and the maximum at higher angle was attributed to the form factor of the phase-separated PS domains.

New SAXS data of a triblock copolymer with a different middle block (poly(ethylene/propylene)) are presented here. Besides the features described above, the scattering patterns of these gels exhibit a number of more pronounced form factor oscillations. These were recorded over a wide range of polymer concentrations (6, 12, and 18%) and molar masses (M_n = 100 000, 200 000, and 300 000; Table 1a) and at different PS contents (20, 35, and 50%; Table 1b) using SANS and synchrotron radiation SAXS. This allows one to analyze the effect of these factors on gel morphology.

Experimental Section

Gels are prepared by heating and gentle mixing of the block copolymer with an extender oil and subsequently pressed into plaques as described elsewhere.[1–3] The preliminary SAXS measurements were performed with Ni-filtered Cu Kα radiation on a Kratky-type camera (Rigaku) with a 40-μm entrance slit installed on a Rigaku Rotaflex rotating anode, operated at 7.5 kW. All data were obtained with infinite slit geometry using a linear position-sensitive proportional detector (Braun OED-50M) to measure the scattered intensity. These data were desmeared and corrected for background scattering using the FFSAXS5 program by Vonk, as reported in ref 3. Scattering measurements with a point focus on bulk and oriented samples were obtained on the X33 camera[4,5] of the European Molecular Biology Laboratory (EMBL) in HASYLAB on the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY) at Hamburg. SANS measurements were performed on the SANS facility[6] of the Risø National Laboratory using neutrons monochromatized with a mechanical velocity selector with a wavelength of λ = 0.94 nm and a full width at half-maximum $d\lambda/\lambda$ = 0.18 using a sample–detector distance of 6 m.

Experiments were also conducted with 4 × 2 × 0.2 cm^3 pieces of gel stretched along their largest dimension using a special device placed in a small oven that maintained the temperature within ±3 °C from room temperature to 180 °C.

Results and Discussion

Phenomenological Description of the Scattering Patterns. The small-angle scattering data obtained for different molar masses and concentrations of triblock copolymers, as well as at different PS contents, exhibit similar general features: two maxima in the low-angle region, a strong one, and another that depends on concentration and molar mass, followed by a steep decrease of intensity and one or two broad maxima in the tail of the small-angle region (Figures 1 and 2). There is also an inflection in the region of the steep intensity decrease for the gels with the lowest (6%) block copolymer concentration. This inflection is more pro-

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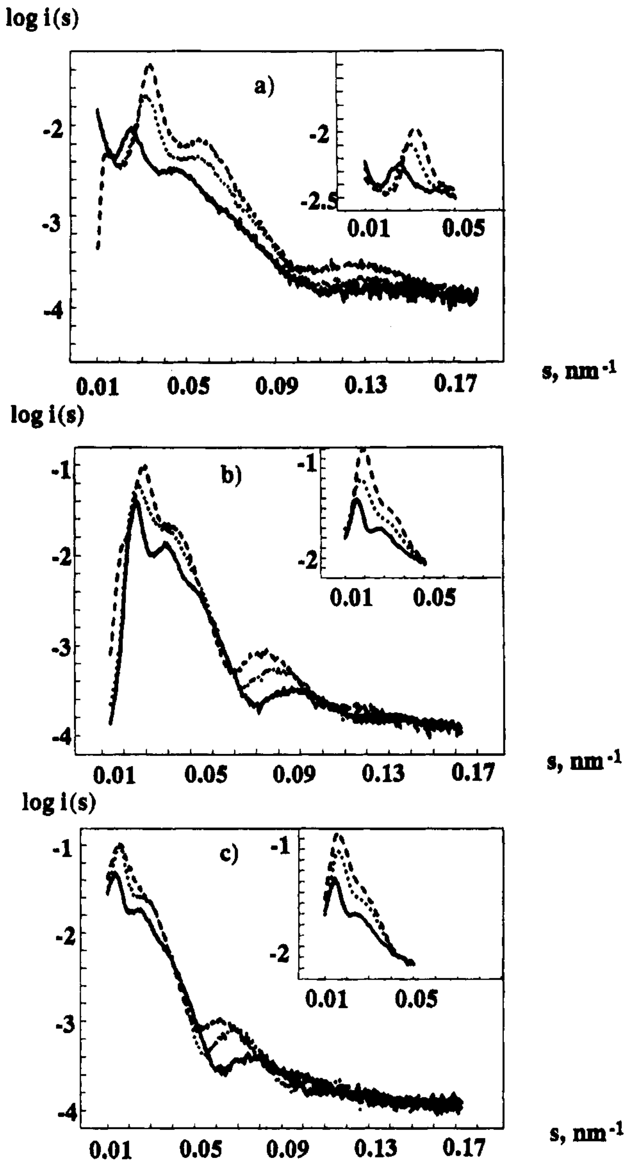

Figure 1. SAXS curves for triblock copolymer gels with PEP midblock and 35% of PS in the macromolecule (first series, Table 1a). Molecular weights are M_n = 100 000 (a), 200 000 (b), and 300 000 (c). Line styles used are (—) for 6%, (···) for 12%, and (– –) for 18% of triblock copolymer in gel. The corresponding SANS curves in the region of the interference maxima are shown as insets.

nounced for the higher molar mass copolymers (M_n = 200 000 and 300 000) than for the lowest one (M_n = 100 000).

These scattering patterns can be qualitatively understood as resulting from a distribution of well-defined regions with higher electron density, corresponding to the PS domains, embedded in a homogeneous medium. As a result of the low PS concentrations the distances between the spheres are much larger than their radii and the intradomain scattering or form factor can be separated from the interferences arising from the interdomain scattering. The interference maxima associated with the large interdomain distances will thus be confined to the small-angle region, whereas the form factor which contains the contribution of the smaller intradomain distances extends over a broad angular range. This is also confirmed by deformation experiments at moderate elongation (Figure 2d): the form factor maxima remain unchanged, whereas there is a clear shift in the position of the interference maxima toward smaller angles (for the direction of stretching) or larger angles (for the perpendicular direction). The appearance of the minima between the interdomain maxima and intradomain maxima provides further evidence for this view. The last minimum is located just beyond the steep intensity decrease (Figures 1 and 2) and originates from the zero point of the form factor contribution of a uniform sphere.

The overall dependence of the scattering pattern on polymer concentration is identical in the different series (Table 1). The interparticle interference maxima shift to higher s-values at increasing concentration (s is the magnitude of the scattering vector, given by $s = 2(\sin\theta)/\lambda$, 2θ is the scattering angle), suggesting a more compact arrangement of the PS domains. The shift toward smaller s-values with increasing polymer concentration of the two maxima of the form factor implies an increase in the size of the PS domains. At constant PS content in the polymer, an increase in polymer concentration in the gel results in a larger amount of PS per domain. Simultaneously there is an increase in the number of PS domains resulting in smaller interdomain distances D ($D = R_0 = 1.22/s_{\mathrm{int}}$; see the explanation of eq 9 in this paper). The estimated ratio of the domain radii for two different concentrations ($R_1{}^3/R_2{}^3 \propto c_1/c_2$) is larger than the observed value, pointing to a slower increase of the domain radius and the formation of new domains. The constant length of the midblocks implies a more compact chain packing in the latter arrangement which can be accounted for by a smaller weight percent of solvent in the gel.

Some trends can be found in the variation of the intensity of the first interference maximum and the appearance of the second one with increasing polymer concentration. In the series with constant PS content (Table 1a) the gels with the lowest molar mass block copolymers (M_n = 100 000) are characterized by an increase in intensity and a sharper first interference maximum. A second maximum also appears which results from increased order in the gel with increasing polymer concentration from 6 to 18 mass % of copolymer. The behavior of the gels of triblock copolymers with M_n = 200 000 is different: the middle, 12% mass concentration system corresponds to a broader first maximum and a less defined second one, while the 6% and 18% systems are more highly ordered. For the highest molecular mass the most disordered state is obtained at 18%. The most disordered system also occurs at 18% for a series of different concentrations using polymer with M_n = 200 000 and PS contents of 20 and 50% but occurs at 12% for 35% PS (Figure 3).

Comparison of the PS-*block*-PEB-*block-PS* gels (M_n = 240 000) with 6, 12, and 18% PS indicates that the most disordered system corresponds to a concentration close to 18% (Figure 2c). These observations will be discussed in more detail in light of models accounting for the morphology of the triblock copolymer gels.

As already mentioned, the form factor oscillations are better defined for triblock copolymer gels with a PEP midblock than with a PEB midblock. Moreover, the definition of these maxima improves with increasing concentration for gels of M_n = 100 000 and 200 000 with a PEP midblock and for gels of M_n = 100 000 with a PEB midblock. They are most clearly defined in the 12% gel with M_n = 300 000 and a PEP midblock and M_n = 240 000 and a PEB midblock as reported earlier.[3]

In most of the present experiments two side maxima are observed, but for the sample with the largest PS

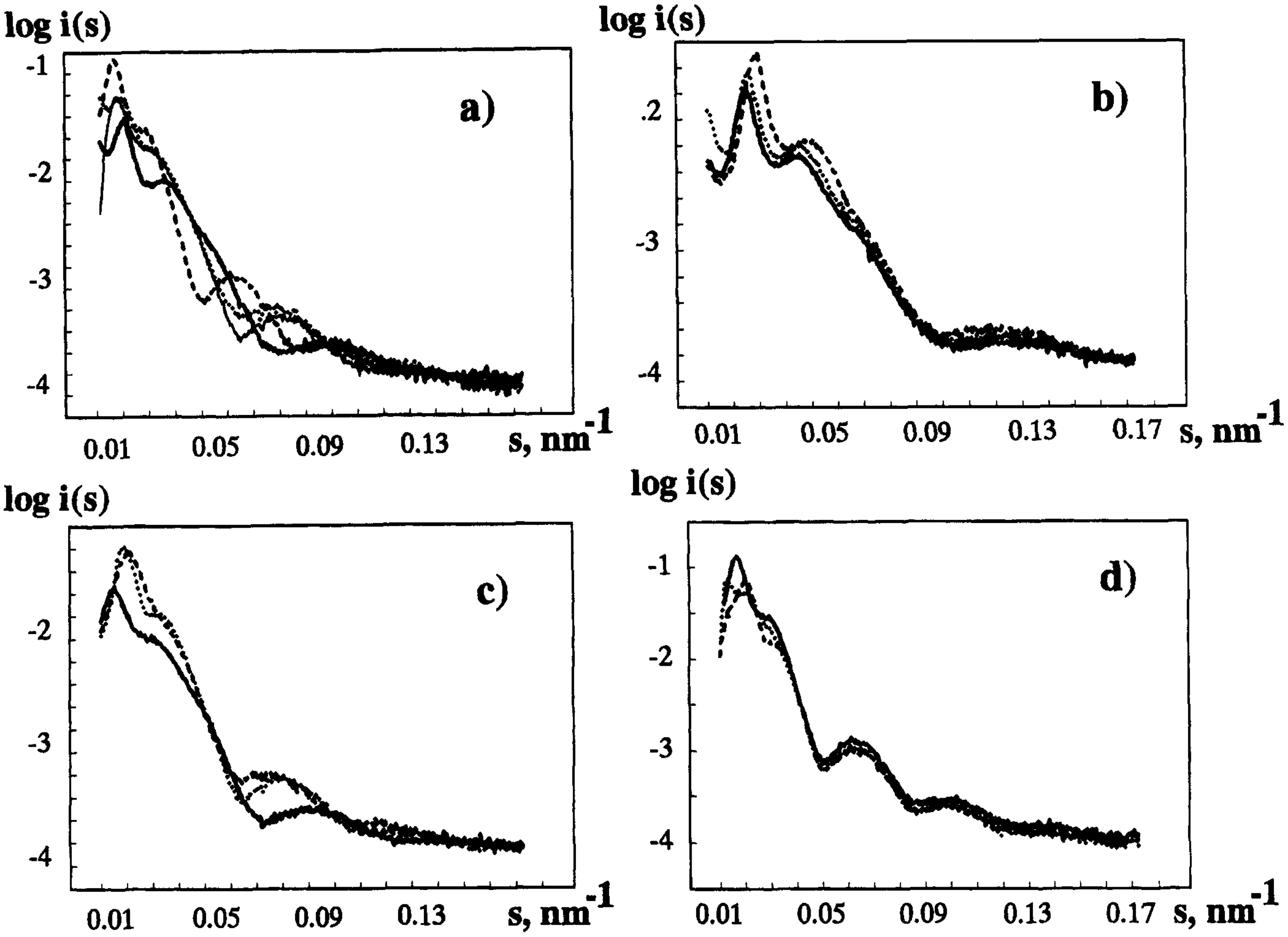

Figure 2. SAXS curves for gels: (a) 12% triblock copolymer of M_n = 200 000, PEP midblock, and different PS contents: (—) for 20% of PS, (···) for 35% from a first series and (thin —) for the same gel from a second series, and (– –) for 50% of PS. (b) Different copolymer concentrations of M_n = 100 000, PEB midblock, and 35% of PS: (—) for 7% gel, (···) for 8.5% gel, and (– –) for 12% gel. (c) Different copolymer concentrations of M_n = 240 000, PEB midblock, and 35% of PS: (—) for 6% gel, (···) for 12% gel, and (– –) for 18% gel. (d) 12% triblock copolymer of M_n = 200 000, PEP midblock, and 50% of PS: original (—) and stretched 2 times, as measured in the direction of stretching (···) and perpendicular to stretching (– –). No changes are observed in the PS domain form factor region.

content there is also a third maximum, suggesting the presence of well-shaped PS domains with nearly identical sizes. Increasing amounts of PS result in larger PS domains, but as the molar mass of polymer is constant this is accompanied by a reduction of the midblock size. In spite of this, the intersurface distance (i.e., the difference between the interdomain distance and the diameter of the domains, $\Delta = D - 2r_0$) is nearly constant for different styrene contents (Table 1b).

Stretching of Gels. All gels were stretched to a maximum of 2.5 times their original length. In the region of the maxima of the form factor the SAXS curves of the deformed and undeformed samples coincide (Figure 2d) for both vertical and horizontal sections of a two-dimensional scattering pattern. This is a common feature for the two series of samples with constant PS content and with constant molar mass. It is an additional argument in favor of the assignment of the form factor maxima and proves that moderate elongation only results in the rearrangement of the PS domains without alteration of their size and shape. Larger deformations (>200%) do, however, distort the PS domains.

Refinement of the Form Factor. As the SAXS curves allow a clear-cut separation of the inter- and intradomain scattering, the form factor of the PS domains can be extracted from the tail of the scattering curve, which is free of contributions from interdomain scattering, and refined. Following the method proposed by Glatter,[7] the distance distribution function $p(r)$ of the scattering particles in the case of an approximately monodisperse system of scatterers is given by the equation

$$I(s) = 4\pi\int_0^\infty p(r)\,\frac{\sin 2\pi sr}{2\pi sr}\,dr = 4\pi\int_0^\infty \sum_{\nu=1}^{n} c_\nu\varphi_\nu(r)\,\frac{\sin 2\pi sr}{2\pi sr}\,dr \quad (1)$$

and is obtained by minimizing the discrepancy between the functional on the right-hand side and the experimental intensity, adjusting the coefficients c_ν in the expansion of $p(r)$. The functions $\varphi_\nu(r)$ are cubic splines. (In the present work the implementation of the method described in ref 8 was used.) The shape of the distance distribution function (Figure 4) unambiguously points to a spherical shape for the PS domains.

Modeling the Scattering

Two approaches have been used to model the scattering from these gels. In the first, one starts from a short-range order liquid system where all orientations

Table 1. Characteristics of Triblock Copolymer Gels[a]

a. Poly(ethylene/propylene) Midblock, 1st Series (Different Molar Masses, PS Content: 35 mass %)

	M_n = 100 000			M_n = 200 000			M_n = 300 000		
	6%	12%	18%	6%	12%	18%	6%	12%	18%
D_x, nm	48.8	39.4	37.0	72.5	68.6	60.4	90.6	79.3	79.3
D_n, nm	47.8	40.8	37.4	75.1	66.1	61.8	83.3	76.6	75.1
D_{mean}, nm	48.3 ± 0.5	40.1 ± 0.7	37.2 ± 0.2	73.8 ± 1.3	67.4 ± 1.3	61.1 ± 0.7	87.0 ± 3.6	78.0 ± 1.3	77.2 ± 2.1
r_x, nm	6.6 ± 0.1	6.8 ± 0.1	7.2 ± 0.1	10.4 ± 0.1	11.5 ± 0.1	12.2 ± 0.1	11.5 ± 0.1	13.1 ± 0.1	14.8 ± 0.1
$\Delta = D_{mean} - 2r_x$, nm	35.2 ± 0.5	26.5 ± 0.7	22.9 ± 0.2	53.0 ± 1.3	44.5 ± 1.3	36.7 ± 0.7	64.1 ± 3.6	51.8 ± 1.3	47.6 ± 2.1

b. Poly(ethylene/propylene) Midblock, 2nd Series (M_n = 200 000; Different PS Content, mass %)

	20			35			50		
	6%	12%	18%	6%	12%	18%	6%	12%	18%
D_x, nm		59.5			61.9			72.5	
D_n, nm	72.6	61.3	57.2	75.1	66.1	58.9	83.3	73.7	67.2
D_{mean}, nm	72.6 ± 0.9	60.4 ± 0.9	57.2 ± 0.9	75.1 ± 2.1	64.0 ± 2.1	58.9 ± 2.1	83.3 ± 0.6	73.1 ± 0.6	67.2 ± 0.6
r_x, nm	8.5 ± 0.1	9.2 ± 0.1	10.2 ± 0.1	10.8 ± 0.1	11.5 ± 0.1	12.1 ± 0.1	13.7 ± 0.1	14.1 ± 0.1	15.3 ± 0.1
$\Delta = D_{mean} - 2r_x$, nm	55.6 ± 0.9	42.0 ± 0.9	36.8 ± 0.9	53.5 ± 2.1	43.1 ± 2.1	34.7 ± 2.1	55.9 ± 0.6	44.9 ± 0.6	36.6 ± 0.6

c. Poly(ethylene/butylene) Midblock (PS Content: 35 mass %)

	M_n = 100 000			M_n = 240 000		
	7%	8.5%	12%	6%	12%	18%
D_x, nm	46.9	45.2	41.6	81.3	63.5	57.8
r_x, nm	7.0	7.1	7.6	9.7	11.2	12.2
Δ, nm	32.9	31	26.4	61.9	41.1	33.4

[a] Interdomain distances (D_x, D_n, and D_{mean}—derived from the position of first interference maxima of SAXS or SANS or their averaged values, respectively; equation $Ds = 1.22$ or condition $\sin(Ds)/(Ds) = \max$ was used); radii of PS domains (r_x), derived from the position of maxima of the form factor; intersurface distance (Δ) between the PS domains. Note that at constant copolymer molar mass the intersurface distance (last line in the Table 1b) does not depend on the PS content (or midblock length) but depends on the concentration of the triblock copolymer (or amount of solvent), which evidences the dilute regime for the midblock chains.

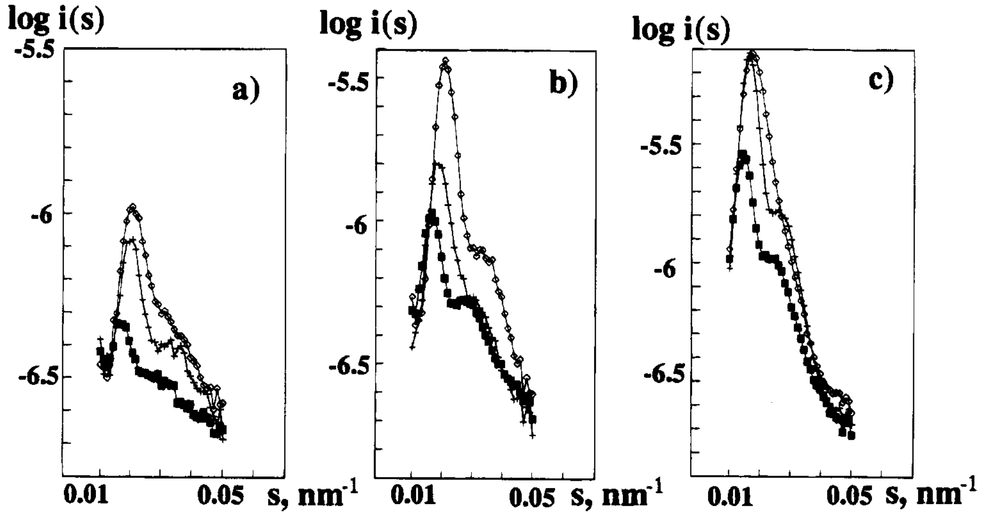

Figure 3. SANS curves for triblock copolymer gels with M_n = 200 000, PEP midblock, and different PS contents in the macromolecule (second series): (a) −20%, (b) −35%, and (c) −50% of PS. The gels of 6% copolymer are represented by ■, 12% by +, and 18% by ◇. The contour length of the midblock is decreasing from a to c, while the size of the PS domains is increasing (Table 1b).

of particles around a central core are equiprobable followed by the introduction of some nearest-neighbor coordination (Figure 5a). Alternatively, one can start from a strict local coordination and take into account a restricted correlation length and distortions of the coordination.

The first approach can be represented by a model of a liquid with hard-sphere (HS) interactions, as already successfully applied to micellar solutions and precipitates in metallic alloys.[9,10] Note that here, however, we consider imaginary hard spheres with a core consisting of the denser PS domain and an outer shell that has the same electron density as the surrounding medium (i.e., zero contrast).

In this case the experimental intensity is approximated by

$$I(s) = KN\langle P(s,r_0,\sigma)\rangle S(s,R,\eta) \tag{2}$$

where K is a constant depending on the type of radiation and sample properties, N is the number of scattering particles, and

$$\langle P(s,r_0,\sigma)\rangle = \int_0^\infty \frac{1}{\sigma(2\pi)^{1/2}} \exp\left(-\frac{(r-r_0)^2}{2\sigma^2}\right) P(s,r)\,\mathrm{d}r \tag{3}$$

is the averaged form factor $P(s,r)$ corresponding to the excess electron density of PS cores with mean radius r_0

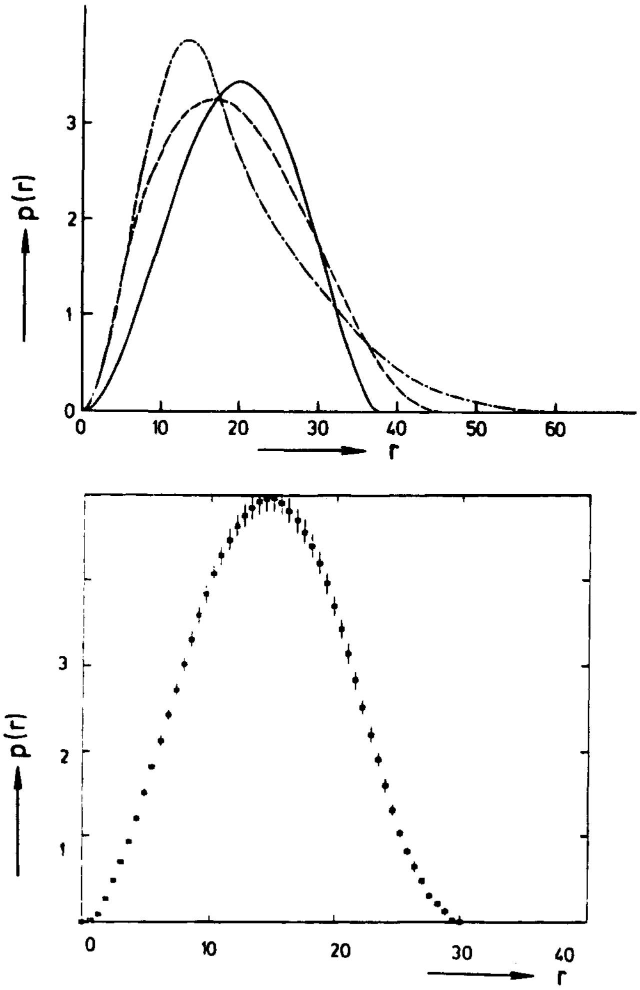

Figure 4. (a) Distance distribution functions for a uniform sphere (—), a prolate (– • –) and an oblate (– –) ellipsoid (picture is reproduced from p 178 of ref 7) and (b) a typical experimental distance distribution function for PS domains. Distance r inside the particle is given in nanometers.

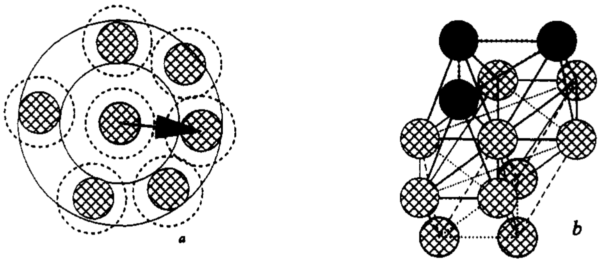

Figure 5. Scheme of liquid-type order: (a) liquid of hard-spheres—only the first coordination sphere is shown, and no angular correlation is accounted for; (b) an alternative liquid-like order with strong angular correlation can be built up by introducing the distance distortions in the local crystalline system of PS domains, formed in between close-packed compact regions of dissolved midblocks and solvent (not shown in the picture). This results in eight tetrahedral units each of four PS domains arranged around the central common domain (coordination model).

and dispersion factor σ.

$$P(s,r_0) = (4\pi r_0^3/3)^2\{3/(2\pi s r_0)^3[\sin(2\pi s r_0) - 2\pi s r_0 \cos(2\pi s r_0)]\}^2 \quad (4)$$

R is the radius of the fictitious hard sphere, usually close to half the typical distance between interacting particles, and η is the hard-sphere volume fraction. $S(s,R,\eta)$ is the structure factor for a monodisperse system, given by

$$S(s,R,\eta) = [1 + 24\eta G(A)/A]^{-1} \quad (5)$$

where $A = 4\pi sR$ and

$$G(A) = \alpha/A^2(\sin A - A\cos A) + \beta/A^3(2A\sin A + (2 - A^2)\cos A - 2) + \gamma/A^5\{-A^4\cos A + 4[(3A^2 - 6)\cos A + (A^3 - 6A)\sin A + 6]\} \quad (6)$$

The parameters α, β, and γ are

$$\alpha = (1 + 2\eta)^2/(1 - \eta)^4$$
$$\beta = -6\eta(1 + \eta/2)^2/(1 - \eta)^4 \quad (7)$$
$$\gamma = 1/2\eta(1 + 2\eta)^2/(1 - \eta)^4$$

The parameters R, η, and r_0 were adjusted in order to obtain the best fit of the measured curve by minimizing the functional

$$\chi^2 = 1/(n - p)\sum[I^{\text{meas}}(s_i) - I^{\text{mod}}(s_i)]^2/\sigma_i^2 \quad (8)$$

where the sum is calculated over n experimental points, p is the number of fitting parameters, $I^{\text{meas}}(s_i)$ are the measured intensities, σ are their standard deviations, and $I^{\text{mod}}(s_i)$ are the model intensities.

The second approach is based on a continuous phase of connected large particles still with zero contrast relative to the surrounding medium with a dispersed phase of small PS domains. This corresponds to the fact that during gelation the segregation of dissolved midblocks results in the formation of regions filled with solvent and midblocks. As the concentration of end blocks is low (≤20%) the midblock/solvent regions can be considered to consist of large particles.[3] Thus, locally the continuous midblock/solvent phase can be considered as a close-packed system of large particles, with the small insoluble PS domains arranged around a large particle taken as the origin.

Three situations can be considered for the arrangement of the small domains around a central small domain.[3,11] In two of these the local coordination is represented by the arrangement of eight regular tetrahedral units, each formed by four PS domains, around the common central domain (Figure 5b). The third case corresponds to a locally hexagonal arrangement of small domains. The first two arrangements represent a macroscopic isotropic order in the gel in a more natural way than the third one. This is also why we use the term locally hexagonal to emphasize that we only deal with local order.

The SAS intensity of the short-range order was modeled with Debye's formula:

$$I(s) = K\langle P(s,r_0,\sigma)\rangle[N + 2\sum Z_k \sin(2\pi s R_k)/(2\pi s R_k)] \quad (9)$$

The sum in brackets represents the interference factor $S(R_k,s)$, similar to the one defined in eq 2, of a distribution of N spheres with mean radius r_0 and standard deviation on the radius σ. The distribution is characterized by a discrete set of k classes of distances R_k with frequency Z_k. The value of r_0 can be derived from the position of the maxima of the form factor of a sphere which occur at $2\pi s r_0 = 5.76, 9.10, ...$[12] The values of R_k and Z_k can be derived directly from the models of

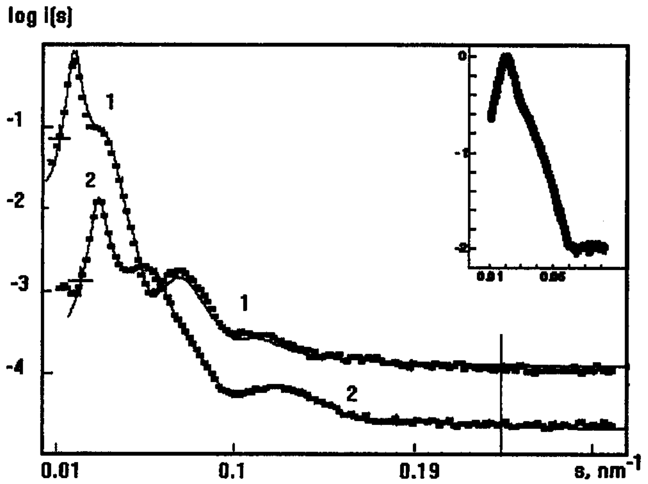

Figure 6. Fitting of SAXS curves by the HS model for 18% triblock copolymer gel with a PEP midblock and $M_n = 300\ 000$ (1) and $M_n = 100\ 000$ (2). Curve 2 represents one of the best fits (suppressed midblock conformation) and curve 1 one of the worse fits (unstretched conformation) for the HS model (see Table 2 and the last section of the paper). In the inset the typical situation (good fit) for the coordination model is shown.

short-range order and geometrical considerations, the region under consideration being limited by its correlation length. All interdomain distances can be related to R_0, the distance between nearest neighbors. R_0 defines the position of the maximum s_{int} of the main term of the sum in the brackets, i.e., $\sin(2\pi sR_0)/(2\pi sR_0)$, which gives $R_0 = 1.22/s_{\mathrm{int}}$.[12] Disorder can be introduced by replacing the old discrete set R_k of distance classes with frequencies Z_k ($0 \leq k \leq M$) of the undistorted model by a new set defined by Gaussians around R_k with standard deviation $R_k(1/\xi)^{1/2}$ to obtain a distorted model:

$$\sum_i \varphi_k \exp[-\xi(R_k - R_i)^2/(R_k)^2] = Z_k$$

$$Z_i = \sum_k f_k(R_i) = \sum_k \varphi_k \exp[-\xi(R_k - R_i)^2/(R_k)^2] \qquad (10)$$

Here ξ defines the degree of disorder and is the adjusted parameter, k is the index of the old system of distances for the model, and i is the index of a new set of distances R_i, more frequently arranged within the correlation length. The first equation in eq 10 means that the previous amount of domain pairs Z_k at distance R_k is now distributed at the new set of different (equidistant) distances R_i ($1 \leq i \leq L$). The number L of different distances in the distorted local coordination model is chosen as $L \approx 10M$. The value of φ_k is derived from this equation. The second equation represents a new number of domain pairs at distance R_i as a sum of M contributions, f_k, from Gaussian distributions of distances around each R_k from the old set of distances. The value of ξ was varied between 30 and 80, and $\sigma = 0.1r_0$ was used in the present calculations.

Comparison of the Models. Analysis of the low-angle part of the SAS pattern in terms of the χ^2-criterion in eq 8 makes clear that both the HS and the coordination models result in a fair agreement with the experimental data (Figure 6).

The HS model emphasizes the short-range order and the absence of crystalline order in the system. It is applicable to the whole concentration range and reproduces the first and second interference maxima. Comparison of Figures 1, 2, and 7 indicates that there are slight deviations at the higher concentrations of the higher molar mass polymer gel. The interpretation of the radius of the HS (R, approximately half the distance between the PS domain centers) and especially of the HS volume fraction (η, a measure of the degree of order) in terms of molecular parameters is more complicated for the case of connected PS domains than for separated particles[9,10] and will be discussed in a forthcoming paper.[11]

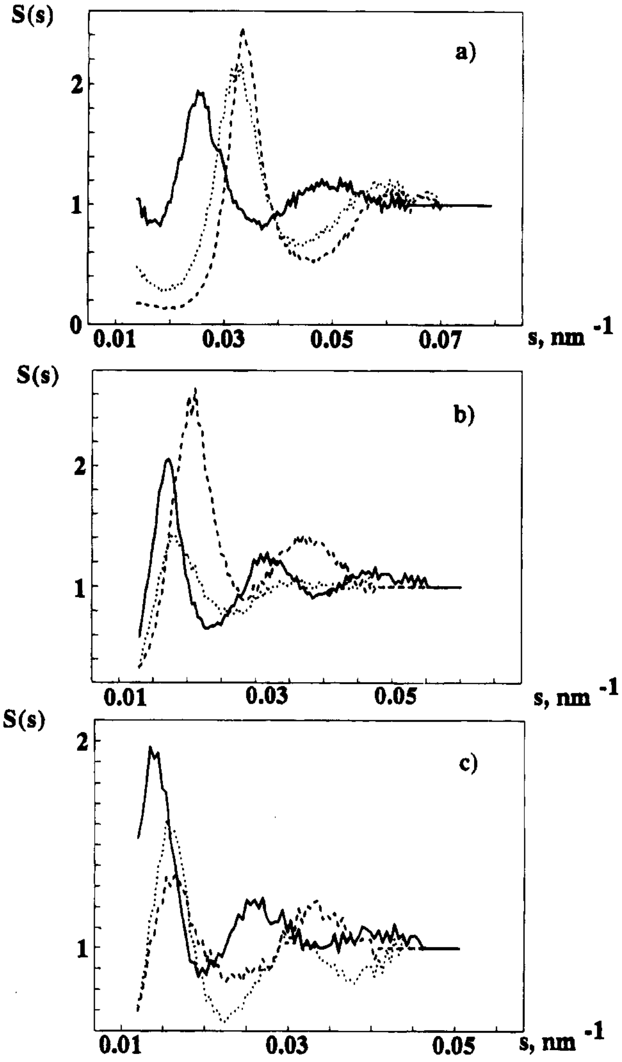

Figure 7. Experimental interference functions for gels based on $M_n = 100\ 000$ (a), 200 000 (b), and 300 000 (c) polymers with PEP midblock. 6% gels are represented by —, 12% by ···, and 18% by – –.

The model of short-range order with coordination involves physically meaningful aspects of a spatial network and relies on the parameters that are obtained from the experimental data: the mean radius r_0 of the PS domains, approximated by a system of ideal monodisperse spheres, the correlation length or number of coordination shells to be taken into account, and the estimate of the principal interdomain distance R_0.

The restrictions on the domains are somewhat artificial as only the first coordination sphere is considered and the disorder in terms of coordination angles is only taken into account through distortions of the interdomain distances. In spite of these limitations all features of the experimental scattering curves are reproduced (inset in Figure 6).

Short-Range Order and the Conformational State of the Midblock. Knowing the form factor and the polydispersity σ of the spherical domains (Table 2), one can derive the experimental structure factors

$$S(s) = I(s)/\langle P(s,r_0,\sigma)\rangle \tag{11}$$

which characterize the degree of short-range order in a system and by mutual comparison of these investigate the concentration dependence of disorder in the gels.

Figure 7 exhibits the structure factors derived for the set of gels in Table 1a which also gives the averaged values of the interdomain and intersurface distances between neighbors. The dependence of the extent of order as monitored by the first maximum of the structure factor on polymer concentration implies the existence of an ordering force. The domains are interconnected by midblocks dissolved in the extender oil. If c^* is the triblock copolymer concentration at which the conformation of the midblock is close to the statistical coil of a free polymer chain (Figure 8), then any deviation from the equilibrium end-to-end distance, $\langle r_{ll}{}^2\rangle^{0.5}$, will induce a counterforce that will act on the PS domains connected to this midblock. Unless the midblocks are equally stretched (for higher solvent contents) or compressed (for lower solvent contents) at any point of the gel network where the midblock concentration deviates from c^*, a local stress point will appear. The counterforce will result in a more uniform distribution of interdomain distances (i.e., a less distorted local coordination) and thus act as an ordering factor.

Concentrations above and below c^* will thus result in a more ordered arrangement of the nearest PS domains. Assuming that conditions for dissolving the midblocks are independent of molar mass, the concentration c^* can be predicted for all gels with different molar masses if only one value is known. Using the relationship $\langle r_{ll}{}^2\rangle = Nl^2$, where l is the segment length and N the number of segments in the chain, one can calculate c^* from the known values of the intersurface distances and the molar mass ratios of copolymer molecules (e.g., $\langle r_{ll}{}^2\rangle_{M_n=200\,000} = 2\langle r_{ll}{}^2\rangle_{M_n=100\,000}$).

The experimental values of the intersurface distances are given in Table 3a. For each molar mass the lines corresponding to the polymer concentrations corresponding to the most disordered gels contain three values. The calculated intersurface distances based on the assumption that the concentrations c^* for other molecular weights have been correctly derived are also given. There are obvious discrepancies between the experimental and calculated values. These can be reduced by taking into account that the conformational state of the ends of the midblock chain in the vicinity of the surface of the PS domains do not behave as statistical coils. Hence, the double of the length of this end region (t) should be subtracted from the intersurface distance. This is equivalent to minimizing

$$\Phi(t) = \left(r_1 - 2t - \frac{r_2 - 2t}{\sqrt{2}}\right)^2 + \left(r_1 - 2t - \frac{r_3 - 2t}{\sqrt{3}}\right)^2 \tag{12}$$

where $\langle r_{ll}{}^2\rangle_{M_n=100\,000} = r_1{}^2$, $\langle r_{ll}{}^2\rangle_{M_n=200\,000} = r_2{}^2$, $\langle r_{ll}{}^2\rangle_{M_n=300\,000} = r_3{}^2$. A value of t = 8.5 nm leads to a significantly better fit as indicated in Table 3b.

This model is, of course, still oversimplified as it neglects the polydispersity of the molar mass of the copolymer and of the blocks. Further, the contour length of the midblocks that form a statistical coil is uncertain, and there may be other effects due to the

Table 2. Parameters of the Hard-Sphere (HS) Model for Triblock Copolymer with a PEP Midblock[a]

	M_n = 100 000 (35% PS)			M_n = 200 000 (35% PS)			M_n = 300 000 (35% PS)			M_n = 200 000 (different PS content, 12% of the total polymer)		
	6%	12%	18%	6%	12%	18%	6%	12%	18%	20% PS	35% PS	50% PS
r_{mean}, nm	6.24 ± 0.03	6.42 ± 0.02	6.83 ± 0.02	9.95 ± 0.03	10.72 ± 0.04	11.64 ± 0.04	11.4 ± 0.04	12.9 ± 0.05	13.43 ± 0.07	8.78 ± 0.04	10.6 ± 0.07	13.93 ± 0.07
Δr, nm	1.19 ± 0.08	1.91 ± 0.04	1.94 ± 0.03	2.33 ± 0.07	2.83 ± 0.08	2.91 ± 0.08	2.85 ± 0.09	2.92 ± 0.09	4.4 ± 0.15	2.61 ± 0.09	3.9 ± 0.15	3.5 ± 0.13
η	0.33 ± 0.015	0.39 ± 0.005	0.46 ± 0.005	0.40 ± 0.007	0.33 ± 0.009	0.39 ± 0.007	0.28 ± 0.016	0.35 ± 0.16	0.28 ± 0.10	0.34 ± 0.17	0.21 ± 0.02	0.35 ± 0.017
L, nm	40.7 ± 0.7	33.2 ± 0.5	32.7 ± 0.4	63.3 ± 0.4	68.2 ± 0.7	51.3 ± 0.5	74.2 ± 1.1	65.7 ± 0.8	68.4 ± 1	51.5 ± ± 0.7	50.9 ± 1.4	60.7 ± 1.1
χ^2, %	6.2	3.3	2.2	2.7	4.8	6	6.7	8.2	8.9	4.5	9.6	10

[a] r_{mean} = mean radius, averaged over Gaussian distribution of radii with full width at half-height $\Delta r = 2(2 \ln 2)^{1/2}\sigma$; η = volume fraction of HS; L = double radius of averaged HS, approximately correlating with interparticle distance in Table 1a and 1b ($D \approx 1.22L$); χ^2 = discrepancy factor for HS model. Note the correlation between the polymer concentration, corresponding to minimal volume fraction η of HS, and concentration of polymer in the most disordered gel for each molar mass (see the last section of this paper).

Table 3. Comparison of Intersurface Distances Δ between PS Domains, Regarded As End-to-End Distances of the Midblock in a Conformation Close to a Statistical Coil[a]

a. Poly(ethylene/propylene) Midblock, 1st Series (Different Molar Masses, 35 mass % of PS Block Content)

	M_n = 100 000			M_n = 200 000			M_n = 300 000		
	Δ, nm	Δ, nm [based on 12% gel of $M_n = 2 \times 10^5$]	Δ, nm [based on 18% gel of $M_n = 3 \times 10^5$]	Δ, nm [based on 6% gel of $M_n = 1 \times 10^5$]	Δ, nm	Δ, nm [based on 18%gel of $M_n = 3 \times 10^5$]	Δ, nm [based on 6% gel of $M_n = 1 \times 10^5$]	Δ, nm [based on 12% gel of $M_n = 2 \times 10^5$]	Δ, nm
6%	35.2 ± 0.5	31.4	27.5	53.0 ± 1.3			64.1 ± 3.6		
12%		26.5 ± 0.7		49.8	44.5 ± 1.3	38.8		51.8 ± 1.3	
18%			22.9 ± 0.2			36.7 ± 0.7	60.9	54.5	47.6 ± 2.1

b. Poly(ethylene/propylene) Midblock, 1st Series (Different Molar Masses, 35 mass % of PS Block Content)

	M_n = 100 000			M_n = 200 000			M_n = 300 000		
	Δ, nm	Δ, nm [based on 12% gel of $M_n = 2 \times 10^5$]	Δ, nm [based on 18% gel of $M_n = 3 \times 10^5$]	Δ, nm [based on 6% gel of $M_n = 1 \times 10^5$]	Δ, nm	Δ, nm [based on 18% gel of $M_n = 3 \times 10^5$]	Δ, nm [based on 6% gel of $M_n = 1 \times 10^5$]	Δ, nm [based on 12% gel of $M_n = 2 \times 10^5$]	Δ, nm
6	18.3 ± 0.5	19.5	17.7	36.1 ± 1.3			47.2 ± 3.6		
12		9.6 ± 0.7		25.9	27.6 ± 1.3	25.1		34.9 ± 1.3	
18			6.0 ± 0.2			19.8 ± 0.7	31.7	33.8	30.7 ± 2.1

[a] Values in a on diagonals (for each certain molecular mass) are taken from Table 1a or (nondiagonal) recalculated based on a supposed equilibrium end-to-end distance for other molar masses. Values in b are on diagonals for a certain molar mass are intersurface distances from Table 3a reduced by the length $2t$ (see eq 12); others were recalculated from diagonal values in the same way as in Table 3a.

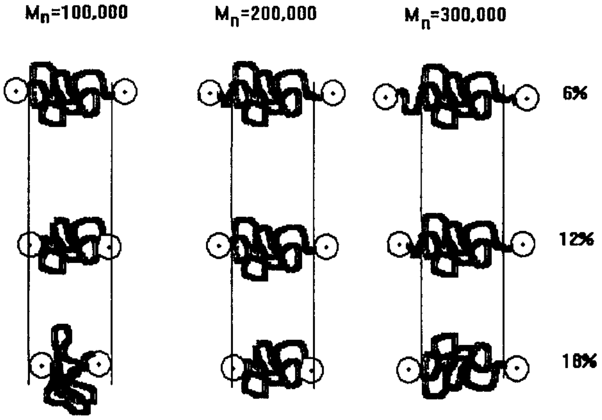

Figure 8. Scheme of end-to-end distances for gels of different molecular weights and the same end block/midblock ratio. The distance between parallel lines represents the equilibrium end-to-end distance for the dilute solution.

semidilute regime for polymer chains in the vicinity of the surface of the PS domains.

Additional data can be used to check the proposed models. A temperature increase, for instance, is expected to alter the order by modifying the equilibrium end-to-end distance. Above a certain threshold this should lead to a decrease of the statistical segment length and thus improve the order of the most disordered gel system. In contrast in the systems where the concentration is higher than c^* (i.e., where the midblock is compressed relative to the equilibrium end-to-end distance) a decrease in order due to increased Brownian motion is expected. SANS data obtained at different temperatures confirm this prediction (Figure 9). The upper curve, corresponding to the concentration c^*, displays a pronounced increase of the second interference maximum and a sharpening of the first one at higher temperatures. Contrary to that at $c > c^*$ (lower curve on Figure 9), there is almost no difference between the high-temperature SANS curve and the one obtained at room temperature.

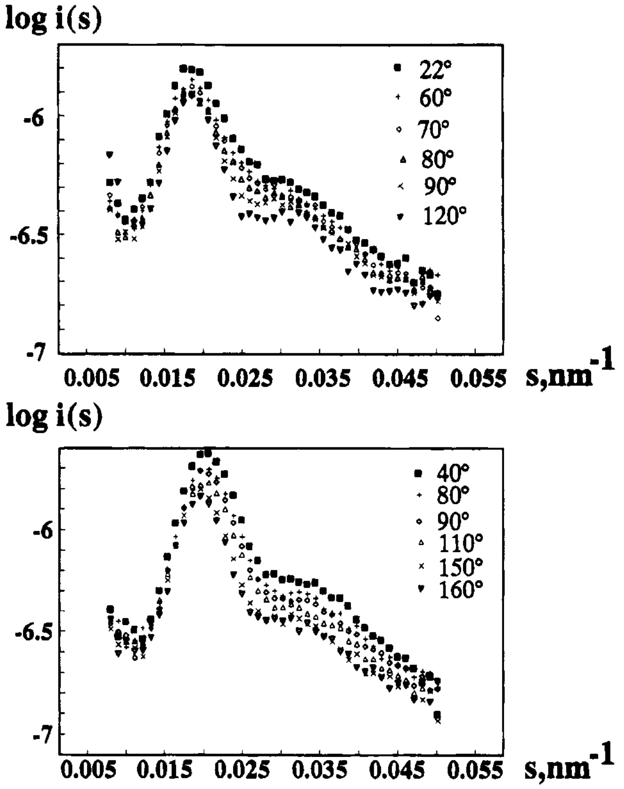

Figure 9. Temperature behavior of the first interference maximum of a SANS curve for the system close to the most disordered state (upper curve, 12% gel of M_n = 200 000 polymer) and for the gel with suppressed conformation of the midblock (lower curve, 18% gel of M_n = 200 000 polymer).

Conclusions

The morphology of triblock copolymer gels can be described as follows: PS end blocks form spherical domains with small polydispersity of radius in a homogeneous medium of dissolved midblock and solvent. The conformation of the midblock can be close to that of a statistical coil in good solvents or compressed or stretched.

In the latter two cases the resulting elastic force increases the order of the PS domains. This order is liquidlike, with a mean interdomain distance that is 2–3 times larger than the mean diameter of the domains. SAXS and SANS data reveal a high coordination order which can be accounted for by two models. The first is a liquid of denser PS cores surrounded by a hard-sphere shell that is contrast-matched with the medium and with a radius corresponding to 80–85% of half the interparticle distance. The distribution of neighbors in the first coordination shell determines the scattering. The second is a coordination model starting from crystalline order in a limited region of space and involving distortions of the interdomain distances.

Moderate stretching (≤150%) of the gel samples does not affect the shape of the PS domains and is entirely reversible.

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