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Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) Nanospheres with Cross-Linked Shells

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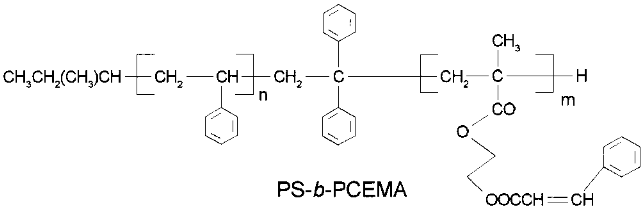
ABSTRACT: Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate), PS-*b*-PCEMA, forms spherical micelles with PCEMA corona and PS core in THF/acetonitrile with 10%, by volume, of THF. Nanospheres with cross-linked PCEMA shells are obtained by photolyzing the sample with UV light. Despite the PCEMA corona, the degree of intermicellar fusion is low at CEMA conversions less than ~40%. The nanospheres, with greater than ~10% CEMA conversions, are dispersible and structurally stable in THF or toluene which solubilizes both PS and un-cross-linked PCEMA.

I. Introduction

Many techniques are available for the preparation of polymeric spheres. Micrometer-sized spheres are produced mainly by emulsion and suspension polymerization in water[1] or in organic solvents.[2] More recent development involved their preparation from precipitation polymerization[3] and the "activated swelling" method.[4] Nanometer-sized particles with approximately spherical shapes are sometimes referred to as microgels.[5] Nanometer-sized spheres or nanospheres can be prepared by microemulsion[6] or precipitation polymerization.[7]

Polymeric nanospheres can also be prepared by cross-linking block copolymer micelles.[8−18] Using this method and diblocks with a block which is cross-linkable by an added initiator, different researchers have succeeded in preparing micelles (or nanospheres) with cross-linked cores[8−11] and coronas.[12] We prepared diblock copolymers such as polystyrene-*block*-poly(2-cinnamoylethyl methacrylate), PS-*b*-PCEMA



PS-*b*-PCEMA

which contain photochemically self-cross-linkable PCEMA blocks. Using these diblocks in the absence of any external initiators, we recently prepared hairy nanospheres,[13−15] shaved nanospheres,[16] porous nanospheres,[17] and hollow nanospheres.[18] In this paper, we report the preparation of nanospheres with cross-linked coronas from PS-*b*-PCEMA. While water-soluble nanospheres with cross-linked shells as those prepared by Thurmond II et al.[12] may have potential applications in controlled drug release etc, our study was aimed only at demonstrating the suitability of diblocks containing a photo-cross-linkable block for the preparation of nanospheres with cross-linked shells and at expanding the repertoire of nanostructures obtainable from such diblock copolymers.

II. Experimental Section

Polymer Synthesis and Characterization. Two PS-*b*-PCEMA samples were used in this study. While the numbers of styrene and CEMA units are all 8.2×10^2 in polymer I, they are 1.08×10^3 and 1.16×10^3, respectively, in polymer II. The precursor to PS-*b*-PCEMA was PS-*b*-P(HEMA-TMS), where P(HEMA-TMS) denotes poly(2-trimethylsilylethyl methacrylate). PS-*b*-P(HEMA-TMS) was prepared by anionic polymerization as described in detail previously.[19,20] The TMS group hydrolyzed readily in methanol. Reacting polystyrene-*block*-poly(2-hydroxylethyl methacrylate) with cinnamoyl chloride yielded PS-*b*-PCEMA. The sample was characterized by GPC, NMR, and light scattering.

Instrumentation and Techniques. GPC analysis was done using THF as the eluant and Waters HT-4 ultra-styragel column. Light scattering was done using a Brookhaven model 9025 instrument equipped with an argon ion laser operated at 488 nm. All light scattering measurements were carried out at room temperature. Photolysis was achieved with light from a 500-W mercury lamp passed through a 260-nm cutoff filter.

Micelle Preparation. Polymer II, 75 mg, was dissolved in 7.5 mL of distilled THF. Acetonitrile (67.5 mL, Aldrich, Spectrograde) was then added. The micellar solution was equilibrated at room temperature for 1 day before UV photolysis. The final polymer solution concentration was 1.00 mg/mL. A similar procedure was used for preparing 100 mL of polymer I micelle solution at 1.00 mg/mL.

Micelle Cross-Linking. PS-*b*-PCEMA micelle solution in THF/acetonitrile (1.00 mg/mL) was irradiated at 22 °C under vigorous stirring. Samples (2.00 mL each) were taken at different irradiation times. Of the 2.00 mL, 0.20 mL was diluted with THF and used for absorbance analysis at 274 nm to determine the conversion of the aliphatic double bonds of CEMA.[13] Then, 0.80 mL was used for the dynamic light scattering measurement. The rest of the sample was dried. To it was then added 0.50 mL of THF for GPC analysis of micellar samples of polymer II. Cross-linked polymer micelles were purified by precipitation in methanol.

Viscosity Measurements. Viscosities of THF/acetonitrile mixtures were measured at room temperature (22 °C) using a Cannon Ubbelohde type viscometer following a method described previously.[19] The viscosities of THF and acetonitrile at 22 °C were taken to be 0.470 and 0.347 cP, respectively.[21]

Light Scattering and Transmission Electron Microscopic (TEM) Studies. Dynamic light scattering measurements were performed of cross-linked PS-*b*-PCEMA micelles at the scattering angle of 90° immediately after a sample was taken from the irradiation cell. Dynamic light scattering data

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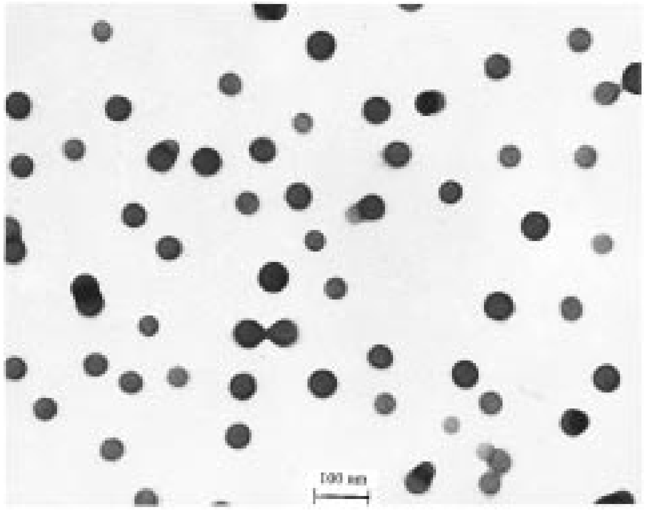

Figure 1. TEM image of polymer II micelles sprayed from THF/acetonitrile with 10%, by volume, of THF.

were analyzed following the method of cumulants[22] to obtain hydrodynamic radii R_h of the nanospheres.

For TEM measurements, several drops of a micellar or nanosphere solution were added into a tube containing a capillary open end and a male ground joint close to the other end. The tube was inserted into a socket with the capillary end located at the narrowed exit end of the socket. As the solution dripped out of the capillary, air, introduced from the sidearm of the socket and gushing out of the exit, broke the fine droplet and brought the particles into contact with a carbon-coated copper grid. Sprayed micelles were stained with OsO_4 or RuO_4 overnight. For routine TEM experiments, a Hitachi-7000 transmission electron microscope (TEM) was operated at 10^5 V. For observing a specimen at different TEM sample stage tilting angles, a Zeiss EM902 instrument was used. The Hitachi-7000 microscope was used preferentially due to its higher-quality images.

III. Results and Discussion

PS-*b*-PCEMA Micelles in THF/Acetonitrile. Formation of PS-*b*-PCEMA micelles in THF/acetonitrile was judged from the bluish tinge of such a solution. Illustrated in Figure 1 is a TEM image of polymer II micelles. These micelles seem spherical with a dark PCEMA shell and a gray PS core. Illustrated in Figure 2 is the image of the same sample at the TEM sample stage tilting angle of 45°. This image suggests that the micelles have the spherical cap shape on the carbon-coated copper grids. This was probably caused by the flattening of the micelles and the spreading of micellar chains on the carbon-coated copper grids after spraying from THF/acetonitrile (AN) with 90% AN. The radius of these deformed micelles is ~24 nm. Similar TEM images and radii were obtained for polymer I micelles.

Micelle formation was also confirmed by our dynamic light scattering experiments. In THF/AN with 90% AN, the hydrodynamic radii, R_h, for polymer I and II micelles are 31 and 34 nm, respectively. These values are larger than the TEM radii, because the micelles are swollen in the solvent mixture.

Photochemical Reactions and Cross-Linking Kinetics of CEMA. CEMA dimerizes due to photoinduced cycloaddition.[23,24] The dimerization can occur between two CEMA units of the same chain, which should change the solubility of the PCEMA corona but does not effect micellar structural “locking in”. PCEMA cross-links because of dimerization between CEMA groups of different chains of the same micelle. In THF/acetonitrile, PCEMA makes up the corona. Bond formation between CEMA groups of chains of different micelles is also possible. This causes nanospheres to fuse.

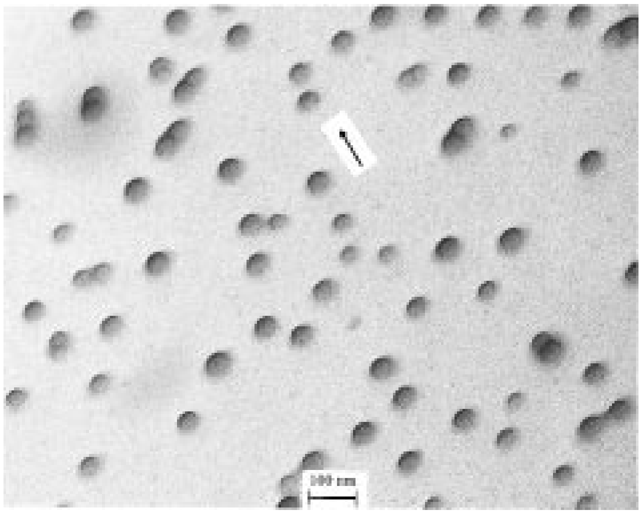

Figure 2. Image of polymer II micelles sprayed from THF/acetonitrile with 10% THF at a TEM sample stage tilting angle of 45°. The sample stage tilting direction is indicated by an arrow in the figure.

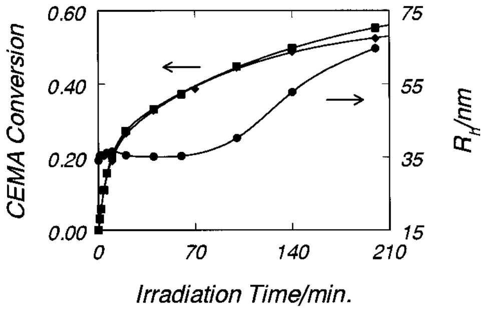

Figure 3. PCEMA conversion, (■), as a function of photolysis time for polymer II micelles. The conversions were calculated from $[A(0) - A(t)]/A(0)$ where $A(0)$ and $A(t)$ and denote the absorbances of the polymer at 274 nm at time zero and t, respectively. Also shown is the variation in the hydrodynamic radius, R_h (•), of polymer II micelles as a function of photolysis time. The PCEMA cross-linking kinetic data agreed well with those (◆) of polymer I micelles at low CEMA conversions.

The extent of the three types of dimerization was difficult to assess quantitatively. Our later analysis of the properties of the photolysis product will show that intermicellar fusion is insignificant at low CEMA conversions. Shown in Figure 3 are the overall disappearance rates of the CEMA groups due to the three types of dimerization as followed by UV absorbance decrease at 274 nm.[13] The close agreement between the CEMA conversion kinetic data for the polymer I and II micelles was fortuitous, because different amounts of polymer were irradiated, and no effort was made to focus the irradiation beam and adjust the position of the irradiation cell so that the samples were photolyzed under exactly the same conditions.

Nanospheres with Cross-Linked Shells. Illustrated in Figure 4 is a TEM image of polymer II micelles sprayed from toluene at a CEMA conversion of 30%. Most of the cross-linked micelles are seen as individual particles with a diameter of ~24 nm here. Further TEM studies revealed that a CEMA conversion of ~10% was sufficient to lock in the polymer I and II micellar

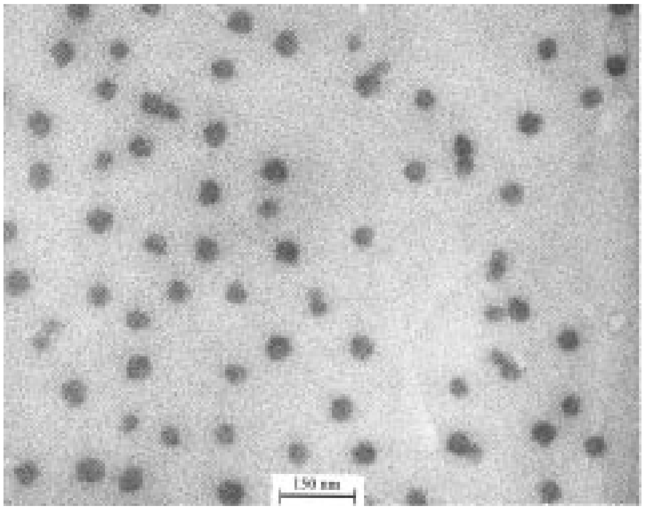

Figure 4. TEM image of polymer II micelles at a CEMA conversion of 30% sprayed from toluene. This sample was stained with RuO_4 to improve contrast.

structure. Since toluene dissolves both PS and un-cross-linked PCEMA, the stability of the particles in toluene suggests the "locking in" of the micelles and the extensive interchain CEMA dimerization in a micelle. The fact that most cross-linked micelles exist as individual particles suggests that the extent of intermicellar CEMA dimerization is low.

The cross-linked micelles or nanospheres remain dispersed in the THF/acetonitrile mixture, in which they were prepared, when stirred. At high CEMA conversions, e.g., >30%, the cross-linked micelles settled with time, e.g. in 1 or 2 h, if not stirred. Precipitation could also be induced sometimes by transferring the micelle solution from one flask to another. The precipitated nanospheres can be separated, dried, and redispersed in THF or toluene. The particles, however, become less dispersible after long storage times, e.g., longer than 1 week, probably due to interparticle chemical fusion via the PCEMA shells in the solid state.

Invariance of R_h Values at Low CEMA Conversions. Also illustrated in Figure 3 is the variation in the hydrodynamic radius, R_h, of polymer II micelles as a function of photolysis time or CEMA conversion. At irradiation times shorter than 60 min or CEMA conversions less than ∼40%, R_h for polymer II micelles remained approximately constant. Similar results were obtained for polymer I micelles, and the R_h values for these micelles at the CEMA conversions of 3.3%, 6.1%, and 15.2% were 31, 31, and 32 nm, respectively, which compare well with 31 nm for the un-cross-linked micelles. These results confirm that there was a low degree of intermicellar fusion at low CEMA conversions.

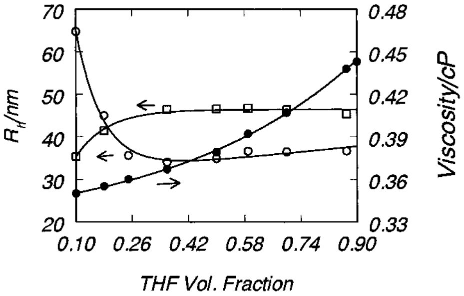

Figure 5. Variation in R_h of polymer II micelles at the CEMA conversions of 11% (□) and 55% (○) as a function of THF volume fraction in THF/acetonitrile mixtures. Also plotted are the viscosities (●) of the solvent mixtures at different compositions.

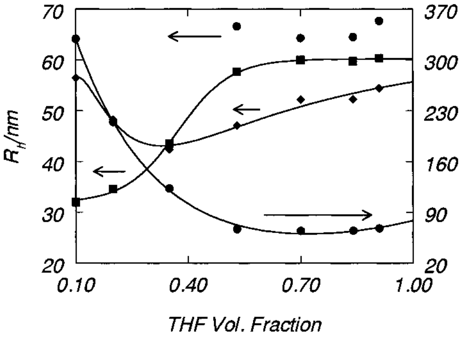

Figure 6. Variation in R_h of polymer I micelles at CEMA conversions of 15% (■), 38% (◆), and 52% (●) as a function of THF volume fraction in THF/acetonitrile mixtures. The data points (●), at the top for polymer I micelles at the CEMA conversion of 52% are plotted against the left axis.

The dynamic light scattering measurements were carried out immediately after each sample was taken. This was especially important for the micelles with high CEMA conversions, e.g. >30%, because these micelles were not stable in THF/AN for a long period of time and the R_h values increased with time after the micelles were transferred to a scattering cell where the solution was not stirred. In cases, the micelles were seen to settle immediately after such a solution was transferred into a new flask. This micellar instability must have derived from the reduced solubility of the PCEMA corona in THF/acetonitrile after extensive inter- and intrachain CEMA dimerization. The cross-linked micelles were thus only kinetically stable in the THF/AN with 90% AN.

R_h Increase at High CEMA Conversions. Data from Figure 3 show a drastic R_h increase at high CEMA conversions for polymer II micelles, which suggests nanosphere fusion. Similar results were observed for polymer I nanospheres. At the CEMA conversions of 39% and 52%, the R_h values measured were 46 and 326 nm immediately after the micellar solutions were transferred into the light scattering cells, which are substantially larger than the initial R_h value of 31 nm for polymer I micelles.

Figures 5 and 6 show the variation in the R_h values of the freshly photolyzed micelles in different THF/AN mixtures with THF content change. Also shown in Figure 5 are the viscosities of different THF/AN mixtures, which were used in R_h calculation. For samples with high CEMA conversions, e.g., >40%, the general trend is that R_h decreases with THF content and then increases. For polymer I micelles with a CEMA conversion of 52%, R_h decreased from 326 nm in THF/AN with 90% AN to 64 nm in THF/AN with 30% AN. R_h then increased slightly to 68 nm in THF/AN with 9% AN. The drastic initial decrease in R_h with THF content suggests the dissociation of fused PS-*b*-PCEMA nanospheres. Thus, most of these fused particles at high CEMA conversions were held together by the van der Waals forces or the fusion occurred due to the reduced solubility of the cross-linked PCEMA corona. The slight increase in R_h with THF content at high THF content is due to the swelling of the cross-linked dissociated nanospheres.

R_h Variations with THF Contents at Low CEMA Conversions. At the CEMA conversions of ∼13%, R_h

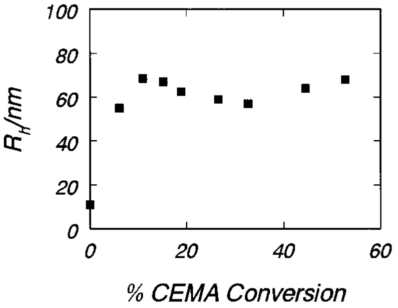

Figure 7. Variation in the R_h values of polymer I micelles in THF as a function of CEMA conversion.

for polymer I and II micelles increased with THF content in THF/AN. Since most micelles exist as individual particles at low CEMA conversions and THF swells both PCEMA and PS, this increase with THF content is expected. What are more surprising are the different degrees of swelling for the cross-linked polymer I and II micelles by THF. At a CEMA conversion of 15%, R_h increased from 32 to 62 nm for polymer I micelles when THF content increased from 10% to 91%. R_h of the polymer II micelles at the CEMA conversion of 11% only increased from 35 to 45 nm. We do not know the exact reason why polymer II nanospheres are held more tightly in THF/AN with high THF contents except the speculation that more interchain bonds are formed in polymer II micelles due to the longer PCEMA block.

R_h Values at Higher THF Contents. For polymer I, the R_h values of the nanospheres in THF/AN with 84% THF from Figure 5 are 60, 52, and 64 nm at CEMA conversions of 15%, 38%, and 52%, respectively. This R_h decrease and increase pattern with CEMA conversion at conversions greater than ~11% is more clearly seen in Figure 7, in which R_h in THF at different CEMA conversions are plotted. R_h increases with CEMA conversion below the conversion of ~11%, because the micellar chains are locked in gradually and a micelle not fully locked is broken into pieces in THF. The value of ~11% at which R_h reaches a maximum may correspond to the CEMA conversion where the micelles are just locked in. R_h subsequently decreases probably because the degree of nanosphere swelling in THF decreases with CEMA conversion. The R_h value rises with CEMA conversion again at values higher than ~40% probably due to intermicellar fusion.

The R_h value of polymer II nanospheres at a CEMA conversion of 55% in THF/AN with 87% THF is 37 nm, which is lower than 45 nm for nanospheres with a CEMA conversion of 11%. This lower R_h value at a CEMA conversion of 55% does not necessarily suggest the absence of intermicellar fusion. First, the R_h values were determined at a scattering angle of 90°. It is only at low scattering angles that the contribution from the fused micelles to light scattering intensity and thus R_h is emphasized. Second, micelles at different CEMA conversions are swollen to different degrees. In fact, the TEM result of Figure 8 shows that some fusion did occur for polymer II nanospheres at a CEMA conversion of 47%. This becomes clearer as one compares the TEM images of Figures 4 and 8.

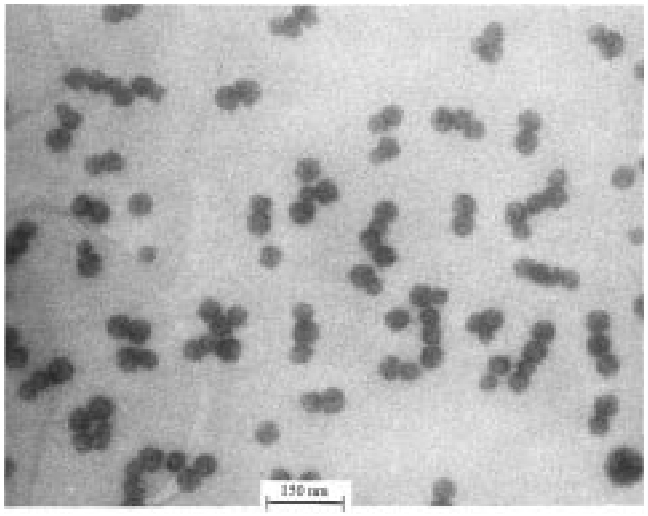

Figure 8. TEM image of polymer II nanospheres at a CEMA conversion of 47% sprayed from toluene.

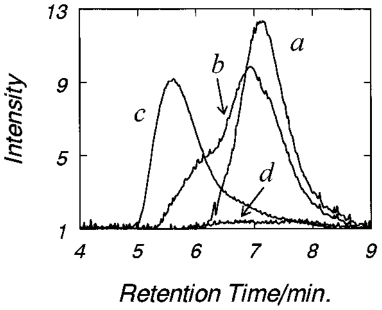

Figure 9. Evolution of GPC chromatograms of the polymer II micelles as a function of CEMA conversion. The chromatograms were recorded at CEMA conversion of 0% (a), 3.1% (b), 5.8% (c), and 11.0% (d), respectively.

Gradual "Lock in" of the Micellar Structure. TEM studies indicated that the micellar structure was locked at a CEMA conversion of ~10%. Some insight into the structural evolution of the particles as a function of irradiation dosage was obtained from the GPC data, Figure 9, of the cross-linked polymer II micellar samples taken at different irradiation times. At a CEMA conversion of 3.1%, there was a small fraction of chains with molar masses higher than that of the single chains. The average molar mass of the eluted chains increased at a CEMA conversion of 5.8%, and the unimolecular chain population decreased. Samples with a CEMA conversion of 11% did not show any peak for fused or cross-linked chains, and the unimolecular chain population was very low.

The unimolecular chain population decreases with CEMA conversion because the number of cross-linked chains increases with CEMA conversion. The molar mass of the eluted cross-linked chains increases initially with CEMA conversion because the chains in a micelle dimerize, trimerize, and form larger and larger aggregates. No cross-linked chains are seen at a CEMA conversion of 11% because the nanospheres with all chains locked in are not eluted out of the GPC column.

Static Light Scattering Studies of the Nanospheres. Static light scattering studies were performed for polymer II nanospheres in toluene. The specific refractive index increments of PS-*b*-PCEMA diblocks in toluene can be calculated from an empirical relation[20]

$$\nu = 0.0938 + 0.029w_{PS} - 0.0115{w_{PS}}^2 \text{ mL/g} \quad (1)$$

Using the weight fraction of 0.27 for PS, we calculated a ν value of 0.101 mL/g. Since our previous study demonstrated that ν changed little with CEMA double

Table 1. Characteristics of the PS-*b*-PCEMA Sample Used

polymer	(n/m) by NMR	$\bar{M}_w/\bar{M}_n$ by GPC	$\bar{M}_w \times 10^{-5}$ by LS	$10^{-2}\ n$	$10^{-2}\ m$
I	1.00	1.10	3.0	8.2	8.2
II	0.93	1.10	4.1	10.8	11.6

Table 2. Weight-Average Molar Masses, $\bar{M}_w$, Radii of Gyration, R_G, and Hydrodynamic Radii, R_h, Determined by Light Scattering for Polymer II Nanospheres in Toluene at Different CEMA Conversions

$\bar{M}_w$/(g/mol)	R_G/nm	R_h/nm [a]
	CEMA Conversion = 30%	
4.5×10^7	44	49
	CEMA Conversion = 35%	
4.2×10^7	44	53
	CEMA Conversion = 43%	
7.4×10^7	55	75

[a] R_h values were determined at a scattering angle of 90°.

bond conversion,[20] the ν value of the diblock was used to approximate that of the nanospheres.

Using the ν value of 0.101 mL/g, we obtained a $\bar{M}_w$ value of 4.5×10^7 g/mol for a polymer II nanosphere sample at a CEMA conversion of 30% following the Zimm method (Table 2). Using this nanosphere molar mass and the molar mass of 4.1×10^5 for the diblock, the aggregation number for the nanospheres should be 1.1×10^2.

Since the specific refractive indices of PS and PCEMA in toluene are different, we should, in principle, correct the molar mass of the nanospheres determined by light scattering.[25] We did not carry out this correction based on two considerations. First, we only needed an estimate of the nanosphere molar mass. Second, the specific refractive indices of PS and PCEMA are 0.112 and 0.094 mL/g, respectively, which are different but sufficiently close.

The radius of such dry solid nanospheres can be calculated using

$$R_d = \left(\frac{3\bar{M}_w}{4\pi N_A \rho}\right)^{1/3} \tag{2}$$

where is N_A Avogardro's number. At a molar mass of 4.5×10^7 g/mol and assuming a density of 1.0 g/mL for the dry nanospheres, we calculated a R_d value of 26 nm, which is the same, within experimental error, as the radius of ~24 nm determined by TEM from Figure 1. The agreement between the radius calculated from light scattering molar mass and the TEM radius again points to the insignificant fusion of different micelles at the CEMA conversion of 30%.

Also shown in Table 2 are the weight-average molar mass, $\bar{M}_w$, the radius of gyration, R_G, and the hydrodynamic radius, R_h, determined for the sample at a CEMA conversion of 35%, and the values agreed with those determined at a CEMA conversion of 30%. Thus, insignificant fusion occurred for samples at a CEMA conversion as high as 35%.

In toluene, the radius of gyration, R_G, determined for the nanospheres at the CEMA conversions of 30% and 35% was 44 nm, which is smaller than the hydrodynamic radius R_h of 49 and 53 nm determined from dynamic light scattering. For perfect homogeneous spheres, the R_h/R_G value should be ~1.29. The theoretical R_h/R_G value is larger than 1.15 ± 0.05 for our samples. The difference is reasonable, because our nanospheres are not homogeneous but have a core–shell structure. In fact, the R_h/R_G value of is in qualitative agreement with the spherical shape of the particles.

At the CEMA conversion of 43%, the, $\bar{M}_w$, R_G, and R_h values for the nanospheres all increased. This suggests some fusion of the nanospheres in agreement with results of Figure 8.

IV. Conclusions

PS-*b*-PCEMA micelles with PS cores were shown to cross-link to yield nanospheres with cross-linked shells. The micellar structure was locked in at a CEMA conversion of ~10%. The degree of intermicellar fusion was low at CEMA conversions less than ~40%. The nanospheres prepared are stable in good solvents such as THF and toluene for PCEMA and can be easily redispersed after drying.

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