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Water-Soluble Nanospheres of Poly(2-cinnamoylethyl methacrylate)-*block*-poly(acrylic acid)

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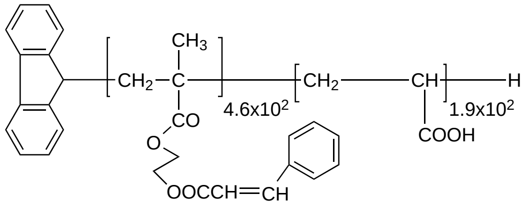
ABSTRACT: Poly(2-cinnamoylethyl methacrylate)-*block*-poly(acrylic acid) (PCEMA-*b*-PAA), with PCEMA photo-cross-linkable and PAA water soluble, were synthesized and characterized. The polymer formed spherical micelles in DMF/water with PCEMA as the core and PAA as the corona. The photo-cross-linking of the micelles yielded water-soluble nanospheres. The nanospheres were characterized by transmission electron microscopy (TEM) and light scattering. Dynamic light-scattering studies revealed that the nanospheres could readily take up organics in water. Coagulation of the nanospheres could be induced by the addition of divalent cations. These properties may allow the use of the nanospheres as the traps for organics in contaminated waters.

I. Introduction

In a block-selective solvent, i.e. a solvent which solubilizes one but not the other block, a diblock copolymer may form micelles with the soluble block in contact with the solvent to stabilize the collapsed insoluble block.[1,2] The micelles can be spherical,[3,4] cylindrical,[4−6] or vesicular.[6,7] Recently our group has reported the synthesis of diblock copolymers with photo-cross-linkable blocks.[8−11] By utilizing these polymers, diblock micelles with a photo-cross-linkable block forming the insoluble core have been cross-linked to produce permanent nanostructures such as star polymers,[3,4] nanospheres,[4] and nanofibers.[4,12]

"Nanospheres" are spherical objects with a relatively large cross-linked core and a thin corona. They have been previously produced by cross-linking the core of crew-cut micelles in organic solvents only.[4,13−15] In this paper, we report the preparation of water-soluble nanospheres from poly(2-cinnamoylethyl methacrylate)-*block*-poly(acrylic acid) (PCEMA-*b*-PAA)



in water/DMF mixtures with PCEMA as the cross-linked core and PAA as the corona.

II. Experimental Section

Materials and Reagents. Tetrahydrofuran (THF) was dried by refluxing in the presence of potassium and benzophenone under argon. Dichloromethane was dried over CaH_2 and distilled prior to use. Monomer 2-(trimethylsiloxy)ethyl methacrylate (HEMA-TMS) was prepared following a literature method,[16] dried with CaH_2, and distilled over triethylaluminum (TEA). Monomer *tert*-butyl acrylate (*t*BA) was filtered through an alumina column, dried with CaH_2, and then distilled over TEA. Fluorene was sublimated prior to use. Fluorenyllithium was prepared by reacting equal molar amounts of fluorene with *n*-butyl lithium in THF at 0 °C for 5 min. All other reagents were used as received. All solvents were purchased from BDH and all reagents were purchased from Aldrich unless otherwise stated.

Polymer Synthesis. P(HEMA-TMS)-*b*-P*t*BA was prepared by sequential living anionic polymerization initiated with fluorenyl lithium at −78 °C in THF using the standard vacuum line technique. HEMA-TMS and *t*BA were each polymerized for 4 h. The living polymerization was then terminated by the addition of several drops of methanol. TMS groups were removed overnight, through the addition of more methanol at room temperature to the polymerization mixture to achieve a THF/methanol volume ratio of 75/25, to produce poly(2-hydroxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PHEMA-*b*-P*t*BA).

The conversion of the PHEMA block of the copolymer to PCEMA was accomplished by reacting the polymer with 1.2 molar equiv of cinnamoyl chloride in dry pyridine at room temperature overnight. The polymer solution was filtered and was added to excess methanol to precipitate out PCEMA-*b*-P*t*BA. The polymer powder was dried at room temperature under vacuum.

PCEMA-*b*-PAA was prepared by the selective cleavage of the *tert*-butyl esters of the P*t*BA block following a literature method.[17] PCEMA-*b*-P*t*BA and iodotrimethylsilane (1.3 molar equiv of *t*BA) were reacted in dry dichloromethane under argon for 80 min. The mixture was then evaporated to dryness. After redissolving the mixture in dichloromethane/methanol (20/1), 500 mL of a 2% aqueous sodium metabisulfate ($Na_2S_2O_5$) solution was added and the slurry was stirred overnight. Dichloromethane was evaporated by gentle heating the next morning, causing the polymer to precipitate in the aqueous $Na_2S_2O_5$ solution. The precipitate was again dissolved in dichloromethane/methanol, washed with water, and reprecipitated in water by evaporating off dichloromethane. The polymer was lastly purified by adding its dichloromethane/methanol solution into a 30/70 mixture of isopropyl alcohol and hexanes. The polymer precipitate was collected by filtration, washed with hexanes, and then dried overnight under vacuum.

Nanosphere Preparation. PCEMA-*b*-PAA (0.20 g) was dissolved in 20 mL of DMF and filtered through a 0.45-μm Teflon membrane filter (Chromatographic Specialties Inc.) to remove any particulate matter or undis-

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solved polymer. An equal volume of water (Barnstead Nanopure) was then added dropwise at a rate of 1 drop per 5 s with continuous stirring to induce micelle formation.[6] Additional water was added in one aliquot afterward to achieve a water/DMF volume ratio of 80/20 and a polymer concentration of ~2.0 mg/mL. The solution was stirred for 18 h, filtered into an irradiation cell maintained at 20 °C, bubbled with argon for 20 min, and then photolyzed with light from a 500 W mercury lamp which had passed through a 260 nm cutoff filter. During irradiation, samples at 1.0 mL each were removed for UV absorbance analysis to determine the conversion of the aliphatic double bonds of PCEMA. The irradiation continued until 15% conversion was achieved.

After cross-linking, the water in the DMF/water mixture was removed by rotary evaporation, yielding a concentrated solution of the nanospheres in DMF. The nanospheres were then precipitated in ether. The particles were allowed to settle and the either was decanted off. After washing with hexanes, the particles were collected by filtration and dried under vacuum.

Polymer Characterization. The conversion from PHEMA-*b*-P*t*BA to PCEMA-*b*-P*t*BA and then to PCEMA-*b*-PAA was followed by ^{1}H NMR using a Bruker ACE-200 instrument. ^{1}H NMR also gave the ratio between the numbers of repeat units of the two blocks of PCEMA-*b*-P*t*BA. GPC analysis was done for PCEMA-*b*-P*t*BA only using THF as the eluent. The instrument used was a Varian Model 5000 instrument equipped with a refractive index detector and a Waters Styragel HT4 column. The specific refractive index increment, dn_r/dc, of PCEMA-*b*-P*t*BA or PCEMA-*b*-PAA was measured with the use of a Phoenix Precision Instrument system. Both static and dynamic light scattering was conducted using a Brookhaven Model 9025 light scattering instrument equipped with a 10-mW helium−neon laser.

Nanosphere Characterization. Nanospheres were characterized by TEM and light scattering. TEM measurements were conducted on a Hitachi H-7000 instrument operated at 10^5 V. TEM samples were prepared by aspirating a fine spray of a dilute nanosphere solution (0.2 mg/mL) in a DMF/water mixture onto a carbon-coated copper grid. The samples were then stained overnight with OsO_4.

To determine the molar mass of the nanospheres by light scattering, the nanospheres were dissolved by stirring in DMSO at 80 °C overnight. The samples were centrifuged at 4.5×10^3 rpm for 30 min before light scattering measurements.

Dynamic Light Scattering. Solutions at a concentration of typically ~0.1 mg/mL were used for dynamic light-scattering measurement. Solutions in water were obtained by dialyzing DMSO solutions against water. Dynamic light-scattering data were analyzed following the method of cumulants.[18] The logarithm of the first-order electric field correlation function, $g^{(1)}(\tau)$, was fitted using

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

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

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

In eq 2, *q* is the scattering wave vector with its magnitude given by

$$q = \frac{4\pi n_0 \sin(\theta/2)}{\lambda_0} \tag{3}$$

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 hydrodynamic radius, R_h, was obtained using

$$R_h = \frac{kT}{6\pi\eta\langle D\rangle_z} \tag{4}$$

with η being the viscosity of the solvent used at 22 °C; and kT the thermal energy.

DMSO/Water Mixtures. Viscosities of DMSO/water mixtures were measured at room temperature (22 °C) using a Cannon Ubbelohde type viscometer. Since the flow times were all above 200 s, no kinetic energy corrections were made in calculating the viscosities from the flow time values. The viscosity η_m of a mixture was calculated by ratioing the flow time t_m of the mixture to that t_0 of water using

$$\eta_m = (t_m\rho_m/\rho_0 t_0)\eta_0 \tag{5}$$

where ρ_m and ρ_0 were the densities of the solvent mixture and water, respectively; η_0, the viscosity of water at 22 °C, was calculated to be 0.96 cP from the equation which represented the best fit to the viscosities of water at 20, 25, and 30 °C reported in ref 19a.

Refractive indices, n_m, of the solvent mixtures were calculated using the following approximate equation

$$n_m = v_1 n_1 + v_2 n_2 \tag{6}$$

where v_1 and v_2 were the volume fractions of DMSO and water, respectively. The refractive indices of DMSO and water, n_1 and n_2, were 1.479 and 1.333.[19b]

III. Results and Discussion

Polymer Synthesis. The polymer was synthesized according to Scheme 1. The structures of PHEMA-*b*-P*t*BA, PCEMA-*b*-P*t*BA, and PCEMA-*b*-PAA were verified by their ^{1}H NMR spectra as illustrated in Figure 1. The P*t*BA signals are weak in the PHEMA-*b*-P*t*BA spectrum, because DMSO-d_6 was used as the solvent in this case. DMSO-d_6 did not dissolve P*t*BA and caused micelle formation from PHEMA-*b*-P*t*BA with P*t*BA as the core. Proton peaks of the core block of micelles are frequently not seen, as the mobility there is low.[3]

The ratio, 2.46, between the number of CEMA to that of *t*BA units was obtained from analyzing the spectrum of PCEMA-*b*-P*t*BA in deuterated chloroform. Both PCEMA and P*t*BA peaks are now clearly seen and can be satisfactorily assigned as shown in Figure 1. The disappearance of the ethylene peaks of the hydroxylethyl group at 4.1 and 3.6 ppm and the emergence of the doubles at 4.2 ppm for the ethylene group of CEMA suggests the complete cinnamation of PHEMA, in agreement with our previous observation.[3,10]

The $(CH_3)_3SiI$ and $Na_2S_2O_5$ treatment clearly did not remove any cinnamoyl groups, as no peaks at 4.1 and 3.6 ppm are observed in the spectrum of PCEMA-*b*-PAA in DMSO-d_6 in Figure 1. The cleavage of the 2-cinnamoylethyl group from PCEMA is even less likely, as ester bonds of primary alkyls are more stable toward the $(CH_3)_3SiI$ attack.[17] The cleavage of the *tert*-butyl groups was obvious as judged from the physical properties of the PCEMA-*b*-P*t*BA sample treated with $(CH_3)_3SiI$

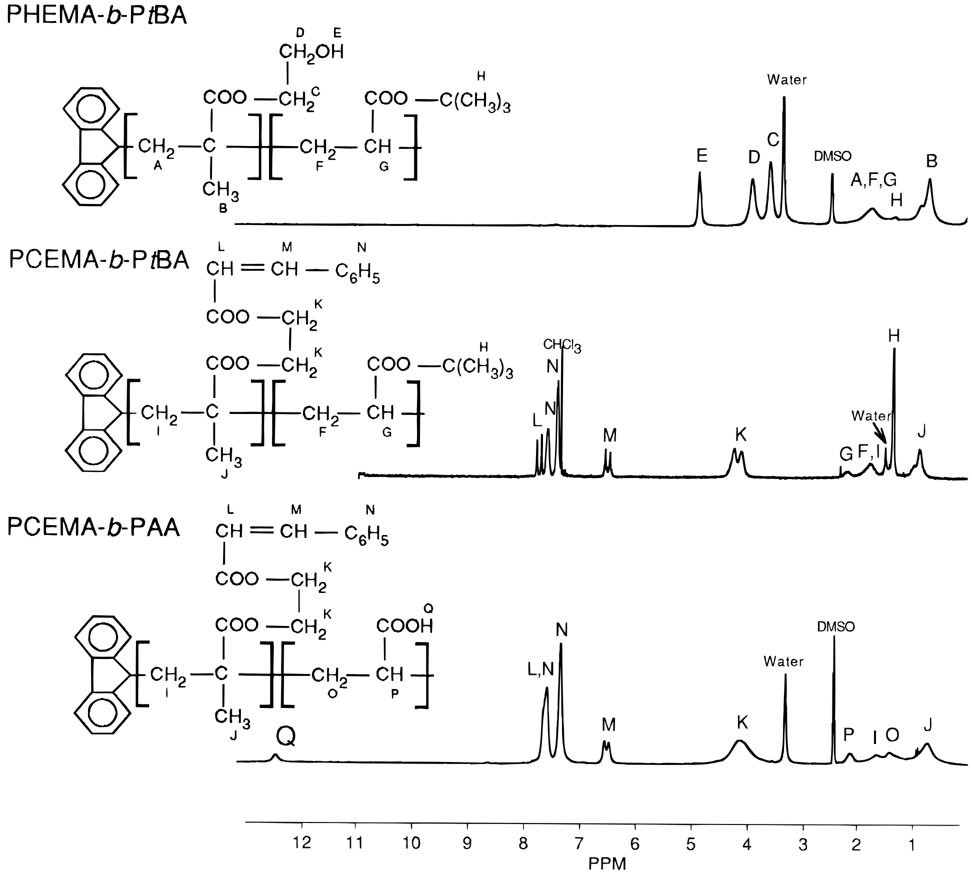
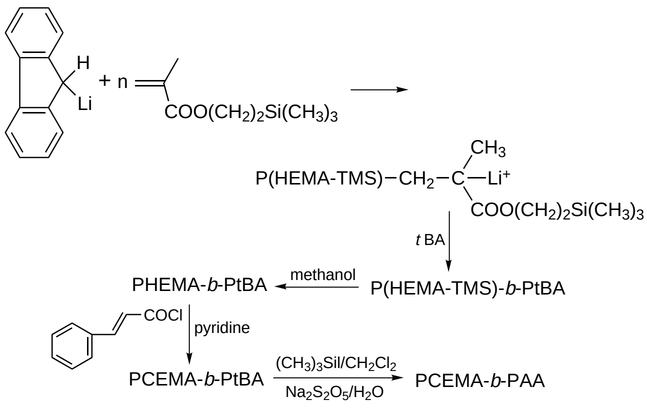


Figure 1. ^{1}H NMR spectra of PHEMA-*b*-P*t*BA (in DMSO-d_6), PCEMA-*b*-P*t*BA ($CDCl_3$), and PCEMA-*b*-PAA (DMSO-d_6).

Scheme 1



and $Na_2S_2O_5$. While PCEMA-*b*-P*t*BA was perfectly soluble in chloroform, the dissolution of the treated sample was slow and the final solution formed had a bluish tinge to it, suggesting micelle formation. As PCEMA is soluble in chloroform and is still intact in the sample treated with $(CH_3)_3SiI$ and $Na_2S_2O_5$, the insoluble block of the micelle must have been PAA. Unambiguous evidence for *tert*-butyl cleavage is obtained from the absence of a singlet at 1.4 ppm for the *tert*-butyl group in the NMR spectrum of PCEMA-*b*-PAA in DMSO-d_6, which now solubilizes the polymer. Further evidence for PAA formation is the direct observation of the carboxylic proton peak at 12.3 ppm. In summary, the selective cleavage of *tert*-butyl group by the $(CH_3)_3SiI$ and $Na_2S_2O_5$ treatment is expected, as this has been well documented[17] and practiced in our group[20] before.

Polymer Characterization. The analysis of the PCEMA-*b*-P*t*BA block copolymer by GPC gave a polystyrene equivalent molar mass of 6.0 × 10^4 g/mol and $\bar{M}_w/\bar{M}_n = 1.09$. Static light scattering was done for both PCEMA-*b*-P*t*BA and PCEMA-*b*-PAA, with concentrations between ~12 and ~1 mg/mL and scattering angles varying from 30° to 150°. The weight-average molar masses, $\bar{M}_w$, are summarized in Table 1. By using the CEMA to AA unit ratio, n/m, of 2.46 determined from NMR, the n and m values were calculated and was also included in Table 1.

Due to the low P*t*BA or PAA weight fractions in PCEMA-*b*-P*t*BA and PCEMA-*b*-PAA, the correction to the apparent molar masses determined from the Zimm plots of these samples should be minor and was thus been ignored. The close agreement between the n and m values determined for PCEMA-*b*-P*t*BA before and after *tert*-butyl group hydrolysis suggests the high selectivity of the hydrolysis reaction and the absence of any side reactions such as cross-linking or chain scission.

UV Cross-Linking of PCEMA-*b*-PAA Micelles. PCEMA cross-linked due to the photodimerization of CEMA groups of different chains.[21,22] The disappearance of the CEMA groups can be followed by UV spectrophotometry, as CEMA absorbed strongly at 274 nm.[3] Figure 2 shows the kinetics of the CEMA conversion as a function of UV exposure time. Since the targeted application for nanospheres in this study was the take up of organics, the cross-linking density of the PCEMA cores should be sufficiently low to allow the easy penetration of organics into the core. All the nanospheres studied here had a CEMA conversion of 15%.

Different CEMA groups of the same chain can also dimerize, which does not lead to cross-linking. Due to the expected extensive interpenetration of different

Table 1. Polymer and Nanosphere Characterization by Light Scattering

polymer	solvent	η/cP	dn_r/dc (mL/g)	$10^{-5}\bar{M}_w$ (g/mol)	10^{-2} n	10^{-2} m	R_G (nm)	R_h (nm)
PCEMA-*b*-P*t*BA	CH_2Cl_2		0.136	1.47	4.7	1.91		
PCEMA-*b*-PAA	DMF		0.143	1.31	4.5	1.84		
nanospheres	DMSO	1.99[a]	0.110	75			34	42 ± 2
nanospheres	water	0.96[b]						48[c]
nanospheres in water/DMSO	2.5% of DMSO	1.00						62[c]
nanospheres in water/DMSO	5.0% of DMSO	1.06						62[c]

[a] Viscosity at 25 °C from ref 19b. [b] Viscosity at 22 °C. [c] Values at 90°. R_h values decreased by about 10% upon increasing the scattering angle from 45° to 150°.

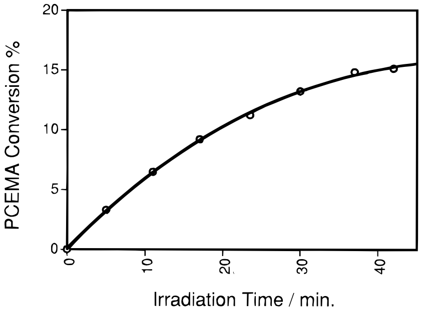


Figure 2. Conversion of the double bond of CEMA as a function of UV irradiation time.

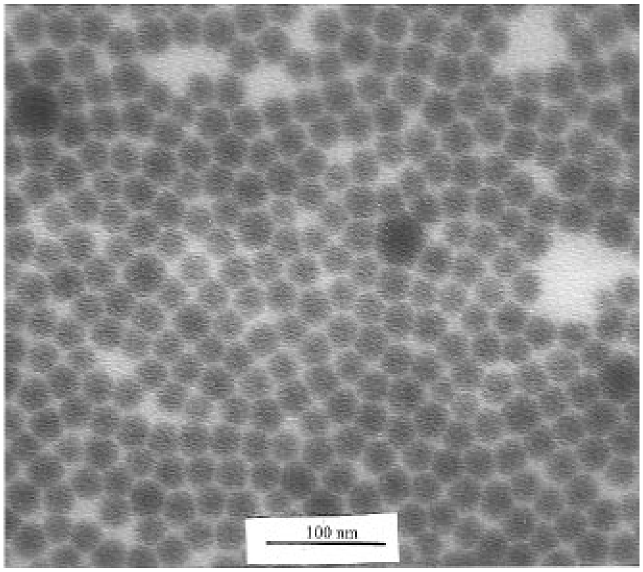


Figure 3. TEM image of nanospheres. The TEM specimen was prepared by spraying a dilute nanosphere solution in DMF/water with 80% water.

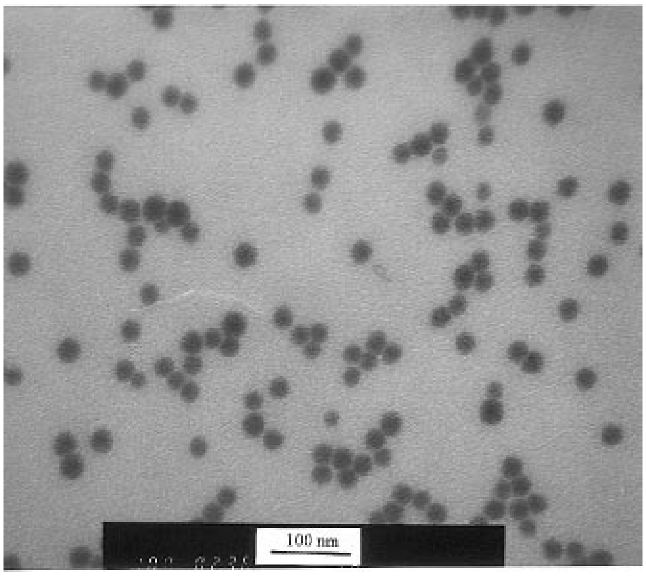


Figure 4. TEM image of aqueous PCEMA-*b*-PAA micelles.

PCEMA chains in the core of micelles, the intrachain dimerization probability should be low. For this reason, we will interchange cross-linking density with CEMA double conversion in our discussion.

TEM Characterization of Nanospheres. Nanosphere powder obtained as described in the Experimental Section could be dispersed in hot DMSO but not in water. Once dispersed in DMSO, water could be added to the DMSO solution and dialysis against water could be employed to prepare aqueous solutions of the nanospheres. The insolubility of the nanospheres directly into water was understandable, as the diblock copolymer itself did not directly disperse in water either. The direct dispersion of the nanospheres in water should be possible for samples with higher PAA contents.

Illustrated in Figure 3 is a TEM image of the nanospheres sprayed from a DMF/water mixture with 20% DMF. Since the sample was stained with OsO_4, which reacted with the aliphatic double bonds of PCEMA, the PCEMA regions should appear as dark domains. It is evident from Figure 3 that we indeed had cross-linked spherical micelles and produced nanospheres. The fact that a sphere had a uniform darkness across its whole cross section area suggests the absence of phase-separated PAA in the spherical region and PCEMA actually makes up the cores. The nanospheres have an extremely narrow size distribution and an average core diameter ~20−30 nm.

Unfortunately, we could not see the shell here. This is, however, expected, as the dry shell layer should be very thin compared to the diameter of the core due to the 10% weight fraction of PAA in the diblock. This also explains why these cross-linked block copolymer micelles are called nanospheres, as the cross-linked cores are dominant in size.

Attempts were made to see the PAA shell layer by staining PAA with CsOH. We were indeed able to see spheres with thin dark shells. Due to the thinness of the coronas, the pictures did not have good resolution and is thus not shown here.

TEM images were also taken of the un-cross-linked micelles from water as illustrated in Figure 4. The dimensions of the un-cross-linked micelles are consistent with those obtained for the nanospheres indicating that the cross-linking of the particles did not alter the size or shape of the polymer micelles.

Nanosphere Characterization by Static and Dynamic Light Scattering. The dn_r/dc value of PS-*b*-PCEMA was found previously not to change significantly with PCEMA cross-linking.[3] This may be approximately true for PCEMA-*b*-PAA. Assuming the same dn_r/dc for the PCEMA-*b*-PAA diblock and the PCEMA-*b*-PAA nanospheres, the weight-average molar mass of the nanospheres was determined by static light scattering in DMSO following the Zimm method to be

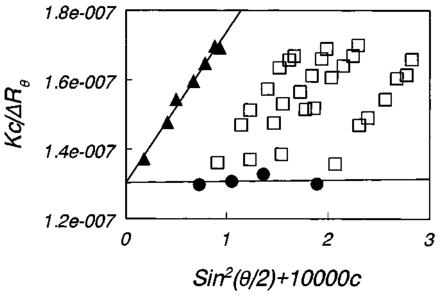


Figure 5. Zimm plot of PCEMA-*b*-PAA nanospheres in DMSO. The angles used were 50°, 80°, 90°, 110°, 125°, 140°, and 150°. The concentrations used were 7.3×, 10.5×, 13.6×, and 18.9 × 10^{-5} g/mL, respectively.

7.5 × 10^6 g/mol (Figure 5). Ratioing the molar masses of the nanospheres and the diblock yields 57 arms for the nanospheres. The radius of gyration, R_G, determined in DMSO for the nanospheres was 34 nm.

Dynamic light-scattering analysis was performed of the nanospheres in DMSO at 35°, 60°, 90°, and 150°. The average hydrodynamic radius, R_h, from four angles was 42 ± 4 nm. The fact that R_G is less than R_h is consistent with the spherical structure of the particles.

The $\bar{M}_w$ value of 7.5 × 10^6 g/mol is consistent with the molar mass estimated from the TEM nanosphere radius R ~15 nm. Assuming a density, ρ, of 1.0 g/mol for such nanospheres, they should have a molar mass, M, ~8.5 × 10^6 g/mol according to

$$M = {}^4/_3 N_A \rho \pi R^3 \tag{7}$$

where N_A is the Avogadro number.

In water, R_h at 90° was 48 nm. Increasing the scattering angle from 60° to 150°, R_h decreased from 55 to 46 nm. This angular dependence of R_h suggests there were large particles in the system. This was probably caused by the fusion of some nanospheres in water. Some fusion occurred as the PAA layer was thin in these nanospheres.

Takeup of Organics in Water By the Nanospheres. The ability of the nanospheres to take organics in water was tested by comparing the R_h values of nanospheres in water and DMSO/water mixtures. The addition of 2.5% by volume of DMSO to an aqueous solution followed by overnight equilibration increased the R_h of the nanospheres to 62 nm as measured at the scattering angle of 90°. This corresponded to a volume increase of 116%, suggesting considerable uptake of DMSO from water by the nanospheres. Addition of more DMSO to a total volume fraction of 5.0% did not lead to further increase in R_h as shown in Table 1. This is because the nanosphere cores were saturated with DMSO at the DMSO volume fraction of 2.5% already.

Nanospheres as Potential Traps for Organics in Polluted Water. PCEMA-*b*-PAA nanospheres at the acrylic acid unit concentration of 1.0 × 10^{-6} mol in 2.0 mL of water precipitated out readily with the addition of ~2.0 molar equiv of divalent cations such as Ca^{2+}, Ba^{2+}, and Cu^{2+}. The cations could be introduced either as salts such as $BaCl_2$ and $CuSO_4$ or as hydroxides. The interparticle fusion is believed to be caused by the bonding of the acrylic acid groups of different nanospheres to the same divalent cation.[6]

The precipitated out nanospheres remain insoluble in all organic solvents tested including DMF, THF, and hexanes. They, however, readily redispersed with the addition of precipitants or complexing reagents for the cations. Nanospheres precipitated with $BaCl_2$ could, for example, be redispersed with the addition of Na_2SO_4. The effect of Cu^{2+} could be counteracted with the addition of EDTA. These properties of the nanospheres make them ideal candidates as the traps for organics in contaminated water.

The advantages of nanospheres over water-soluble diblock micelles as traps for organic contaminants are obvious. First, they benefit from the lack of a critical micellar concentration (cmc) and remains stable at concentrations below the cmc of un-cross-linked micelles. This advantage becomes apparent when a large pool of water is to be cleaned with the traps. Then, the cross-linked micelles, after harvesting by precipitation with the addition of divalent cations, can be extracted with organic solvents to remove the loaded contaminants and be reused after redispersion. The un-cross-linked micelles of PCEMA-*b*-PAA, on the other hand, cannot survive the extraction process.

In addition to the organic trap application, they can also be used as drug carriers in controlled drug delivery, for example.[23]

IV. Conclusion

PCEMA-*b*-PAA with 4.6 × 10^2 units of CEMA and 1.9 × 10^2 units AA was synthesized and characterized. The polymer formed spherical micelles in water/DMF mixtures with PCEMA as the core and PAA as shell. Photo-cross-linking of the PCEMA core led to our first preparation of water-soluble block copolymer nanospheres. The spherical shape of the particles were confirmed by TEM. The nanospheres had an extremely narrow size distribution and an average aggregation number of 57.

The nanospheres can readily take up organics from water. They precipitate out from water upon the addition of divalent cations. The precipitated nanospheres can be extracted with organic solvents without noticeable dissolution and redispersed by the addition of precipitants or complexing reagents for the cations. These properties may prove ideal for the use of the nanospheres as traps for organics in contaminated water.

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