Cross-Linked Nanospheres of Poly(2-cinnamoylethyl methacrylate) with Immediately Attached Surface Functional Groups

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ABSTRACT: A polyisoprene-*block*-poly(2-cinnamoyethyl methacrylate) (PI-*b*-PCEMA) sample with a narrow molar mass distribution was prepared and characterized. The sample formed spherical micelles in hexanes/THF with 20% of THF by volume. After photo-cross-linking of the PCEMA core took place, the PI corona block was cleft by ozone and $(CH_3)_3P$ treatment to produce PCEMA nanospheres with surface carbonyl groups or PCEMA−CO nanospheres. These spheres were stable without any added surfactant in a good solvent for PCEMA. Reaction of the carbonyl groups with cyclopentadiene catalyzed by pyrrolidine yielded fulvene-covered nanospheres, PCEMA−FV nanospheres, which possessed better solubility in organic solvents than the PCEMA−CO spheres. This work represents the first attempt at the preparation of cross-linked nanospheres with immediately attached surface functional groups from block copolymers. When appropriately functionalized, these nanospheres should be useful as solid lubricant or support for catalysts.

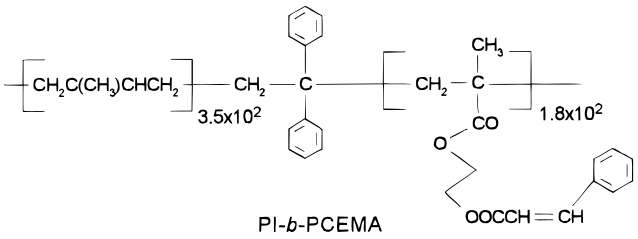
I. Introduction

Many techniques are available for preparing polymeric spheres of various sizes. Micrometer-sized spheres are mainly produced by emulsion and suspension polymerization in water[1] or in organic solvents.[2] More recent development involved their preparation by precipitation polymerization[3] and from the "activated swelling" method.[4] Nanometer-sized spheres are also referred to as microgels.[5] They can be prepared by microemulsion[6] or by precipitation polymerization.[7] With notable exceptions,[3,7] the preparation of polymeric spheres of various sizes always involved the use of either ionic or steric stabilizers.

Polymeric nanospheres can also be prepared by cross-linking block copolymer micelles. Previous efforts involved the cross-linking of the core block of diblock copolymer micelles using thermal initiators[8] or photoinitiators.[9,10] These strategies worked well in the solid state in which the rate of domain fixation was much faster than that of micelle chain exchange.[11] In the solution phase, insoluble products were frequently obtained due to the fusion of different micelles during micelle cross-linking. We recently prepared diblock copolymers with self-photo-cross-linkable blocks, which photo-cross-linked without any additives such as an initiator.[12−14] Using these diblocks, soluble nanospheres with narrow size distributions were always prepared.[14−16] From these diblocks, we also prepared cross-linked polymeric monolayers (brushes),[17−19] nanofibers,[20] and thin films with tunable nanochannels.[21]

Nanospheres prepared from block copolymer micelles are stabilized in solution by the corona block due to steric stabilization.[22] When diblock nanospheres are cast from a solution, a film forms after solvent evaporation due to the intermixing between the corona chains of different nanospheres. We were curious about the consequence of cleaving the corona block off a dilbock copolymer nanosphere in a solution and the prospect for "nonsticky" nanospheres as solid lubricant. It was for these and for the potential use of these nonsticky nanospheres as catalyst support that we initiated the preparation of highly cross-linked nanospheres with surface functional groups, i.e. spheres derived from the cleaving of the corona block of diblock nanospheres.

The diblock copolymer used was polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate), PI-*b*-PCEMA. Micelles were prepared from this polymer with PCEMA as the core and PI as the corona. After the PCEMA cores were cross-linked photochemically, the PI block was cleaved by ozonolysis to produce PCEMA nanospheres with surface carbonyl groups or PCEMA−CO nanospheres. The ability to tailor the surface properties further and change surface functional groups was demonstrated by reacting the carbonyl groups with cyclopentadiene catalyzed by pyrrolidine. This reaction yielded fulvene-covered nanospheres or PCEMA−FV nanospheres.



PI-*b*-PCEMA

II. Experimental Section

Reagents and Materials. Isoprene was distilled over *n*-butyllithium before use. Hexane (Omni solvent, EM Science) was washed repeatedly with concentrated sulfuric acid until the sulfuric acid phase became colorless. It was then washed with a dilute $NaHCO_3$ solution and water until the water phase became neutral. After being dried over $CaCl_2$ and refluxed with potassium, it was distilled over *n*-butyllithium. The procedures for the preparation of HEMA-TMS, where HEMA-TMS denotes ((trimethylsilyl)oxy)ethyl methacrylate, and the purification of styrene, THF, and 1,1-diphenylethylene (DPE) were described previously.[23] All other reagents were used as received.

Polymer Synthesis. The precursor polymer, PI-*b*-P(HEMA-TMS), to PI-*b*-PCEMA was prepared by sequential anionic polymerization using the standard high vacuum technique.[24]

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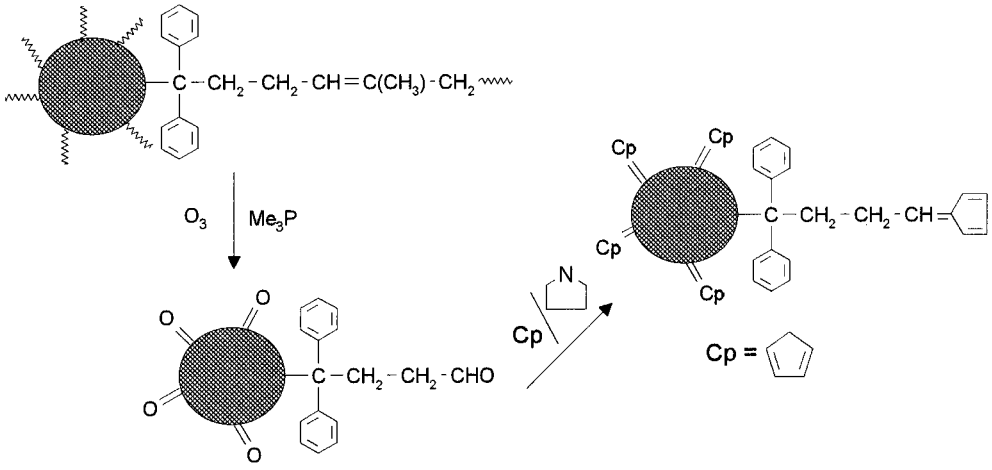
Scheme 1



A three-neck round-bottom polymerization flask with LiCl was baked under high vacuum. To it was then charged distilled hexane. Isoprene was polymerized in hexane at room temperature for 2 days using *sec*-butyllithium as the initiator. After the addition of DPE, hexane was removed and THF was added by cryodistillation under vacuum. The second monomer, HEMA-TMS, was polymerized in THF at −78 °C for 2 h before the polymerization was terminated with methanol.

After the mixture was warmed to room temperature, more methanol was added to achieve a THF/methanol volume ratio ~75/25. Also added was 1 drop of concentrated hydrochloric acid and 2,6-bis(*tert*-butyl)-4-methylphenol. The mixture was stirred overnight to hydrolyze the TMS group. PI-*b*-PHEMA was purified by precipitation into water and rinsed with methanol. PI-*b*-PCEMA was obtained by reacting PI-*b*-PHEMA with cinnamoyl chloride in pyridine overnight at room temperature. The resulting polymer was purified by repeated precipitation from methanol.

Polymer Characterization. GPC analysis was done on a Varian Model 5000 HPLC instrument using a Styragel HT 4 (Waters) column calibrated by monodisperse polystyrene standards (Polymer Laboratories). The ratio in the number of isoprene to CEMA units, n/m, was determined using ^{1}H NMR. The absolute weight-average molar mass was measured using a Brookhaven model 9025 light scattering instrument in chloroform using a He-Ne laser. The difference Δn_r between the refractive indices of a polymer solution and pure chloroform at 633 nm was determined using a differential refractometer (Precision Instruments Company) equipped with a band-pass filter at room temperature. The specific refractive index increment ν or dn_r/dc, where n_r and c represent the refractive index and concentration of a polymer solution, was obtained from the slope of a straight line yielded by plotting Δn_r vs c.

Micelle Preparation and Cross-Linking. PI-*b*-PCEMA was dissolved in distilled THF. Micelles formed upon the addition of sufficient hexanes (analytical reagent, BDH). While micelles, as judged from their characteristic bluish tinge, started to form in hexanes/THF with 50% hexanes by volume, we prepared micelles in hexanes/THF with 80% hexanes. The typical polymer concentrations used were between 2.0 and 5.0 mg/mL.

Micelle solutions were purged with argon before cross-linking by light which had passed a 260-nm cutoff filter from a 500-W mercury lamp. Vigorous stirring was rendered by a magnetic stirrer throughout irradiation.

Micelle Cross-Linking Kinetics. At various times, 2.00 mL was taken from an irradiated sample consisting of 100 mL of a PI-*b*-PCEMA solution at 2.00 or 5.0 mg/mL in hexanes/THF with 20% THF. Of the 2.00 mL, 0.200 mL was used after dilution by THF for CEMA content analysis spectrophotometrically at 274 nm. Then 1.50 mL was evaporated to dryness with a gust of nitrogen and then dissolved in 0.30 or 1.00 mL of THF for GPC analysis.

Ozonolysis. Cross-linked micelles of PI-*b*-PCEMA were dissolved in methylene chloride and then cooled to −40 °C. Ozone was then bubbled through it for several minutes. The ozone-saturated solution was stirred for 30 min before excess ozone was blown off by nitrogen. Excess trimethyl phosphite and a trace amount of 2,6-bis(*tert*-butyl)-4-methylphenol were then added. Trimethyl phosphite was added to reduce the ozonides formed to carbonyl or ketone groups. 2,6-Bis(*tert*-butyl)-4-methylphenol functioned as a free radical scavenger.

Reaction with Cyclopentadiene. PCEMA−CO nanospheres (~50 mg), with PI freshly cleft and precipitated out from methanol, were redispersed in ~5 mL of methylene chloride. They were then reacted at room temperature for 1 day with 2.0 mL of freshly distilled cyclopentadiene using pyrrolidine (1.3 mL) as the catalyst (Scheme 1).[35] The solution eventually turned bright yellow. To the solution were then added 0.90 mL of acetic acid, which turned the solution red, and 20 mL of diethyl ether to precipitate the nanospheres. The nanospheres were centrifuged out, rinsed with ether, redissolved in DMSO, and precipitated out from ether again. The precipitate was rinsed with methanol until the solution phase became colorless and then dried.

TEM Studies. TEM measurements were conducted on a Hitachi H-7000 instrument operated at 1.0×10^5 V. TEM samples of cross-linked PI-*b*-PCEMA micelles were prepared by aspirating a fine spray of a dilute solution (~0.1 mg/mL) in a hexanes/THF (80/20) mixture onto a carbon-coated copper grid. Due to the high tendency for PCEMA−CO nanospheres to aggregate and their low stainability by OsO_4, TEM specimens of these samples showing individual nanospheres could not be obtained by the spraying method. Instead, individual nanospheres were observed by embedding the samples in a polymer matrix. This involved mixing ~1.0 mg of the nanospheres with ~0.2 g of PCEMA in 4 mL of chloroform. Several drops of the solution were then dispensed on water surface. After solvent evaporation, the thin polymer film containing PCEMA−CO nanospheres was transferred on to a copper grid.

Dynamic Light Scattering Measurement. Solutions at the concentration typically ~0.1 mg/mL were centrifuged at 4.5×10^3 rpm for 15 min, and the supernatant was then used for dynamic light scattering measurement. Dynamic light-scattering data were analyzed following the method of cumulants.[25] The viscosities used for chloroform and DMSO at 24 °C were 0.55 and 2.0 cP, respectively.[26]

III. Results and Discussion

Polymer Characterization. Illustrated in Figure 1 is the ^{1}H NMR spectrum of the PI-*b*-PCEMA sample in $CDCl_3$. Since the PCEMA peaks have been assigned previously[14] and PI is a well-studied polymer and its peak assignment can, for example, be found in ref 24, we did not assign all the peaks in Figure 1 but only assigned three which were of importance to our discussion. From the intensities of peaks b and c, the efficiency of 1,4-addition, y, in Figure 1, was calculated to be 94%. This is in good agreement with the expected value of 93% for isoprene polymerization in a nonpolar

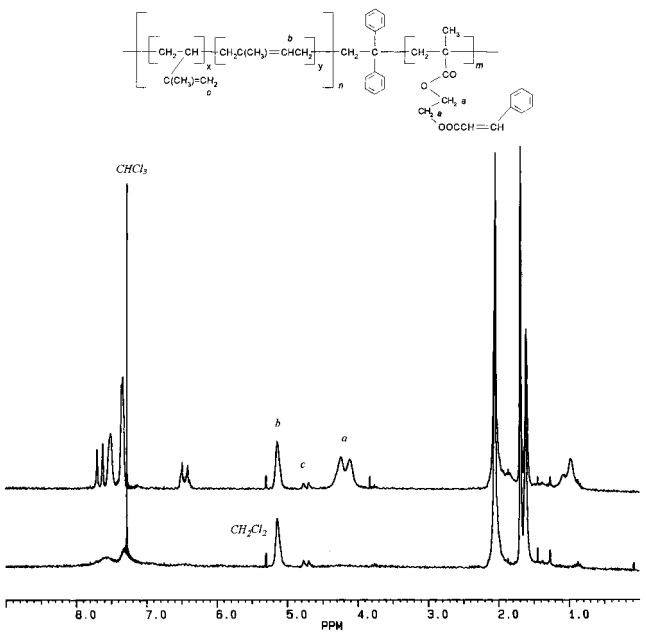


Figure 1. NMR spectrum of PI-*b*-PCEMA in $CDCl_3$. Also shown (bottom) is that of PI-*b*-PCEMA micelles at the cross-linking density of 38%.

Table 1. Characteristics of the PI-*b*-PCEMA Sample

n/m from NMR	$\bar{M}_w/\bar{M}_n$ from GPC	$10^{-4}\bar{M}_w$ (g/mol) from GPC	dn_r/dc (mL/g)	$10^{-4}\bar{M}_w$ (g/mol) from LS	$10^{-2}n$	m
1.94	1.12	2.74	0.128	7.0	3.5	178

solvent.[24] The ratio between the numbers of isoprene to CEMA units, n/m, for the diblock was calculated from the intensities of peaks b and a and the y value to be 1.94 (Table 1).

GPC measurement of PI-*b*-PCEMA using monodisperse PS as the standards yielded a single peak with $\bar{M}_w/\bar{M}_n = 1.12$. Plotting light scattering data following the Zimm method yielded the apparent weight-average molar mass $\bar{M}_w$ of 7.0×10^4 g/mol. Assuming that n/m varied little from chain to chain, we neglected the diblock correction to the apparent molar mass.[27] Using n/m determined from NMR and $\bar{M}_w$ from light scattering, the numbers of isoprene and CEMA units in the chain were calculated to be 3.5×10^2 and 178, respectively.

Cross-Linking of PI-*b*-PCEMA Micelles. PCEMA cross-links due to the multiple dimerization of two CEMA groups of different chains.[28] The disappearance of the CEMA groups was followed by UV spectrophotometry, as CEMA absorbed strongly at 274 nm. 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 PCEMA chains in the micellar cores, the intrachain dimerization probability should be low. For this, we interchange cross-linking density with CEMA double conversion in our discussion.

Several batches of samples at concentrations between 2.0 and 5.0 mg/mL were prepared with cross-linking densities between 20 and 50%. Illustrated in Figure 2 is the relative decrease in the concentration of the aliphatic double bond of CEMA as a function of UV irradiation time for two of the irradiated samples at concentrations of 2.0 and 5.0 mg/mL in hexanes/THF with 20% THF. As irradiation time increases, the CEMA conversion increases.

At the same irradiation time, CEMA conversion was always higher for the sample with a lower concentration. This is expected. Our irradiation cell had a pathlength ~20 cm. At polymer concentrations of 2.00 and 5.0 mg/mL, light at ~274 nm should be absorbed completely in both cases. At an equal incident photon flux, the CEMA conversion rate should be higher for the more dilute sample.

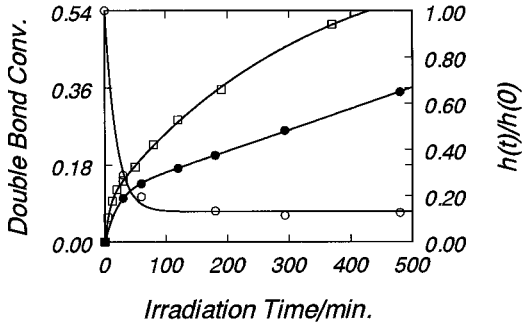


Figure 2. Plot of CEMA double bond conversion as a function of UV irradiation time. The irradiated samples consisted of a 100 mL solution at 5.0 (●) or 2.00 (□) mg/mL in hexanes/THF with 80% hexanes by volume. Also plotted is the decrease in the relative height, $h(t)/h(0)$, of the GPC unimer peak (○) as a function of irradiation time for the more concentrated sample.

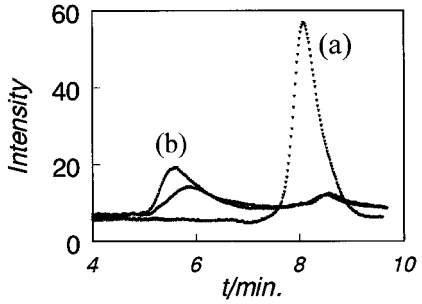


Figure 3. Comparison between the GPC chromatogram of PI-*b*-PCEMA (a) and those of PI-*b*-PCEMA micelles at the cross-linking densities of 17% (b) and 35% (unlabeled). The irradiated sample had a concentration of 2.00 mg/mL.

Illustrated in Figure 3 is the comparison between the gel permeation chromatograms of PI-*b*-PCEMA micelles at 0%, 17%, and 35% cross-linking densities. As irradiation time increased, the unimer peak centered ~8.2 min shifted to longer times. This is expected, as the intramolecular cross-linking of the PCEMA block of a unimer was supposed to produce a "tadpole molecule" which possessed a smaller hydrodynamic volume than the diblock copolymer chain.[29] The presence of PI homopolymer in the system would also contribute to the observed shift in the single chain peak, as the PI homopolymer would normally have a lower molar mass than the diblock.

Although an equal amount of polymer was injected, the total area of the peaks of the single chains and micelles for a cross-linked sample was significantly lower than that of the unirradiated sample. This was most likely caused by the fact that some of the cross-linked micelles did not elute out of the column. The decrease in dn_r/dc of the cross-linked micelles relative to THF could also have contributed to the decreased peak intensity. This contribution should, however, be minor as dn_r/dc of a sample in chloroform at the cross-linking density of 38% was 0.112 mL/g, which represented a small decrease from 0.125 mL/g for an un-cross-linked sample. The relative difference between dn_r/dc for the cross-linked and un-cross-linked sample should be even smaller in THF, the solvent used for GPC analysis. The refractive indices of THF and chloroform are 1.407 and 1.446; dn_r/dc for the cross-linked and un-

cross-linked sample in THF should be 0.151 and 0.164 mL/g, respectively, following a first-order approximation.[27]

As PCEMA cross-linking density increased from 17% to 35%, the micellar peak area decreased substantially (Figure 3). This suggests that more micelles were retained by the GPC column as the cross-linking density increased. The particles which did not come out were the larger ones. They formed probably due to micelle fusion during photolysis. Micelle fusion was possible partially because the residual double bonds of PI chains could cross-link. The probability for the reaction between different isoprene units should, however, be low as PI absorbed negligibly above 260 nm. Micelle fusion could occur also due to the cross-linking of different PCEMA cores, as was reported by Saito et al.[8] when the micelles were not kinetically frozen. In hexanes/THF with 20% THF, the PCEMA cores of our micelles should be swollen, and the micelles may not be kinetically frozen on the time scale of photolysis.

As PCEMA cross-linking density increased, the micellar GPC peak shifted to longer retention times or smaller hydrodynamic volumes. Micelle size shrink due to reduced swelling with an increase in the core cross-linking density is expected. The other possible reason was that larger particles or fused micelles were more likely to undergo intermicellar fusion due to their larger surface areas. The preferred further fusion of the larger particles would have made them too large to be eluted from the GPC column.

Quantitative analysis of the single chain peak height at irradiation time t relative to that of the unirradiated sample yielded the $h(t)/h(0)$ results shown in Figure 2 for the sample at the concentration of 5.0 mg/mL. The same trend was observed for the other set of samples irradiated at a concentration of 2.00 mg/mL. That $h(t)/h(0)$ leveled off quickly suggested the swift locking in of the micelles by photo-cross-linking.

Properties of Cross-Linked PI-*b*-PCEMA Micelles. Cross-linked micelles of PI-*b*-PCEMA were soluble in solvents such as chloroform, THF, and toluene, which were good for both PI and PCEMA. Illustrated in Figure 1 is the comparison between ^{1}H NMR spectra of the PI-*b*-PCEMA diblock and a cross-linked micelle sample with the cross-linking density of 38% in $CDCl_3$. That most of the peaks of PCEMA in the cross-linked micelles did not show suggested that the PCEMA block resided in the core, where polymer segmental mobility was low. That the PI peaks appeared normal suggested that the PI chains made up the corona. Also shown at 5.3 ppm is the peak of the added internal standard, CH_2Cl_2. At an equal mass concentration with the same amount of CH_2Cl_2 added, that the ratios between the intensity of peak b and that of CH_2Cl_2 were approximately the same for a PI-*b*-PCEMA and the cross-linked micelle sample suggested that PI was mostly in the corona.

The cross-linking of PCEMA could also be appreciated from our FTIR results shown in Figure 4. Upon UV irradiation, the carbon−carbon double bond peak at 1635 cm^{-1} decreased substantially.

GPC analysis of the cross-linked PI-*b*-PCEMA micelles gave a weight-average molar mass of 6.0×10^5 g/mol and $\bar{M}_w/\bar{M}_n = 1.29$ against PS standards. It is well-known that linear polymers cannot be used to calibrate GPC columns to obtain the molar mass of cross-linked micelles due to the drastic segmental density difference in the two cases. The molar mass was

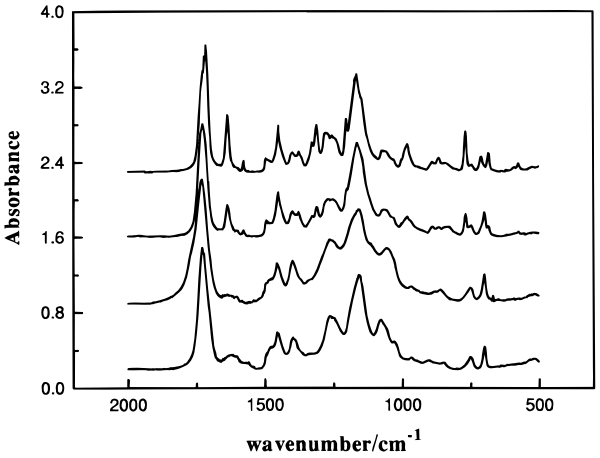


Figure 4. Comparison between FTIR spectra of PI-*b*-PCEMA (top) and PI-*b*-PCEMA micelles at the cross-linking density of 50% before (second from the top) and after (third from the top) ozone and $(CH_3)_3P$ treatment. Also shown is the FTIR spectrum (bottom) of PCEMA−FV nanospheres chemically modified with cyclopendiene.

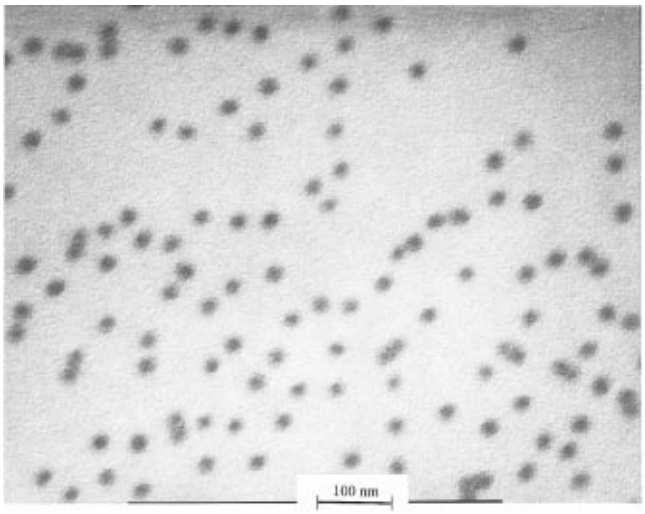


Figure 5. TEM image of PI-*b*-PCEMA micelles at the cross-linking density of 20% prepared in hexanes/THF with 20% THF.

only used to calculate the hydrodynamic radius of the micelles using[14]

$$R_h = \left(\frac{0.409 \times 10^{-2} \bar{M}_w^{1.714}}{\pi N_A}\right)^{1/3} \quad (1)$$

From eq 1, we obtained a R_h value of 26 nm.

Illustrated in Figure 5 is a TEM image of such micelles. The picture clearly shows that all micelles are spherical and have a very sharp radius distribution of ~12 nm. This sharp distribution revealed by TEM is in contradiction with the large $\bar{M}_w/\bar{M}_n$ value of 1.29 we obtained by GPC. This again points to the possible existence of fused micelles in the system. Actually, fused micelles are seen in Figure 5. TEM results are not conclusive as the micelles could have fused during specimen preparation.

Dynamic light scattering was used to determine the hydrodynamic radius R_h of the cross-linked micelles. The R_h value was 35 nm (Table 2), substantially larger than the GPC value of 26 nm, and was scattering-angle independent.

The substantially larger R_h value from dynamic light scattering again pointed to the existence of fused

Table 2. Properties of Cross-Linked PI-*b*-PCEMA Micelles and PCEMA Nanospheres, Where Light Scattering Experiments Were Performed in Chloroform

sample	$\bar{M}_w$/(g/mol) by GPC	$\bar{M}_w/\bar{M}_n$ by GPC	R_h/nm by LS	R_G*/nm by LS	ν (mL/g)	$\bar{M}_w$* (g/mol)
micelles of PI-*b*-PCEMA[1]	6.0×10^5	1.29	35	40	0.112	1.13×10^7
PCEMA−CO nanospheres[a]			22			
PCEMA−FV nanospheres			23[b]			

[a] The PCEMA cross-linking density was 38%. [b] Value determined at the scattering angle of 150°.

micelles in the system. The GPC value was lower, because some large fused micelles were not eluted out of the column and analyzed. Samples for light-scattering measurements were purified by centrifugation, which did not lead to any polymer loss as verified by our UV absorbance analysis of samples before and after centrifugation.

The specific refractive index increment of PI-*b*-PCEMA micelles at the cross-linking density of 38% in chloroform was determined to be 0.112 mL/g. Using $\nu = 0.112$ mL/g, the apparent molar mass of the micelles was determined to be 1.13×10^7 g/mol from the Zimm method. Again by assuming there was little fluctuation in the chemical composition from micelle to micelle, we neglected the correction of the molar mass of the micelles. From $\bar{M}_w = 1.13 \times 10^7$ g/mol, the apparent aggregation number for the micelles is thus 159.

The apparent radius of gyration, R_G, determined for the sample was 40 nm, which was larger than the R_h value of 35 nm. That $R_G/R_h > 1$ suggested that the micelles were not perfectly spherical, in contradiction with the TEM result. Furthermore, the TEM radius of ~12 nm was too small to explain the molar mass of 1.13×10^7 g/mol. Assuming a density ρ of ~1.0 g/cm^3, the radius of a solid PI-*b*-PCEMA micelle, R_s, as estimated from

$$(4/3)\rho N_A \pi R_s^3 = \bar{M}_w^* \qquad (2)$$

should be ~17 nm. This again suggests the presence of some fused micelles in this system.

Evidences for PI Cleaving. Ozonolysis was traditionally used to cleave double bonds of small molecules for fragment analysis to establish molecular structures. The reaction of double bonds with ozone yields ozonide. The ozonide can be either reduced or oxidized by reacting with a reductant or an oxidant. We used a reductant, $(CH_3)_3P$, to cause carbonyl group formation from decomposed double bonds.[30]

The PI block should completely disintegrate by ozonolysis, because most double bonds of PI are in the polymer backbone. PCEMA cores also contained some un-cross-linked CEMA units. These double bonds might also cleave. Their cleavage should not, however, affect the integrity of the nanospheres when the cross-linking densities were high, as the cinnamoyl groups are only pendant to the chains.

Cleavage of the PI block of the PI-*b*-PCEMA cross-linked micelles was demonstrated by our NMR, IR, and dynamic light scattering results. Dynamic light scattering showed that the R_h decreased from 35 nm for cross-linked PI-*b*-PCEMA micelles to 22 nm for PCEMA−CO nanospheres in chloroform. This R_h decrease is equivalent to a 4-fold decrease in volume. Considering that the weight fraction of PI in PI-*b*-PCEMA was only ~$^1/_3$, this suggested that the packing density of PI chains in chloroform was ~$^1/_9$ that of PCEMA, a value quite reasonable. This was, however, only an estimation, as not all micelles were spherical in this system due to micelle fusion.

Neither PCEMA nor PI NMR signals were observed for the PCEMA−CO nanospheres. The absence of signals from PCEMA was expected as the mobility of the PCEMA block was low in the cross-linked core. The absence of the PI signals suggested the cleavage of the PI block.

The comparison between the IR spectra of cross-linked PI-*b*-PCEMA micelles and PCEMA−CO nanospheres is shown in Figure 4. That the double bond absorption peaks at 1635 and 980 cm^{-1} decreased and a shoulder at 1781 cm^{-1} appeared next to the carbonyl groups of PCEMA at 1715 cm^{-1} indicated the occurrence of the first reaction shown in Scheme 1. The survival of some double bonds of PCEMA after the ozone and $(CH_3)_3P$ treatment is manifested by the residual IR peak at 980 cm^{-1}, characteristic of the out-of-plane bending motions of the hydrogen atom next to the *trans* double bond of CEMA.

Properties of PCEMA−CO Nanospheres. After cleaving the PI block, the nanospheres remained dispersed in methylene chloride. Once precipitated from methanol, they could still be redispersed as individual nanospheres in methylene chloride, THF, or other good solvents for PCEMA. Once the precipitate was vacuum dried, aggregates were formed which did not fully dissolve in any organic solvents tested. This was probably due to the strong van der Waals forces between the surface carbonyl groups or the reaction between the residual ozonides on different nanosphere surfaces. Thus, not fully dried nanospheres were used for all physical measurements. The difficulty in obtaining soluble dry PCEMA−CO nanospheres explained why static light-scattering measurements were not made to determine the molar mass of the nanospheres.

Drying a solution of PCEMA−CO nanospheres in CH_2Cl_2 on a glass slide did not lead to the formation of a homogeneous film but left a cloudy sample on the slide. On the other hand, a transparent film formed upon drying a cross-linked PI-*b*-PCEMA micelle solution in CH_2Cl_2. This property difference clearly demonstrates the validity of our prediction that bear nanospheres might not be as "sticky" as diblock nanospheres due to the lack of interparticle chain penetration.

Freshly prepared PCEMA−CO nanospheres with a cross-linking density of 50% were shown by TEM to be perfectly spherical (Figure 6) and have an average radius of ~9 nm, which represents a decrease from ~12 nm for PI-*b*-PCEMA micelles.

Reactivity of the Carbonyl Groups of PCEMA−CO Nanospheres. The use of the nanospheres as solid lubricants or catalyst supports requires the chemical modification of the surface functional groups. While many reactions were possible for the surface carbonyl groups, we demonstrated that the carbonyl groups could react with cyclopentadiene to produce fulvene-modified nanospheres or PCEMA−FV nanospheres (Scheme 1). This reaction was chosen as the reaction conditions were mild and easy to fulfill.[31]

The occurrence of the reaction could be judged from the color change of the nanospheres (the solution turned

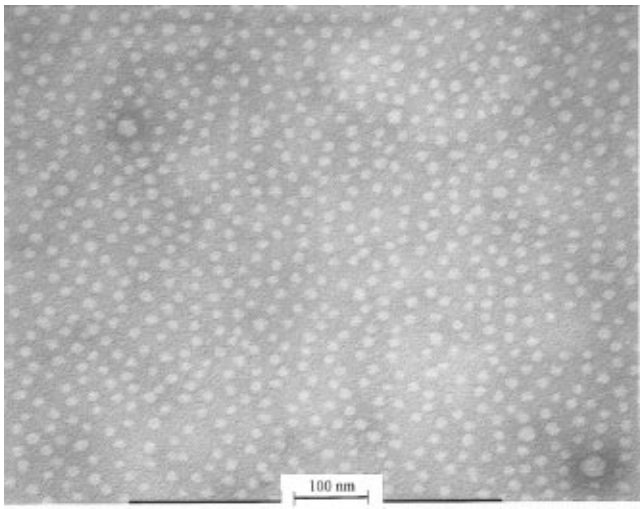


Figure 6. TEM image of PCEMA nanospheres with carbonyl surface groups. The nanospheres appeared lighter as they were dispersed in a stained PCEMA film.

yellow and the solid turned red) as cyclopentadiene was added to the nanospheres in the presence of pyrrolidine. FTIR (Figure 4) showed that the carbonyl peak at 1781 cm^{-1} disappeared, and a broad peak at 1625 cm^{-1} characterizing fulvene formation appeared after the reaction.

Properties of PCEMA−FV Nanospheres. In contrast to the carbonyl-covered nanospheres, vacuum-dried fulvene-covered nanospheres were completely soluble in DMSO when heated at 80 °C for 1 day. This increased solubility suggests the reduction in the adhesion between different nanospheres and the potential to even further reduce nanosphere adhesion for solid lubricant applications.

Dynamic light scattering studies were performed in DMSO for a PCEMA−FV nanosphere sample derived from PI-*b*-PCEMA micelles cross-linked at a concentration of 5.0 mg/mL to a cross-linking density of 50%. At the scattering angle of 150°, the determined R_h was 23 nm, which was, within experimental error, the same as 22 nm for PCEMA−CO nanospheres. This suggests that the nanospheres retained their integrity after fulvene attachment and remained dispersed.

Unfortunately, the R_h values for this sample had angular dependence. This is expected, as there were substantial intermicellar fusion in this sample due to the high polymer concentration used for irradiation, e.g. 5.0 vs 2.0 mg/mL for the other samples. In fact, the same angular dependence was observed for the PI-*b*-PCEMA micelles cross-linked at a concentration of 5.0 mg/mL. We have not attempted the preparation of another PCEMA−FV nanosphere sample, as the angular dependence of R_h does not change our conclusion that the PCEMA−CO nanosphere carbonyl groups are active and the reaction between the carbonyl groups with a reasonably mild reagent should not affect the integrity of the nanospheres.

IV. Conclusion

PI-*b*-PCEMA with a narrow molar mass distribution was prepared and characterized. The polymer formed spherical micelles in hexanes/THF. After photo-cross-linking the PCEMA core, the PI block of the cross-linked micelles were cleft by ozone and $(CH_3)_3P$ treatment to produce PCEMA−CO nanospheres, as verified by our light-scattering, FTIR, and NMR results. Evaporation of the solvent from such a nanosphere solution could not lead to the formation of a homogeneous polymer film, as expected, due to the lack of interparticle chain mixing. The carbonyl groups of the nanospheres were shown to be labile toward further reaction. The conversion of surface carbonyl groups to fulvene increased the solubility of the nanospheres in organic solvents possibly due to the decreased inter-sphere adhesion. This suggests the potential for further surface property modification of the nanospheres to enable their use as solid lubricant or catalyst supports.

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References and Notes

(1) See, for example: Billmeyer, F. W., Jr. *Textbook of Polymer Science*; Wiley & Sons: New York, 1984.
(2) See, for example: Ito, K. In *Polymeric Materials Encyclopedia—Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p. 3927.
(3) See, for example: Li, K.; Stöver, H. D. H. *J. Polym. Sci.: Polym. Chem.* **1993**, *31*, 3257.
(4) See, for example: Ugelstad, J.; Schmid, R.; Aune, O.; Bjorgum, J.; Kilaas, L.; Strenstad, P. In *Polymeric Materials Encyclopedia—Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 4501.
(5) Funke, W. In *Polymeric Materials Encyclopedia—Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 4360.
(6) See, for example: Gan, L. M.; Chew, C. H. In *Polymeric Materials Encyclopedia—Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 4321.
(7) See, for example: Chen, H.; Ishizu, K.; Fukutomi, T.; Kakurai, T. *J. Polym. Sci.: Polym. Chem.* **1984**, *22*, 2123.
(8) (a) Saito, R.; Ishizu, K.; Fukutomi, T. *Polymer* **1990**, *31*, 680. (b) *Ibid.* **1992**, *33*, 1712.
(9) Tuzar, Z.; Bahadur, P.; Kratochvil, P. *Makromol. Chem.* **1981**, *182*, 1951.
(10) Wilson, D. J.; Riess, G. *Eur. Polym. J.* **1988**, *24*, 617.
(11) (a) Ishizu, K.; Onen, A. *J. Polym Sci.: Polym. Chem.* **1989**, *27*, 3721. (b) Ishizu, K.; Kuwahara, K. *Ibid.* **1993**, *31*, 661.
(12) Liu, G.; Hu, N.; Xu. X.; Yao, H. *Macromolecules* **1994**, *27*, 3892.
(13) Hu, N.; Liu, G. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 949.
(14) Guo, A.; Liu, G.; Tao, J. *Macromolecules* **1996**, *29*, 2487.
(15) Tao, J.; Stewart, S.; Liu, G.; Yang, M. *Macromolecules* **1997**, *30*, 2738.
(16) Henselwood, F.; Liu, G. *Macromolecules* **1997**, *30*, 488.
(17) Liu, G.; Xu, X.; Skupinska, K.; Hu, N.; Yao, H. *J. Appl. Polym. Sci.* **1994**, *53*, 1699.
(18) (a) Tao, J.; Guo, A.; Liu, G. *Macromolecules* **1996**, *29*, 1618. (b) Ding, J.; Tao, J.; Guo, A.; Stewart, S.; Hu, N.; Birss, V. I.; Liu, G. *Marcomolecules* **1996**, *29*, 5398.
(19) Ding, J.; Birss, V. I.; Liu, G. *Macromolecules* **1997**, *30*, 1442.
(20) (a) Liu, G.; Qiao, L.; Guo, A. *Macromolecules* **1996**, *29*, 5508. (b) Liu, G. *Nanofibers. Adv. Mater.* **1997**, *9*, 437.
(21) Liu, G.; Ding, J.; Guo, A.; Herfort, M.; Bazett-Jones, D. *Macromolecules* **1997**, *30*, 1851.
(22) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.
(23) Liu, G.; Smith, C. K.; Hu, N.; Tao, J. *Macromolecules* **1996**, *29*, 220.
(24) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983.
(25) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(26) Lide, D. R. *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, FL, 1995.
(27) Huglin, M. B. *Light Scattering from Polymer Solutions*; Academic Press: London, 1972.
(28) Guillet, J. E. *Polymer Photophysics and Photochemistry—An Introduction to the Study of Photoprocesses in Macromolecules*; Cambridge University Press: Cambridge, U.K., 1985.
(29) Tao, J.; Liu, G. *Macromolecules* **1997**, *30*, 2408.
(30) Lee, J.-S.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2602.
(31) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

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