Star and Cylindrical Micelles of Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) in Cyclopentane

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Received August 26, 1996; Revised Manuscript Received December 23, 1996[⊗]

ABSTRACT: Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) samples with n/m larger than 9.0, where n and m stand for the numbers of styrene and of CEMA units in a chain, formed essentially star micelles and those with n/m between 7 and 8.2 formed mixtures of star and long cylindrical micelles in cyclopentane with PCEMA as the core and PS as the shell. UV cross-linking of the PCEMA cores of these micelles at 50 °C yielded star polymers and nanofibers. This probably represents the first preparation of cross-linked block copolymer cylindrical micelles or nanofibers in the solution phase. While we have previously prepared star polymers using this approach, this study shows the robustness of this method in producing star polymers with as many as 4.5×10^2 arms and a molar mass of 9.9×10^7 g/mol. Detailed study showed that UV cross-linking only locked in the structure of the micelles and did not change their aggregation numbers. This allowed us to determine the molar masses of the cross-linked micelles in toluene, in which uncross-linked micelles would have disintegrated, and to equate them to those of the uncross-linked micelles in cyclopentane. The aggregation numbers of the star micelles in cyclopentane were found to follow theoretical scaling laws.

I. Introduction

In a block-selective solvent, a diblock copolymer may form spherical micelles with the insoluble block as the core and the soluble block as the corona.[1−5] How the aggregation number and size of these micelles change with the numbers of repeat units n and m for the soluble and insoluble block has been of much theoretical study in the past 2 decades.[6−13]

All theoretical approaches started by formulating the change in the free energy of a system when micelles formed due to the association of free or single chains. The free energy was then minimized with respect to a change in a parameter of interest such as the aggregation number f, the radius of the micellar core R_c, or the thickness of the corona L to obtain theoretical expressions for f, R_c, and L. In the scaling approaches,[6−8] only the dominant contributions to the total free energy of the system were considered. In numerical approaches,[9−10] f, R_c, and L were calculated for model systems by taking all energy terms into consideration. Theoretical relations of f, R_c, and L were obtained for such model systems by correlating f, R_c, and L values of a series of samples. Regardless of the theoretical approaches, the general relations for f and R_c can be written as

$$f \approx m^{\alpha} n^{\beta} \tag{1}$$

and

$$R_c \approx m^{\gamma} n^{\lambda} \tag{2}$$

While the α, β, γ, and λ values have been found for cases when a homopolymer which has the same structure as one constituent block of the diblock is used as the solvent,[11−13] we will only discuss the situation when the block-selective solvent consists of small molecules.

From the scaling approaches, β and λ values were always found to be zero. For star micelles with the corona block much longer than the core block, α and γ were found by both Zhulina et al.[7] and Halperin[8] to be $^4/_5$ and $^3/_5$, respectively. On the extreme of crew-cut micelles with the corona block much shorter than the core block, α and γ were found by de Gennes[6] to be 1 and $^2/_3$. Zhulina and Birshtein[7] found that the scaling relations for f and R_c remained the same regardless if a Θ or good solvent was used for the corona block. Assuming a constant segmental density across the corona, Noolandi and Hong[9] computed the f and R_c values for micelles formed from three series of polystyrene-*block*-polybutadiene (PS-*b*-PB) samples in n-heptane, a Θ solvent for PB, with each series possessing the same PB weight fraction. Correlating the f and R_c values for each of the series yielded composition independent α and γ values of 0.90 and 0.64. These α and γ values are intermediate between those of star and crew-cut micelles. The surprising ones are the scaling relations derived from the numerical results of Nagarajan and Ganesh.[10] They modeled three systems. For a system with the corona block in a good solvent, the α, β, γ, and λ values were found to be 1.19, −0.51, 0.73, and −0.17, respectively. In a Θ solvent, these values changed to 1.10, −0.24, 0.70, and −0.08.

There have been several attempts made to test the theoretical scaling relations mentioned above in the past decade. Bluhm and Whitmore[14] determined the radius of gyration R_G of three PS-*b*-PB samples in heptane aimed at testing scaling relations established by Noolandi and Hong[9] for R_c and L. Since R_G was nontrivially related to R_c and L, the comparison between the experimental data and theory could not be more than qualitative. Xu et al.[15] studied micelles of polystyrene-*block*-poly(ethylene oxide) in water aimed at testing some theoretical models. Since a number of their polymers formed "micelle clusters", the inability to determine the sizes and aggregation numbers of the spherical micelles directly made their study ambiguous. McConnell et al.[16] and Bahadur et al.[17] studied micelles of a number of PS-*b*-PI samples in block-selective solvents for PI (polyisoprene); neither the aggregations numbers nor the R_c values determined followed any of the theoretical scaling relations. In their cases, samples with PS weight fractions as high as 71% were used. At

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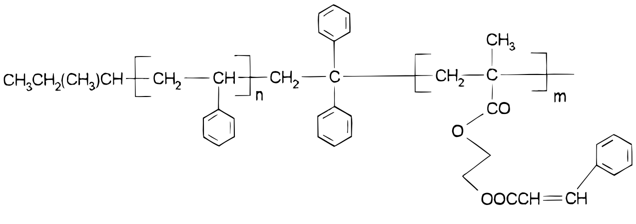
[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

such high insoluble block weight fractions, the formation of cylindrical[18−22] or vesicular micelles[22−23] rather than spherical micelles could have been possible. The formation of cylindrical micelles would explain why some of the f values determined by Bahadur et al. were abnormally high. Then, micellar morphological transitions could be accompanied by sudden changes in f values as observed by McConnell et al.

Antonietti et al.[18] determined the f values for four PS-*b*-PVP samples in selective solvents for PS with PVP (poly(vinylpyridine)) weight fractions less than 33%. For cases when star micelles were formed, f scaled following eq 1 with $\beta = 0$ and α between 1.5 and 2.0. This represented a m dependence much stronger than that predicted by any existing theory. This strong m dependence was somewhat resonated by the results of Qin et al.[24] measured for PS-*b*-PMA micelles in a dioxane/water mixture containing 20% of water by volume, where PMA denoted poly(methacrylic acid) and was the soluble block. In their case, the α value was 1.89. But their f values also had a n dependence with β equal to -0.86. Zhang et al.[25] determined the R_c and f values for a series of crew-cut micelles of PS-*b*-PAA [poly(acrylic acid)] in water. The R_c values followed eq 2 with $\gamma = 0.40$ and $\lambda = -0.15$, values far off from the theoretically predicted values. Although no experimental scaling relation was established for the f values, it was obvious to see that their f values did not follow any of the existing scaling relations either. While the reasons for the discrepancy between the theoretical and experimental results could be manifold, the most likely reason was that the systems mentioned in this paragraph did not reach thermodynamic equilibrium. The chain exchange kinetics of PS-*b*-PAA micelles in water was, for example, so slow that the micelles remained intact after eluding out of GPC columns.[26]

Khougaz et al.[27] determined the aggregation numbers of 15 PS-*b*-PANa samples with short PS and long PANa [poly(sodium acrylate)] blocks after heating the star micelles in boiling 2.5 M sodium chloride solution for prolonged times. Excluding two abnormal data points, their f data could be fitted by eq 1 with $\beta = 0$ and α equal to either 0.80 or 1.0. The correlation coefficients generated in the two cases were 0.86 and 0.83. Due to the large deviation of the correlation coefficients from 1, the results could not be used to conclude which model, star vs crew-cut model, was better, despite the fact that the polyelectrolyte star model should be more appropriate there.[28] The α value generated lay at least in the neighborhood of the theoretically predicted values. In conclusion, most experimental results obtained so far were far off from theoretical predictions. The validation of some and the invalidation of other theoretical models would require data of far better quality.

This study was initiated aimed at another test of existing theories. Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) samples were used partially because these polymers were available, as we used them previously to prepare various nanostructures including cross-linked polymer brushes,[29−32] star polymers,[33] nanospheres,[33] and nanofibers.[34] Then, we could cross-link the PCEMA core of PS-*b*-PCEMA star micelles photochemically. If the cross-linking only locked in the structure of the star micelles and did not change their aggregation numbers, the cross-linked micelles could be studied in a much wider choice of solvents including those in which uncross-linked micelles would disintegrate. The cross-linked micelles could also be separated from unimers by GPC fraction. This would allow the more accurate determination of the molar masses of micelles by light scattering.



PS-*b*-PCEMA

A total of nine polymers were used in this study. Unfortunately, only six of the samples with $n/m \geq 9.0$ formed essentially spherical micelles in cyclopentane with PCEMA as the core and PS as the corona. The m dependence of the f and R_c values agreed with theoretical scaling relations. The other interesting aspect of this study has been in the discovery of wormlike or cylindrical micelle formation from the other PS-*b*-PCEMA samples with n/m between 7.0 and 8.2. Since the PCEMA block was photocross-linkable, the cross-linking of the PCEMA cores of these cylindrical micelles yielded "permanent" cylindrical micelles or nanofibers. Since our previous preparation of nanofibers were achieved by cross-linking the PCEMA cylindrical domains in PS-*b*-PCEMA films,[34] this study represents the first report, as far as we know, of the preparation of cross-linked cylindrical micelles from a diblock micellar solution.

II. Experimental Section

Polymer Synthesis and Characterization. The detailed procedures for polymer synthesis and characterization have been described previously.[33,35] The polymers were synthesized by anionic polymerization. Styrene was polymerized at −78 °C in THF using *sec*-butyllithium. 1,1-Diphenylethylene (DPE) and lithium chloride, both at 3.0 equiv to *sec*-butyllithium, were then added. DPE reacted with polystyryl anions to convert them to the sterically more hindered PS-DPE anions. Lithium chloride was used to improve the polydispersity of the second block. The second block was prepared by initiating the polymerization of (trimethylsiloxy)ethyl methacrylate (TMSEMA) with PS-DPE anions. The trimethylsilyl protecting groups were removed by hydrochloric acid catalyzed hydrolysis of PS-*b*-PTMSEMA in a THF/methanol mixture to produce PS-*b*-PHEMA. To attach cinnamoyl groups, PS-*b*-PHEMA was reacted with cinnamoyl chloride in pyridine.

GPC analysis was done with THF as the eluant. The Styragel HT-4 (Waters) column was calibrated using polystyrene standards. The ratio in the number of styrene to CEMA units, n/m, was determined using ^{1}H NMR. The absolute weight-average molar masses were measured in toluene using a Brookhaven Model 9025 light scattering instrument equipped with a 632-nm He−Ne laser. All diblocks are denoted by two numbers separated by a hyphen with the first number representing the number of styrene units, n, and the second the number of CEMA units, m.

PS-*b*-PHEMA prepared this way may contain some homopolystyrene. Homopolystyrene was removed from PS-*b*-PHEMA by extraction in refluxing cyclohexane.

Micelle Preparation and Cross-Linking. Around 100 mg of PS-*b*-PCEMA was dispersed in 50 mL of cyclopentane (95%, Aldrich) by gentle heating. The mixture was then filtered and refluxed for 1−3 days before irradiation at 50 °C to cause 40% of the aliphatic double bond of PCEMA to photodimerize. The decrease in double bond concentration with irradiation time was monitored by UV spectrophotometry, as PCEMA had a strong adsorption peak at 274 nm [$\epsilon = 2.8 \times 10^4$ L/(mol·cm)]. The heating was used to ensure that micellar equilibrium was established and also to make cyclopentane a better solvent for the PS block, as the Θ temperature for PS in cyclopentane is 19.6 °C.[36] Cross-linked micelles were isolated by precipitation from methanol.

Fractionation of Cross-Linked 1640-182 Micelles. Micelles of 1640-182 contained a small fraction of short cylinders and were purified by precipitation fractionation. About 80 mg of the sample was dissolved ~10 mL of cyclohexane containing ~0.1 mL of THF at 36 °C. Upon cooling to room temperature, the high molar mass fraction, ~20 mg, precipitated and was removed by centrifugation. The major fraction, ~50 mg, was induced to precipitate by adding another 10 mL of cyclohexane to the supernatant. It was fraction 2 of 1640-182 micelles that was used in all physical studies unless otherwise specified.

Micelle Characterization. Micelles were cross-linked before any physical studies were performed. Transmission electron microscopy (TEM) was used to identify the morphology of the cross-linked micelles. Light scattering done in toluene was used to determine their hydrodynamic radii, the radii of gyration, and the weight-average molar masses. GPC using THF as the eluant was used to estimate the size distribution of the cross-linked star micelles with relatively low molar masses.

TEM specimen were prepared by spraying dilute cyclopentane solutions of the cross-linked micelles onto carbon-coated copper grids.[23] Or one drop of a micelle solution was dispensed on water surface first to allow micelle film formation after solvent evaporation. The micellar particle film was then transferred onto a carbon-coated copper grid. The specimen were stained by OsO_4 vapor overnight before viewing by TEM.

Star polymers, except that from 1640-182, were fractionated by GPC to remove the unimers. We did not attempt the separation of 1640-182 and cylindrical micelles from their unimers, because cylindrical micelles were not eluted out of the GPC columns, and the 1640-182 micelles were not resolved from their unimers.

All light scattering measurements were carried out in toluene at room temperature. For samples with R_G below 30 nm, dust was removed by filtration through 0.40-μm filters. The scattering angles used were between 20 and 150°. For samples with R_G above 30 nm, their toluene solutions were centrifuged at 4.5×10^3 rpm for 10 min, and the supernatant was then used for light scattering analysis. The scattering angles used for these samples were all below 90°.

Solutions at the concentration typically ~0.3 mg/mL were used for dynamic light scattering measurement. Dynamic light scattering data were analyzed following the method of cumulants.[37] The logarithm of the first-order electric field correlation function, $g^{(1)}(\tau)$, was fitted using

$$\ln g^{(1)}(\tau) = 1 - K_1\tau + {}^1/_2 K_2\tau^2 + ... \tag{3}$$

where K_1 is related to the z-average diffusion coefficient $\langle D\rangle_z$ by

$$K_1 = q^2\langle D\rangle_z \tag{4}$$

In eq 4, q is the scattering wave vector with its magnitude given by

$$q = \frac{4\pi n_0 \sin(\theta/2)}{\lambda_0} \tag{5}$$

where θ is the scattering angle, n_0 the refractive index of toluene, and λ_0 the wavelength of the laser beam at 632.8 nm. The z-average hydrodynamic radius, R_h, was obtained for each sample at at least three angles using

$$R_h = \frac{kT}{6\pi\eta\langle D\rangle_z} \tag{6}$$

with η being the viscosity of toluene, i.e. 0.59 cP, at 20 °C,[36] and kT being the thermal energy.

Table 1. Characterization of Polymers

laboratory code	(n/m) by NMR	$\bar{M}_w/\bar{M}_n$ by GPC	$10^{-4}\bar{M}_w$ by GPC	$10^{-4}\bar{M}_w{}^*$ by LS	$10^{-2}n$	$10^{-2}m$
813-59	13.8	1.17	9.6	10.0	8.1	0.59
267-22	12.0	1.10	2.9	3.4	2.7	0.22
342-34	10.1	1.14	3.8	4.4	3.4	0.34
122-12	9.9	1.13	1.5	1.6	1.22	0.12
204-22	9.6	1.09	2.5	2.7	2.04	0.22
1640-182	9.0	1.10	21.8	21.8	16.4	1.82
309-38	8.2	1.10	3.3	4.2	3.1	0.38
1209-152	7.9	1.10	14.8	16.5	12.1	1.52
750-107	7.0	1.12	10.0	10.6	7.5	1.07

An indication of the width of the size distribution of the micelles is obtained from

$$PD = K_2/K_1^{\,2} \tag{7}$$

where K_2 is the second-order cumulant obtainable from eq 3.

III. Results and Discussion

Polymer Characterization. All polymer samples had narrow molecular weight distributions as indicated by their low polydispersity indices (Table 1) determined by GPC. Since the GPC column was calibrated using monodisperse PS standards, the weight-average molar masses of the diblocks were included in Table 1 only to double check the light scattering results.

The specific refractive index increments, ν, of the diblocks in toluene at 632 nm were calculated from an empirical expression established before[31]

$$\nu = 0.0938 + 0.0299w_{PS} - 0.0115w_{PS}^{\;2} \text{ mL/g} \tag{8}$$

where w_{PS} is the weight fraction of PS in a diblock. Light scattering determination of the apparent molar masses, $\bar{M}_w{}^*$, of the polymers made use of

$$Kc/\Delta R_\theta = (1/\bar{M}_w{}^*)[1 + (R_G q)^2/3] + 2A_2c \tag{9}$$

where K was the optical constant of the system, c was the polymer concentration, A_2 the second virial coefficient, and ΔR_θ the Rayleigh ratio. The $\bar{M}_w{}^*$ values were obtained from the $Kc/\Delta R_\theta$ values by extrapolating to zero c and θ using a software provided by Brookhaven Instruments following the Zimm method. Since the molecular weight determination of the diblocks was straightforward, a Zimm plot was not shown here. Instead, a Zimm plot will be shown for the data of a star polymer later on.

The apparent molar masses, $\bar{M}_w{}^*$, determined from the Zimm plot should be further corrected, as eq 9 is applicable to homopolymers only. This diblock correction was not done as we believed that the correction should be small due to the facts that the ν values for PS and PCEMA, being 0.094 and 0.112 mL/g, were very close and that the n/m values should not vary much for the same sample from chain to chain.[38] Using n/m values determined from NMR and $\bar{M}_w{}^*$ from LS, the weight-average n and m values were calculated and are presented in Table 1.

TEM Characterization of Cross-Linked Micelles. TEM analysis was done for all the samples. The results showed that only five of the nine samples, with $n/m \geq 9.6$ (Table 2), formed pure spherical micelles. Illustrated in Figure 1 is a TEM image of the 813-59 star polymer. As the sample was prepared using the spraying method, individual micelles are observed. These are clearly star polymers with a small dark PCEMA core surrounded by a gray PS shell.

Table 2. Characterization of Cross-Linked PS-*b*-PCEMA Micelles

laboratory code	$10^{-6}\bar{M}_w$ by LS	f	R_G^*/nm S	R_C/nm^c	R_h/nm DLS	K_2/K_1^2 from DLS	$10^{-6}\bar{M}_w$ (g/mol) GPC	$\bar{M}_w/\bar{M}_n$ from GPC
				Star Micelles				
813-59	9.7	97	37.0	8.4	50	0.07	1.46	1.16
267-22[a]	1.76	52	14.0	4.9	19.3	0.04	0.62	1.20
342-34	3.1	70	20.3	6.2	24.7	0.04	1.09	1.13
122-12[a]	0.71	44	9.0	3.9	12.9	0.07	0.29	1.13
204-22[a]	1.40	52	12.3	4.9	17.8	0.06	0.53	1.18
1640-182	99[b]	4.5×10^2	75	20	101	0.06		
				Cylindrical Micelles				
309-38	5.0	118	31		27.0	0.05		
1209-152	134	7.8×10^2	131		107	0.10		
750-107	124	1.13×10^3	116		95	0.10		

[a] Significant errors in these R_G values are expected, as the $Kc/\Delta R_\theta$ values did not vary much with $\sin^2(\theta/2)$. [b] $\bar{M}_w$ determined by light scattering was divided by 1.21, and the correction factor was derived from the presence of cylindrical micelles. The f and R_G values were calculated based on the corrected $\bar{M}_w$ value. [c] Core radius of dry micelles.

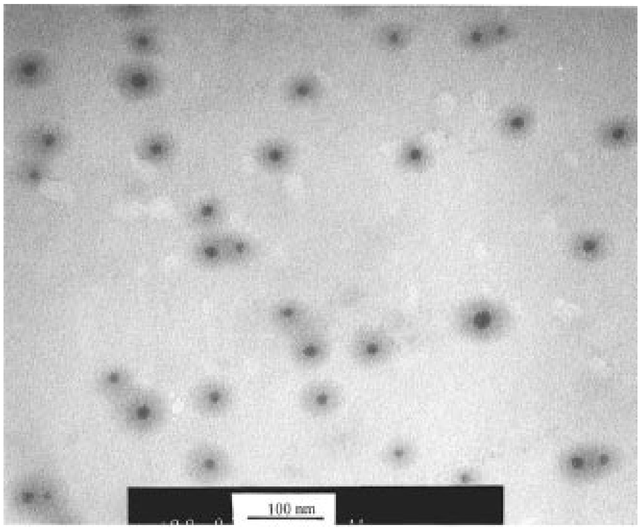


Figure 1. TEM image of cross-linked 813-59 micelles.

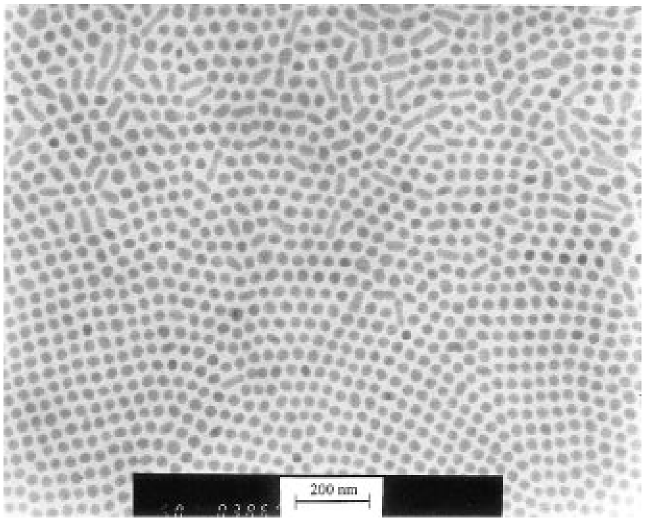


Figure 2. TEM image of cross-linked 1640-182 micelles.

The sample 1640-182 with $n/m \geq 9.0$ formed star micelles containing a small fraction of short cylinders. Illustrated in Figure 2 is a TEM image of cross-linked 1640-182 micelles.

For 309-38 with $n/m = 8.2$, the major component was still star micelles but the few cylinders observed were long with aspect ratios upto 50. Long and large quantities of cylinders were found in 1209-152 and 750-107 micelles. A TEM image showing the morphologies of 750-107 micelles is illustrated in Figure 3.

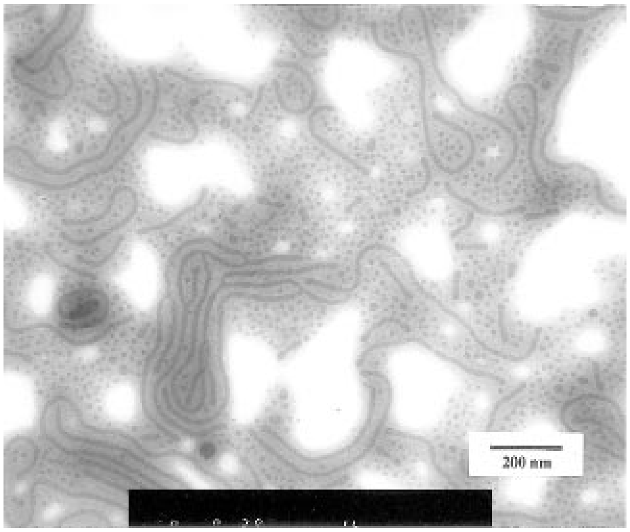


Figure 3. TEM image of cross-linked 750-107 micelles.

Static Light Scattering Characterization of Micelles. The molar masses, $\bar{M}_w$, and radii of gyration, R_G, of all cross-linked micelles were determined from static light scattering in toluene and the results are summarized in Table 2. Cyclopentane was not used as the solvent, because the highest purity of cyclopentane we could purchase still contained 5% of other hydrocarbons and the use of a mixed solvent for determining the molar mass of a polymer requires the troublesome dialysis of a solution against the solvent mixture. Furthermore, we have so far determined the specific refractive index increments of PS-*b*-PCEMA in toluene only.

Illustrated in Figure 4 is the Zimm plot for the 1640-182 star polymer. In calculating $\bar{M}_w^*$ of diblock micelles, their ν values were assumed to be approximately the same as their precursor diblocks, an assumption verified previously.[33] The molar masses determined from the Zimm method were the apparent values, but we did not carry out the further diblock correction of these values for reasons explained before.

For testing scaling relations, the molar masses of the star micelles should be obtained. Cross-linked micelles of 1640-182 consisted mainly of star polymer with a small fraction of cylinders. The population of the cylinders can be estimated from a TEM image by particle counting. We counted a total of 1400 particles in Figure 2, with 1309 being star micelles, 88 doublets, 2 triplets, and 1 quadruplet. By a quadruplet, we refer to a cylinder whose length was ~4 time the diameter of a star micelle. Similarly, doublets and triplets are

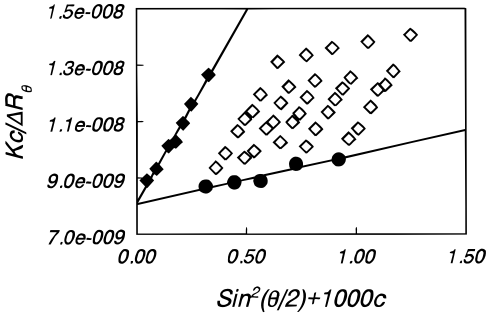


Figure 4. Plot of $Kc/\Delta R_\theta$ vs $\sin^2(\theta/2)$ (◆) and c (●) for cross-linked 1640-182 micelles in toluene. The scattering angles used were 25, 35, 45, 50, 55, 60, and 70°. The concentrations used were 0.92×10^{-3}, 0.73×10^{-3}, 0.56×10^{-3}, 0.45×10^{-3}, and 0.315×10^{-3} g/mL, respectively.

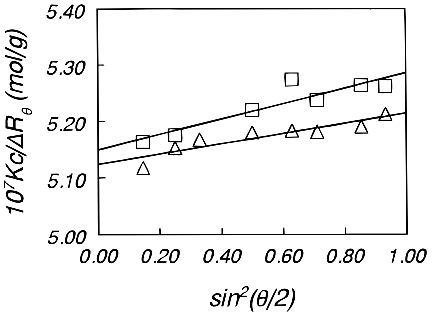


Figure 5. Plot of $Kc/\Delta R_\theta$ vs $\sin^2(\theta/2)$ for cross-linked, (△), and uncross-linked, (□), 267-22 micelles at 0.355 mg/mL in cyclohexane.

cylinders with aspect ratios approximately equal to 2 and 3, respectively. According to the definition of weight-average molar mass, the observed molar masses of 1640-182 micelles, $\bar{M}_w$*, should be related to the molar masses of the star micelles, $\bar{M}_w$, by

$$\bar{M}_w^* = \frac{\sum_{i=1}^{4} l_i (i\bar{M}_w)^2}{\sum_{i=1}^{4} l_i (i\bar{M}_w)} \qquad (10)$$

where the upper summation index of 4 stands for the largest aspect ratio of a cylinder observed; l_i are the number of particles counted for a particular type of micelles with an aspect ratio of i. Using eq 10 and the particle set shown in Figure 2, we obtained

$$\bar{M}_w^* = 1.21\bar{M}_w \qquad (11)$$

for 1640-182 micelles. The value shown in Table 2 is the $\bar{M}_w$ value for the 1640-182 star micelles. Due to the limited number of particles counted and some arbitrariness involved in classifying the cylinders into different multiplets, eq 10 is approximate but definitely represents an improvement over the direct use of $\bar{M}_w$* for the molar mass of the 1640-182 micelles. As for the coefficient of 1.21 in eq 11, we expect the error to be within ±10%, as we obtained an value of 1.25 for another set of samples.

Micelle Structure "Lock in" by Photocross-Linking. The f values of cross-linked star micelles are assumed to be the same as those of the uncross-linked ones originally stable in cyclopentane, and these values are used to test scaling relations. The validity of the assumption that the photocross-linking of the PCEMA block only "locked in" the structure of micelles and did not change their aggregation numbers, f, can be appreciated from the following considerations.

In a previous paper describing the preparation of star polymers and nanospheres from PS-*b*-PCEMA with large and small n/m, we reported that the phase separation between PCEMA core and PS shell was sharp and the photocross-linking reaction was selective.[33] We also showed that the hydrodynamic radius of micelles of a sample before and after photocross-linking was, within experimental error, constant. In this study, we showed that f did not change with photocross-linking by carrying out static light scattering study of 267-22 in cyclohexane before and after UV irradiation. Cyclohexane instead of cyclopentane was used here again because cyclopentane was not pure enough for light scattering measurement.

Plotted in Figure 5 are the $Kc/\Delta R_\theta$ values, for cross-linked (unimers not removed) and uncross-linked 267-22 micelles at an equal concentration, c, of 0.355 mg/mL, vs $\sin^2(\theta/2)$. Extrapolating to zero θ, we obtained the $1/\bar{M}_w + 2A_2c$ values of $5.1_3 \times 10^{-7}$ and $5.1_5 \times 10^{-7}$ g/mol for cross-linked and uncross-linked 267-22 micelles, respectively, where c stands for polymer (unimer and micelle mixture) concentration and A_2 denotes the second virial coefficient. If neglecting the $2A_2c$ term due to the low polymer concentration used, we obtained the apparent molar masses of 1.95×10^6 and 1.94×10^6 g/mol for cross-linked and uncross-linked 267-22 micelles. These values are, within experimental error, the same and suggest the validity of our assumption that PCEMA cross-linking did not change the aggregation number of PS-*b*-PCEMA micelles.

Aggregation Numbers. The aggregation numbers f of micelles were calculated by ratioing the molar masses of micelles to those of the diblocks (Table 2). Correlating f with n and m to obtain the accurate α and β values as defined in eq 1 would have required more data points. We tried to see what α would be if β was assumed to be zero as predicted by de Gennes,[6] Zhulina and Birshtein,[7] Halperin,[8] and Noolandi and Hong.[9] Illustrated in Figure 6 is the ln f-vs-ln m plot for the six star polymers. Linear regression analysis yielded

$$\ln f = 1.14 + 0.92 \ln m \qquad (12)$$

with a correlation coefficient of 0.975. The slope of 0.92 is in good agreement with the value of 0.90 derived by Noolandi and Hong[9] and is between 0.80 and 1.00 as predicted by Halperin[8] and de Gennes.[6]

We also attempted the fitting of the f data by

$$f = a_0 + a_1 m^{\alpha} n^{\beta} \qquad (13)$$

with exponents α and β defined by various theories. When choosing the α and β values for the Nagarajan and Ganesh theory,[10] we recognized that some arbitrariness was involved, as cyclopentane at 50 °C was between an athermal (good) and a Θ solvent for PS.

The a_0 and a_1 values generated from such fittings together with the correlation coefficients R_{val} are shown in Table 3. It is obvious that all theories could be used to explain the data. Judged from the expectation that $a_0 = 1$ as $m \rightarrow 0$, the theory of de Gennes[6] seems to explain the data the best. This assertion, however, needs to be confirmed by more experimental data covering a wider range of m values.

Scaling Relation for R_c. Since the weight fraction, w_{PCEMA}, of PCEMA in PS-*b*-PCEMA is known from

Table 3. Parameters Generated from Fitting f and R_c Values with Different Theoretical Relations

model	a_0	a_1	R_{val}
f Data			
de Gennes: $\alpha = 1, \beta = 0$	−8.0	2.5	0.991
Noolandi & Hong: $\alpha = 0.90, \beta = 0$	−23	4.2	0.987
Halperin: $\alpha = 0.80, \beta = 0$	−74	7.6	0.948
Nagarajan & Ganesh: $\alpha = 1.19, \beta = -0.51$	−61	45	0.990
R_c Data			
de Gennes: $\gamma = 2/3, \lambda = 0$	−0.11	0.63	0.995
Noolandi & Hong: $\gamma = 0.64, \lambda = 0$	−0.47	0.73	0.994
Halperin: $\alpha = 3/5, \lambda = 0$	−1.1	0.93	0.993
Nagarajan & Ganesh: $\gamma = 0.73, \lambda = -0.17$	−1.6	1.71	0.995

NMR measurements, we calculated the core radius of dry PS-*b*-PCEMA star micelles using the following relation by assuming the density of 1.0 g/mL for PCEMA

$$R_c = \left(\frac{3\bar{M}_w w_{PCEMA}}{4\pi N_A}\right)^{1/3} \tag{14}$$

where N_A is Avogardro's number. The R_c values calculated were shown in Table 2. The calculated R_c values of 813-59 and 1640-182 star micelles are in good agreement with those estimated from Figures 1 and 2. The TEM R_c values were not used for testing the scaling relations, as the error involved with measuring the radius of the small cores by a ruler would have been large.

When in cyclopentane, the core might be slightly swollen by the solvent and the core radius might increase by a factor φ. We assume the same expansion factor, φ, for all micellar cores. According to eq 2 and assuming $\lambda = 0$, plotting either $\ln(\varphi R_c)$ or $\ln R_c$ vs $\ln m$ should generate the same slope γ. We thus plotted $\ln R_c$ vs $\ln m$ (Figure 6), yielding

$$\ln(R_c/\text{nm}) = -0.31 + 0.63 \ln m \tag{15}$$

with a correlation coefficient of 0.994. The γ value of 0.63 is in good agreement with 0.64, the value predicted by Noolandi and Hong[9] and is between 0.60 and $^2/_3$, the values predicted by Halperin[8] and de Gennes.[6]

We also attempted the fitting of the R_c data by

$$R_c = a_0 + a_1 m^{\gamma} n^{\lambda} \tag{16}$$

with exponents α and β defined by various theories. The a_0 and a_1 values generated from such fittings together with the correlation coefficients R_{val} are again shown in Table 3. It is obvious that all theories can be used to explain the data. Judged from the expectation that $a_0 \rightarrow 0$ as $m \rightarrow 0$, the theory of de Gennes explained the data the best. Again, this assertion needs to be confirmed by more experimental data.

Scaling Relation for *L*. Due to the large n/m ratios, our cross-linked micelles are essentially star polymers. The shell thickness L of a star polymer in a good solvent should scale according to[39]

$$L \approx n^{3/5} f^{1/5} \tag{17}$$

where n is the number of styrene units in a diblock.

The shell thickness L was calculated using

$$L = R_h - R_c \tag{18}$$

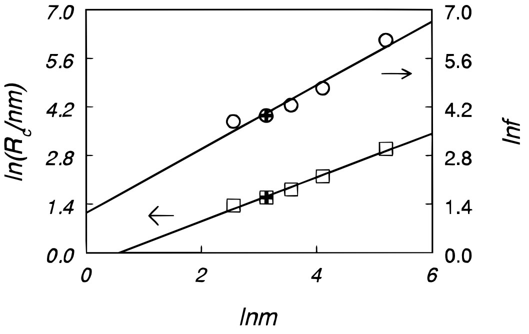


Figure 6. Plot of $\ln(R_c/nm)$ (□) and $\ln f$ (○) vs $\ln m$ for the star micelles. Since the data points of 267-22 micelles coincide with those of 204-22 micelles, the + signs are used to represent the data of 267-22 micelles.

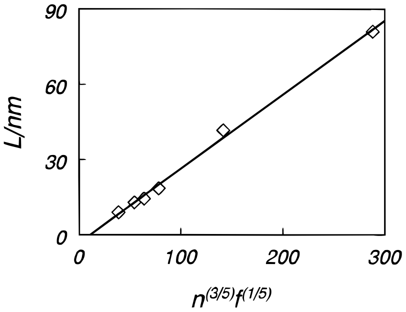


Figure 7. Plot of L vs $n^{3/5}/f^{1/5}$ for the star polymers.

where R_h was the hydrodynamic radius of micelles determined from dynamic light scattering, and R_c the core radius of the dry micelles. In toluene, the micellar cores should be swollen, the use of R_c in eq 18 to calculate L thus represented an approximation. However, we expected the error introduced by the use of eq 18 to be small. This was true first because the error in using R_c to approximate the core radius in toluene should be relatively small, e.g. within 50%, as the cross-linking density of PCEMA was high, i.e. ~40%. Then, the L values were much larger than R_c. A 50% error in the R_c value only meant a 10% error in the L value.

Plotted in Figure 7 are L vs $n^{3/5}f^{1/5}$ for our star polymers. Linear regression analysis yielded

$$L/nm = -3.3 + 0.30 n^{3/5} f^{1/5} \tag{19}$$

with a correlation coefficient of 0.998. Considering that 1640-182 star polymer had 4.5×10^2 arms, this probably represented the first test of scaling relation 17 over such a large f range.

Characterization of Cross-Linked PS-*b*-PCEMA Star Micelles by GPC. Star micelles of all samples but 1640-182 were analyzed by GPC to see their size distributions and PS-equivalent molar masses. The GPC molar masses should, however, not be overinterpreted, as it was long recognized that the true molar masses of micelles should be significantly higher than those determined by GPC due to the much higher average segmental density inside a micelle than that in a polymer coil. The low polydispersity indices, $\bar{M}_w/\bar{M}_n$, suggest that our micelles had narrow size distributions.

Formation of Wormlike Micelles. Wormlike micelle formation in block-selective solvents from block copolymers has been reported on several occasions.[18−22] Only on two occasions[19,22] have these structures been verified with electron microscopy. In other cases, cylindrical structures were deduced only from light scattering results. Zhang and Eisenberg's results[22] suggest that a diblock copolymer in water may have most of the morphologies it has in the solid state by changing the relative lengths of the two blocks. In the solid state, the two blocks of a diblock copolymer normally segregate into different phases, due to their incompatibility. The domain structures of a $(A)_n-(B)_m$ diblock vary depending on the relative composition of the two diblocks.[40] At a volume fraction below roughly 17% for the B block, it will exist as spheres dispersed in the continuous A phase. As the B content is gradually increased to 60% by volume, the B domain successively changes its shape from spheres to cylinders, double diamonds, and lamella. Zhang and Eisernberg found spherical, cylindrical, vesicle micelle formation in water from polystyrene-*block*-poly(acrylic acid) as the PS or the insoluble block content was increased. The spherical, cylindrical, vesicle micelles corresponded to spherical, cylindrical, and lamellar phases in the bulk state.

Our results confirm the trend observed by Zhang and Eisenberg,[22] i.e. that cylindrical micelles formed at a higher insoluble block content than spherical micelles did. The n/m range over which cylindrical micelles formed coincided with that over which cylindrical phases formed from PCEMA in bulk.[34] In bulk, 1209-152 and 750-107 were previously shown to form cylindrical domains of PCEMA dispersed in the continuous matrix of PS. Irradiation of thin films of 1209-152 and 750-107 and the subsequent separation of the different cylindrical domains by solvent enabled us to prepare nanofibers.[34] This study shows that nanofibers can be prepared in the solution phase as well.

Since cylindrical micelle formation in cyclopentane and PCEMA cylindrical phase formation in the bulk occurred in the same n/m range, we checked if the cylindrical micelles in cyclopentane were derived from the separation of different PCEMA cylindrical domains in bulk. The 750-107 micelles were prepared in THF/cyclopentane with 97% by volume of cyclopentane. In this mixture, the micelles of 750-107, as indicated by TEM measurements, were perfectly spherical. The micellar mixture was then extracted with water several time to remove THF. As THF was extracted, the initial bluish micellar solution turned whitish. TEM results showed that spherical to cylindrical micelle transformation accompanied this process. Thus, cylindrical micelles were the thermodynamically stable aggregates of 750-107, and most probably of 1209-152, and 309-38 as well in cyclopentane.

R_h/R_G for Different Samples. For perfect homogenous spherical particles, R_h/R_G should be 1.29. Diblock copolymer micelles possess core-shell structures and are inherently not homogeneous. Despite this, R_h/R_G are all ∼1.29 for the six samples with $n/m \geq 9.0$. This ratio decreased to 0.87 for 309-38 micelles and ∼0.80 for 1209-152 and 750-107 micelles. For cylinders[18]

$$R_G/R_h = \frac{1}{\sqrt{3}}[\ln(L_c/d) + 0.38] \qquad (20)$$

where L_c and d are the length and diameter of the cylinders, respectively. That R_h/R_G decreased with the increasing aspect ratio of micelles as confirmed by TEM results was thus expected.

Effect of Fractionation Precipitation of the 1640-182 Star Polymer. Star polymer of 1640-182 was purified by fractionation precipitation. In this subsection, the properties of the sample before and after fractionation will be compared so that a confidence level can be established for this purification procedure.

Before fractionation, the sample had a K_2/K_1 value of 0.06, suggesting that this sample was monodisperse already. The R_h, R_G, and $\bar{M}_w$ (before correction by eq 11) determined for the sample were 100 nm, 100 nm, and 1.16×10^8 g/mol, respectively. These values changed to 101 nm, 75 nm, and 1.20×10^8 g/mol after fractionation. Thus, fractionation barely changed the molar mass of the system. Since R_h/R_G increased significantly with this fractionation treatment, this suggests that the fractionation was effective in removing a small amount of long cylindrical micelles in the original system.

V. Conclusion

TEM results have shown that PS-*b*-PCEMA with low polydispersity indices and $n/m \geq 9.0$ formed star micelles in cyclopentane with PCEMA as the core. Long cylinders were found in micellar samples of diblocks with n/m between 7.0 and 8.2. The TEM results were confirmed by the measured R_h/R_G values for the micelle samples.

The structure of the star and cylindrical micelles could be locked in by photocross-linking the PCEMA block of the micelles to produce star polymers and nanofibers. This represents the first preparation of cross-linked block copolymer cylindrical micelles or nanofibers in the solution phase. While the preparation of star polymers from cross-linkable diblock copolymers has been reported,[33] this work shows the robustness of this method in producing star polymers with as many as 4.5×10^2 arms and a molar mass of 9.9×10^7 g/mol.

Since the photocross-linking did not perturb the aggregation numbers, we have extrapolated the aggregation numbers of the star micelles in cyclopentane from those of the star polymers determined in toluene. The aggregation numbers and the core radii of the star micelles could be explained by existing theoretical scaling relations. We also obtained the shell thicknesses of the star polymers and showed that they obeyed eq 17 derived by Daoud and Cotton.[39] For differentiating different scaling relations, another systematic study with more samples covering a larger m range would be required.

Acknowledgment. The authors are grateful to NSERC of Canada for financially sponsoring this research. The TEM images were obtained by Dr. J. Ding and two of the polymers used here were synthesized by Dr. A. Guo for another project. Contributions made by them are also cordially acknowledged.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surf. Colloid. Sci.* **1993**, *15*, 1.

(2) For papers dealing with the effect of temperaure and solvent composition change on micelle formation, see, for example: (a) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. Macrmolecules 1996, 29, 220. (b) Quintana, J. R.; Janez, M. D.; Villacampa, M.; Katime, I. *Macromolecules* **1995**, *28*, 4139. (c) Zhou, Z.; Chu, B.; Peiffer, D. G. *Macromolecules* **1993**, *26*, 1876. (d) Zhou, Z.; Chu, B.; Peiffer, D. G. *Langmuir* **1995**, *11*, 1956. (e) Siqueira, D. F.; Nunes, Wolf, B. A. *Macromolecules* **1994**, *27*, 4561. (f) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975. (g) Ünal, H. I.; Price, C.; Budd, P. M.; Mobbs, R. H. *Eur. Polym. J.* **1994**, *30*, 1037. (f) Astafieva, I.; Khougaz, K.; Eisenberg, A. *Macromolecules* **1995**, *28*, 7127.

(3) For papers examining the polarity and structures of micellar cores, see, for example: (a) Prochazka, K.; Martin, T.; Munk, P.; Webber, S. E. *Macromolecules* **1996**, *29*, 6518. (b) Kiserow,

D.; Prochazka, K.; Radireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 461.
(4) For papers examining chain stretching in micelles, see, for example: Cogan, K. A.; Gast, A. P.; Capel, M. *Macromolecules* **1991**, *24*, 6512.
(5) For papers examining micelle dynamics, see, for example: (a) Smith, C. K.; Liu, G. *Macromolecules* **1996**, *29*, 2060. (b) Wang, Y.; Kausch, C. M.; Chu, M.; Quirk, R. P.; Mattice, W. L. *Macromolecules* **1995**, *28*, 904. (c) Procházka, K.; Bednár, B.; Mukhtar, E.; Svoboda, P.; Trnëná, J.; Almgren, M. *J. Phys. Chem.* **1991**, *95*, 4563.
(6) de Gennes, P. G. In *Solid State Physics, Supplement 14*: Liebert, J., Ed.; Academic Press: New York, 1978.
(7) Zhulina, E. B.; Birshtein, T. M. *Vysokomol. Soedin* **1985**, *27*, 511.
(8) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(9) Noolandi, J.; Hong, M. H. *Macromolecules* **1983**, *16*, 1443.
(10) Nagarajan, R.; Ganesh, K. *J. Chem. Phys.* **1989**, *90*, 5843.
(11) Liebler, L.; Orland, H.; Whjeeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(12) Whitmore, D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(13) Meier, D. J. *J. Polym Sci.: Part C* **1969**, *26*, 81.
(14) Bluhm, T. L.; Whitmore, M. D. *Can. J. Chem.* **1985**, *63*, 249.
(15) Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.
(16) McConnell, G. A.; Gast, A. P.; Huang, J. S.; Smith, S. D. *Phys. Rev. Lett* **1993**, *71*, 2102.
(17) Bahadur, P.; Sastry, N. V.; Marti, S.; Riess, G. *Colloid Surf.* **1985**, *16*, 337.
(18) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(19) (a) Price, C.; Chan, E. K. M.; Hudd, A. L.; Stubbersfield, R. B. *Polym. Commun.* **1986**, *27*, 196. (b) Price, P. *Pure Appl. Chem.* **1983**, *55*, 1563.
(20) Utiyama, H.; Takenaka, K.; Mizumori, M.; Fukuda, M.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1974**, *7*, 515.
(21) Zhou, Z.; Chu, B. *Macromolecules* **1988**, *21*, 2548.
(22) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(23) Ding, J.; Liu, G. *Macromolecules*, in press.
(24) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z. *Macromolecules* **1994**, *27*, 120.
(25) Zhang, L.; Barlow, R. J.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6055.
(26) Zhong, X. F.; Varshney, S. K.; Eisenberg, A. *Macromolecules* **1992**, *25*, 7160.
(27) Khougaz, K.; Astafieva, I.; Eisenberg, A. *Macromolecules* **1995**, *28*, 7135.
(28) Dan, N.; Tirrell, M. *Macromolecules* **1993**, *26*, 4310.
(29) Liu, G.; Hu, N.; Xu, X.; Yao, H. *Macromolecules* **1994**, *27*, 3892−3895.
(30) Hu, N.; Liu, G. *J. Macromol. Sci.—Pure Applied Chem.* **1995**, *A32*, 949.
(31) Tao, J.; Guo, A.; Liu, G. *Macromolecules* **1996**, *29*, 1618.
(32) Ding, J.; Tao, J.; Guo, A.; Stewart, S.; Hu, N.; Liu, G. *Macromolecules* **1996**, *29*, 5398.
(33) Guo, A.; Tao, J.; Liu, G. *Macromolecules* **1996**, *29*, 2487.
(34) Liu, G.; Qiao, L.; Guo, A. *Macromolecules* **1996**, *29*, 5508.
(35) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. *Macromolecules* **1996**, *29*, 220.
(36) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989.
(37) Koppel, D. E. *J. Chem. Phys.* 1972, 57, 4814.
(38) Benoit, H.; Froelich, D. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: London, 1972.
(39) Daoud, M.; Cotton, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 531.
(40) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

MA9612788