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Heat-induced transition of polystyrene-*block*-poly(ethylene-*co*-propylene) micelles in decane and in dioxane

D. Hlavatá*, J. Stejskal, J. Pleštil, Č. Koňák and P. Kratochvíl
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

and M. Helmstedt
Universität Leipzig, Fakultät für Physik und Geowissenschaften, D-04103 Leipzig, Germany

and H. Mio and P. Laggner
Institute of Biophysics and X-Ray Structure Research, Academy of Science, A-8010 Graz, Austria
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Dissolution of polystyrene-*block*-poly(ethylene-*co*-propylene) (PS–PEP) in decane, a selective solvent for the PEP block, and dioxane, a selective solvent for the PS block, at room temperature leads to formation of metastable micellar structures, which convert into stable micelles with molar mass reduced several times after heating above ~50°C. By comparing small-angle X-ray scattering (SAXS) and light scattering (LS) data, the following models of micellar structures are suggested: At room temperature, dissolution of PS–PEP in decane yields aggregates of micelles. These are detected by LS, while SAXS reflects the molar mass of individual micellar cores formed by PS blocks. At elevated temperature, these compound particles disaggregate and then reorganize into equilibrium micelles of reduced molar mass. Solutions of PS–PEP in dioxane at room temperature have a different character. The molar masses of the observed particles determined by SAXS are in a good agreement with LS results, so we can exclude aggregation of micelles in this solvent. Nevertheless, also here, after heat treatment, both SAXS and LS yield a molar mass that is about 5 times lower than that determined for unheated solutions. Metastable structures surviving from the solid-state morphology after dissolution in a selective solvent at room temperature may convert to classical equilibrium micelles only after heating.

(Keywords: block-copolymer micelles; light scattering; small-angle X-ray scattering)

INTRODUCTION

Block copolymer micelles[1] formed by polystyrene-*block*-poly(ethylene-*co*-propylene) (PS–PEP) in selective solvents have recently been studied[2–6]. This is partly due to the commercial availability of the diblock copolymer, and partly because of the complex and interesting behaviour that the micelles exhibit, which is not completely understood yet. Also, the role of these copolymers in the steric stabilization of poly(methyl methacrylate) dispersion particles has been studied[7–9]. Such particles can be visualized as micelles 'stuffed' with a polymer[9].

The behaviour of PS–PEP copolymer in solvents selective for the PEP block, viz., in decane and in diisopropyl ether, has been described in our previous communication[2]. The diblock copolymer forms micelles that have a PS core and a PEP shell in these solvents. It was observed that the turbidity of the solutions prepared at room temperature is substantially reduced after heating of the solution, the change being irreversible. The structures obtained by direct dissolution in decane at room temperature are metastable and retain the structural features of micelles that exist in solid-state morphology. After heating, they convert to equilibrium micelles, the molar mass of which is reduced several times[2]. The concept of *frozen* micelles has been introduced to explain the existence of the metastable state. Such micelles or micellar structures cannot exchange unimers, and they are likely to exist in the cases when the insoluble blocks are strongly entrapped within the micellar core, i.e. if the core is compact (unswollen) or in the glassy state, as it is with PS–PEP in decane[2].

Observation of metastable micellar structures has already been described in the literature concerning the micellar solutions of copolymers composed of PS and aliphatic blocks. Stacy and Kraus[10] found a substantial decrease of the association number in micellar solutions of polystyrene-*block*-polybutadiene in hexane, heptane and decane after heating and subsequent cooling. By small-angle neutron scattering, Higgins *et al.*[11] obtained

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* To whom correspondence should be addressed

Table 1 Characterization of PS-PEP diblock micelles in decane (selective solvent for PEP) and in dioxane (selective solvent for PS). M_w is the mass-average molar mass, R_h the hydrodynamic radius, R_c the radius of the core, and ϕ_c the degree of swelling of the core

Solvent/History	$10^{-6}M_w$ (g mol^{-1}) SLS	SAXS[a]	SAXS[b]	R_h (nm) DLS	R_c (nm) SAXS	ϕ_c SAXS
Decane[c]						
Unheated	65.7	30.6	33.2	71	18.2	1.45
Heat-treated	8.7	9.0	14.4	42	13.8	1.45
Dioxane						
Unheated	~100	110	127	110[d]	36.0	1.20
Heat-treated	35	26	26	32[d]	21.3	1.20

[a] From the differential scattering cross-section at zero angle
[b] From the position of the maxima on scattering curves
[c] Taken from ref. 2
[d] Taken from ref. 9

similar results for micelles of polystyrene-poly(ethylene-*co*-propylene) in dodecane. Price *et al.*[12] observed formation of work-like micelles during dissolution of polystyrene-*block*-polyisoprene in *N*,*N'*-dimethylacetamide at room temperature. In dilute solutions these micelles are converted into spherical micelles when heated above 70°C.

In micellar solutions of PS–PEP dissolved in decane at room temperature, approximately twice as high values of molar mass, M_w, were determined on the basis of light scattering (LS) than by small-angle X-ray scattering[2] (SAXS) (see *Table 1*). This discrepancy leads us to the assumption that in these solutions micellar aggregates are present together with single micelles. These large objects are observable by means of LS but their contribution to the X-ray scattering intensity is not detectable in the range of scattering vector covered by our SAXS experiments.

In order to confirm this assumption, the structural changes that occur during the heating of micellar solutions and subsequent cooling down were studied by LS and SAXS as complementary methods. The behaviour in a solvent selective for the PEP blocks (decane) is compared with that of reversed micelles in a solvent selective for the PS blocks (dioxane).

EXPERIMENTAL

Materials

The PS–PEP diblock copolymer was a commercial sample manufactured by the Shell Chemical Co. under the trademark Kraton G 1701. The mass-average molar mass was[2] $M_w = 1.05 \times 10^5$ g mol^{-1}, mass-to-number molar mass ratio $M_w/M_n = 1.24$, and the copolymer contained 34 wt% of PS. The solvents, decane and dioxane, were used without further treatment. The basic solutions were prepared by dissolution of 0.2 g of the diblock copolymer in 10 ml of decane or dioxane in sealed glass ampoules. These ampoules were used directly for LS experiments, while SAXS measurements were performed in glass capillaries. The kinetics of the transition process was studied using these 2% solutions. For determination of M_w of micelles, solutions in the concentration range 0.0005–0.020 g cm^{-3} were prepared.

Small-angle X-ray scattering

Some preliminary measurements of the scattering curves were performed on a conventional Kratky camera using the sequential mode of the data collection. Data on the dynamics of the process were taken on a Kratky compact camera (A. Paar, Graz, Austria) equipped with a position-sensitive detector (OED-50, MBraun, Munich, Germany) using Ni-filtered Cu K$_\alpha$ radiation (wavelength $\lambda = 1.54$ Å) from an X-ray tube with rotating anode (Rigaku RU-200).

For the determination of precise values of micellar parameters, the measured intensities were converted to absolute scale by means of a Lupolen standard, and the differential cross-section $\mathrm{d}\Sigma(q)/\mathrm{d}\Omega$ (where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector and θ is the scattering angle) was then obtained by means of Glatter's desmearing program ITP[13,14]. Structure changes occurring during the heat-induced transition were described using the measured (smeared) intensities on a relative scale.

Mass-average molar mass, M_w, was determined from the differential cross-section extrapolated to zero scattering angle:

$$M_w^{(a)} = \frac{N_A}{c(\Delta b)^2}\frac{\mathrm{d}\Sigma(0)}{\mathrm{d}\Omega} \qquad (1)$$

Here N_A is the Avogadro constant, c is the polymer concentration and Δb is the excess scattering amplitude. Alternatively, M_w was evaluated from the geometric radius of the micellar core, R_c, calculated from the position of the side maximum, assuming that these cores are dense enough and monodisperse:

$$M_w^{(b)} = \frac{4\pi N_A R_c^3}{3 w_c \bar{v}_c \phi_c} \qquad (2)$$

Here w_c and $\bar{v}_c$ are the mass fraction and the partial specific volume of the core, respectively, and ϕ_c is the degree of swelling of the core. The details of the evaluation procedures are described in our foregoing papers[2,15].

Light scattering

Light scattering experiments were made with the ALV apparatus using an Adlas 300 mW laser (532 nm), Newport Liquid Crystal Controller model 932-CX, Thorn EMI photomultiplier and ALV-5000 Multiple Tau Digital Correlator. The temperature of the sample immersion bath (xylene) was controlled within ±0.01°C with a Lauda Externregler R22 thermostat. The light scattering was measured at an angle of 90°. The temperature changes of the viscosity and of the refractive index of individual solvents were evaluated by interpolation of the published data[16]. The hydrodynamic radii were calculated by the cumulant method and/or by CONTIN.

RESULTS AND DISCUSSION

Native solutions of the diblock copolymer, prepared by dissolution in decane or in dioxane at room temperature, were slowly heated and then cooled down to room temperature, and the scattering of the samples was recorded during the whole process. The same temperature history was followed in both LS and SAXS experiments.

Micelles with PS core in decane

According to preliminary measurements on a conventional Kratky camera at IMC, Prague, only small changes in the innermost part of the SAXS curves were observed below ~50°C. Above this temperature, the position of the side maximum attributed to scattering from the dense PS core[17] is shifted to higher q values (*Figure 1*). This means that the size of the micellar core decreases due to the release of polymer chains and resultant reduction of the association number. The disaggregation of complex structures is then expected in the region of 30–50°C.

Precise SAXS measurements of the heat-induced transition of PS–PEP in decane were taken using a compact Kratky camera equipped with rotating anode and position-sensitive detector (PSD), which makes it possible to study the process in more detail (*Figure 2*). Variation of the SAXS curves is characterized by means of the sum of intensities in the q range of 0.015–0.030 Å^{-1} where the changes induced by the increasing temperature are most pronounced.

The SAXS measurements were performed according to the time and temperature regime given in *Figure 3* and they were followed by the measurement of LS intensities and hydrodynamic radii, R_h, according to the same scheme. LS intensities, I, were measured at 90° and they were normalized to the intensity of a benzene standard, I_b.

The most interesting feature of this picture is the different dependence of the intensities determined by the two scattering methods. While changes of the sum of SAXS intensities, which are sensitive to the dimensions of single micelles, are observable at temperatures above ~50°C, LS intensities, sensitive to the presence of aggregates, exhibit a remarkable decrease in the temperature region between 40 and 50°C.

At room temperature the CONTIN analysis reveals the presence of two modes, which would correspond to spherical particles with radius 50–60 nm (individual micelles) and 400–500 nm (micellar aggregates). The average hydrodynamic radii obtained from dynamic light scattering increase in the temperature region 40–50°C (*Figure 3*), which is believed to reflect the swelling processes. At 50°C and/or at higher temperature, the decrease in the hydrodynamic radii is observed until a single peak in the CONTIN analysis is reached, in accord with the expected conversion into equilibrium micelles.

In the solid state, the polystyrene blocks form spherical cores[2], which are embedded in the continuous matrix of PEP chains. We believe that occasional microcrystalline regions can be formed in PEP matrix. These could survive the dissolution in decane at room

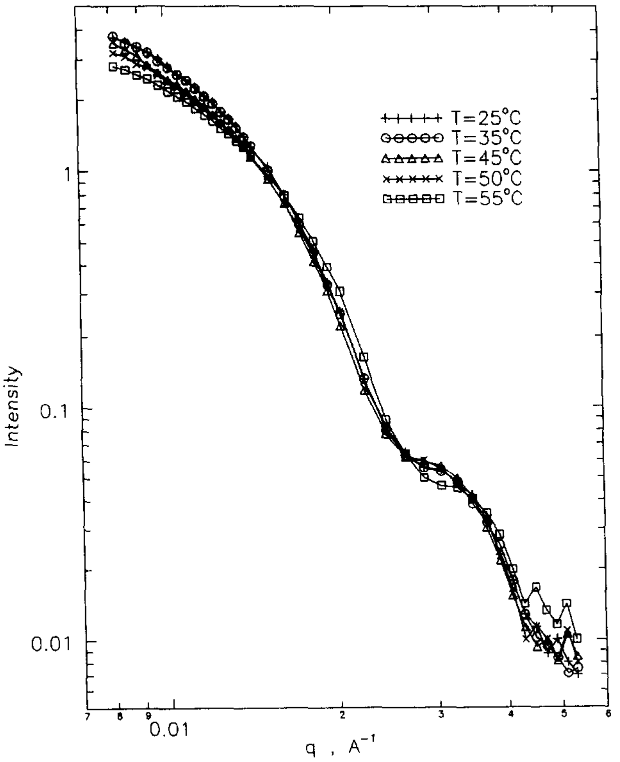

Figure 1 Temperature variation of SAXS curves of PS–PEP in decane at 25–55°C

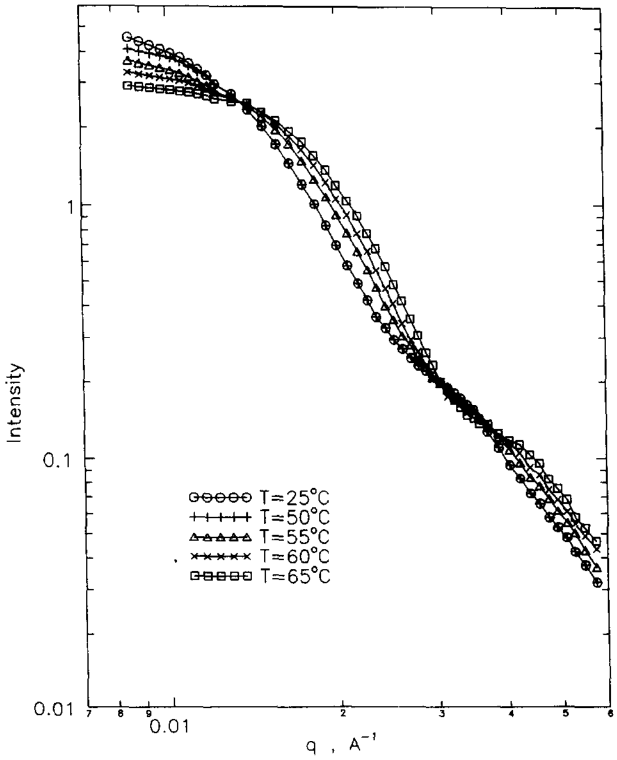

Figure 2 Temperature variation of SAXS curves of PS–PEP in decane at temperatures above 50°C using PSD

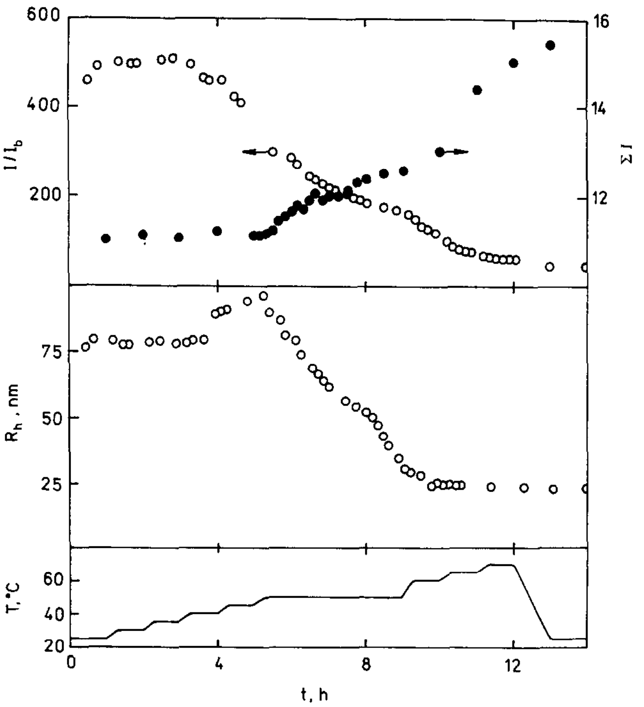

Figure 3 Time and temperature dependence of the sum of SAXS intensities, ΣI, in the q range 0.015–0.030 Å^{-1}, LS intensities normalized to benzene standard, I/I_b, and hydrodynamic radius, R_h, of PS–PEP in decane

temperature and would later cause the formation of loosely connected aggregates of micelles (*Figure 4*). Such aggregates are identified by light scattering, while SAXS observes much smaller individual micellar cores in the aggregated structure.

After increase of temperature, the semicrystallites decompose and the individual micelles are liberated. However, below ca. 50°C, these micelles are still frozen and reflect the solid-state morphology. Only after the temperature has been increased above ca. 55°C does the core structure become loosened, and exchange of the unimers results in formation of the equilibrium micelles. The equilibration is faster at higher temperature. Above ca. 105°C, the micelles finally decompose and a true solution of unimers is formed[9].

On cooling below ca. 50°C, the equilibrium micelles get frozen again in a new state. There are no free unimers in solution and the critical micelle concentration becomes immeasurably low. Again, the micelles do not aggregate in decane at room temperature. On the other hand, the aggregates reappear after the polymer has been precipitated, dried and redissolved in decane at room temperature again.

The use of a strong source of X-rays and PSD makes it possible to reveal another detail on the SAXS curves measured in a stable state, i.e. before heating and after heating with subsequent cooling down back to room temperature. These curves, corrected for slit collimation errors, are given in *Figure 5*. On these curves, two maxima corresponding to the scattering on the PS core[2] were detected at $q_1 = 0.032$ Å^{-1} and $q_2 = 0.051$ Å^{-1} for native solutions and at $q_1 = 0.044$ Å^{-1} and $q_2 = 0.068$ Å^{-1} for the solutions after the heating-induced transition. The values of q_1/q_2 equal 0.63 and 0.65 in native and heated solutions, respectively. These values are very close to the theoretical value 0.63 for the particle scattering function of uniform homogeneous spheres[17].

In native solutions, the radius of these spheres, R_c, calculated according to the relation[17] $R_c = 5.76/q_1$ or $R_c = 9.1/q_2$, equals 18.0 or 17.8 nm, respectively, and is in very good agreement with the radius of PS spheres found in dry copolymer, $R_c = 16.0$ nm, if the degree of swelling $\phi_c = 1.45$ is taken into account[2]. This finding confirms our assumption that micellar cores obtained by dissolution of PS–PEP in decane at room temperature correspond to the solid-state PS microdomains, and only the increase in temperature above the glass transition of the PS core[2] enables the transformation to the equilibrium state.

Micelles with PEP core in dioxane

Dioxane is a solvent selective for polystyrene, i.e. it does not dissolve PEP blocks. Assuming again the existence of the solid-state structure, in which PS cores

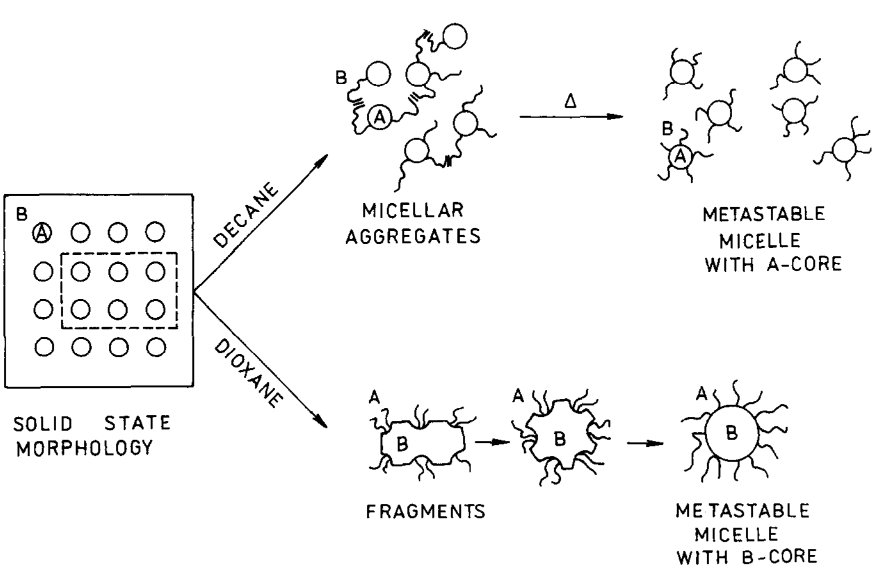

Figure 4 Schematic sketch of dissolution of PS–PEP diblock copolymer in decane, a selective solvent for the PEP matrix (B), and dioxane, a selective solvent for PS spheres (A)

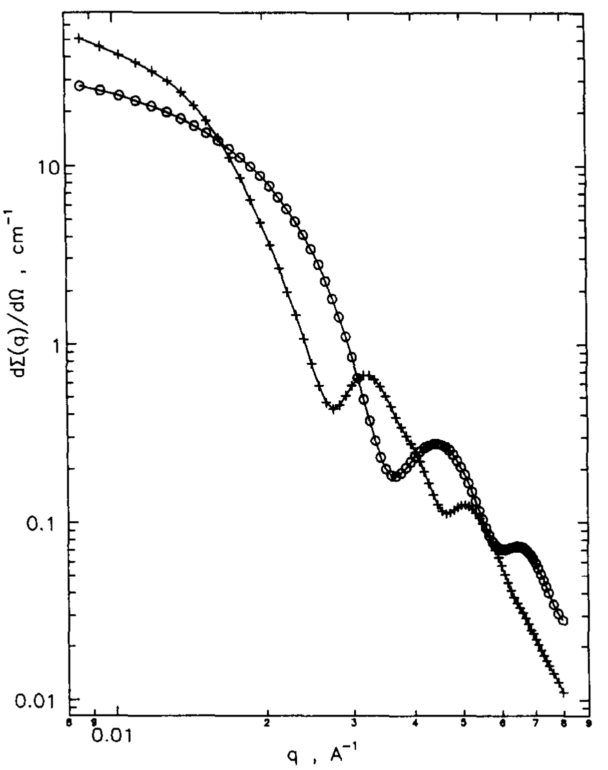

Figure 5 Desmeared differential cross-section $d\Sigma(q)/d\Omega$ of PS–PEP in native (+) and heated (O) decane solutions

are located in a matrix of PEP chains[2], one would expect that only swelling of the diblock copolymer will occur. It is thus rather surprising to find that the diblock copolymer dissolves easily at room temperature to yield a well defined turbid solution and that its turbidity is substantially and irreversibly reduced as the solutions are heated to 100°C and cooled down again. In other words, the same type of behaviour is observed as in decane.

The following interpretation is offered: The PS cores in the solid-state structure are swollen by dioxane. The swelling pressure exerts a strong force on the rubbery matrix, which may eventually decompose into smaller fragments (*Figure 4*). The liberated PS blocks start to form shells of the future micelles. The decomposition of the solid-state structure proceeds until a convenient size and shape of resulting objects is obtained. Note that, like in the previous case, only separation of the chains, but *no exchange of mass* leading to the formation of the equilibrium structure, occurs.

In our preceding paper[9], changes of micellar parameters in PS–PEP dioxane solutions induced by heating were studied by LS. It was found that both hydrodynamic radius and molar mass were reduced several times after heating, the change being even more pronounced than in decane solutions. Measurement of SAXS curves also indicates these changes (*Figure 6*) but, unlike in decane, the molar masses of PS–PEP micelles in dioxane determined by means of LS and SAXS are in good accord (see *Table 1*, where for comparison also the results for PS–PEP micellar solution in decane presented in our previous paper[2] are summarized). No aggregates are thus detected and the remarkable change of the micellar mass observed after heating of the solutions prepared at room temperature can be attributed to the reduction of the association number only.

Structure changes occurring during the process are characterized, as in the case of decane, by the temperature dependence of the sum of intensities, ΣI, in the q range 0.009–0.018 Å^{-1}, where the SAXS curves differ remarkably from each other. In addition to this, also the temperature dependence of the intensities extrapolated

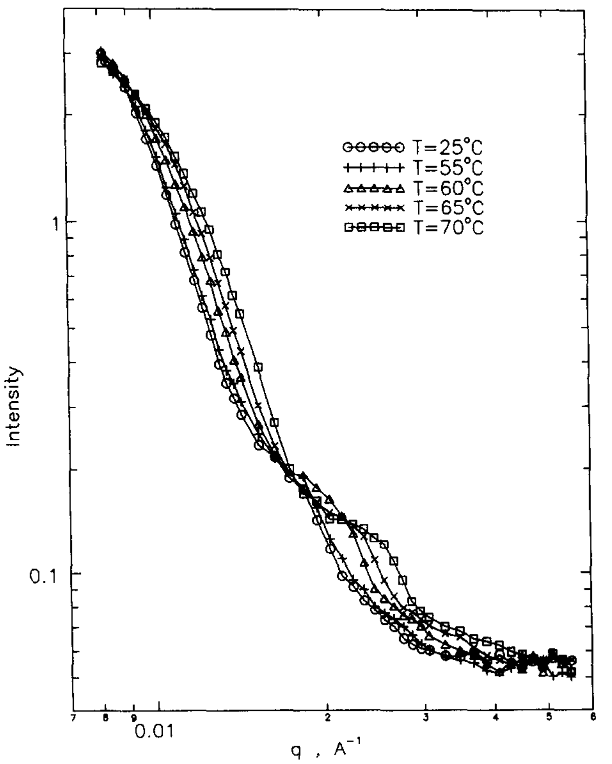

Figure 6 Temperature variation of SAXS curves of PS–PEP in dioxane

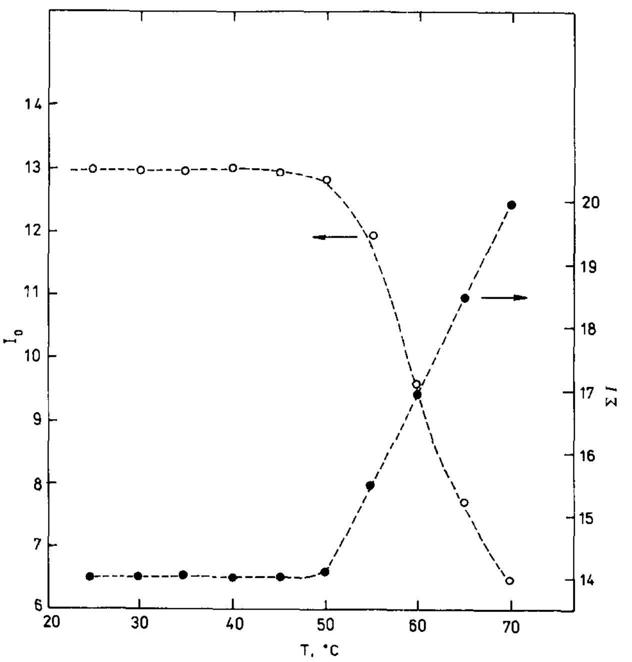

Figure 7 Temperature dependence of the sum of SAXS intensities, ΣI, for q = 0.008–0.012 Å^{-1} and intensities extrapolated to zero scattering angle, I_0, of PS–PEP in dioxane. Samples were measured at given temperatures for 30 min; the interval between individual measurements was 5 min

to zero scattering angle, I_0, is given here because, unlike in decane, the innermost part of the scattering curves is not affected by the presence of aggregates.

The variations of ΣI and I_0 with temperature are shown in *Figure 7*. Comparison of the values determined by SAXS and the temperature dependence of LS intensities I/I_b (*Figure 8*) indicates that the onset of the heat-induced transition in PS–PEP micellar solutions in dioxane is in the temperature region of 50–55°C.

Investigation of the process by means of SAXS was, in contrast to LS, performed for experimental reasons at temperatures below 70°C but, as the transition is not a function of temperature only but also of time, the SAXS curves were taken for longer times than is necessary for LS measurements. Nevertheless, both diagrams, one based on LS and the other on SAXS data, have the same course: values of the variables describing the structural changes are constant below ca. 50°C and then monotonical decrease (I/I_b and I_0) or increase (ΣI) until the equilibrium state is reached.

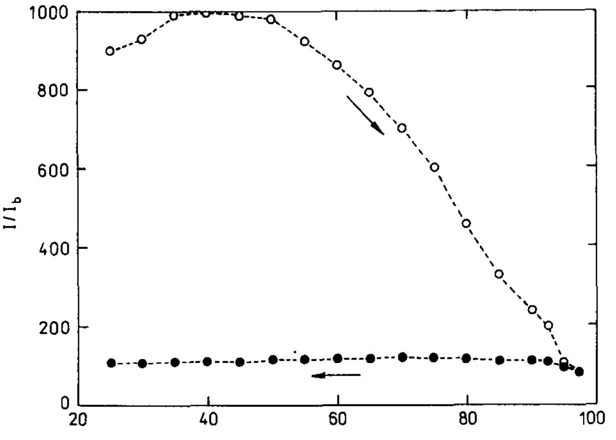

Figure 8 Temperature dependence of LS intensities of PS–PEP in dioxane normalized to benzene standard, I/I_b. Temperature is varied by 0.25°C min^{-1}

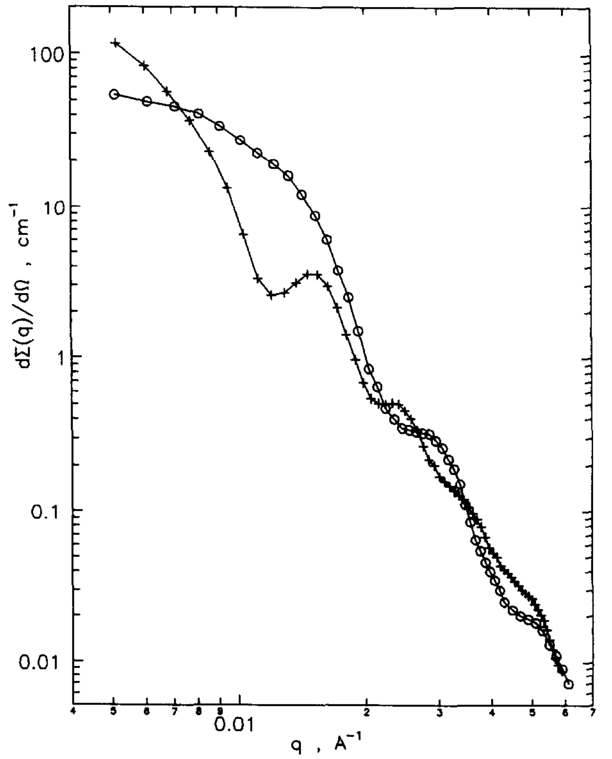

Figure 9 Desmeared differential cross-section $d\Sigma(q)/d\Omega$ of PS–PEP in native (+) and heated (O) dioxane solutions

SAXS curves of both native and heated micellar solutions of PS–PEP in dioxane exhibited, similarly to the corresponding decane solutions, two side maxima, which can be attributed to the form factor of homogeneous uniform spheres (*Figure 9*). From the values of $q_1 = 0.016\,\text{Å}^{-1}$ and $q_2 = 0.025\,\text{Å}^{-1}$ found for native solutions and $q_1 = 0.027\,\text{Å}^{-1}$ and $q_2 = 0.040–0.045\,\text{Å}^{-1}$ for heated solutions, the radius of the dense PEP core in native dioxane solution was determined to be 36.0 nm; its value dropped to 21.3 nm after heating. The ratio(q_1/q_2) was determined to be 0.64 for native and heated solutions, i.e. very close to the theoretical value for spheres (see above). In other words, in both solvents, decane and dioxane, monodisperse spherical micelles are detected, their size being dependent on the thermal history.

CONCLUSIONS

In the solid state, block copolymers with incompatible sequences form microdomain structures. When selective solvents are used for dissolution, the morphology existing in the solid state may be to some extent preserved even in the solutions. This is especially true when the insoluble blocks are in an unswollen or glassy state.

The presence of metastable structures of this type should be suspected when block copolymers dissolve at room temperature and the solutions irreversibly change their properties (e.g. turbidity, viscosity) after being heated.

With PS–PEP diblock, dissolution at room temperature yields a solution of metastable structures with both decane (selective solvent for PEP) and dioxane (selective solvent for PS). In the former solvent, aggregates of micelles with PS core are formed; in the latter, large metastable micelles with PEP core result. Combination of SAXS and LS appears to be a good method for determination of the character of these large objects. While LS intensity is influenced by the presence of aggregates, SAXS is sensitive predominantly to the dimensions of individual micelles.

The metastable 'frozen' structures are converted on increasing temperature into equilibrium micelles with the corresponding cores, but become frozen again in the new state upon cooling. The presence of the frozen micelles should be suspected also in the cases when the critical micellar concentration was reported to be immeasurably low. Under these conditions, there are no unimer molecules in solution.

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