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Star-shaped micelles of polyisobutylene–polystyrene–polyisobutylene triblock copolymer in hexane solution

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Polyisobutylene–polystyrene–polyisobutylene (PIB–PS–PIB) triblock copolymer was synthesized and studied in dilute hexane, toluene and tetrahydrofuran solution by the laser dynamic light scattering method. Star-shaped micelles were observed in hexane which is a good solvent for the PIB segments but a bad solvent for the PS segments. The diameters of the hard core and the micelle were estimated and the size and the size distribution of micelles were also determined by dynamic light scattering. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Star-shaped polymers, built up at least from three linear polymer chains ('arms') connected to a central 'core' region, represent a special class of branched polymers.

The starpolymers decrease the viscosity of lubricating oils in a wide temperature range and increase the viscosity index[1]. Study of the process leading to various shape of micelles formed from different block copolymers in a block-selective solvent is an extensive research area of polymer science. Micelles may form if the hard segment of a block copolymer does not dissolve in the solvent in question[2–9]. The formation of micelles from the poly(vinylpyridene) polystyrene–poly(vinylpyridene)[7] polystyrene–polyisoprene polystyrene[8] triblock, and from the polystyrene–poly(2-cinnamoyethyl-methacrylate)[9] diblock has been observed. The micelles formed from di- or triblock copolymers possess a loose branched[8], spherical[7,9] or cylindrical[9] shape. Most of the triblocks investigated were hard–soft–hard type. In the case of the soft–hard–soft copolymers a microphase separation was expected in an appropriate solvent and the hard segments were supposed to be linked to each other physically and reversibly. Our model block copolymers were the polyisobutylene–polystyrene–polyisobutylene (PIB–PS–PIB) triblock. The hard segment of these block copolymers, i.e., the polystyrene segments, do not dissolve in hexane which is a model solvent for aliphatic lubricating oils[1].

EXPERIMENTAL

Polyisobutylene–polystyrene–polyisobutylene triblock copolymer

The block-copolymerization was carried out in a 1000 ml three-necked flask in a Dry-Box, at −80°C, under dry nitrogen atmosphere. The reaction mixture was stirred with a mechanical stirrer. The details of the polymerization, polymer preparation and characterizations have been published[3]. Styrene, pyridine and *p*-dicumyl chloride (pDCC) were dissolved in a mixture of methylcyclohexane/CH_2Cl_2 (60:40, v/v). The volume of the solution was 600 ml. The polymerization was started by adding $TiCl_4$ as a coinitiator to the solution. After a period of time a sample was taken from the mixture, and 'in situ' isobutylene was added to the living polystyrene (PS) reaction mixture and the polymerization was terminated with precooled methanol. The polymer was purified by precipitation from its hexane solution with methanol.

A waters size-exclusion chromatograph (SEC) equipped with a Waters differential refractometer, u.v.-detector and five Ultrastyrogel columns (7.8 × 300 mm) was used for the determination of the molecular weights and molecular weight distributions. The system was calibrated with polystyrene and polyisobutylene standards, and tetrahydrofuran was used as the eluent.

The hexane and tetrahydrofuran solutions of the copolymers were examined by dynamic and static light scattering performed on a Brookhaven Light Scattering device equipped with a BI-9000 digital correlator. The light source was a solid-state, vertically polarized laser operating at 533.4 nm. Both dynamic and static measurements were performed at 25°C. The refractive indices of hexane solutions of the triblock were measured with a Rayleigh type interferometer (Carl Zeiss, Jena, Germany). The specific refractive index increment (d*n*/d*c*) of the triblock in hexane at 538 nm was found to be 0.15 ml/g.

^1H n.m.r. spectra were recorded on a Bruker 360 MHz instrument.

Measurements and data analysis

The autocorrelation function of the scattered light intensity was acquired in the homodyne mode[10]. The normalized autocorrelation function:

$$C(\tau) = [\langle I(0)I(\tau)\rangle - \langle I\rangle^2]/\langle I\rangle^2 \qquad (1)$$

where at long delay times (τ) all correlation is lost, and the measured autocorrelation function is equal to the square of the average intensity ($\langle I\rangle^2$). In our calculations a

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measured baseline of four baseline channels was used for normalization.

In the simplest case (monodisperse):

$$C(\tau) = A + Be^{-2\Gamma\tau} \qquad (2)$$

where $\Gamma = 1/\tau_c$, and τ_c is the characteristic decay time of the autocorrelation function and A and B are constants. Γ can be determined by a single exponential fit, and contains information on the temporal fluctuations of the concentration, which are related to the motion of the particles. So the diffusion coefficient:

$$D = \Gamma/q^2 \qquad (3)$$

where q is the magnitude of the scattering wave vector, which can be specified by the Bragg condition:

$$q = 4\pi n/\lambda_i \sin(\Theta/2) \qquad (4)$$

where n is the refractive index of the solvent, λ_i is the wavelength of the incident light in vacuo and Θ is the scattering angle. On certain conditions (Newtonian fluid, spherical particles) the Stokes–Einstein relation between the diffusion coefficient and the hydrodynamic diameter (d_H) of particle can be used to determine d_H:

$$D = kT/(3\pi\eta d_H) \qquad (5)$$

where k is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the solvent.

In the case of polydisperse systems the experimentally determined autocorrelation function can be expressed in a more complex way:

$$C(\tau) = \int G(\Gamma) e^{-\Gamma\tau} \, d\Gamma \qquad (6)$$

where $G(\Gamma)$ represents the distribution of decay times owing to the distribution of sizes. The moments of decay time distribution (and particle size distribution) can be determined by a simple data analysis technique, by the method of cumulants:

$$\ln C(\tau) = -\Gamma_{avr}\tau + (\mu_2\tau^2)/2 - \ldots \qquad (7)$$

where Γ_{avr} and μ_2 are the first and the second moments of the distribution, respectively. From these moments the polydispersity index of particle size distribution can be easily expressed:

$$\text{polydispersity} = \mu_2/\Gamma^2 \qquad (8)$$

For full particle-size distribution studies the NNLS (non-negative constraint least-squares) calculation combined with multiple-pass analysis was employed.

RESULTS AND DISCUSSION

No micelles formation was recognized in toluene or tetrahydrofuran, which are good solvents for both the PIB and the PS segments. The effective diameter determined for the PIB–PS–PIB block copolymer by dynamic light scattering (DLS) in tetrahydrofuran was 5.5 nm. However, when the PIB–PS–PIB block copolymer was dissolved in hexane, which is a bad solvent for the PS segment, an opaque solution was formed. The correlation functions were obtained at least in four different angles in the range of 60–155°. The typical correlation function obtained at 90° for the PIB–PS–PIB copolymer is shown in *Figure 1*.

The size distribution for the PIB–PS–PIB block copolymer in hexane at 90° was evaluated by the NNLS method (*Figure 2*). The size distributions were unimodal in the concentration range applied (0.5–2 mg/ml).

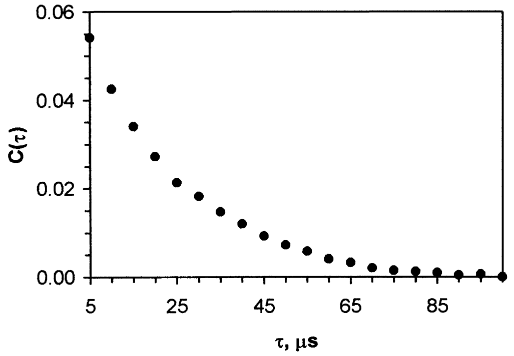

Figure 1 A typical correlation function for the PIB–PS–PIB triblock in hexane at ambient temperature obtained at $\Theta = 90°$. The length of the PS and the PIB segments are 6700 and 10 300 g/mol by SEC and ^{1}H n.m.r., respectively

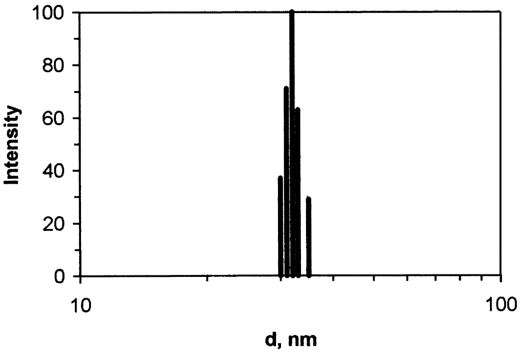

Figure 2 Size distribution of micelles formed from the PIB–PS–PIB triblock determined by DLS in hexane ($\Theta = 90°$). The length of the PS and the PIB segments are 6700 and 10 300 g/mol by SEC and ^{1}H n.m.r., respectively. Effective diameter, 34 nm; polydispersity, 0.11

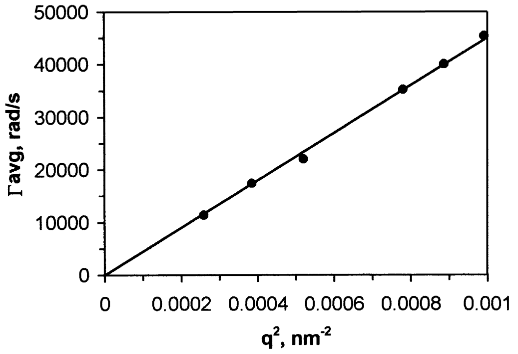

Figure 3 Γ–q^2 plot for the PIB–PS–PIB triblock in hexane. The length of the PS and the PIB segments are 6700 and 10 300 g/mol by SEC and ^{1}H n.m.r., respectively

On *Figure 3*. the $\Gamma - q^2$ plot is presented for the triblock copolymer. This plot indicates that the diffusion coefficient is independent of the angles, which suggests a compact, spherical structure.

Estimation of the aggregation number and number of arms

The dependence of the diffusion coefficient and the effective diameter on the concentration of the PIB–PS–PIB block copolymers was investigated in the 0.5–2 mg/ml concentration range (*Figure 4*).

The data clearly show that the diffusion coefficient and the effective diameter of micelles do not depend

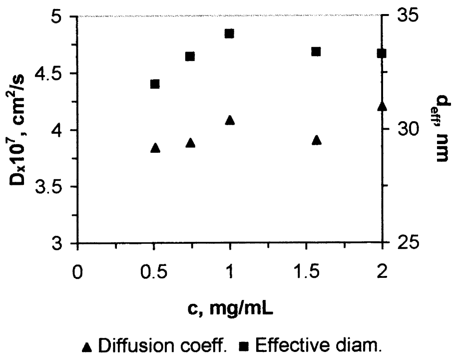

Figure 4 Dependence of the effective diameter (d_{eff}) and the diffusion coefficient (D) on the concentration of the PIB–PS–PIB triblock in hexane. The lengths of the PS and the PIB segments are 6700 and 10 300 g/mol by SEC and ^{1}H n.m.r., respectively

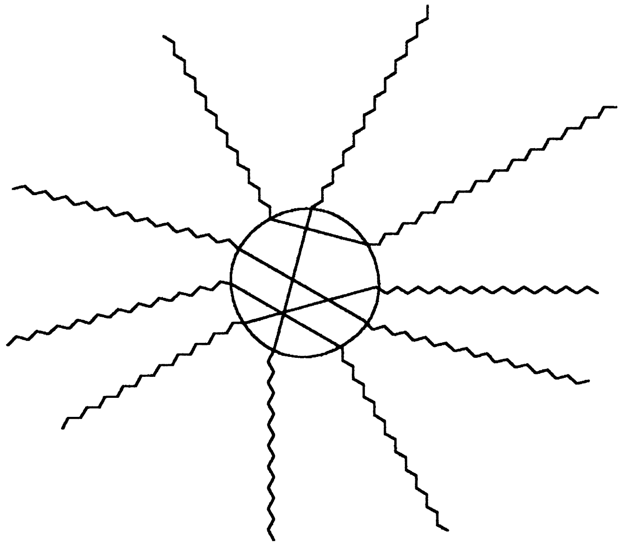

Figure 5 A proposed schematic structure of micelles formed from the PIB–PS–PIB triblock in hexane. The circle represents the hard core formed from the PS segments. The estimated diameter of the hard core $R_c = 5.3$ nm and the effective diameter of the whole micelle $d_{\mathrm{eff}} = 34$ nm

significantly on the concentration. These facts indicate that the size of the micelles in the concentration range employed does not increase with the increasing concentration of the PIB–PS–PIB block copolymer. Since the effective diameter is approximately independent of the concentration of the triblock copolymer, it can be concluded that the aggregation number does not vary significantly in the concentration range investigated. This makes it possible to estimate the aggregation number in hexane by static light scattering experiments using the Zimm-plot analysis.

The aggregation number and the number of arms can be expressed mathematically in the following way:

$$f = M_{\mathrm{w,a}}/M_{\mathrm{w,u}} \tag{9}$$

where f is the number of unimers in the micelle, i.e., the aggregation number; $M_{\mathrm{w,a}}$ and $M_{\mathrm{w,u}}$ are the molecular weights of the aggregate and the unimer, respectively.

$M_{\mathrm{w,a}}$ was determined by static light scattering measurements using the Zimm-plot, and $M_{\mathrm{w,u}}$ was obtained by SEC analysis.

The number of arms (n_a) for the triblock copolymer is $n_a = 2f$.

The aggregation number of the PIB–PS–PIB copolymer in hexane is $f \approx 39$ and $n_a \approx 78$ ($M_{\mathrm{w,a}} = 930\,000$ g/mol and $M_{\mathrm{w,u}} = 24\,000$ g/mol).

Theoretically, the R_H/R_G value (where R_H and R_G are the hydrodynamic radius and radius of gyration, respectively) should be 1.29 for a homogeneous sphere[9]. The measured R_H/R_G value was 1.25, which supports the former conclusion, namely that the PIB–PS–PIB block copolymer forms spherical micelles in hexane.

Estimation of the size of the hard core of micelles

The size of the hard core of the micelles (R_c) can be estimated by the following formula[9]:

$$[3M_{\mathrm{w,a}} w_{\mathrm{PS}}/(4\pi N_A \rho_{\mathrm{PS}})]^{1/3} = R_c \tag{10}$$

where $M_{\mathrm{w,a}}$ is the weight-average molecular weight of the micelles; w_{PS} is the weight fraction of polystyrene in the triblock; ρ_{PS} is the density of amorphous polystyrene which is about 1.05 g/ml[11]; and N_A is Avogadro's number. The calculated R_c for the hard core of the micelle is $R_c = 5.3$ nm.

The schematic structures of micelles formed from the PIB–PS–PIB is shown on *Figure 5*.

CONCLUSION

Microphase separations of the PIB–PS–PIB triblock copolymer solutions were recognized in hexane (i.e., a bad solvent for the PS segment). The size and size distribution of micelles were determined by dynamic light scattering measurements and micelle formation was observed. In addition, on the basis of DLS and static light scattering experiments it was concluded that spherical, compact star-shaped micelles with a polystyrene hard core were formed.

This block copolymer may be applied directly as an oil additive under the T_g of the hard segments.

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