Polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) Tadpole Molecules

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Received September 24, 1996[⊗]

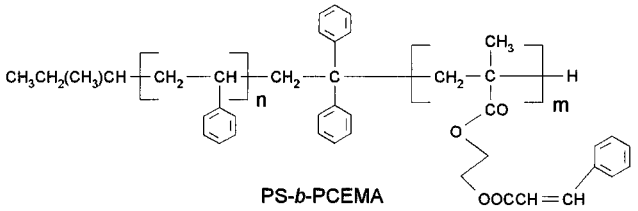
ABSTRACT: In THF/cyclopentane (CP) or THF/cyclohexane (CH) mixtures with sufficiently high CP or CH contents, polystyrene-*block*-poly(2-cinnamoylethyl metharylate) (PS-*b*-PCEMA) forms micelles with PCEMA as the core. Coexisting with the micelles are unimer chains. The unimers are expected to have the tadpole conformation with the PS block assuming the normal random-coil conformation and the PCEMA block clustering together like a globule. Photo-cross-linking the PCEMA globule of the unimers enabled our first preparation of permanent tadpole molecules from diblock copolymers. The tadpole conformation has been confirmed by our GPC, light scattering, and NMR study.

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. Micelles with different aggregation numbers, f, and unimers with $f = 1$ always coexist. While micelles may have different shapes ranging from spheres,[1, 2] cylinders,[3−5] and vesicles,[5,6] to donuts,[7] a unimer would probably always resemble a tadpole with the insoluble block clustering together to form a globule and the soluble block assuming the normal random coil conformation, as first hypothesized by Sadron.[8]

The easiest way to verify that a diblock unimer contains a normal and a collapsed block is probably to show that a diblock shrinks in size in a block-selective solvent. This has been difficult because the critical micelle concentration of a diblock copolymer is normally very low to allow the use of scattering techniques for determining unimer sizes in a block-selective solvent. The way to circumvent this has been in studying the collapsing of multiblock or graft copolymer unimers to extrapolate the behavior of diblock copolymers.[9−11]

We have recently synthesized diblocks with photo-cross-linkable blocks including polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA),[2,12] poly(cinnamoylethyl methacrylate)-*block*-poly(acrylic acid) (PCEMA-*b*-PAA),[13] and poly(isobutyl vinyl ether)-*block*-poly[(vinyloxy)ethyl cinnamate].[14−15] Like other diblocks, PS-*b*-PCEMA and PCEMA-*b*-PAA formed spherical or cylindrical micelles in selectively poor solvents for PCEMA with PCEMA as the core. Photo-cross-linking the micelles enabled our preparation of star polymers,[2,4] nanospheres,[2,13] and nanofibers[4,16] from the diblock copolymers. Also present with these nanostructures must have been some intramolecularly cross-linked unimers or tadpole molecules. In this paper, we report the preparation and separation of these tadpole molecules by GPC fractionation from cross-linked PS-*b*-PCEMA micelles and the study of the tadpoles confirming their structure. This represents the first preparation and isolation of diblock tadpole molecules.



PS-*b*-PCEMA

Experimental Section

Polymers. Three polymers, 902-281, 229-74, and 240-48, were used in this study, where the numbers before and after a hyphen represent the numbers of styrene and CEMA units in a diblock. The synthesis and characterization procedures for these polymers have been described in detail previously[2] and will thus not be repeated here.

Instrumentation and Techniques. GPC analysis was done with THF as the eluant. The Styragel HT-4 (Waters) column was calibrated using polystyrene standards. Light scattering was done using a Brookhaven model 9025 instrument equipped with a 632-nm He−Ne laser. All light scattering measurements were carried out in toluene at room temperature. The scattering angles used were between 30° and 150°, and the polymer concentrations used were between ∼1 and 10 mg/mL. Photolysis was achieved with light from a 500-W mercury lamp which had passed through a 260-nm cutoff filter.

Micelle and Unimer Cross-Linking. Micelle and unimer mixtures were prepared by dissolving the polymers in THF first. Cyclopentane (CP) or cyclohexane (CH) was then added to achieve the desired THF/CP or THF/CH ratio. The final polymer solution was typically 100 mL, and the concentration was ∼2.0 mg/mL.

Sample 229-74 was cross-linked in THF/CH with 10% THF and 240-48 in THF/CP with 3% THF. The cross-linking of 902-281 was done in THF/CP with 40% THF to increase the weight fraction of unimers in the mixture. Cross-linking kinetics was followed by taking samples, 2.0 mL each, at various irradiation times. Of the 2.0 mL, 0.50 mL was used for UV absorbance analysis at 274 nm to obtain PCEMA double-bond conversion. The rest was blown dry with nitrogen and dissolved in 0.50 mL of THF for GPC analysis.

Tadpole Isolation. The weight fraction of tadpoles in the cross-linked 229-74 sample was ∼5% and ∼25% for 902-281. The tadpoles were isolated from the cross-linked micelles by tedious GPC fractionation. It is, however, expected that fractionation precipitation can be used in the future for larger scale unimer preparation.

Results and Discussion

GPC, light scattering, and NMR were used to show that tadpole molecules were indeed prepared. GPC was

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

S0024-9297(96)01422-2 CCC: $14.00

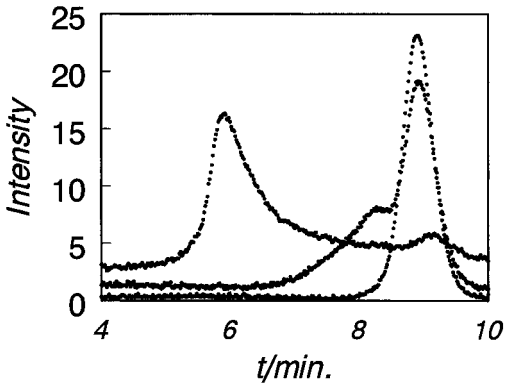


Figure 1. Comparison of the gel permeation chromatograms of 240-48 micelles irradiated for 0 (lowest curve), 2, and 60 min (highest) in THF/CP with 3% THF.

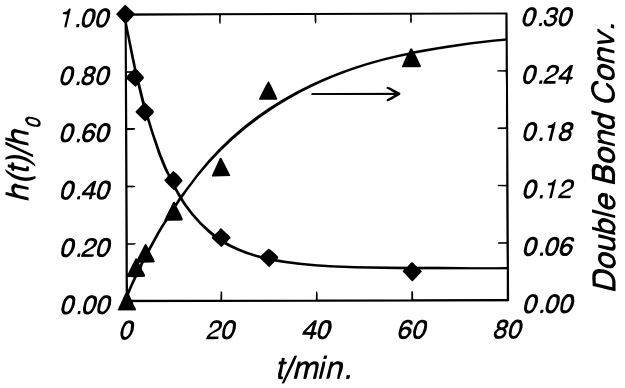


Figure 2. Plot of the height of the unimer peak at irradiation time t relative to that at time zero, $h(t)/h_0$, against t (◆). Also plotted is PCEMA double-bond conversion vs t.

used to monitor the evolution in the chromatograms of cross-linked PS-*b*-PCEMA products as a function of irradiation time. Light scattering was used to show that the radius of gyration of a tadpole molecule was smaller than that of the diblock in toluene, a good solvent for both PS and PCEMA. The compactness or the immobility of the cross-linked PCEMA block was judged from the ^{1}H NMR peak broadening of PCEMA.

Micelle and Unimer Cross-Linking. Illustrated in Figure 1 is the comparison between the gel permeation chromatograms of the 240-48 micelle sample at three different irradiation times. The micelles were prepared in THF/CP with 3% THF. GPC was run using THF as the eluant. Before UV irradiation, the GPC peak of the diblock was Gaussian with a retention time of ~9.0 min. Two-minute irradiation caused 3.5% of the CEMA double bonds to disappear as analyzed by UV spectrophotometry. GPC analysis indicated a 22% decrease in the height of the peak corresponding to single PS-*b*-PCEMA chains and the appearance of a shoulder on the high molar mass side. After 60 min of irradiation, the micelle structure appeared to be locked in and the micelles were eluted out as a high molar mass peak with a retention time of ~5.8 min. The single-chain peak was now weak.

Quantitative analysis yielded Figure 2 where the decrease in the single-chain peak height relative to that of the unirradiated sample, $h(t)/h_0$, is plotted as a function of irradiation time t. Also plotted in Figure 2 is the PCEMA double-bond conversion as a function of t. The $h(t)/h_0$ data could be well fitted by the following exponential function:

$$h(t)/h_0 = 0.112 + 0.86 \exp(-t/\tau) \quad (1)$$

with $\tau = 9.5$ min. The good fit of the single-chain peak height data by an exponential function is fortuitous, as the single-chain peaks were never deconvoluted from those of the partially cross-linked samples to obtain the accurate peak heights. Also, no attempt was made to correct for the volume change caused by sample taking at various irradiation times.

The single-chain peak height, following eq 1, initially decreased with irradiation time and eventually leveled off. The single-chain peak was initially high, as micelle chains were not all cross-linked. Those which were not cross-linked were eluted out by THF as single chains and contributed to the intensity of the single-chain peak in GPC. As irradiation progressed, all micelle chains should eventually get locked in. What were left of the single chains should be the intramolecularly cross-linked unimers or tadpole molecules which were originally in equilibrium with micelles before irradiation started.

To really obtain tadpole molecules, one should thus irradiate a micellar sample sufficiently long so that the residual single chains are all intramolecularly cross-linked unimers. In a sufficiently block-selective solvent, a unimer should have a relatively compact PCEMA block. On the other hand, the PCEMA block in a micelle core is expected to assume approximately the random-coil conformation due to the extensive mixing between different chains. Single chains extracted out of a partially cross-linked micelle would thus not be tadpole molecules due to the loose conformation of the PCEMA block. For this, the micelles and unimers of 229-74 were irradiated to obtain a CEMA conversion of 38% and those of 902-281 a conversion of 26%, and the single chains were then separated to produce tadpoles. Due to the longer PCEMA blocks in 229-74 and 902-281 than in 240-48, we expect the CEMA conversions used for these samples should be sufficiently high to lock in all micelle chains in micelles.

Change in the Position of the GPC Single-Chain Peaks. A closer examination of Figure 1 reveals that the position of the 250-45 single-chain peak shifted toward longer retention times or lower hydrodynamic radius as irradiation proceeded. This is in agreement with the expectation that as irradiation dosage increased, the PCEMA block of the unimers got more tightly locked up due to higher intrachain cross-linking densities. At high radiation dosages, unimer chains are tadpole molecules.

One may also suggest that the single-chain peak position shift was caused by the homo-PS chains present in a sample. As the irradiation dosage increases, the diblock chains cross-link and the contribution made by the homo-PS chains to the intensity of the single-chain peak increases. Since homo-PS generally possesses lower molar masses than the diblock chains, the gradual shift in the unimer peak to lower hydrodynamic radius is thus expected.

The homo-PS explanation for the unimer peak shift is unlikely to be true, or at least not completely true, becuase all samples used in this study were extracted carefully with hot cyclohexane to remove homo-PS from PS-*b*-PHEMA. Despite this, a more convincing argument would require the demonstration that the molar mass of the irradiated single chains remains unchanged from that of the diblock while their size decreases with irradiation.

Table 1. Characteristics of 902-281 Tadpoles and the PS-*b*-PCEMA Samples Used

code	n/m by NMR	$\bar{M}_w/\bar{M}_n$ by GPC	$10^{-4}\bar{M}_w$ (g/mol) by GPC	$10^{-4}\bar{M}_w$ (g/mol) by LS	$10^{-2}n$	$10^{-2}m$	R_G/nm
229-74	3.1	1.10	3.1	4.3	2.3	0.74	
240-48	5.0	1.08	3.0	240	48	0.23	
902-281	3.2	1.09	9.7	16.5 ± 0.7	9.0	2.81	19.1 ± 0.7
902-281 tadpoles				15.9 ± 0.2			14.2 ± 1.0

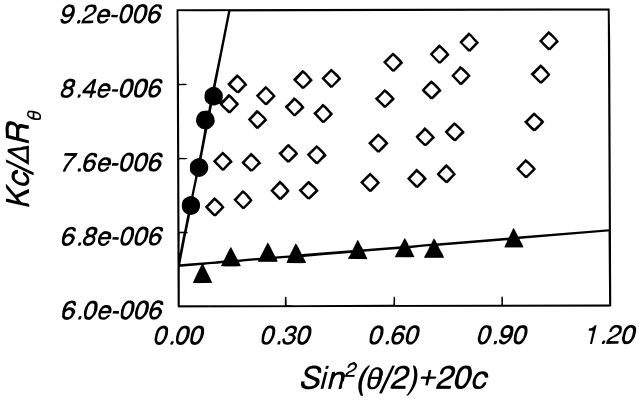


Figure 3. Zimm plot for data from one of the light scattering measurements of 902-281 tadpole molecules. Scattering angles used were 30°, 45°, 60°, 70°, 90°, 105°, 115°, and 150°. The polymer concentrations used were 1.76×10^{-3}, 2.92×10^{-3}, 3.82×10^{-3}, and 4.99×10^{-3} g/mL.

Light Scattering Studies of 902-281 Tadpole Molecules. Static light scattering can be used to determine both the molar mass, $\bar{M}_w$, and the radius of gyration, R_G, of the tadpole molecules, which can then be comapred with those of un-cross-linked diblock copolymers. To make a meaningful comparison of the R_G values, the R_G values should be sufficiently large, e.g., >10 nm, so that they can be determined with accuracy by light scattering. The sample 902-281 meets this criterion.

The micelles of 902-281 prepared in THF/CP with 60% CP were irradiated to obtain a cross-linking density of 26%. At 60% CP, the unimer fraction for 902-281 was found to be ~25%, and its GPC peak was well resolved from that of the cross-linked micelles. The unimer fraction was concentrated by GPC fractionation using THF as the eluant.

The dn/dc value for 902-281 was calculated to be 0.107 mL/g from an empirical relation established previously:[12]

$$\mathrm{d}n/\mathrm{d}c = 0.0938 + 0.0299w_{PS} - 0.0115w_{PS}^2 \text{ mL/g} \quad (2)$$

where w_{PS} is the PS weight fraction of 0.56 for the sample. Since our previous study has shown that the photo-cross-linking did not change the dn/dc of a sample, the dn/dc value of the 902-281 tadpole sample was assumed to be the same as that of the diblock.

Light scattering measurements were performed twice in toluene for the intramolecularly cross-linked unimer and for the unirradiated diblock copolymer. The $\bar{M}_w$ and R_G values were obtained following the Zimm method without resorting to further diblock correction.[12] Illustrated in Figure 3 is the Zimm plot for the data of the tadpole sample from one of the light scattering runs. The averages for the R_G and $\bar{M}_w$ values from the two runs for the tadpoles are $(1.59 \pm 0.02) \times 10^5$ g/mol and 14.2 ± 1.0 nm, and these for the diblock are $(1.65 \pm 0.07) \times 10^5$ g/mol and 19.1 ± 0.7 nm.

A closer examination of Figure 3 also shows that the uncertainty for the $Kc/\Delta R_\theta$ vs $\sin^2(\theta/2)$ slope is relatively large. This is reflected in the relatively large uncertainty margin in R_G. The relatively large uncertainty in R_G is caused by the small R_G value determined. Despite the experimental uncertainty, the difference between the R_G's of the tadpole and the diblock is real. The fact that the molar mass of the tadpoles remains close to that of the un-cross-linked sample and the R_G of the tadpoles is considerably smaller than that for the un-cross-linked diblock clearly suggests the tadpole conformation for the intramolecularly cross-linked PS-*b*-PCEMA unimers. This tadpole conformation is also retained in toluene, a good solvent for both PCEMA and PS.

UV absorbance analysis was also carried out on the tadpole sample and yielded a CEMA double-bond conversion of ~22%, which, within experimental error, was the same as 26%, the overall CEMA conversion for the unimer and micelles.

NMR Characterization of Tadpole Molecules. ^{1}H NMR was run on the 902-281 tadpoles to check the mobility of the PCEMA protons. If the PCEMA block is highly intramolecularly cross-linked, its proton signals should be broad and the intensity low. The low intensity and broad peak for the PCEMA block were indeed observed for the 902-281 tadpoles, but the signals were still visible, suggesting that the PCEMA block was swollen by deuterated chloroform. This is quite understandable, as the tadpoles were prepared in THF/CP with 40% THF in which the PCEMA block should have been quite swollen by THF. When swollen, the chance for the dimerization of CEMA groups which are not adjacent in the chain sequence decreases and that for the dimerization of CEMA groups which are close neighbors in the chain sequence increases. The dimerization of close neighbors increases chain stiffness but does not help to compact the PCEMA block. A less compact block may have some mobility for the individual segments.

We also cross-linked micelles of 229-74 in THF/cyclohexane with 10% THF. Due to the low THF content, the core of the unimers in this case was expected to be very compact in the mixed solvent. Photolysis should have caused extensive dimerization of CEMA units which were not adjacent units in the chain sequence and locked in the compact conformation. Illustrated in Figure 4 is the comparison between the ^{1}H NMR spectrum of the intramolecularly cross-linked unimer against that of the unirradiated diblock in deuterated chloroform in the δ 4−10 region. Although the PS peaks in these two cases are comparable in intensity, the PCEMA peaks of the tadpole molecules disappeared completely. A drastic intensity reduction was also observed for the PCEMA backbone proton peaks located at ~δ 1. The spectra in the δ 0−4 region were not shown as some solvent peaks also showed up in this region. UV analysis indicated that the CEMA content in this sample was 20% of that of the un-cross-linked diblock. The CEMA content of 20% suggested either an unusually high CEMA conversion, i.e., 80% instead of the overall 38% conversion for the micelle and

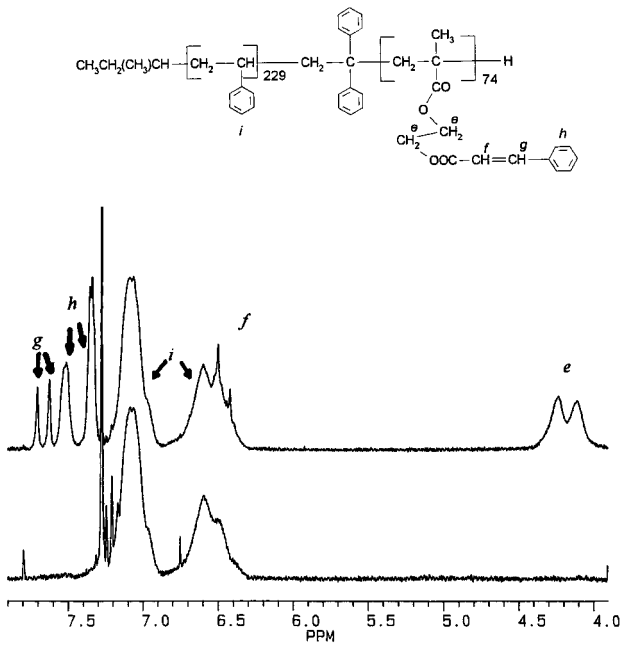


Figure 4. Comparison between the ^{1}H NMR spectra of 229-74 (top) and its tadpole molecules (bottom) in $CDCl_3$.

unimer mixture, in the tadpoles or that the single-chain fraction contained some PS homopolymer or PS-*b*-PCEMA chains with shorter PCEMA blocks. Regardless of the explanation for the unusually low CEMA content in the tadpoles, the fact that CEMA was present in the tadpole sample and not seen by ^{1}H NMR at all suggested a very compact conformation for the PCEMA block.

Micelle Characteristics. As far as this study was concerned, the shapes and the aggregation numbers of the micelles prepared were irrelevant. Despite this, we demonstrated by transmission electron microscopy that the micelles were spherical in all the examined cases.

Conclusions

Unimers of PS-*b*-PCEMA in THF/CH or THF/CP with sufficiently high CH or CP contents can be intramolecularly cross-linked to lock in the PCEMA block in the globule conformation to produce tadpole molecules. Cross-linked unimers should have the expected tadpole shape as confirmed by GPC, light scattering, and NMR.

Acknowledgment. The authors would like to thank NSERC of Canada for its Research Grant Program for financial support of this work.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1992**, *15*, 1.
(2) Guo, A.; Liu, G.; Tao, J. *Macromolecules* **1996**, *29*, 2487.
(3) Price, P. *Pure Appl. Chem.* **1983**, *55*, 1563.
(4) Tao, J.; Stewart, S.; Liu, G. *Macromolecules*, in press.
(5) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(6) Ding, J.; Liu, G. *Macromolecules* **1997**, *30*, 655.
(7) Ding, J.; Liu, G.; Yang, M. *Polym. Commun.*, in press.
(8) Sandron, Ch. *Pure Appl. Chem.* **1962**, *4*, 347.
(9) Bresler, S. E.; Pyrkov, L. M.; Frenkel, S. Ya.; Laius, L. A.; Klenin, S. I. *Vysokomol. Soedin.* **1962**, *4*, 250.
(10) Gallot, Y.; Leng, M.; Benoit, H.; Rempp, P. *J. Chim. Phys.* **1962**, *58*, 1093.
(11) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1775.
(12) Tao, J.; Guo, A.; Liu, G. *Macromolecules* **1996**, *29*, 1618.
(13) Henselwood, F.; Liu, G. *Macromolecules* **1997**, *30*, 488.
(14) Liu, G.; Hu, N.; Xu, X.; Yao, H. *Macromolecules* **1994**, *27*, 3892.
(15) Hu, N.; Liu, G. *J. Macromol. Sci. - Pure Appl. Chem.* **1995**, *A32*, 949.
(16) Liu, G.; Qiao, L.; Guo, A. *Macromolecules* **1996**, *29*, 5508.

MA961422P