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Star Polymers and Nanospheres from Cross-Linkable Diblock Copolymers

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ABSTRACT: Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) formed micelles in THF/cyclohexane or chloroform/cyclohexane mixtures with the PCEMA block as the core. Depending on the relative length of the PS and PCEMA block, star and crewcut micelles were prepared. Upon UV irradiation, the PCEMA block selectively cross-linked to form star polymers and nanospheres from the corresponding star and crewcut micelles. The cross-linked micelles were characterized by solution and solid-state NMR, FTIR, GPC, TEM, and dynamic and static light scattering.

I. Introduction

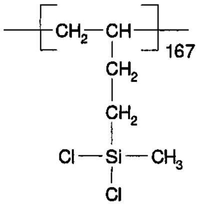
Star polymers are macromolecules consisting of more than three linear polymer chains of approximately equal lengths joined together at one end of each chain to a chemically-bonded core.[1] In a star polymer, the core radius should be much smaller than the dimension, e.g. the root-mean-square end-to-end distance, of the individual chains or arms. If the core size is much larger, such an entity is called a "nanoparticle", as its property will be dominated by the cross-linked nanometer-sized core. If the nanoparticles are approximately spherical in shape, they are referred to as "nanospheres".

Star polymers and nanospheres may have important industrial applications. Star polymers, possessing better processibility than their linear counterparts, have, for example, been used as melt strength improvers.[2] Star polymers may also self-assemble into unique morphologies such as the honeycomb morphology, as observed recently.[3] Nanospheres as defined here, resembling dendrimers, may be useful as drug carrying reagents in controlled drug release[4,5] or as support for industrial catalysts.[6]

Star polymers[1] and star and crewcut micelles[7,8] have attracted much attention in the past. The study of star and crewcut micelles has led to the establishment of scaling relations between their radius and molecular parameters such as the number of segments in each chain.[9−11] Research in star polymers has included the theoretical and experimental establishment of the relation between the mean-square radius of gyration of a star polymer and that of a linear polymer of the same molar mass.[1,12,13]

Three methods have been traditionally used for preparing star polymers. The earliest method used multifunctional small molecules to terminate either living anionic or cationic polymerization.[1] Silicon tetrachloride $SiCl_4$ can, for example, be used to terminate the living anionic polymerization of styrene to produce a star polymer with four arms, i.e. $f = 4$. Using this method, star polymers with 18 arms have been synthesized.[14] The main limitation with this method has been in the synthetic difficulty facing the preparation of star polymers with more arms. Recently, star polymers with 280 arms have been claimed to be prepared using this method.[12] In that case, perhydrosilylated poly(1,2-butadiene) was used to terminate the anionic polymerization of butadiene. When 280 arms are attached to a perhydrosilylated chain, the chain would definitely be stretched to avoid crowding of the PB arms. Since the PB arms were not much longer than the perhydrosilylated PB chain, one could hardly call such a polymer a star polymer, as it would have resembled more closely a grafted polymer.

Figure 1. Star polymer and a nanosphere.



$$-\!\!\left[CH_2-\underset{\underset{\underset{\underset{\underset{Cl}{|}}{Cl-\overset{|}{Si}-CH_3}}{CH_2}}{|\;CH_2}}{|}}{CH}\right]_{167}\!\!-$$

In the second method, a difunctional monomer such as divinylbenzene is used to terminate the living anionic or cationic polymerization of a monofunctional monomer such as styrene.[1,15] The difunctional monomer cross-links to form a tightly bound core with the polymerized monofunctional monomer as the arms, if the concentration of the difunctional monomer is 2−5 times that of the initiator. The main disadvantage with this technique is the large polydispersity in the f distribution of the final star polymer.

The third method is a variation on the second. Instead of adding a difunctional monomer after a monofunctional monomer is polymerized, a difunctional monomer is cross-linked first to form cross-linked microparticles by living polymerization. The living anionic or cationic centers in the microparticles are then used to polymerize a monofunctional monomer.[1] The drawback for this technique again lies with the wide f distribution.

Other than the above methods, Long et al.[16] attempted the synthesis of star polymers by the hydrolysis and condensation of trialkoxysilyl-terminated PS oligo-

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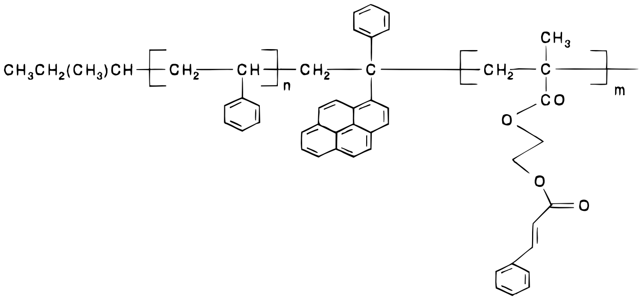
mers. This method was not successful, as the reaction led to insoluble products.

Nanospheres as defined here are similar in structure to microgels. Microgels, i.e cross-linked particles of the nanometer scale, have been traditionally prepared by microemulsion polymerization.[17] Microgels can also be prepared by controlling the degree of copolymerization of a mixture of mono- and difunctional monomers.[18] This approach is less desirable, as one normally ends up with a mixture of microgels, linear polymer chains, and gelled polymers.

In our approach, a diblock copolymer with a photo-cross-linkable block was used as the starting material. Depending on the relative length of the core and the corona blocks, star (hairy) and crewcut micelles were prepared with the cross-linkable block as the core.[7] Upon cross-linking the core, star and nanospheres were then produced from the corresponding hairy and crewcut micelles.

The diblock copolymers used in this study were polystyrene−pyrene−poly(cinnamoylethyl methacrylate) (PS-*b*-PCEMA):



Polymer I: $n = 276$, $m = 90$.

Polymer II: $n = 302$, $m = 570$.

where PCEMA is the photo-cross-linkable block[19−22] and pyrene was introduced at the junction point of the two blocks to facilitate fluorescence studies of diblock micelles described elsewhere.[23] As polymers I and II were rich in PS and PCEMA, respectively, we hoped that the cross-linked micelles formed from these polymers would approximate star polymers and nanospheres. They are, by no means, strict star polymers and nanospheres, as n/m ratios are neither much larger than 1 or close to zero, where n and m stand for the numbers of styrene and CEMA units in a diblock, respectively. This can, however, be improved later by using diblocks with more extreme n/m values. The primary objective of this research was thus to demonstrate the feasibility of the proposed method.

It should be pointed out that Procházka et al.[24] and Wilson et al.[25] have previously attempted the preparation of cross-linked micelles. They prepared polystyrene-*block*-polybutadiene (PS-*b*-PB) micelles with PB block as the core. Photoinitiators such as benzoyl peroxide were then added to the micellar solution to initiate the photo-cross-linking of the PB block. Their method was unsuccessful, as the resultant micelles became insoluble in organic solvents once the resultant polymer was dried. Furthermore, they never intended the photo-cross-linking of micelles as a synthetic technique but as a method to stabilize micelles for physi−chemical studies. The concept of star polymers and nanospheres was thus not introduced by them in whatever fashion.

II. Experimental Section

The synthesis and characterization of polymers I and II have been described previously.[22] Their properties are summarized in Table 1.

Preparation of Cross-Linked Micelles. Polymer I (0.240 g) was dissolved in 6.0 mL of freshly-distilled THF. To it was then added 54 mL of spectrograde cyclohexane. The micelle solution was refluxed for 4 to 5 h to establish micelle size distribution equilibrium. After the solution was purged with argon for 15 min at room temperature, the solution was irradiated, with light passed through a 260 nm cutoff filter from a 500-W mercury lamp, to cross-link the PCEMA block. Vigorous stirring was rendered by a magnetic stirrer throughout the irradiation process to afford the uniform cross-linking of the micelles. After 80 min, the irradiated sample was precipitated out from an excess amount of methanol, filtered, and dried under reduced pressure as a powder.

Polymer II micelle solutions were prepared by dissolving the polymer (0.24 g) in 18.6 mL of chloroform first and then adding cyclohexane to a volume ratio of 31/69. The micelle solution was stirred at 50 °C for 2 h and then irradiated for 80 min while the temperature was maintained.

Kinetics of Micelle Cross-Linking. For following the cross-linking kinetics of polymer I and II micelles, ~2 mL of sample was taken at a designated irradiation time. Part of the sample was then diluted for absorbance measurement at 274 nm on a Perkin-Elmer photodiode spectrophotometer. For FTIR measurement, ~0.5 mL of the sample was mixed with ~0.2 g of potassium bromide. After solvent evaporation under vacuum, a disk was made from the powdery mixture for measurement on a Mattson FTIR (Model 4030) instrument.

NMR Measurement. Solution ^{1}H NMR measurements were carried out on a Bruker ACE-200 instrument, and solid-state ^{13}C NMR measurements on a Bruker AMX-300 instrument. To compare the proton peak intensity of the PS block of cross-linked polymer I micelles relative to that of un-cross-linked polymer I, solutions of the two samples were prepared under exactly the same conditions, e.g. at equal concentrations and volumes, in $CDCl_3$ containing premixed CH_2Cl_2. The ratio of the PS peak intensity to that of the CH_2Cl_2 was then used to characterize the amount of PS present.

GPC Measurement. All GPC measurements were carried out in THF on a Varian Model 5000 HPLC instrument. Zorbax PSM 300-S and 1000-S columns were used in series and calibrated using monodisperse polystyrene standards (Polymer Laboratories).

Dynamic Light Scattering Measurement. The hydrodynamic radii R_h of micelles were determined, at 21.0 ± 0.5 °C, by photon correlation spectroscopy using an ALV spectrometer equipped with an ALV-5000 full digital correlator (280 channels) over the time range from 10^{-7} to 10^3 s. Both the incident beam, from an Addas Nd-YAG laser with emission at 532 nm, and the scattered beam were polarized vertical to the scattering plane. The typical micelle concentration used was between 0.3 and 1 mg/mL, and the scattering angle θ was between 15 and 45°.

The intensity autocorrelation function was analyzed by inverse Laplace transformation using a program called Contin to obtain the distribution $P(\tau)$ in and the average $\langle\tau\rangle$ of relaxation times τ. τ is related to the relaxation rate Dq^2 by

$$\tau = 1/(Dq^2) \tag{1}$$

where D is the diffusion coefficient of micelles, and q, the magnitude of the scattering vector, is related to the wavelength of the laser beam λ and the refractive index n of the solvent by

$$q = \frac{4\pi n}{\lambda}\sin(\theta/2) \tag{2}$$

At a given D, the hydrodynamic radius R_h was calculated using

$$R_h = \frac{kT}{6\pi\eta D} \tag{3}$$

or

$$R_h = \frac{kTq^2\tau}{6\pi\eta} \quad (4)$$

where kT refers to the thermal energy at temperature T and η is the zero-shear-rate viscosity of the solvent used, which we determined experimentally. The distribution in R_h, $P(R_h)$, was obtained on the basis of $P(R_h) \propto P(\tau)$.

In cases of binary solvent mixtures, n was calculated from the refractive indices n_1 and n_2 of the individual solvents using[26]

$$(1/\rho)(n_r - 1) = (w_1/\rho_1)(n_1 - 1) + (w_2/\rho_2)(n_2 - 1) \quad (5)$$

where w_1 and w_2 are the weight fractions of components 1 and 2, respectively; ρ_1 and ρ_2, their densities. The refractive indices for THF, cyclohexane, and chloroform at 532 nm have been approximated by 1.4050, 1.4266, and 1.4459, their values at the sodium emission line.[27]

Static Light Scattering. The absolute weight-average molar masses and the radii of gyration of cross-linked micelles were determined using a Brookhaven Model 9025 light scattering instrument equipped with a 10-mW helium–neon laser. The solvent used was either toluene or THF and the scattering angles used were between 20 and 150°. The difference in the refractive indices Δn_r of a cross-linked micellar solution and the solvent was determined using a differential refractometer (Precision Instruments Co.) equipped with a band-pass filter centered at 633 nm. The specific refractive index increment ν or dn/dc of cross-linked polymer II micelles was obtained from the intercept when plotting Δn_r versus concentration c.[26]

Transmission Electron Microscopy Measurement. One or two drops of a dilute solution, ~0.5% by wt, of cross-linked polymer I or II micelles in THF was carefully dispensed on the surface of distilled water. Due to the miscibility between THF and water, THF rapidly mixed with water. A thin polymer film was left on the water surface. The film was transferred onto copper grids coated with carbon. After drying under vacuum, the samples were stained by OsO_4 vapor overnight and analyzed on a Hitachi H-7000 instrument operated at 75 000 V.

III. Results and Discussion

Micelle Cross-Linking by the PCEMA Block. Cinnamate derivatives have been widely used in the photolithography industry. Upon irradiation at 274 nm, the aliphatic double bond of two cinnamate groups undergo photodimerization to produce a cyclobutane ring.[28,29] If two cinnamate groups of different chains dimerize, cross-linking takes place.

Under our irradiation conditions, the fact that only the PCEMA block was photoactive was clearly demonstrated by our FTIR results. As irradiation time increased, the absorbances at 1635 and 980 cm^{-1} decreased, Figure 2, relative to the peak at 1165 cm^{-1}. The 1635 and 980 cm^{-1} peaks are characteristic of the aliphatic $-C{=}C-$ stretching and the $=C-H$ out-of-plane bending vibrations of PCEMA,respectively. The absorbance at 1165 cm^{-1} did not decrease, as it is characteristic of the $-CO-O-$ (acetyl oxygen) stretching of the ester groups in PCEMA.[30]

That the PS block was not photoactive has been confirmed by our ^1H NMR studies of the cross-linked polymer I micelles. In $CDCl_3$, a good solvent for both PS and PCEMA, we determined the intensities of the PS peaks, at δ 7.15 (broad, 3H) and δ 6.60 (broad, 2H), of cross-linked polymer I micelles to be the same, within experimental error, as those of an un-cross-linked polymer I sample at an equal concentration.

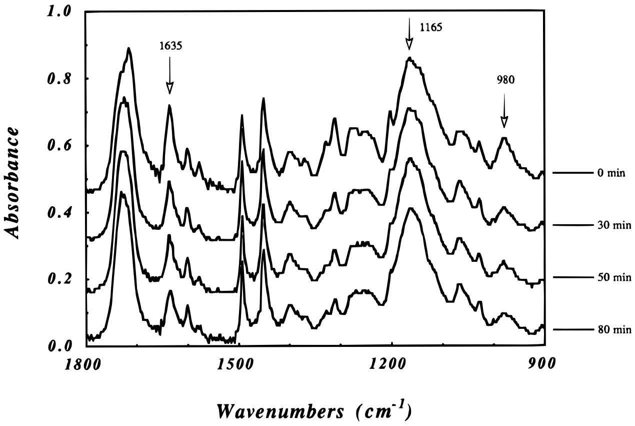


Figure 2. Change in the IR absorption spectrum of polymer I micelles in the 900–1800 cm^{-1} region as a function of irradiation time t.

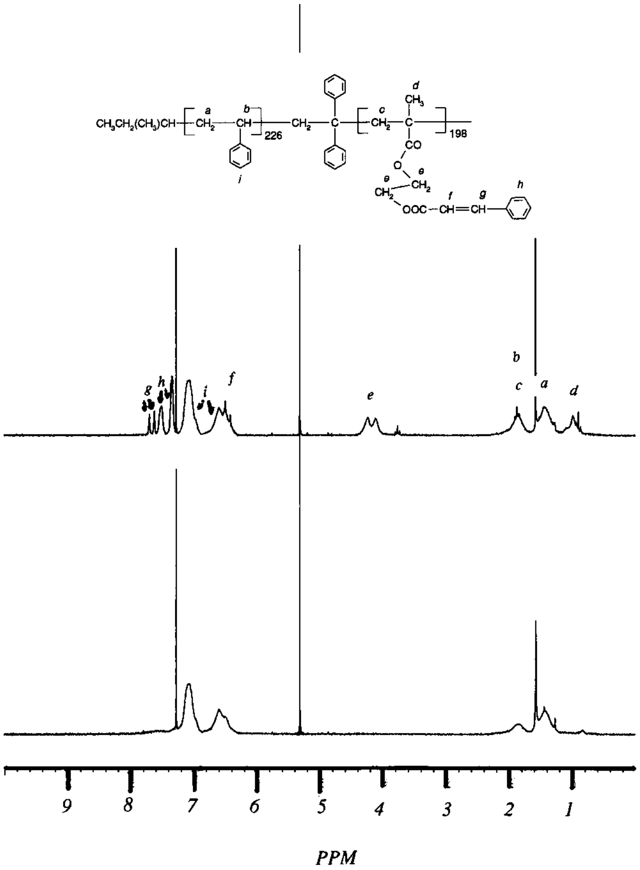


Figure 3. Comparison between the ^1H NMR spectra of polymer I (top) and cross-linked polymer I micelles (bottom) in $CDCl_3$. The PCEMA peaks became weak or invisible in cross-linked polymer I micelles.

Sharp Phase Boundary between the PCEMA Core and the PS Corona. While the PS proton peaks of cross-linked polymer I micelles remained normal in $CDCl_3$, only some of the PCEMA peaks were visible and the visible peaks with very weak, e.g. ~5% of their required intensities (Figure 3). To confirm that the invisible and weak signals were not due to the photodegradation of the PCEMA block, we have obtained the solid-state ^{13}C NMR spectra of polymer I and cross-linked polymer I micelles. The fact that the ^{13}C NMR spectra, Figure 4, of polymer I and cross-linked polymer I micelles are essentially the same suggests that PCEMA did not decompose. In addition, the slight decrease in the intensities of the peaks at 146 and 120 ppm can be well explained by the partial disappearance of the aliphatic double bond carbon atoms of PCEMA.

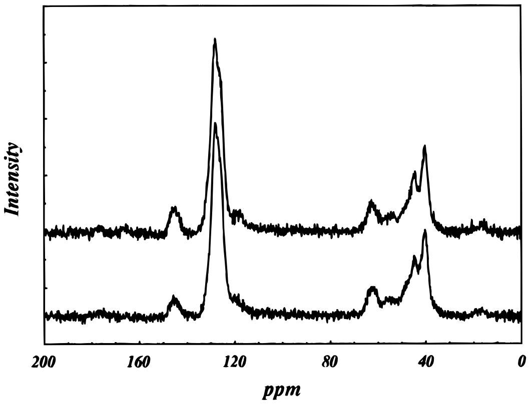


Figure 4. Comparison between the solid-state ^{13}C NMR spectra of polymer I (top) and cross-linked polymer I micelles (bottom).

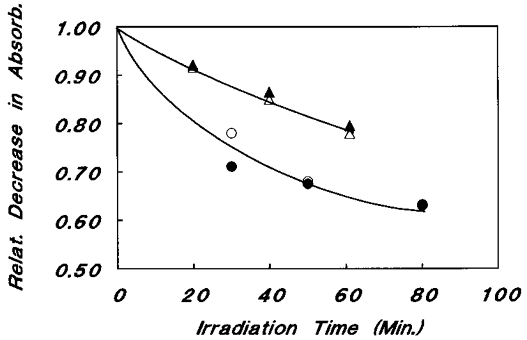


Figure 5. Decrease in $A_{274}(t)/A_{274}(0)$ and $A_{1635}(t)/A_{1165}(t)$ as a function of irradiation time *t*. Circles and triangles represent data obtained for polymers I and II, respectively. Filled triangles and circles represent FTIR data and the rest represent UV data.

Thus, we concluded that the PCEMA ^{1}H peaks are invisible or weak because they were buried in the cross-linked cores of polymer I micelles. In a cross-linked core, the segmental mobility is low and the peaks are excessively broad so as to be very weak or invisible. A similar phenomenon has been observed with the ^{1}H peaks of the core block of un-cross-linked micelles in a block-selective solvent.[31]

The fact that the protons of the PCEMA block in $CDCl_3$ were barely seen suggests that they are almost completely buried in the core. Then, the fact that the protons of PS were almost 100% seen by NMR indicates that PS was exclusively in the corona where the segmental mobility is high. Thus, the phase separation between PS and PCEMA is excellent.

Cross-Linking Kinetics. At 274 nm, we have determined the molar extinction coefficient ϵ of 2.8×10^4 L/(mol·cm) for the CEMA unit in PCEMA, whereas that of the styrene unit in PS is much smaller, i.e. ~700 L/(mol·cm). Since ϵ of the styrene unit is small, the contribution of PS to light absorption at 274 nm is negligible. The rate of absorbance decrease at 274 nm is thus proportional to the rate of CEMA disappearance at low degrees of CEMA dimerization. This decrease is illustrated in Figure 5 in terms of $A_{274}(t)/A_{274}(0)$, where $A_{274}(t)$ and $A_{274}(0)$ are the absorbances of the polymers at 274 nm at irradiation time *t* and zero, respectively, for polymer I and II micelle solutions. The rate of double bond decrease should be proportional to that of cross-linking.

As the peak at 1165 cm^{-1} in the IR region corresponds to the C−O stretching of PCEMA ester groups, its intensity should not change significantly with the dimerization of CEMA. In monitoring the rate of decrease in the absorbance at 1635 cm^{-1}, corresponding to the stretching vibration of the aliphatic double bond of CEMA, we have thus used the 1165 cm^{-1} peak as the reference. The decrease in $A_{1635}(t)/A_{1165}(t)$ as a function of irradiation time *t* for the micelles of polymers I and II is also illustrated in Figure 5, where $A_{1635}(t)/A_{1165}(t)$ is the absorbance at 1635 cm^{-1} relative to that at 1165 cm^{-1}. The fact that the UV data and FTIR data agreed with one another for both samples suggests the validity of our methods.

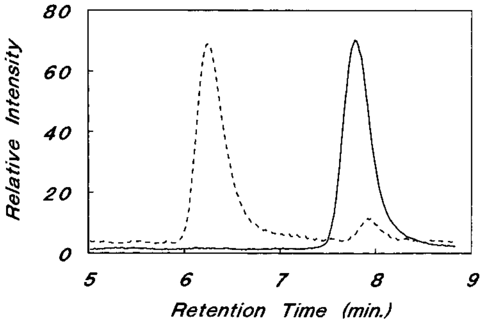


Figure 6. Comparison of GPC chromatograms of polymer I (solid) and cross-linked polymer I micelles (dashed line).

The double bond concentration decreased faster for polymer I than for polymer II. This is reasonable, considering that both solutions had the same concentration, i.e. 4 mg/mL. At this concentration, the incident light at 274 nm would be essentially 100% absorbed by both samples, as the irradiation cell path length is over 20 cm. The relative rate of CEMA disappearance is higher for polymer I since its CEMA content is lower.

Characterization of Cross-Linked Polymer I Micelles by GPC. Shown in Figure 6 is the GPC chromatogram of cross-linked polymer I micelles, obtained using THF as the eluant, for comparison with that of unirradiated polymer I. The cross-linked sample shows two peaks: one with a retention time close to that of polymer I and the other, the major peak, with a much shorter retention time and a PS-equivalent weight-average molar mass of 7.7×10^5 g/mol and a number-average molar mass of 7.0×10^5 g/mol.

The peak with a longer retention time must be due to unimers which were originally in equilibrium with the micelles before micelle cross-linking. Due to irradiation, intramolecular photodimerization took place in the PCEMA block of a unimer, which made its size smaller than an unirradiated polymer I chain in THF and its retention time in the GPC columns longer. The peak with a shorter retention time must have arisen from cross-linked micelles, as un-cross-linked micelles dissociate instantaneously in THF, a good solvent for both PS and PCEMA.

As will be discussed later, un-cross-linked polymer I micelles have some 69 arms. Figure 6 clearly shows that cross-linked micelles have a very narrow size distribution, i.e. with a polydispersity of 1.10 against PS standards. This probably represents the most monodisperse star polymer ever prepared with such a high number of arms.

Molar masses for star polymers from GPC, which are calibrated using linear polymer standards, have been long recognized to be much lower than their true values, as star polymers have a higher segmental density in a solution than a linear counterpart.[11,12] Due to this, we can only estimate the hydrodynamic radius R_h of cross-

Table 1. Characterization of Polymers I and II

sample	n/m by NMR[a]	$\bar{M}_w/\bar{M}_n$ by GPC	$\bar{M}_w$ (g/mol) by LS
I	3.07	1.10	5.0
II	0.53	1.07	18.0

[a] The symbols n and m denote the numbers of repeat units in the PS and PCEMA blocks of each polymer, respectively.

linked polymer I micelles using the fact that a star polymer and a linear polymer chain with an equal retention time should have an equal R_h. The R_h of a linear PS chain of the weight-average molar mass $\bar{M}_w$ can be calculated using[32]

$$R_h = 3\sqrt{\frac{0.3[\eta]\bar{M}_w}{\pi N_A}} \tag{6}$$

where N_A is the Avogardro constant and $[\eta]$ is the instrinsic viscosity of the sample in the eluant. According to Appelt and Meyerhoff,[33] PS in the molar mass range of 1.3×10^5 and 40×10^6 g/mol in THF obeys

$$[\eta] = (1.363 \times 10^{-2})\bar{M}_w^{\ 0.595} \tag{7}$$

Using eqs 6 and 7, we calculated a hydrodynamic radius R_h of 298 Å for PS with $\bar{M}_w = 7.7 \times 10^5$ g/mol. As our cross-linked polymer I micelles possess a PS-equivalent $\bar{M}_w$ of 7.7×10^5 g/mol, their average R_h is, thus, 298 Å.

GPC could not be used for characterizing cross-linked polymer II micelles, as they could not be eluted out of the columns. These particles could not be eluted as they are both larger and less likely to deform than cross-linked polymer I micelles.

Dynamic Light Scattering Studies. We have also determined the average R_h of cross-linked polymer I micelles by dynamic light scattering (DLS) in THF and obtained a value of 253 Å. This is in reasonable agreement with the GPC value of 298 Å, considering that completely different techniques were used.

We then examined the effect of photo-cross-linking on micellar properties. Before cross-linking, we obtained an average R_h value of 228 Å for polymer I micelles in a THF/cyclohexane mixture with a cyclohexane volume fraction of $f_c = 0.90$. After cross-linking, R_h changed to 217 Å (Table 2). If the average aggregation number $\bar{n}_{ag}$ had changed significantly during the micelle cross-linking process, we would have seen a much larger change in R_h. The small change in R_h of the cross-linked sample could be due to experimental errors or can be explained by the possible shrinkage of the micelle core upon cross-linking. The insignificant R_h change suggests that photo-cross-linking only "locked in" the structure of an un-cross-linked micelle and did not change the micelle aggregation number.

Results of Table 2 further show that the dimension of cross-linked micelles is larger in THF than in THF/cyclohexane or chloroform/cyclohexane mixtures. This increase in size is quite understandable, as the cores are not as swollen in the binary solvent mixtures as in THF. It should also be noted that the degree of swelling seems to be larger for cross-linked polymer II micelles, as the degree of cross-linking is lower for polymer II micelles. The lower degree of cross-linking and the higher degree of swelling also explains the higher mobility of CEMA segments in cross-linked polymer II micelles, as revealed by the stronger ^{1}H NMR signals of PCEMA.

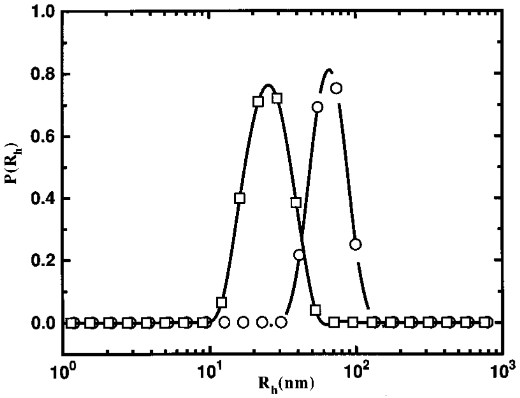


Figure 7. Distribution in R_h of cross-linked polymer I (□) and II (○) micelles as revealed by dynamic light scattering.

Illustrated in Figure 7 are the distributions in R_h for cross-linked polymer I and II micelles obtained from dynamic light scattering measurements. The distributions are narrow, in agreement with the GPC result for cross-linked polymer I micelles. The absence of a unimer peak for the cross-linked polymer I micelle mixture derived from the fact that a light scattering spectrophotometer is much less sensitive to unimers than GPC is, as unimers are much smaller and scatter much less light than micelles.

Static Light Scattering Studies. For measuring the weight-average molar masses of the cross-linked micelles of polymers I and II, we determined the specific refractive index increment ν of cross-linked polymer II micelles in toluene. This was 0.101 mL/g, which is, within experimental error, the same as 0.100 mL/g for polymer II. The agreement suggests that the photodimerization of some 20% of the aliphatic double bonds of PCEMA did not affect ν of polymer II significantly. Because of this, we did not repeat the ν measurement for cross-linked polymer I micelles. Instead, we used the ν value for un-cross-linked polymer I in toluene, i.e. 0.108 mL/g.[4]

For a diblock, the apparent molar mass $\bar{M}_w$*, obtained from plotting light scattering data following the Zimm method, is related to the true $\bar{M}_w$ value by[26]

$$\bar{M}_w^*/\bar{M}_w = \frac{1}{\nu^2}[\nu_1\nu_2 - (\nu_1\nu_2 - \nu_2^{\ 2})w_{PS}^{\ 2} - (\nu_1\nu_2 - \nu_1^{\ 2})(1 - w_{PS})^2] \tag{8}$$

where ν_1 and ν_2, 0.0938 and 0.112 mL/g, are the specific refractive index increments of PCEMA and PS, respectively,[22] ν is that of the diblock, and w_{PS} is the weight fraction of PS in a diblock. Partial dimerization of the

Table 2. Characterization of Cross-Linked and Un-cross-Linked Micelles by Dynamic Light Scattering at 21 ± 0.5 °C

sample	solvent	solvent viscosity (cP)	diffusion coefficient (cm²/s)	R_h (Å)
un-cross-linked polymer I micelles	THF/cyclohexane, $f_c = 0.90$[a]	0.801	1.19×10^{-7}	228
cross-linked polymer I micelles	THF/cyclohexane, $f_c = 0.90$	0.801	1.26×10^{-7}	217
cross-linked polymer I micelles	THF	0.486	1.78×10^{-7}	253
cross-linked polymer II micelles	chloroform/cyclohexane, $f_c = 0.69$	0.690	0.76×10^{-7}	413
cross-linked polymer II micelles	THF	0.486	0.69×10^{-7}	641

[a] The symbol f_c denotes the volume fraction of cyclohexane.

Table 3. Characterization of Cross-Linked Micelles by Static Light Scattering

sample	solvent	$10^{-6}\bar{M}_*$ (g/mol)	$\bar{M}$ (g/mol)	$\bar{n}_{ag}$	R_g (Å)	$10^6 A_2$ [(cm^3·mol)/g^2]
polymer I	THF	3.4			200	11.2
polymer I	toluene	3.2	3.5	69	180	9.7
polymer II	toluene	30	32	1.8×10^2	603	1.4

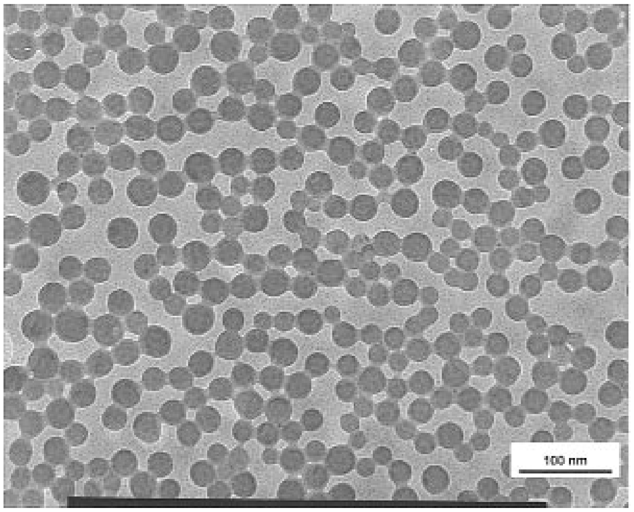


Figure 8. Transmission electron micrograph of cross-linked polymer I micelles.

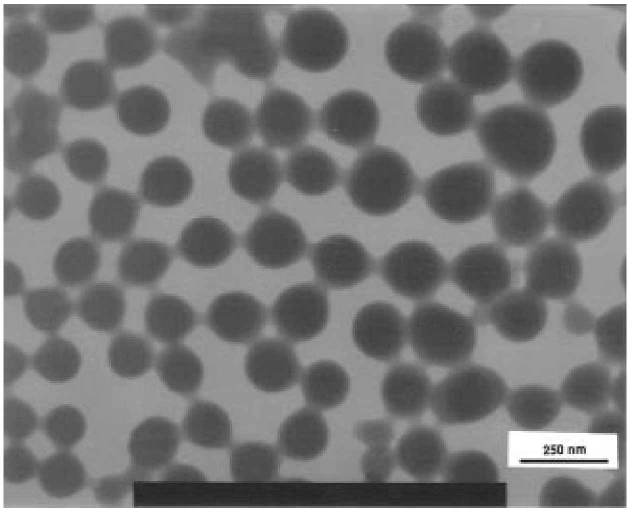


Figure 9. Transmission electron micrograph of cross-linked polymer II micelles.

CEMA aliphatic double bonds makes cross-linked micelle polymers with at least three components, i.e. PS, and CEMA units which are dimerized and not dimerized. Strictly, we should not use eq 8 for calculating the molar masses of the cross-linked micelles. The $\bar{M}_w$ values calculated from eq 8, Table 3, are thus only the approximate values. Using $\bar{M}_w$ for the cross-linked micelles and those of the polymers, we calculated the aggregation numbers of 69 and 179 for cross-linked polymer I and II micelles, respectively.

Also tabulated in Table 3 are the second virial coefficients A_2 and the radii of gyration R_g of the cross-linked micelles. The R_g values are in both cases smaller than R_h values, in agreement with the observation by Qin et al.[34]

TEM Results. Illustrated in Figures 8 and 9 are the transmission electron micrographs of cross-linked polymer I and II micelles. From the micrographs, we obtained the average radii ~25 and ~85 nm, respectively. These values are comparable with the hydrodynamic radii of 25 and 64 nm measured by dynamic light scattering in THF. The slightly larger TEM radius for cross-linked polymer II micelles can be explained as due to experimental error, because the sample size, i.e. the number of micelles on the graph, is too small to have statistical significance. Furthermore, the size distribution of cross-linked polymer II micelles seems to be relatively broad.

While our TEM radii are comparable with the hydrodynamic radii of cross-linked micelles, Webber and co-workers[34] found that the TEM values were substantially smaller than the hydrodynamic radii of their polystyrene-*block*-poly(methacrylic acid) micelles. Since different systems were studied and different TEM sample preparation techniques were used, we do not want to speculate on reasons for the different results in the two cases.

Star Polymers vs Nanospheres. As mentioned in the Introduction, the polymers used here produced cross-linked micelles which hardly qualify as star polymers and nanospheres. The preparation of star polymers from this polymer should be trivial by using diblocks with even larger *n*/*m* values. We have, for example, recently produced cross-linked micelles with an *n*/*m* value equal to 12 and do not see any obstacles to increasing the *n*/*m* ratio further. The real concern here is how far down we can decrease *n*/*m* for producing nanospheres from PS-*b*-PCEMA. Decreasing the block length of PS at a fixed PCEMA block length may lead to diblock precipitation in a block-selective solvent before *n*/*m* is small enough for crewcut micelle formation. While we have not explored the lower *n*/*m* limit for stable micelle formation from PS-*b*-PCEMA, Eisenberg and co-workers were able to produce crewcut spherical micelles from polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) with 200 units of styrene and 15 units of acrylic acid in water.[35] Replacing the PS block with PCEMA, we should have no trouble with producing nanospheres from PCEMA-*b*-PAA.

IV. Conclusions

We have prepared cross-linked spherical diblock micelles from two PS-*b*-PCEMA copolymers. The spherical shape has been confirmed by TEM results. NMR results have indicated that the PS and the PCEMA blocks were well segregated, with PS as the shell and PCEMA as the core. Dynamic light scattering studies suggested that the photo-cross-linking of PCEMA locked in the structure of micelles and did not lead to any significant change in the aggregation number of micelles. They also showed that cross-linked micelles possessed narrow size distributions, in agreement with GPC and TEM results. Studies by static light scattering yielded aggregation numbers of 69 and 179 for cross-linked polymer I and II micelles, respectively.

Although copolymers with extreme *n*/*m* values were not used here, we expect this method to be equally applicable in these cases for the preparation of star polymers and nanospheres. Since the photo-cross-linking does not modify the aggregation number of micelles, we expect cross-linked micelles to be useful for verifying scaling relations of star and crewcut micelles.

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