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Star-Shaped Nanomicelles of Polyisobutylene-Polystyrene Diblock Copolymers. New Stabilizer for Living Dispersion Polymerization of Styrene

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Summary

Formation of star-shaped nanomicelles of polyisobutylene-polystyrene (PIB-PS) diblock copolymers in hexane solution is reported. The length of the polystyrene segments were varied in the M_n range of 4000-13000 g/mol at approximately constant polyisobutylene segments length. The size and the size distribution of the nanomicelles were investigated by dynamic light scattering. Based on static light scattering measurements the mass-average molecular mass of the micelles and the number of arms were also determined. The synthesized diblock-copolymers were demonstrated to be capable of stabilizing the growing particles which were formed in the living anionic dispersion polymerization of styrene in hexane.

Introduction

When a linear block copolymer is dispersed in a block selective solvent for one of the blocks, micelles of well-defined morphology are formed. Micellization in dilute solutions of different block copolymers in selective solvents has attained great attention in the last years[1-11].

Micellization of block copolymers due to different nature of the blocks makes such copolymers very useful for the application as colloid stabilizers, emulsifiers and antifoaming agents. The same property makes such copolymers important in the emulsion, suspension and ionic dispersion polymerizations[13-15].

The size, the size distribution and the number of arms of the micelles formed in selective solvents determine the applicability of such copolymers.

In this paper we report a star-shaped micelle formation from the polyisobutylene (PIB)-polystyrene (PS) diblock copolymer in hexane, which is a good solvent for the PIB segments and bad for the PS segments. Our aim was to study the size, the size distribution, the number of arms and the shape of micelles formed form the PIB-PS diblock copolymer as a function of the length of the PS segments. The resulted PIB-PS diblock copolymers were tested as steric stabilizers in the living anionic dispersion polymerization of styrene.

Experimental

Synthesis of polyisobutylene-polystyrene diblock copolymers

The block-copolymerizations were performed 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

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stirrer. Isobutylene, pyridine and 2-chloro-2,4,4-trimethylpentane (TMPCl) 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, ”in situ” styrene was added to the reaction mixture. The polymerization was terminated with precooled methanol. The polymer was purified by successive precipitation from its CH_2Cl_2 solution with methanol.

Anionic dispersion polymerization of styrene in hexane

After dissolution of the diblock-copolymers (0.2 g) styrene (5 ml) was added to the solution. The polymerizations were initiated by adding 0.6 ml of 2.5 mol/l n-buthyllithium (nBuLi) to the reaction mixture. After a predetermined interval, the polymerization was terminated with 2 ml of methanol. The dispersions were investigated by dynamic light scattering (DLS), light microscopy and by transmission electronmicroscopy (TEM) in order to determine the size of the particles formed.

Instruments

A Waters Size-Exclusion Chromatograph (SEC) equipped with Waters differential refractometer, UV-detector and five Ultrastyrogel columns (7.8 x 300 mm) was applied for the determination of the molecular weights and molecular weight distributions. The system was calibrated with polystyrene and polyisobutylene standards. Tetrahydrofuran was used as the eluent.

The light scattering experiments were performed with a Brookhaven Light Scattering device equipped with a BI-9000 digital correlator. The light source is a solid state, vertically polarized laser operating at 533.4 nm. All measurements were performed at 25 ^oC.

The refractive indices (dn/dc) of the hexane solutions of the diblock were measured with a Rayleigh- type interferometer (Carl Zeiss, Jena, Germany) at 538 nm.

The light microscope experiments were made on Zeiss AxioTech type microscope. The TEM pictures were taken by a Jeol 2000 FX-II type transmission electron microscope.

Results and Discussion

Formation of nanomicelles from polyisobutylene-polystyrene diblock copolymers in hexane

The dynamic light scattering experiments were performed in tetrahydrofuran (which is a good solvent for both segments) and hexane (which is a bad solvent for the PS segment but good for the PIB segment). The correlation functions on solutions of the PIB-PS diblock were obtained at least in four different angles in the range of 60-155^o and were analyzed by the method of cumulants and the NNLS method (Non-negative Constraint Least Squares). The determined effective diameters by DLS in tetrahydrofuran were in the range of 4-5 nm. However, when dissolving the copolymers in hexane, much larger sizes were obtained indicating the aggregation of the PIB-PS copolymers. A typical micelle size distribution for a PIB-PS block copolymer measured in hexane at 90^o scattering angle is presented in Fig. 1. In all cases the size distributions were unimodal in the concentration range applied (0.5-2 mg/ml).

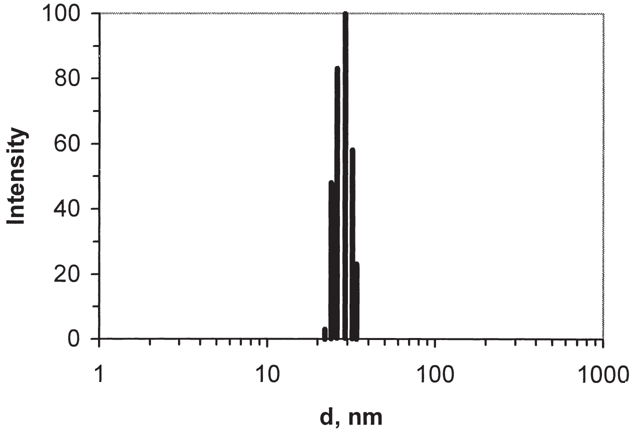


Fig. 1. Size distribution determined by DLS of micelles formed from the PIB-PS diblock in hexane, ($\Theta = 90^o$). The length of the PS and the PIB segments are 4300 and 11000 g/mole by SEC and ^{1}H-NMR, respectively. **The effective diameter: 29 nm. The polydispersity: 0.11.**

Estimation of the aggregation number and number of arms

Plotting the diffusion coefficients and the effective diameters versus the concentration of the PIB-PS diblock copolymer in the range of 0.5-2 mg/ml no significant dependence can be recognized (Fig. 2).

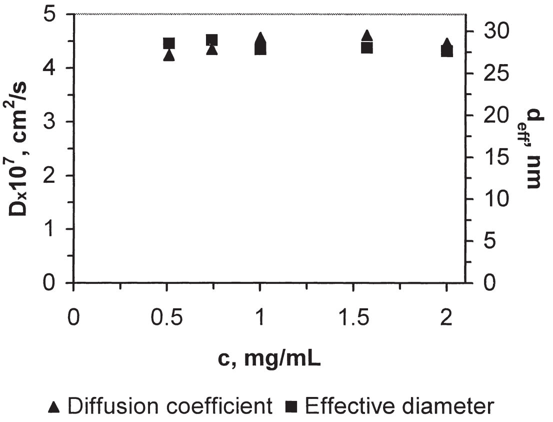


Fig. 2. Dependence of the effective diameter and diffusion coefficient on the concentration of the PIB-PS diblock in hexane. The length of the PS and the PIB segments are 4300 and 11000 g/mole by SEC and ^{1}H-NMR, respectively.

This indicates that the size of the micelles in the concentration range applied does not vary significantly with the concentration of the PIB-PS block copolymer. This observation, i.e., that the micelle sizes is independent of the copolymer concentration, is characteristic of micelle formation by a closed association process. Once the maximum size of the micelle has been reached a further increase in the block copolymer concentration causes the increase of the concentration of the micelles with the same size. Therefore, the aggregation number of the micelle can be determined by static light scattering experiments by means of the Zimm-plot analysis.

The aggregation number and the number of arms can be expressed by Eq. 1.

$$f = M_{w,a}/M_{w,u} \qquad (1)$$

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

$M_{w,a}$ were determined by static light scattering measurements using the Zimm-plot analysis. The number of arms (n_a) for the micelle in the case of the PIB-PS diblock copolymer is $n_a = f$. Theoretically, the R_H/R_g values should be 1.29 for a homogenous sphere (where R_H = hydrodynamic radius and R_g = radius of gyration). The R_H/R_g values are close to this value (see Table 1.) which support the formation of spherical micelles.

Estimation of the size of the hard core of the micelles

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

$$[3M_{w,a}w_{PS}/(4\pi N_A \rho_{PS})]^{1/3} = R_c \qquad (2)$$

where $M_{w,a}$ is the mass-average molecular mass of the micelles; w_{PS} is the mass fraction of polystryrene in the diblock; ρ_{PS} is the density of dry polystyrene (12) (which is 1.05 g/cm^3); and N_A is the Avogadro's number.

The dependence of the size of the hard core (d_c), the hydrodynamic diameter (d_h) and the number of arms of the micelles (f) on the molecular mass of the polystyrene segments (M_n) are presented in Table 1. and Fig. 3. The size of the hard core is levelling off on increasing molecular mass of the PS block. This limits the aggregation number, i.e., the number of arms. The lower the frequency of the arms is the higher the possibility of solvation is, i.e., the hydrodynamic diameter is increasing with the molecular mass of the hard core segments.

Living anionic dispersion polymerization of styrene in hexane in the presence of the PIB-PS diblock copolymer. A new dispersing agent

Our goal was to study the effect of the PIB-PS diblock as stabilizer on the dispersion polymerization of styrene. Anionic dispersion polymerization of styrene in hexane was carried out in the presence of PIB-PS diblock copolymers of varying PS segments in length.

Code	$M_{n[PS]}$ (g/mol)	$M_{n[PIB]}$ (g/mol)	d_c (nm)	d_h (nm)	f	R_h/R_g
PIBPS1	4300	11000	7.8	29	29	1.35
PIBPS2	6500	10300	10.4	33	46	1.39
PIBPS3	9040	8900	10.6	42	34	1.22
PIBPS4	13600	11400	10.7	45	27	1.4

Table 1. The diameter of the hard core, the hydrodynamic diameter and the number of arms of the micelles in hexane solution.

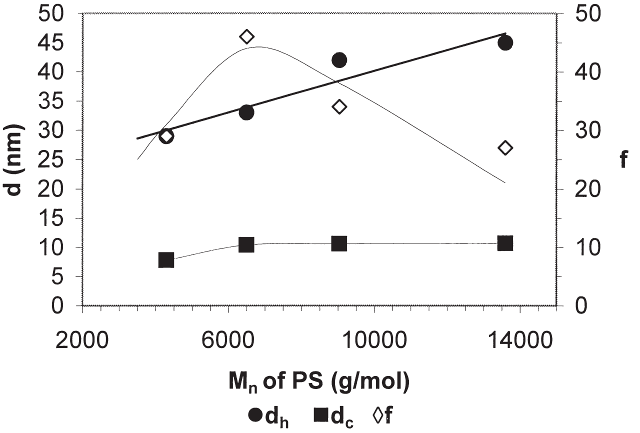


Fig. 3. The dependence of the size of the hard core, the hydrodynamic diameter and the number of arms of the micelles on the molecular mass of the polystyrene (hard) segments in hexane solution.

Without diblock copolymers, a very rough PS precipitate was obtained. By increasing the length of the polystyrene in the diblock, narrower and smaller size of polystyrene particles were obtained under the same conditions. The images obtained with optical microscope and TEM are shown in Fig. 4. This tendency is probably due to the greater adsorption energy of the large polystyrene segments onto the surface of the growing polystyrene particles. In the case of the shorter polystyrene segment the adsorption energy is not sufficient, therefore desorption of the diblock can take place resulting in large particle size and broad particle size distribution. However, the M_n and M_w/M_n of the resulted polystyrene produced with different PIB-PS diblock stabilizers did not change significantly. The M_n of the polystyrene increases with the monomer conversion. Typical SEC traces are shown in Fig.5. The dispersion polymerization seems to be slowly initiated living polymerization. The livingness of the polymerization is proved by plotting the diagnostic lines, i.e., the M_n versus W_p and -ln(1-C) versus time lines (Fig. 6). To interpret the effect of the stabilizer, we postulated that the size of the hard core of the micelles formed from the PIB-PS diblock copolymers is increased by styrene. Therefore, independent DLS experiments were performed on the solution of the diblock copolymers in the presence of styrene. However, these experiments did not show an increase of the size of the micelles, i.e., no swelling of the micelles takes place.

Probably, the nanomicelles originally present in hexane, are collapsed in the presence of polystyrene nuclei, i.e., the unimers of the PIB-PS diblock are attached onto the polystyrene surface. Thus, there should exist an equilibrium between the nanomicelles and unimers (shifted to micelles in the absence of polystyrene particles) and unimers adsorbed onto the polystyrene particles (Scheme 1).

After evaporation the solvent, the bulk polystyrene samples obtained can be re-dispersed to the extent of their initial size, i.e., as they were before preparation, indicating that the stabilizer molecules are attached firmly onto the surface of the polystyrene particles.

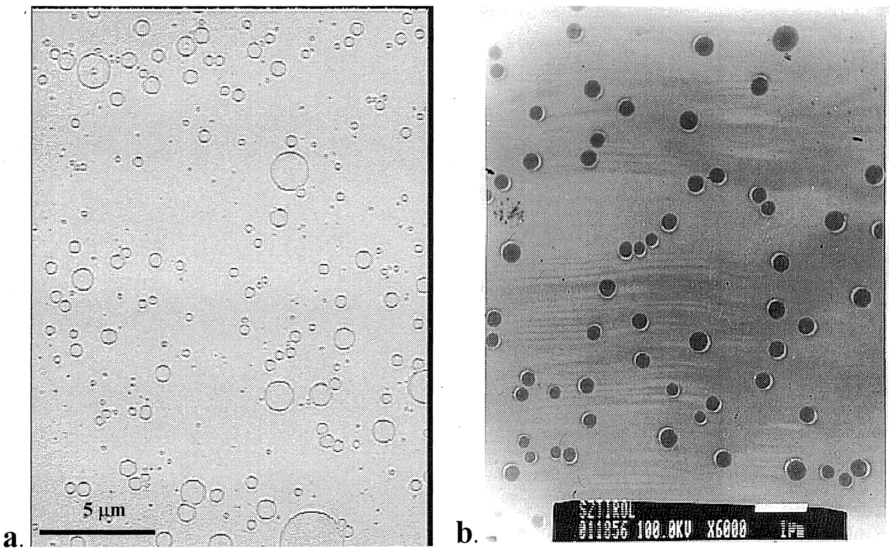
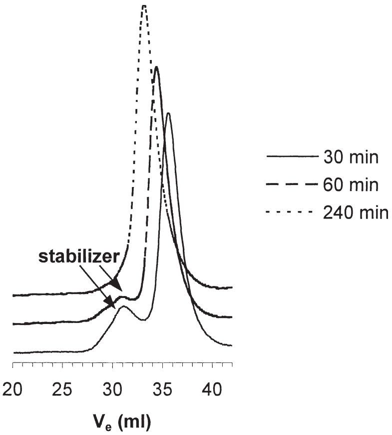


Fig. 4. Optical microscope (a) and transmission electronmicroscope micrograph (b) of polystyrene particles prepared via anionic dispersion polymerization.

Conditions: 4 ml styrene, 0.002 mol nBuLi and 0.2 g **PIBPS1** (a) and 0.2 g **PIBPS4** (b) in 45 ml hexane. T=30 °C, reaction time= 60 min. Composition for **PIBPS1** and **PIBPS4** are in Table 1.



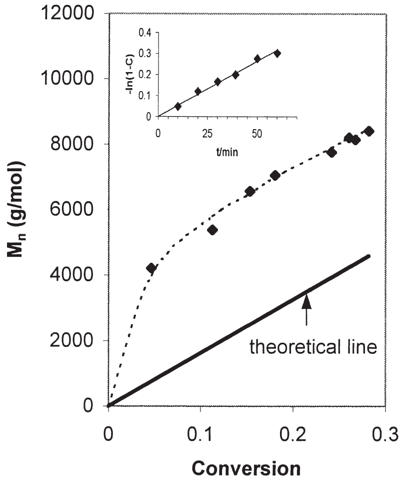
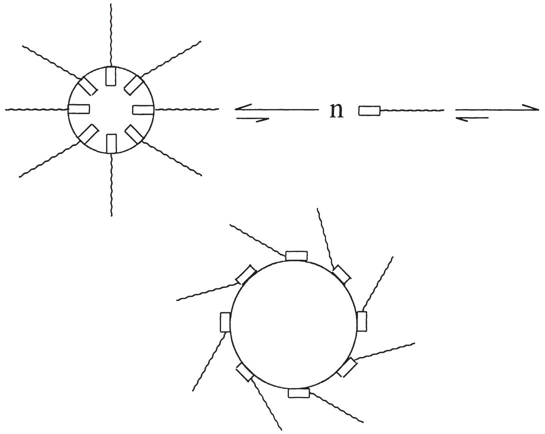


Fig. 5. SEC traces of polystyrene prepared by anionic dispersion polymerization
Conditions: 4 ml styrene, 0.002 mol nBuLi and 0.2 g **PIBPS4** in 45 ml hexane. T=30 °C

Fig. 6. Diagnostic plots for proving the livingness of anionic dispersion polymerization of styrene.
Conditions: 10 ml styrene, 0.005 mol nBuLi and 0.5 g **PIBPS4** in 115 ml hexane. T=30 °C



Scheme 1. Schematic representation of stabilization of polystyrene particles by the PIB-PS diblock copolymers

Conclusion

Formation of star-shaped nanomicelles were recognized in hexane solution of the PIB-PS diblock copolymers. The size and size distribution of the particles were determined by dynamic light scattering (DLS) measurements. On the basis of dynamic and static light scattering, spherical, compact nanomicelles formation is concluded.

The synthesized PIB-PS diblock copolymers were tested as steric stabilizers in the living dispersion anionic polymerization of styrene, and the **PIBPS4** copolymer was proved to be the best stabilizer.

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