3426 *Macromolecules* **2005,** *38,* 3426−3431

Small-Angle Neutron Scattering from Solutions of Diblock Copolymers in Partially Miscible Solvents[†]

Petr Štěpánek,*,[‡] Zdeněk Tuzar,[‡] Frédéric Nallet,[§] and Laurence Noirez[||]

Institute of Macromolecular Chemistry, Heyrovský Sq. 2, 1620 6 Prague 6, Czech Republic,
Centre de recherche Paul-Pascal, CNRS, 115 Avenue du Docteur-Schweitzer, 33600 Pessac, France,
and Laboratoire Léon-Brillouin, laboratoire mixte CEA—CNRS, CEA-Saclay,
91191 Gif-sur-Yvette Cedex, France

Received October 1, 2004; Revised Manuscript Received February 3, 2005

ABSTRACT: We report on small-angle neutron scattering experiments from diblock copolymers A−B dissolved in a mixture of partially compatible solvents a and b (an extended abstract of this work has been published in *Bull. Am. Phys. Soc.* **2004**, March). Block A is polystyrene, while block B is polyisoprene, polybutadiene, or hydrogenated polyisoprene. Solvent a is dimethylformamide, which is a good solvent for block A and a bad solvent for block B, and vice versa for solvent b, namely, cyclohexane. There is a range of temperatures and concentrations somewhat above as well as below the coexistence curve of the two solvents where the samples, though remaining macroscopically homogeneous, are microphase-segregated, presumably between a-rich and b-rich domains separated by interfaces covered with the diblock copolymer. For the various copolymers studied, we find cubic or hexagonal structures with local order only at high temperatures, but long-range ordered structures below the coexistence curve. The characteristic structural dimensions are in the range 60−110 nm and depend on both the polymer concentration and relative amount of solvents. We also show that the chains at the interface are slightly extended, as described by the value $a = 0.65$ of the Flory exponent that exceeds the value for free chains with excluded volume, $a = 0.60$.

Introduction

Colloidal behavior of block and graft copolymers in appropriate solvents is in many respects similar to that of soaps and surfactants in water.[1−3] Block and graft copolymers can form micelles, which are able to, e.g., solubilize otherwise insoluble substances or stabilize particles of colloidal dimensions. Amphiphilic surfactants are known to lower the effective surface tension at the interface between otherwise immiscible solvents, e.g., an organic solvent and water, giving rise to various "water-in-oil" (inverse) and "oil-in-water" (direct) disordered or liquid-crystalline microemulsions.[4,5] Such systems found numerous applications in various branches of industry and everyday life. Similarly, block and graft copolymers can "compatibilize" immiscible homopolymers. A variety of structures resulting from mixtures of homopolymers A and B with a diblock copolymer A−B have been theoretically predicted and experimentally confirmed.[6]

Somewhat similar are the colloidal systems made of a diblock copolymer A−B dissolved in an immiscible mixture of low-molecular-weight solvents a and b, where a is a thermodynamically good solvent selective for block A (and a precipitant for block B) and b is a thermodynamically good solvent selective for block B (and a precipitant for block A). Long-range-ordered, anisotropic nanostructures can be expected, formed by periodically arranged domains of solvents a and b, stabilized by the block copolymer forming a brush on the a/b interface. This model was treated theoretically using the mean-field approximation[7] or the scaling approach.[8] It has been concluded that, depending on the symmetry of the copolymer and other properties of the model, various ordered structures may result, in particular built by periodically stacking lamellar (two-dimensional), cylindrical (one-dimensional), or spherical particles. Very few experiments have been performed so far on diblock copolymers located at the structured interface between two such immiscible liquids. In the experiments reported here, we use small-angle neutron scattering to investigate the structure and other properties of several microscopically ordered solutions of diblock copolymers with polystyrene (A) and polydiene or aliphatic (B) blocks in a mixture of two *partially miscible* solvents, namely, cyclohexane (b) and dimethylformamide (a). These two solvents are fully miscible at temperatures above the coexistence curve, which displays a critical point at temperature $T_c = 51.4$ °C with dimethylformamide critical volume fraction $\phi_{DMF} = 0.327$; below this curve a two-phase region obtains, a DMF-rich liquid-phase coexisting at equilibrium with a cyclohexane-rich phase.

Background

Because of their physicochemical applications and importance in industry, grafted polymer layers have been the subject of many experimental and theoretical investigations since the brush model of Alexander and de Gennes.[9,10] This model predicts the thickness and density profile of the polymer brush as a function of the grafting density and molar mass of the polymer chains attached to the interface. Two basic regimes are described: (1) the low grafting density ("mushroom") regime, where the well-separated chains are randomly coiled, (2) the high grafting density ("brush") regime, where the chains in the grafted layer overlap and form a semidilute solution where the concentration c decreases in a direction z perpendicular to the solid interface as $c(z) \approx z^{-4/3}$.

---

* To whom correspondence should be addressed. E-mail: stepan@imc.cas.cz.

[†] Dedicated to Professor Pavel Kratochvíl on the occasion of his 75th birthday.

[‡] Institute of Macromolecular Chemistry.

[§] CNRS.

[||] CEA-Saclay.

10.1021/ma0479767 CCC: $30.25

Table 1. Characteristics of the Copolymers Used[a]

acronym	composition	M_{PS} [g/mol]	M_B [g/mol]	w_{PS}
S−I(126−39)[b]	poly(styrene-*b*-isoprene)	126000	39 000	0.76
S−EP(41−54)[c]	poly[styrene-*b*-(ethylene-*co*-propylene)]	41000	54 000	0.43
S−EP(45−135)[d]	poly[styrene-*b*-(ethylene-*co*-propylene)]	45000	135 000	0.25
S−B(16−79)[b]	poly(styrene-*b*-butadiene)	16000	79 000	0.17

[a] M_{PS} = molar mass of the polystyrene block, M_B = molar mass of the second block, and w_{PS} = weight fraction of polystyrene. [b] Polymer Source, Inc., Canada. [c] Shellvis 50 from the Shell Co. [d] Shellvis 40, from the Shell Co.

The case of block copolymers adsorbed to a solid interface has been discussed by Daoud,[11] who has shown that for various block copolymers the width of the adsorbed layer is on the order of the radius of a free chain. The local concentration of the interfacial layer is larger for a random copolymer than for a homopolymer. From energy calculations it appears that the easiest multiblock copolymer to adsorb to an interface is a diblock copolymer.

Adsorption of polyelectrolytes to an interface has been treated by Andelman and Joanny.[12] The electrostatic force then modifies the structure of the adsorbed chains; charged chains are stretched as compared to neutral chains with the same chemical compositions but no dissociated charged groups. The effect of interaction of the chains with the surface when the latter is charged was also considered.

The case of diblock copolymers at the interface between two immiscible liquids was first discussed by de Gennes[10] in relation to the brush model. It was concluded that a high grafting density of polymers at a surface may be hard to reach by grafting but that it could be obtained with block copolymers at an interface between two immiscible solvents. Examination of this prediction is one of the purposes of this study.

Cantor has developed[7] a mean-field approach to describe diblock copolymers at the interface between two immiscible liquids. A phase diagram has been derived in terms of the volume fraction of polymer in the system, ϕ_P, and the volume fraction of one of the solvents, ϕ_a. One-phase, two-phase, and three-phase regions exist in the phase diagram where all polymer-containing phases are lamellar. When the volume fraction of the copolymer is small, a three-phase structure appears where the two regions of neat solvents a and b are separated by a single- or multiple-lamellar region of the copolymer where the two blocks are swollen by the respective solvents. Two two-phase regions exist for such solvent compositions where one solvent is absorbed by the lamellar phase but an excess of the other solvent makes a second phase of neat solvent. A single-phase region exists for polymer concentrations and solvent compositions such that both solvents are fully absorbed in the layered structure.

The scaling approach of Dan and Tirrell[8] to diblock copolymers at an interface between two immiscible solvents leads to a description in terms of emulsion droplets containing solvent a dispersed in solvent b, and this phase being in equilibrium with a phase of solvent a. As the concentration of the polymer is increased, the formation of cylindrical microdomains is predicted, which leads to a hexagonal phase. With further increasing the polymer concentration, lamellae appear at the point where the surface density of the phase of cylinders is equal to that of the lamellae. The experiments reported later in this paper were done on samples always in *single-phase* regions, but the lamellar symmetry was never observed.

Experimentally, several studies have been done on *adsorbed* layers by neutron scattering. Brushes of polystyrene chains grafted onto porous silica have been studied.[13,14] It was shown that the interface in a good solvent has essentially a parabolic shape with an exponential tail and that the local structure of the brush is similar to that of a semidilute polymer solution with a typical blob size equal to the distance between grafting sites. Studies of adsorption of poly(dimethylsiloxane) chains on porous silica have shown[15] that the adsorbed polymer chains are stretched and interact strongly. The collapse−stretching transition of the same system was also investigated,[16] as a function of the solvent thermodynamic quality (good to poor) controlled by solvent composition or temperature. In the presence of a poor solvent the interface is dense and of well-defined thickness, whereas a good solvent induces a strong stretching of polymers and a smoother shape of the interfacial profile with large concentration fluctuations.

Capillary wave properties have been studied[17] by light scattering, and interfacial viscoelastic moduli determined, for a film of polybutadiene-*b*-poly(ethylene oxide) at the (macroscopic) interface between cyclohexane and water. Neutron reflectivity was used[18] to study the properties of the same diblock copolymer at the hexadecane/water interface, and it was shown that the copolymer segregates at the interface, with the blocks forming a concentrated region adjacent to a dilute region on either side of the nominal dividing surface.

To the best of our knowledge, no experiment has been done so far to investigate the formation of microphase-separated microstructures in a system of a block copolymer in partially miscible solvents, together with their long-range order properties. In this paper, we present results of a neutron scattering study of semidilute solutions of several diblock copolymers in such a mixture of partially miscible solvents, namely, cyclohexane and dimethylformamide.

Experimental Section

Cyclohexane (CX) and dimethylformamide (DMF) (p.a.) were purchased from Fluka and deuterated solvents (isotopic purity of 99.5%) from Chemotrade, Leipzig. All solvents were used as received. The neutron scattering length densities (10^{10} cm^{-2}) of the solvents are $\rho_{d\text{-CX}} = 6.68$, $\rho_{d\text{-DMF}} = 6.386$, and $\rho_{h\text{-CX}} = -0.277$. The neutron scattering lengths densities ρ (10^{10} cm^{-2}) of polystyrene, polybutadiene, polyisoprene, and hydrogenated polyisoprene (PEP) are 1.43, 0.46, 0.268, and −0.324, respectively. A mixture of *d*-CX and 4% *h*-CX was prepared that has the same scattering length as *d*-DMF. The solvent mixtures were then prepared using appropriate volumes of *d*-DMF and of the mixture *d*-CX/*h*-CX. The coherent scattering curves obtained thus originate solely from the contrast (“film” contrast) between the copolymer and the (uniform) solvent.

Four diblock copolymer samples in which one block was polystyrene and the second block was polybutadiene, polyisoprene, or hydrogenated polyisoprene, i.e., poly(ethylene-*co*-propylene) (further on, PEP), have been used; their properties and characteristics are compiled in Table 1.

The polymer solutions were prepared by dissolving the diblock copolymer in the appropriate mixture of the solvents CX and DMF. The sample cells were sealed with a Teflon stopper and Teflon tape and allowed to homogenize at 60 °C (i.e., above the phase separation temperature of the neat solvents) in an oven with occasional shaking.

We use the following symbols to describe the polymer solvent systems investigated in this work: ϕ_{DMF} = volume fraction of DMF in the solvent mixture CX/DMF, w_{PS} = mass fraction of polystyrene in the diblock copolymer, c = concentration (g/mL) of the diblock copolymer in the solution.

Small-angle neutron scattering experiments were performed at CEA-Saclay on the spectrometer PAXY of the Laboratoire Léon-Brillouin. Measurements were performed with a 128 × 128 multidetector (pixel size 0.5 × 0.5 cm^2), using a nonpolarized, monochromatic (wavelength λ set by a velocity selector) incident neutron beam collimated with circular apertures for two sample-to-detector distances, namely, 1 m (with $\lambda = 6$ Å) and 7 m (with $\lambda = 8$ Å). With such a setup, the investigated range of scattering wave vector modulus is 4×10^{-3} to 4×10^{-1} Å^{-1}. In all the cases reported in this paper, the two-dimensional scattering patterns were isotropic so that they were azimuthally averaged to yield the dependence of the scattered intensity $I(\mathbf{q})$ on the scattering vector $\mathbf{q}$.

The measured curves were corrected by a standard procedure for background scattering and empty cell scattering, and normalized by the path length and transmission of the samples. The transmission values were corrected for the variation of path length in the sample cell as a function of scattering angle. If $T(0) = I_T/I_{T0}$ is the transmission of the sample at scattering angle $\theta = 0$ (I_{T0} is the intensity of the primary neutron beam that has passed an empty cell, and I_T is the intensity of the beam that has passed a sample), it can be shown that the transmission $T(\theta)$ at a nonzero angle is

$$T(\theta) = \exp[(\cos\theta)^{-1} \ln(T(0))] \qquad (1)$$

Further, the incoherent scattering has to be subtracted from the curves. It should be evaluated by measurements on mixtures of pure solvents. Because the pure solvents are not miscible at temperatures below the coexistence curve, the scattering of a mixture of *h*-CX and *d*-CX was measured that had the same calculated incoherent scattering as the polymer-containing mixture of *h*-CX, *d*-CX, and *d*-DMF. Both the corrected scattering curve from the sample and that from the solvent mixture were first normalized by a scattering curve of a reference cell filled with distilled, light water (itself corrected for background scattering and empty cell scattering and normalized by the angle-dependent transmission). This yielded a flat scattering curve for the *h*-CX/*d*-CX mixture that was subtracted from the sample scattering curve.

Results and Discussion

Figure 1 shows the temperature−composition phase diagram of the binary mixture of the two protonated solvents CX and DMF reproduced from literature data.[19]

The arrow in Figure 1 shows the location of the critical point on the coexistence curve, $\phi_{DMF} = 0.327$, $T_c = 51.4$ °C. For the critical composition we have verified that the demixing occurs at the same temperature in a protonated and a deuterated mixture of the solvents, with a precision of 0.1 °C.

When the diblock copolymer is added to a mixed solvent of a certain composition, it forms a homogeneous solution at high temperatures where the two solvents are fully miscible. When on cooling the temperature drops below the coexistence curve, the two solvents do not phase separate macroscopically; instead a microphase-separated system is formed where CX-rich domains coexist with DMF-rich domains, the interface between the domains being presumably covered with the diblock copolymer. In the present case, DMF is a thermodynamically good solvent for polystyrene and a bad solvent for the polydiene or aliphatic block while cyclohexane is a good solvent for the polydiene or aliphatic chain and a Θ to bad solvent for polystyrene, depending on the exact temperature (the Θ temperature[20] of polystyrene in CX is 34.5 °C). The morphology of the microphase-separated structure in principle depends on the composition of the solvent mixture, on the concentration and composition of the diblock copolymer, and on temperature and will be discussed subsequently. In a Flory-like description of the ternary mixture, *six* interaction parameters are involved, and it appears nearly impossible to make quantitative predictions on the structure that a polymer−solvent system of a particular composition will adopt. For a simpler system consisting of a diblock copolymer and a solvent selective for one block (e.g., poly(styrene-*b*-isoprene) in dioctyl phthalate, it was shown[21−23] that it is the balance of the interaction between the solvent and the individual blocks that governs the structure of the microphase-separated system and that this structure can be completely different form that of the neat copolymer in bulk.

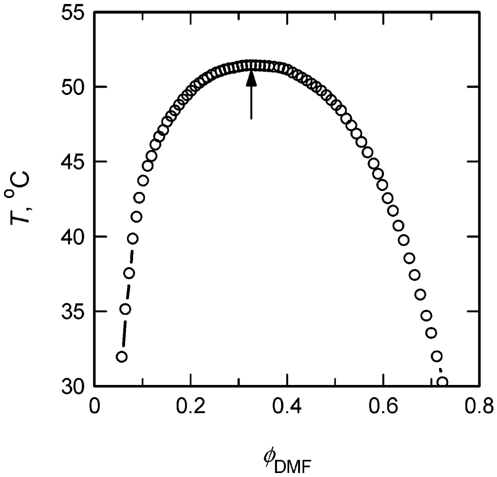

Figure 1. Temperature−composition diagram of the mixture of solvents *h*-cyclohexane and *h*-dimethylformamide (DMF), constructed with experimental data from ref 19. ϕ_{DMF} is the volume fraction of DMF in the mixture. The arrow indicates the critical composition of $\phi_c = 0.327$; the critical temperature is $T_c = 51.4$ °C.

The interfacial structure of the microphase-separated mixture is schematically shown in Figure 2 (the actual long-range structure is different, as will be shown below) for a typical solution of an S−I copolymer in a mixture of CX and DMF with $\phi_{DMF} = 0.1$. In the neutron scattering experiments the contrast between the two solvents was matched as explained above, so that the contrast was given by the periodic stacking, with characteristic size d, of polymer-decorated interfaces as shown in Figure 2. The content of DMF was variable, but DMF was always a minority solvent in the mixture.

Figure 3 shows the $\mathbf{q}$ dependence of the normalized intensity of neutron scattering for the four copolymers at a temperature of 25 °C and at concentrations of copolymer and compositions of solvent given in the caption. For all four copolymers, a maximum of the static structure factor located at $\mathbf{q}_0$ was clearly identifiable whatever the DMF and polymer contents in the investigated range. The characteristic stacking distance d is proportional to $(\mathbf{q}_0)^{-1}$, with the proportionality constant depending on morphology as will be discussed

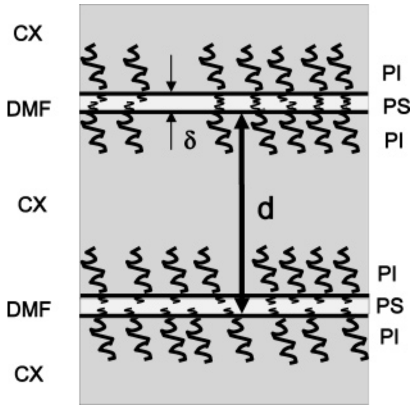

Figure 2. Scheme of the local structure of the microphase-separated mixture of cyclohexane (CX) and dimethylformamide (DMF), with the diblock copolymer poly(styrene-*b*-isoprene) covering the interface between the two solvents. The characteristic distance of the structure is *d*. Abbreviations: PS, polystyrene; PI, polyisoprene.

below, and for all studied systems *d* is in the range 60−110 nm.

For the polymer with the shortest polystyrene block—S−B(16−79), $w_{\mathrm{PS}} = 0.17$—two secondary maxima located at $\mathbf{q}_0\sqrt{2}$ and $\mathbf{q}_0\sqrt{3}$ are observed, suggesting a long-range-ordered cubic structure. Since only two secondary maxima can be unambiguously identified, it is not possible to decide on the type of cubic structure (body-centered or simple cubic), but the face-centered cubic structure can be ruled out, as it would lead instead to a secondary maximum at $\mathbf{q}_0\sqrt{(4/3)}$. For the two polymers with an intermediate relative length of the polystyrene block—S−EP(45−135), $w_{\mathrm{PS}} = 0.25$, and S−EP(41−54), $w_{\mathrm{PS}} = 0.51$—a secondary maximum at $\mathbf{q}_0\sqrt{3}$ is visible, but not at $\mathbf{q}_0\sqrt{2}$, hinting at a 2D structure with hexagonal symmetry. Finally, the polymer with the relatively longest polystyrene block—S−I(126−39), $w_{\mathrm{PS}} = 0.76$—exhibits only a secondary maximum located at $\mathbf{q}_0\sqrt{7}$ that is also hinting at a hexagonally ordered system. The expected peak at $\mathbf{q}_0\sqrt{3}$ can barely be distinguished on the curve, which is probably due to interferences with the form factor of the building units of the structure. This issue will be discussed in greater detail in a forthcoming paper. In a similar way, there is a weak indication of a peak located at $\mathbf{q}_0\sqrt{7}$ in Figure 3b,c, but again the position cannot be quantitatively determined.

Investigation of dilution laws and calculations to be presented in a forthcoming paper show that the structures with hexagonal symmetry cannot be inverted structures; thus, they consist of PS cylinders. The fact that we did not observe a structure with lamellar symmetry does not mean that it does not exist at some particular composition of the solvent and concentration of one of the polymers. It has been shown that already in the case of a diblock copolymer and a single selective solvent a great variety of morphologies can be observed depending on the temperature and polymer composition and concentration. Similarly, it is not possible to predict the morphology in the present case with a mixture of two selective solvents. A more complete investigation of the multidimensional phase diagram (temperature, solvent composition, solvent concentration, polymer composition) is under way and will be presented in a forthcoming paper.

The position of the first maximum, $\mathbf{q}_0$, is related to the center-to-center distance *d* between the stacked particles in the structure by the Bragg law, $d = C/\mathbf{q}_0$, where the constant *C* depends slightly on the morphology of the structure: for 1D lamellar (not observed here) or 3D simple cubic morphology $C = 2\pi$, for 2D hexagonal morphology $C = (4\pi)/\sqrt{3}$, and for body-centered cubic morphology $C = \pi\sqrt{6}$. For the four samples shown in Figure 3, and assuming a body-centered rather than simple cubic structure for the type of cubic structure observed, we thus get the values of *d* listed in Table 2.

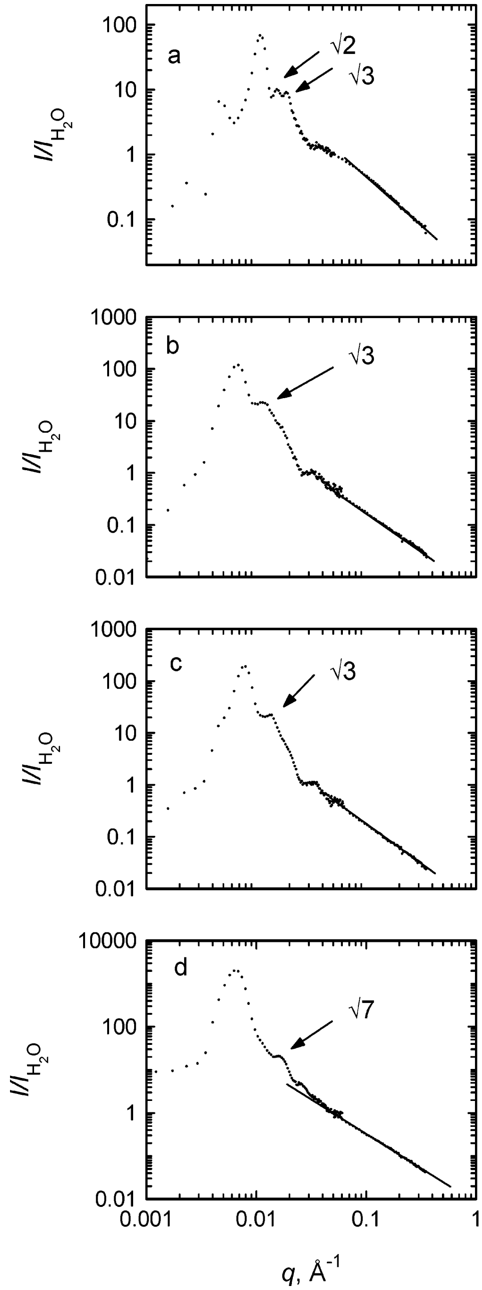

Figure 3. Dependence of the scattered intensity $I(\mathbf{q})$ normalized by scattering of a reference sample of H_2O on the scattering vector $\mathbf{q}$ at a temperature of 25 °C for the four diblock copolymers listed in Table 1, in the following mixtures: (a) S−B(16−79), $c = 0.1$ g/mL, $\phi = 0.08$, (b) S−EP(45−135), $c = 0.02$ g/mL, $\phi = 0.18$, (c) S−EP(41−54), $c = 0.02$ g/mL, $\phi = 0.18$, (d) S−I(126−39), $c = 0.06$ g/mL, $\phi = 0.08$.

For the mixture of solvents without copolymer, the transition from homogeneous mixtures to phase-separated states is a first-order phase transition experimentally indicated by a stepwise increase in turbidity at the cloud point temperature (except at the critical composi-

Table 2. List of Parameters Obtained from the Scattering Curves in Figure 3[a]

sample	*c*, g/mL	ϕ_{DMF}	$\mathbf{q}_0$, nm^{-1}	*d*, nm	m	a
S−B(16−79)	0.10	0.08	0.1110	69.3	−1.50	0.66
S−EP(45−135)	0.02	0.18	0.0684	113.0	−1.47	0.68
S−EP(41−54)	0.02	0.18	0.0792	97.2	−1.53	0.65
S−I(126−39)	0.06	0.08	0.0660	110.0	−1.59	0.63

[a] c = copolymer concentration, ϕ_{DMF} = volume fraction of DMF, $\mathbf{q}_0$ = position of the first maximum of $I(\mathbf{q})$, d = characteristic distance of the structure, m = slope of a straight line fit to the data at large angles in Figure 3, and a = exponent calculated according to eq 2.

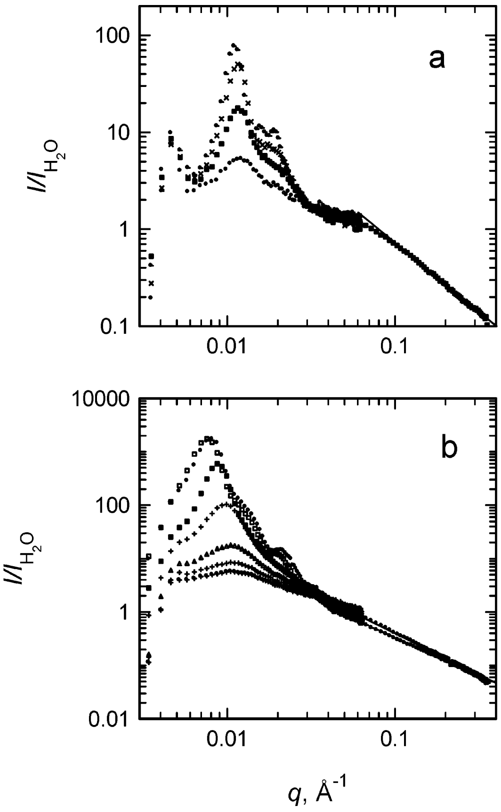

Figure 4. Scattered intensity I as a function of the scattering vector $\mathbf{q}$ for various temperatures: (a) copolymer SB(16−79), c = 0.1 g/mL, ϕ_{DMF} = 0.08, temperatures from top to bottom at $\mathbf{q}$ = 0.01 A^{-1}, 20, 35, 41, and 50 °C, (b) copolymer SI(126−39), c = 0.06 g/mL, ϕ_{DMF} = 0.18, temperatures from top to bottom at $\mathbf{q}$ = 0.01 A^{-1}, 20, 35, 45, 50, 55, and 60 °C.

tion, not discussed here, where the transition is second-order). For mixtures with the diblock copolymer, the evolution of the spectra with temperature may appear more continuous, featuring a progressive buildup of the structure over a temperature range of about 15 °C. Two examples of this process are shown in Figure 4 for solutions of the diblock copolymer S−B(16−79) that orders into a cubic microstructure, and of the diblock copolymer S−I(126−39) that exists as a hexagonal microstructure.

In the latter case, the position, amplitude, and width of the peak at $\mathbf{q}_0$ are displayed as a function of temperature in Figure 5. The peak intensity $I(\mathbf{q}_0)$ increases by about 2 orders of magnitude on cooling from 55 to 40 °C (Figure 5a). At this solvent composition (ϕ_{DMF} = 0.08) the phase separation temperature (cloud point) of the solvent mixture is T_s = 39.6 °C.

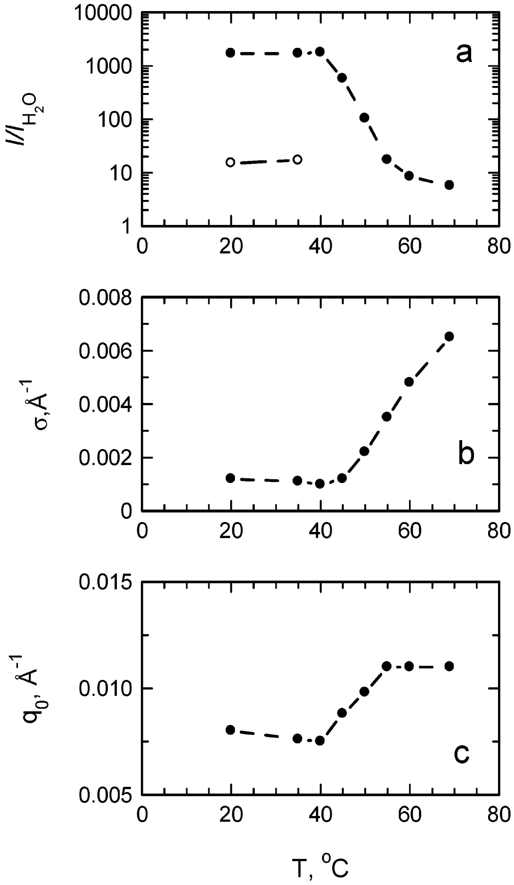

Figure 5. Temperature dependence of the parameters calculated from the scattering curves in Figure 4b: (a) intensity of the first (●) and second (○) maxima, (b) width σ of the first maximum, (c) position $\mathbf{q}_0$ of the first maximum.

This means that the process of creating the microscopically segregated solvent domains evidenced in Figure 4b begins at temperatures *well above* the phase transition temperature of the neat solvents. It is most probably driven by the progressive selective sorption of each solvent to the polymer block for which it is a good solvent. Below T_s the secondary maxima appear, indicating that the microstructure, now thoroughly formed, becomes long-range-ordered. This is also supported by the observation that above T_s the main peak, still broad and describing locally periodic variations in composition, gets progressively sharper as the spatial extent of the local order increases as indicated by its decreasing width σ. Long-rang order eventually obtains below T_s, where the peak becomes resolution-limited (see Figure 5b).

Our assumption that a selective sorption of CX and DMF on PEP or PS, respectively, may be extremely high and thus play a role in microseparation in a block copolymer is based on the experimental data from a polycaprolactam/*m*-cresol/*n*-heptane system.[24,25] The unusually high selective sorption of cresol onto polycaprolactam was documented to take place more than 25 °C above the demixing temperature of a given solvent mixture. Due to virtual isorefractivity of DMF and CX the technique used in ref 24 (and described in detail in ref 26) could not be applied to the present system.

Another driving force creating microscopically segregated solvent domains well above the phase transition temperature of the solvents is the large composition fluctuations in the system observed above the phase separation temperature by static and dynamic light scattering; these results will be reported in a forthcoming paper.

The polymer solutions discussed in this paper are semidilute in the sense that the polymer concentration

Table 3. Temperature Dependence of the Flory Exponent *a*

T, °C	a	T, °C	a	T, °C	a
20	0.639	30	0.661	41	0.665
25	0.650	36	0.659		

exceeds c^*, the crossover concentration (calculated as $c^* = 3M/4\pi N_A R_g^3$, where M is the molar mass of the polymers, R_g the radius of gyration, and N_A the Avogadro number). We have determined by dynamic light scattering experiments, to be discussed in detail in a forthcoming paper, that the correlation length of these semidilute solutions in the homogeneous phase (above 51.4 °C) is typically $\xi = 4-5$ nm. For scattering vectors $\mathbf{q}$ larger than $1/\xi$, i.e., in the large-angle part of the spectra where structure factor features are no longer observable, the scattering curve gives information about chain statistics:[27]

$$S(\mathbf{q}) \approx \mathbf{q}^{-1/a} \qquad (2)$$

where the exponent a is the Flory exponent in the relation between molar mass M and size R, $R \approx M^a$, and has the values $a = 0.6$ for a chain with excluded volume, $a = 0.5$ for a Gaussian chain, and $a = 1$ for a rigid rodlike chain. Figure 3 shows that at large scattering vectors there always exists a linear part of the scattering curve when plotted in logarithmic coordinates. The slope m of the straight line fitted through the linear part of the scattering curve yields the exponent a in eq 2. The values of a are listed in Table 2 for the four samples examined in Figure 3. The value of a is approximately constant with an average value of $a = 0.65$. This value is slightly larger than what would correspond to chains in a good solvent ($a = 0.60$), but is very far from the value for fully extended chains ($a = 1.0$). Thus, we may conclude that the polymer chains at the interface adopt a conformation corresponding to the good solvent by which each block is surrounded. The small increase of the exponent a above the value for plain chains with excluded volume indicates a slight stretching of the chain that could be explained[7] by the fact that one end of the polymer block is anchored at the interface.

Table 3 shows the value of the exponent a for the sample S−I(126−39) (with $\phi_{DMF} = 0.08$, $c = 0.06$ g/mL) at various temperatures.

The value of a stays approximately constant and equal to $a = 0.65$ in the temperature range covering the crossover from disordered to long-range-ordered solutions. This value of the exponent a is similar to that found theoretically for diblock copolymer chains with the junction point constrained to lie at an interface, either flat ($a = 9/14 = 0.64$ in ref 28 or $a = 2/3 = 0.67$ in ref 7) or spherical[11,29] ($a = 2/3 = 0.67$).

Conclusions

We have shown that diblock copolymers at the interface between two immiscible liquids are slightly extended as evidenced by the value $a = 0.65$ of the Flory exponent, which somewhat exceeds the value $a = 0.6$ for coils with excluded volume interaction. Within experimental uncertainty this value appears to be independent of temperature.

On a larger scale, and at temperatures below the coexistence curve of the neat solvents, the mixtures form a microscopically segregated system with long-range order where domains rich in, respectively, cyclohexane and dimethylformamide are separated by interfaces covered with the diblock copolymer. For the rather asymmetric diblock copolymer S−B(16−79) with a styrene content of 17% we have found that it forms a structure with a presumably body-centered cubic symmetry. For all the other diblock copolymers with a styrene content in the range 25−75% a structure with hexagonal symmetry is apparently always formed. The periodicity of the structures is in the range 60−110 nm.

The mixtures of CX and DMF used in this work were off-critical. For such compositions, the phase transition from a homogeneous mixture to the two-phase state below the coexistence curve is first-order. In the presence of the diblock copolymer the transition from a homogeneous semidilute solution to the microscopically ordered state is gradual; it begins approximately 15 °C above the coexistence curve. This is explained by a combined effect of selective sorption of the solvents to the individual blocks of the copolymer and of fluctuations in composition above the phase transition.

Acknowledgment. We acknowledge support of this work by the European Commission under the IHP program. Z.T. and P.S. acknowledge support by Grants 203/04/490, SON/03/E001, and 203/02/1262 of the Grant Agency of the Czech Republic. P.S. and F.N. acknowledge support under the joint agreement CNRS-Czech Academy of Science for international cooperation.

References and Notes

(1) Liu, S. Y.; Armes, S. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1413.
(2) Cogan, K. A.; Gast, A. P. *Macromolecules* **1990**, *23*, 745.
(3) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 31.
(4) Winsor, P. A. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; Ellis Harwood Ltd.: Chichester, U.K., 1974; Vol. 1, Chapter 5.
(5) Huh, C. *J. Colloid Interface Sci.* **1979**, *71*, 408.
(6) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, U.K., 1996.
(7) Cantor, R. *Macromolecules* **1981**, *14*, 1186.
(8) Dan, N.; Tirrell, M. *Macromolecules* **1993**, *26*, 637.
(9) Alexander, S. *J. Phys. (Paris)* **1987**, *20*, 1692.
(10) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(11) Daoud, M. *C. R. Acad. Sci., Ser. IV* **2000**, t.1, 1125.
(12) Andelman, D.; Joanny, J. F. *C. R. Acad. Sci., Ser. IV* **2000**, t.1, 1153.
(13) Auroy, P.; Mir, L.; Auvray, L. *Phys. Rev. Lett.* **1992**, *69*, 93.
(14) Auroy, P.; Auvray, L. *J. Phys. II* **1993**, *3*, 227.
(15) Auvray, L.; Auroy, P.; Cruz, M. *J. Phys. I* **1992**, *2*, 943.
(16) Auroy, P.; Auvray, L. *Macromolecules* **1992**, *25*, 4134.
(17) Milling, A. J.; Hutchings, L. R.; Richards, R. W. *Langmuir* **2001**, *17*, 5305.
(18) Bowers, J.; Zarbakhsh, A.; Webster, J. R. P.; Hutchings, L. R.; Richards R. W. *Langmuir* **2001**, *17*, 140.
(19) Bittrich, H. J.; Kilian B.; Geier K. *Z. Phys. Chem. (Leipzig)* **1979** *260* (1), 59.
(20) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.
(21) Lodge, T. P.; Hanley, K. J.; Pudil, B.; Alahapperuma, V. *Macromolecules* **2003**, *36*, 816.
(22) Hanley, K. J.; Lodge, T. P.; Huang, C. *Macromolecules* **2000**, *33*, 5918.
(23) Lodge, T. P.; Pudil, B.; Hanley, K. J. *Macromolecules* **2002**, *35*, 4707.
(24) Tuzar, Z.; Kratochvíl, P. *Macromolecules* **1977**, *10*, 1108.
(25) Tuzar, Z.; Procházka, O.; Kratochvíl, P. *Eur. Polym. J.* **1981**, *17*, 87.
(26) Tuzar, Z.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1967**, *32*, 3358.
(27) Higgins, J. S.; Benoit, H. C. *Polymers and Neutron Scattering*; Clarendon Press: Oxford, 1994; Chapter 6.
(28) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879.
(29) de Gennes, P. G. *Solid State Phys.* **1978**, *14*, 1.

MA0479767