LIGHT SCATTERING FROM POLYSTYRENE-*block*-POLY(ETHYLENE-*co*-PROPYLENE) IN DECANE AND IN DIOXANE*

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Polystyrene-*block*-poly(ethylene-*co*-propylene) solutions in decane have been investigated by dynamic and static light scattering. The dissolution of the diblock copolymer in a solvent, which is selective of aliphatic blocks, yields well-defined metastable micellar structures. These structures are converted into equilibrium micelles on heating and change into frozen micelles when cooled. A similar pattern is observed also in dioxane, which is a selective solvent for polystyrene blocks.

The supermolecular structures formed by block copolymers have received an increased attention[1 – 9] in last few years. In selective solvents, which dissolve one type of the blocks but precipitate the other, the individual block copolymer molecules (unimers) associate into micelles. The behaviour of diblock copolymer micelles[1] and unimer–micelle equilibria have been recently investigated both theoretically[2 – 4] and experimentally[5 – 9]. Probably most of the experimental work has been done with polystyrene-*block*-poly(ethylene-*co*-propylene) (PS–PEP), which is commercially available. The behaviour of this copolymer in selective solvents has been briefly reviewed in our preceding communication[5]. In decane, which is a selective solvent for the aliphatic block, the formation of micelles with a PS core and PEP shell is anticipated[1]. We have observed[5] that the dissolution at room temperature yielded solutions of metastable micellar structures. These structures were irreversibly converted into much smaller equilibrium micelles after heating of the solutions to 100 °C. The concept of frozen micelles was

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[*] Part II in the series Equilibrium and Non-Equilibrium Copolymer Micelles; Part I: ref.[5].

introduced to account for the existence of the metastable structures, which are believed to be linked to the solid-state morphology before the dissolution.

In this paper, we use light scattering methods to describe the changes occurring during the heating and the following cooling of PS–PEP solutions in decane. The results are compared with those obtained in dioxane, which is a selective solvent for the PS blocks.

EXPERIMENTAL

The PS–PEP diblock copolymer was a commercial sample manufactured by Shell Chemical Company under the trademark Kraton G1701. The weight-average molecular weight was[5] M_w = 1.05 . 10^5, weight-to-number-average molecular weight ratio M_w/M_n = 1.24. The copolymer contained 34 wt.% PS. The solvents, decane and dioxane (purum; Fluka, Switzerland), were used without further treatment. Weighed amounts of the copolymer and of the solvent were sealed in glass ampoules. The light scattering from the solutions has been measured directly in these ampoules.

Dynamic light scattering measurements were performed with a laboratory-made multiangle correlation spectrophotometer equipped with an Argon–Ion and He–Ne laser together with a 100 channel analog Stochastic Analyser NSA 1000 (Metrimex, Hungary). The autocorrelation curves were fitted by a single exponential function. Some independent measurements were also done with an ALV-5000 multibit, multitau autocorrelator covering approximately 8 decades in delay times. The samples were thermostatted during the measurement in silicone-oil bath, which was used as the refractive index matching liquid. The autocorrelation functions were analyzed assuming that the decay times had Pearson distribution[10]. The hydrodynamic radius has been calculated from the Stokes–Einstein equation. The temperature dependences of the refractive index and the viscosity of the solvents were evaluated on the basis of published data[7,11].

Static light scattering was measured with a Fica 50 apparatus. The experimental details are given elsewhere[5]. The refractive index increments of Kraton G1701 in decane at elevated temperatures were calculated by using the temperature dependence reported in the literature[7] as 0.139 $cm^3 g^{-1}$ (90 °C, 546 nm) and 0.146 $cm^3 g^{-1}$ (130 °C, 546 nm). The refractive index increment in dioxane was determined with a Brice–Phoenix BP-2000-V differential refractometer as 0.120 $cm^3 g^{-1}$ (25 °C, 546 nm).

RESULTS AND DISCUSSION

When solutions of the PS–PEP copolymer prepared at room temperature in decane are heated, the intensity of scattered light decreases dramatically (Fig. 1). The change in the integral intensity can be observed both with dynamic and static light scattering apparatus as well as by the naked eye. The intensity of scattered light at the angle 90° is reduced in two steps, each time by about an order of magnitude. The first drop occurs above ca 50 °C, then the intensity nearly levels off in the region 80 – 100 °C, to be followed by another decrease at still higher temperature. The intensity of scattered light does not show any significant changes above 120 °C. When the temperature is lowered, a reversible behaviour is observed down to ca 80 °C. The intensity of scattered light then remains virtually constant during a further decrease down to room temperature.

To explain the observed phenomena, the following hypothesis can be offered (Fig. 2): In solid state, block copolymers form a variety of organized structures with separated regions of the individual blocks. E.g., micelles having a PS core embedded in PEP matrix are anticipated to form a solid-state morphology[5] when the block copolymer contains a major fraction of PEP. When solvents selective of matrix are used to dissolve a diblock copolymer, the micellar cores existing in the solid state (Fig. 2*a*) may survive even in the resulting solution (Fig. 2*b*). Such situation is likely to occur when the contacts between the units of polymer chains within the core are strongly preferred to polymer–solvent interactions (unswollen core) and when the pull of chains in shell on the core exerted after dissolution is weak (moderately swollen shell). The metastable structures (Fig. 2*b*) are converted into equilibrium micelles when heated (Fig. 2*c*). These micelles dissolve to a molecular solution when temperature is further increased (Fig. 2*d*) and/or get into a new frozen state once temperature is decreased (Fig. 2*e*).

When insoluble blocks are strongly bound within the micellar core, the probability that a copolymer molecule (unimer) could be pulled out of and transferred between the individual micelles is low. This is especially true when the core is in the glassy state. No transport of matter will be thus perceptible on a current time scale and the critical micellar concentration will appear as extremely, usually immeasurably, low[5,9]. Such micelles can be regarded as being frozen. Substantial changes in their structure take place when the temperature is increased. The exchange of unimers is then possible and equilibrium micelles are formed. These micelles coexist together with the unimer and may decompose to form a molecular solution when the temperature is further increased. The above reasoning also applies to other types of the solid-state morphology, e.g., to cylindrical domains. In principle, metastable worm-like micelles could then result and, indeed, their occurrence has been reported in the literature[12,13].

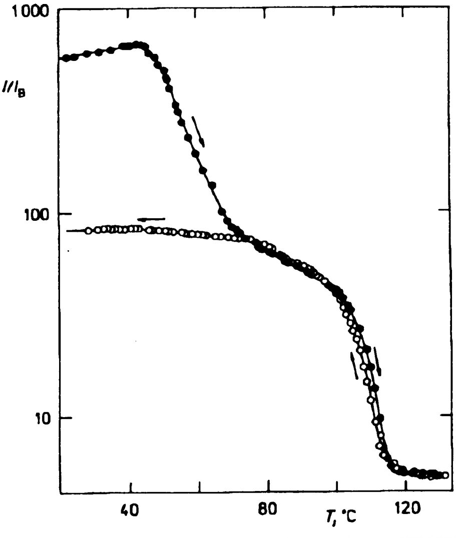


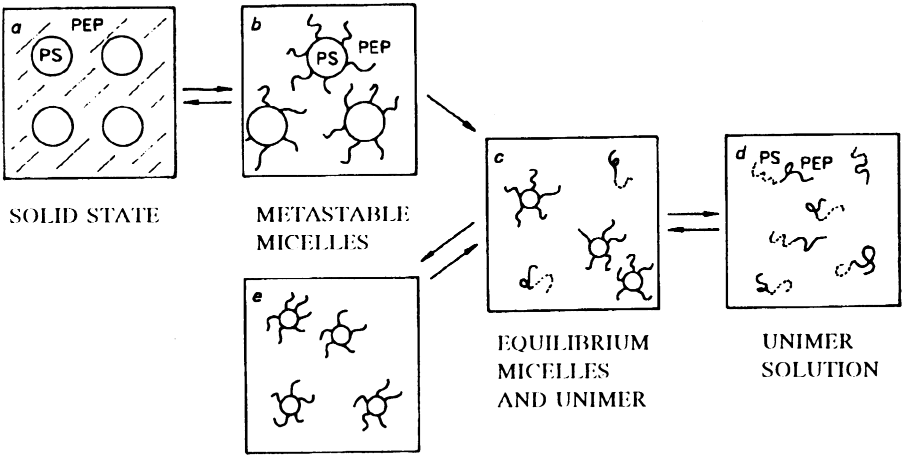
FIG. 1

Relative intensity, I/I_B, of the light scattered at the angle 90° (I_B, the intensity of light scattered by benzene) for PS–PEP diblock copolymer in decane in dependence on temperature during heating (full points) and subsequent cooling (open points). Copolymer concentration, c 0.005 g cm^{-3}; temperature varied by 0.25 °C/min

The features outlined above are observed when the PS–PEP diblock copolymer is dissolved in decane at room temperature. In addition to the intensity of scattered light (Fig. 1), the undergoing changes can be graphically illustrated by monitoring the temperature dependence of hydrodynamic radii, which follows a similar pattern (Fig. 3).

The structures obtained after dissolution at room temperature are, as we assume, in a metastable state[5]. The properties of their solutions do not change throughout, even for months. When the contacts between the insoluble blocks within the core are loosened, the conversion into equilibrium micelles occurs. This transition is reflected by a sudden drop of the hydrodynamic radii above 50 °C (Fig. 3). The dynamics of the process at fixed temperature, 60 °C, is illustrated in Fig. 4. Two different slopes can be fitted in the time dependence of intensity of scattered light plotted in the logarithmic scale. Thus it seems that two processes, a fast followed by a slow one, are involved in the transition. The first one corresponds to the decomposition of the metastable structure, the second seems to be associated with the rearrangement and equilibration of the resulting fragments. The whole process accelerates at higher temperature.

Between 80 – 100 °C, the integral intensity of scattered light and hydrodynamic radius depend on temperature, but no more on time (Figs 1 and 3). The micelles coexist in the thermodynamic equilibrium with unimer (Fig. 2*c*). Their proportion is expected to shift in favour of the unimer as temperature grows. This is reflected by the decrease in the intensity of scattered light (Fig. 1). Due to high differences in molecular weights of the unimer and micelles, only the hydrodynamic radius of the micelles is measured, and, consequently, it does not virtually change in this temperature interval (Fig. 3).



SOLID STATE

METASTABLE MICELLES

EQUILIBRIUM MICELLES AND UNIMER

UNIMER SOLUTION

FROZEN MICELLES

FIG. 2
Dissolution of PS–PEP diblock copolymer in a solvent selective of the matrix

The static light scattering performed at 90 °C with a set of solutions of varying copolymer concentration yields a distorted Zimm plot. The distortion is due to the fact that at a moderate polymer concentration the dissymmetry of scattered light is lower than unity[5]. This otherwise rare behaviour is commonly observed with PS–PEP diblocks in alkanes[5,7,12,14]. Nevertheless, the extrapolation of the data to zero concentration is straightforward and a molecular weight of $M_w = 2.6 \cdot 10^6$ is obtained. Due to the presence of the unimers, the average molecular weight is lower compared to that of heat-treated micelles characterized at room temperature[5], $M_w = 8.7 \cdot 10^6$, where all block copolymer molecules are expected to be incorporated into the micelles.

The growth of the micellar dimensions at 90 – 100 °C (Fig. 3) can be interpreted as a swelling of the micelles on the verge of their decomposition into unimers. The effect is not expected to influence substantially the integral intensity of scattered light

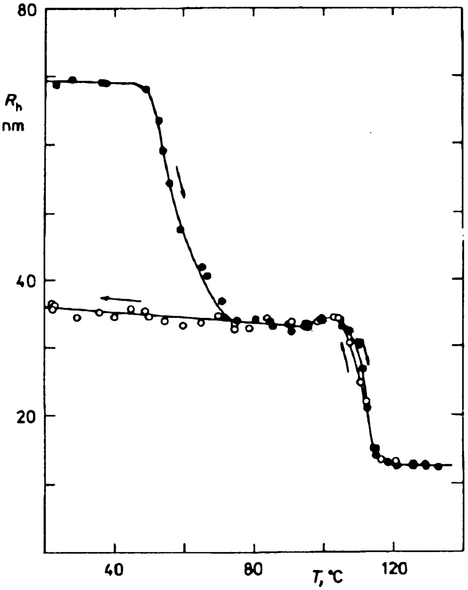


FIG. 3

Hydrodynamic radii, R_h, of PS–PEP diblock copolymer micelles in decane in dependence on temperature. (Solid-state micelles are converted into equilibrium ones, which dissolve as temperature is increased (full points). When temperature is decreased, the equilibrium micelles are formed again and then they get into a new frozen state (open points). Copolymer concentration, c 0.005 g cm^{-3}; temperature varied by 0.25 °C/min.)

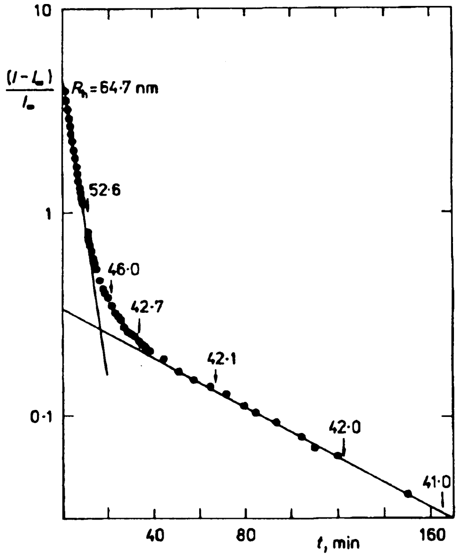


FIG. 4

Time dependence of the intensity of scattered light, $(I - I_\infty)/I_\infty$, from PS–PEP diblock copolymer in decane and the corresponding hydrodynamic radii, R_h, at 60 °C. (Angle of observation 90°, copolymer concentration c 0.005 g cm^{-3}. I_∞ is the equilibrium intensity of scattered light at infinite time; I_∞/I_B = 141.)

(Fig. 1). The further decrease in dimensions above 105 °C (Fig. 3) corresponds to the successive decomposition of micelles into a true molecular solution of unimers or to the reduction of the association number. The apparent mean dimensions of the unimer–micelle mixtures are measured in this temperature range. The process is accompanied by a decrease in the integral intensity of the scattered light as the mean molecular weight of the dissolved species is reduced by an order of magnitude (Fig. 1).

When the measurement of static light scattering is repeated at 130 °C for a set of solutions, the molecular weight estimated from the angular range 60° – 150° is $M_w \approx 2 \cdot 10^5$, i.e., higher than that expected for the unimer[5], $M_w \approx 1.05 \cdot 10^5$. Nevertheless, even this result indicates the practically complete molecular dissolution of the copolymer and the absence of micelles. A strong curvature of the angular dependences of scattered light has been observed at low angles (30° – 45°) in the Zimm plot. In our opinion, this is a consequence of the fact that the micellar solutions were not optically clarified, in order to prevent any undesirable removal of some supermolecular structures. The dust particles present in the copolymer may affect the results of light scattering when the molecular weight of the scatterers is low, which seems to be the case with the solutions of the unimer.

The dissolution and formation of the equilibrium micelles is reversible (Figs 1 and 3). Both the integral intensity and the hydrodynamic radii follow the same path as the temperature is decreased to 80 – 100 °C again. The observed hysteresis (Fig. 1) is probably caused by the finite rate of heating and cooling. On further cooling, no change in dimensions of micelles is observed. Consequently, we assume that below ca 50 °C, where the metastable structures exist, the micelles become frozen (Fig. 2*e*). The uniformity of micelles, often reported in the literature[1], indicates that the micelles were formed in the process reaching the thermodynamical equilibrium. Their transformation into a frozen state, far away from equilibrium conditions, does not change their uniformity.

The association number of the micelles in the frozen state is, of course, fixed. Such micelles can be transferred to other media, e.g., by dialysis against an excess of another selective solvent[15] or from a more volatile selective solvent into another one by preferential evaporation of the solvent with a lower boiling point[1,5], without their association number being changed. Such micelles are conveniently characterized, because their association number is not affected by dilution. The frozen state need not, of course, exist in any system. Whether or not it occurs in a temperature range depends on the nature of solvent and on its interaction with the constituent blocks. E.g., with diisopropyl ether, a direct dissolution to equilibrium micelles with PS core has been observed at room temperature[5]. Therefore, in experiments, it is not always easy to decide whether the micelles are in the equilibrium state or in a frozen state.

Dioxane is a good solvent for polystyrene, while it does not dissolve PEP blocks. In this sense, it is a logical counterpart to decane. Assuming again the existence of the solid state structure, in which PS cores are located in a matrix of PEP chains (Fig. 2), one would expect, that only swelling of the diblock copolymer occurs in dioxane. Rather surprisingly, the diblock copolymer dissolves easily at room temperature to a lightly turbid solution and its turbidity is irreversibly reduced as the solutions are heated to 100 °C and then cooled down again. In other words, the same type of behaviour is observed as in decane.

The entities obtained after dissolution in dioxane at room temperature are larger (R_h = 110 nm, Fig. 5) than those in decane[5] (R_h = 70 nm, Fig. 3). Above ca 50 °C, a pronounced irreversible decrease in the particle size was observed. Unfortunately, above 100 °C, where molecular dissolution to unimers could be expected, the measurement is not feasible due to the boiling point of dioxane (101 °C). When lowering the temperature, a small reduction of the particle size corresponding to deswelling is observed (Fig. 5). The micelles at room temperature are again in the frozen state.

The changes in the hydrodynamic radius after heat treatment are more pronounced in dioxane (Fig. 5; R_h from 110 nm down to 32 nm) than in decane (Fig. 3; R_h from 70 nm down to 36 nm). The molecular weight of micelles obtained after exposure to the elevated temperature is higher in dioxane, $M_w = 32 \cdot 10^6$, than in decane[5] $M_w = 8.7 \cdot 10^6$. This indicates, that the average density of micelles, assuming homogeneous spherical particles, must be much higher in dioxane (0.39 g cm^{-3}) than in decane (0.05 g cm^{-3}). In dioxane, the highly swollen shell is formed by relatively short PS chains contributing little to R_h, while the compact core comprises much longer PEP chains. This results in higher association number and also molecular weight. In decane, a reverse situation may be anticipated, in qualitative agreement with the experimental data.

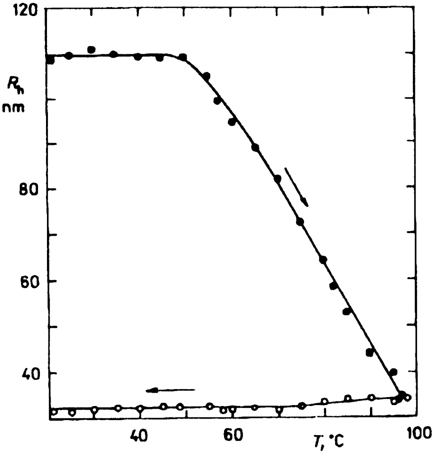


FIG. 5

Hydrodynamic radii, R_h, of PS–PEP diblock copolymer micelles in dioxane in dependence on temperature (for explanation see Fig. 3)

The existence of the metastable micelles in dioxane seems to be well established, although their origin and potential relation to the solid-state morphology is not completely obvious.

CONCLUSIONS

Under specific conditions, non-equilibrium micellar structures are obtained after dissolution of a diblock copolymer in a selective solvent at room temperature. The properties of such metastable structures seem to be remnants of the solid-state morphology of the diblock copolymer with separated domains of the individual blocks. The non-equilibrium micelles convert into equilibrium ones when the temperature is increased sufficiently. They transform into a new frozen state with fixed association number as the solution is cooled down to room temperature again. The presence of metastable (frozen) micelles is to be suspected in cases, when a block copolymer dissolves to a solution, the properties of which are irreversibly changed after heat treatment and subsequent cooling to the dissolution temperature.

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