Tadpoles from the Intramolecular Photo-Cross-Linking of Diblock Copolymers

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ABSTRACT: Preparation of tadpoles or globule−coil diblock copolymers from three coil−coil diblock copolymers is reported. The coil−coil copolymers consist of one poly(*tert*-butyl acrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate) or PtBA-*b*-PCEMA sample and two PtBA-*b*-P(CEMA-*ran*-hCEMA) samples. Here P(CEMA-*ran*-hCEMA) denotes poly[(2-cinnamoyloxyethyl methacrylate)-*ran*-(2-hydrocinnamoyloxyethyl methacrylate)]. The tadpoles are prepared by photo-cross-linking the PCEMA or P(CEMA-*ran*-hCEMA) blocks intramolecularly. Intramolecular cross-linking competes with intermolecular cross-linking. The former is encouraged by adding a diblock copolymer solution at a low pumping speed into a solvent under constant UV irradiation and stirring. The irradiation ensures that the newly added copolymer is immediately converted into tadpoles. The slow copolymer addition ensures that the copolymer concentration in the photoreactor remains low throughout the photolysis process. Factors affecting the purity, yield, and compactness of the tadpoles produced are examined.

I. Introduction

Diblock tadpoles are prepared by cross-linking intramolecularly one block of a coil−coil diblock copolymer.[1] The head or the globule block of a tadpole should normally be less than ∼10 nm, and the tail block assumes the random coil conformation. Scheme 1 illustrates two conformations for a tadpole in a solvent.

Such small nanostructures should have interesting properties and applications. One can imagine, for example, the different micelle formation properties of the tadpoles and their precursory diblock copolymers for their architectural differences.[2] One can imagine also the molecular imprinting of the tadpole heads.[3] The advantages of producing imprinted tadpoles include the fast diffusion of reagents in and out of the tadpole heads. One can imagine further the use of functional tadpole heads in drug delivery[4,5] or for the template synthesis of small inorganic nanoparticles. Despite all of the above, reports on diblock tadpoles are scarce.[1,6–8] This paper reports the preparation of tadpoles from one poly(*tert*-butyl acrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate) or PtBA-*b*-PCEMA sample and two PtBA-*b*-P(CEMA-*ran*-hCEMA) samples (Scheme 2). Here PhCEMA denotes poly(2-hydrocinnamoyloxyethyl methacrylate).

There have been two reports on tadpole preparation. Tao and Liu[1] reported tadpole preparation from PS-*b*-PCEMA, where PS denotes polystyrene. They collapsed the PCEMA block in THF/cyclopentane (CP) with 60 vol % of CP, a selective solvent mixture for PS, to produce first unimolecular micelles or unimers[9,10] in equilibrium with spherical micelles. The mixture was then irradiated to photo-cross-link PCEMA to yield tadpoles and nanospheres (cross-linked spherical micelles). Since only the portion of chains which existed as unimers with a concentration less than the critical micellar concentration (cmc) were converted into tadpoles and the cmc was low, tadpoles were produced only in minute quantities. Pure tadpoles were obtained only after a tedious separation of the tadpoles from the nanospheres by size-exclusion chromatography (SEC).

Hawker and co-workers[7,8] produced tadpoles from poly[styrene-*ran*-(vinylbenzocyclobutene)]-*block*-poly(ethylene glycol) or P(S-*ran*-VBCB)-*b*-PEG. The VBCB units were incorporated into the PS block in <30 mol % to cross-link the P(S-*ran*-VBCB) block at high temperatures, e.g. 250 °C, via VBCB 1,4-cycloaddition or dimerization. The cross-linking reaction was performed in benzyl ether, a good solvent for both P(S-*ran*-VBCB) and PEG. Thus, the preparation did not invoke a prior physical collapsing step for P(S-*ran*-VBCB). Rather, the collapsing of the P(S-*ran*-VBCB) block was accomplished due to covalent bond formation between the different VBCB units. To increase the amount of tadpoles obtainable from each preparation, Hawker and co-workers[7,8] did not use the high dilution method, which is very noneconomical in terms of solvent use and had been used traditionally for the preparation of intramolecularly cross-linked nanoparticles from homopolymers.[11–13] Instead, they used a clever and ingenious flow reactor design. They prepared tadpoles through the slow and gradual addition of P(S-*ran*-VBCB)-*b*-PEG in benzyl ether at room temperature into a solvent reservoir heated at 250 °C. Once in the reservoir or reactor, the diblock copolymer was converted quickly into tadpoles. Since diblock copolymer addition was rate determining, the concentration of the diblock copolymer remained low in the reactor throughout the synthesis, and thus interchain reaction was minimized. The tadpoles did not undergo further intertadpole fusion probably because they possessed surfaces covered by the inert styrene units. Such a strategy ensured that tadpoles were produced at final diblock copolymer concentrations that were thousands of times higher than what could have been possible from the high dilution method.

In the Hawker case, the intramolecular cross-linking was triggered thermally at a high temperature. Our group has used extensively and successfully the photo-cross-linking of PCEMA to prepare various permanent or cross-linked nanostructures including nanospheres,[14] hollow nanospheres,[15] nanofibers,[16–18] nanotubes,[19,20] cross-linked polymer brushes,[21] and thin films containing nanochannels.[22] More recently, these permanent nanostructures have been covalently coupled to yield nanotube multiblocks,[23] supersurfactants,[24] and grafted nanotube arrays.[25] In this paper we examine how to combine the photo-cross-linking chemistry of PCEMA or P(CEMA-*ran*-hCEMA) with the Hawker strategy to prepare tadpoles in large quantities.

II. Experimental Section

Materials. Cinnamoyl chloride (98%) and hydrocinnamoyl chloride (98%) were purchased from Aldrich and were used as received. Pyridine (ACS reagent, Fisher Scientific) was refluxed

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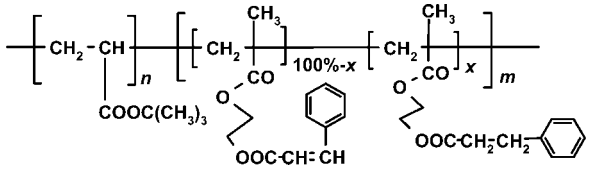
Scheme 1. Two Possible Conformations of Tadpoles

Scheme 2. Chemical Structure of PtBA-*b*-P(CEMA-*ran*-hCEMA)



and distilled over CaH_2 under nitrogen. Cyclohexane (99+% ACS spectrophotometric grade) from Aldrich and chloroform (ACS reagent grade) from Fisher Scientific were used as received.

PtBA-*b*-P(CEMA-*ran*-hCEMA). One PtBA-*b*-PCEMA sample, P1, and two PtBA-*b*-P(CEMA-*ran*-hCEMA) samples, P2 and P3, were used in this work. The hCEMA molar contents in P2 and P3 are 18 and 34 mol % in the P(CEMA-*ran*-hCEMA) blocks, respectively. All these samples were derived from the same PtBA-*b*-PHEMA precursor. Here PHEMA denotes poly(2-hydroxyethyl methacrylate). PtBA-*b*-PHEMA was obtained from the hydrolysis of PtBA-*b*-P(HEMA-TMS) with P(HEMA-TMS) denoting poly(2-trimethylsiloxyethyl methacrylate). PtBA-*b*-P(HEMA-TMS) was synthesized by sequential anionic polymerization.[26]

To prepare P3, 160 mg of PtBA-*b*-PHEMA containing 0.62 mmol of hydroxyl groups was dissolved in 2.5 mL of dry pyridine. Cinnamoyl chloride (88 mg or 0.52 mmol) was then added to the solution. The mixture was stirred overnight under nitrogen before it was dropped onto ice to precipitate the polymer. The polymer was washed with excess water and dried overnight in a vacuum oven. To hydrocinnamate the remaining HEMA units, the dry polymer was dissolved in 2.0 mL of dry pyridine and reacted overnight with excess hydrocinnamoyl chloride (0.25 mL or 1.67 mmol). The polymer was recovered by precipitation onto ice, washed with excess water, and dried in a vacuum oven. P2 was prepared similarly, and P1 was prepared by reacting PtBA-*b*-PHEMA with excess cinnamoyl chloride.

Tadpole Preparation. Tadpoles were prepared by pumping a diblock copolymer solution in chloroform/cyclohexane (CF/CH) into a CF/CH solvent mixture regulated at 22 °C under constant stirring and irradiation. Here the CH volume fraction f_{CH} in the solution was lower than or equal to that of the solvent mixture. The solution pumping speed was controlled by a MPP-100 variable flow minipump. The polymer solution sizes used were 5.0, 20.0, and 20.0 mL, and the corresponding solvent sizes were 95.0, 80.0, and 13.3 mL, respectively. Irradiation was achieved by a focused beam that had passed through a 270 nm cutoff filter from a 500 W mercury lamp in an Oriel 6140 lamp housing powered by an Oriel 6128 power supply. To enable some equilibration time between the added diblock copolymer and its new salvation medium, the tip of the diblock copolymer addition needle was wrapped by a piece of aluminum foil in the shape of a trumpet that was ~1.5 cm long to block the UV beam. Thus, the newly added sample was irradiated only after it had diffused away from the protection of the aluminum foil into illuminated regions of the flask. In all experiments, irradiation was continued for another 4−8 h after diblock copolymer solution addition. The irradiated samples were dried by rota-evaporation and further dried under vacuum for storage. In some cases, the dried samples were redissolved in tetrahydrofuran and then precipitated into methanol/water at v/v = 9/1 to purify the samples.

Light Scattering Measurements. Light scattering measurements were performed on a Brookhaven BI-200 SM instrument equipped with a He−Ne laser (632.8 nm) at 22 °C. All samples were clarified by filtration through 0.1 or 0.2 μm Whatman PTFE syringe filters before measurements. To estimate the cmc of P1 or P1 tadpoles, 3.1 mg of P1 or a P1 tadpole sample was dissolved in 30 mL of a CF/CH mixture with f_{CH} = 64%. This stock solution was then diluted with the same CF/CH mixture to give solutions with different concentrations. The solutions were filtered through 0.1 μm Whatman PTFE syringe filters, and the scattered intensities were measured at 30° as a function of P1 or P1 tadpole concentration. For molecular weight determination, the specific refractive index increment of P1 was determined in butanone following procedures reported already.[14]

Table 1. Molecular Properties of PtBA-*b*-PCEMA or P1

SEC M_w/M_n	d*n*/d*c* (g/mol)	LS $10^{-5}M_w$ (g/mol)	NMR *n*/*m*	*n*	*m*
1.20	0.166	1.75	1.23	510	420

Other Analyses. All ^{1}H NMR measurements were carried out on a Bruker Advance-300 instrument in $CDCl_3$. SEC analyses were performed at 30 °C on a Waters 515 system equipped with two columns (Waters HT-4 and μStyragel 500 Å columns) and a Waters 2410 differential refractometer. The system was calibrated by monodisperse polystyrene standards, and THF was used as the eluant at a flow rate of 1.00 mL/min. Some of the SEC traces were deconvoluted into a cross-linked micelle or dimer peak and a tadpole peak, and the peak areas were evaluated using the PeakFit software. CEMA double-bond conversions were monitored by absorbance changes at 274 nm using a Varian-300 spectrophotometer.[14]

Photolysis of Tadpole Micelles. P1 tadpoles were prepared in CF/CH at f_{CH} = 64% with a PCEMA double conversion of 26%. After drying, the sample was redispersed at 1.0 mg/mL in 3.0 mL CF/CH with f_{CH} = 64% or f_{CH} = 72% to prepare tadpole micelles. The samples were equilibrated for 1 h under stirring before they were photolyzed in a Hellma quartz cell under stirring for 1 h. The absorbance changes before and after the photolysis for the samples were checked by analyzing solutions diluted by CF/CH to 3.00 g from initial aliquots of ~50 mg. SEC samples were obtained by drying the samples by rota-evaporation and then redisperseing them in 0.2 mL of THF.

III. Results and Discussion

One PtBA-*b*-PCEMA and two PtBA-*b*-P(CEMA-*ran*-hCEMA) samples were examined for tadpole preparation. These samples rather than PS-*b*-PCEMA samples, which were investigated in our prior study,[1] were employed here for sample availability. Some hCEMA units were incorporated into the PCEMA block in order to check whether hCEMA without a cross-linkable double bond would concentrate on the surfaces of the tadpole heads and help prevent them from intertadpole cross-linking.

Polymer Characterization. Since all of the polymers were derived from the same PtBA-*b*-PHEMA copolymer, only the PtBA-*b*-PCEMA sample or P1 was characterized thoroughly. Table 1 summarizes the characteristics of P1. SEC analysis based on polystyrene standards gave a polydispersity index M_w of 1.20 for this sample. Using the measured specific refractive index increment M_w of 0.166 mL/g in butanone, we determined by light scattering (LS) a weight-average molar mass M_w of 1.75×10^5 g/mol. Proton NMR analysis in $CDCl_3$ yielded an tBA to CEMA repeat unit number ratio *n*/*m* value of 1.23. Combining the LS M_w and NMR *n*/*m* values, we obtained the weight-average numbers of repeat units of 510 and 420 for PtBA and PCEMA, respectively.

PtBA-*b*-P(CEMA-*ran*-hCEMA) samples were obtained by reacting a fraction of the hydroxyl groups of PtBA-*b*-PHEMA with a controlled amount of cinnamoyl chloride and then the rest of the hydroxyl groups with excess hydrocinnamoyl chloride. The hCEMA molar fractions *x* in the P(CEMA-*ran*-hCEMA) blocks for samples P2 and P3 were determined by ^{1}H NMR to be 18% and 34%, respectively.

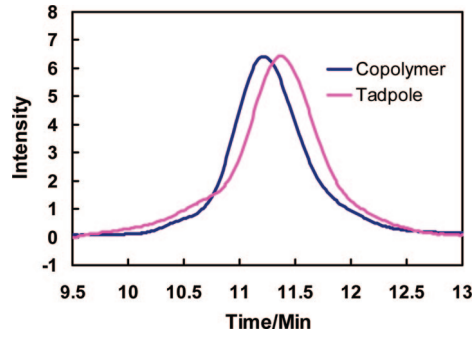


Figure 1. Comparison of SEC traces for P1 and P1 tadpoles.

Tadpole Preparation. Tadpoles were prepared by adopting the Hawker strategy[8] involving the addition of a diblock copolymer solution gradually into a solvent under constant UV irradiation and stirring. After each preparation, the solvent was removed by rota-evaporation, and the resultant solid sample was dried under vacuum before its redispersion in solvents for further characterization by SEC and NMR.

Figure 1 compares the SEC traces for P1 and a P1 tadpole sample. The tadpole sample was prepared by pumping, at 0.22 mL/min, 20.0 mL of a P1 solution in CF/CH into 13.3 mL of solvent. Both the solution and solvent had $f_{CH} = 64\%$, and the solution P1 concentration was 3.0 mg/mL. The CF/CH mixture was used because it was selective for PtBA and collapsed the PCEMA block for the insolubility of PCEMA in CH. The pronounced shift in the SEC peak to "a lower molecular weight" suggests tadpole formation or the locking-in of the PCEMA block in a collapsed state even in the SEC eluant THF, a good solvent for both PtBA and un-cross-linked PCEMA.

A quantitative analysis revealed that the SEC peak "molecular weight" of the tadpoles was 1.11×10^5 Da, which represented a 21% reduction from the peak molecular weight of 1.40×10^5 Da for the diblock copolymer. Our previous LS analyses of PS-*b*-PCEMA tadpoles showed that the LS molecular weight of the tadpoles was the same as their precursory diblock copolymer.[1] The PS-*b*-PCEMA SEC peak shifted because the tadpoles had a smaller radius of gyration than their precursory diblock copolymer. The explanation should remain valid here for the PtBA-*b*-PCEMA system.

To calculate the hydrodynamic volume V_p of a sample at its chromatogram peak, we relate its peak PS-equivalent molecular weight M_p and V_p by[27]

$$V_p = \frac{[\eta]_p M_p}{2.5} \tag{1}$$

Here the intrinsic viscosity $[\eta]_p$ of PS with molecular weight M_w can be calculated from[28]

$$[\eta]_p = 1.10 \times 10^{-2} M_p^{0.725} \quad \text{mL/g} \tag{2}$$

The combined use of eqs 1 and 2 yielded a volume V_p reduction of 33% for this tadpole sample relative to its diblock copolymer precursor P1. This is a very impressive size decrease considering that it resulted probably from the collapsing of only the PCEMA block of the copolymer. It remains interesting to determine using a previously established method[29] the degree of collapsing for a PCEMA homopolymer under such conditions.

While no peak was found for cross-linked micelles or nanospheres in the SEC trace of Figure 1, the tadpole peak had a larger shoulder than the diblock copolymer precursor peak at the higher molecular weight end. The shoulder was deconvoluted from the tadpole peak using a commercial software. Figure 2 shows the deconvoluted peaks. The molecular weight at the maximum of the high-molecular-weight peak was approximately twice that of the tadpole peak. Thus, the shoulder was derived

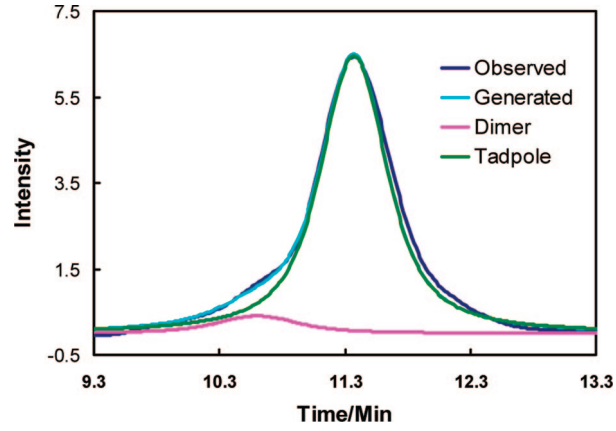


Figure 2. Comparison of the SEC trace (blue) for the P1 tadpole sample with its deconvoluted dimer (red) and tadpole (green) peaks. Also shown is the simulated P1 tadpole trace (cyan).

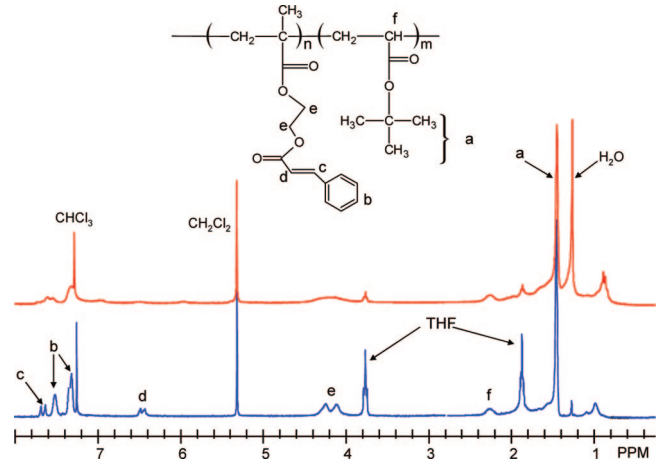


Figure 3. Comparison of ^{1}H NMR spectra of P1 (blue) and P1 tadpoles (red) in $CDCl_3$.

probably from dimers formed during tadpole preparation. The dimer population for this tadpole sample was estimated from the ratio between the area of the dimer peak to the total area of the dimer and tadpole peaks, and it was 7%. Since the diblock copolymer precursor contained already some dimers, which were formed probably for PCEMA cross-linking during sample storage, the amount of dimers formed during tadpole preparation should be <7%. Thus, the tadpoles from such a preparation were >93% in population or purity. They were free of cross-linked micelles despite the fact that the polymer concentration in the final irradiated mixture was 1.80 mg/mL, which was 27 times the cmc value of 0.067 mg/mL for the diblock copolymer in CF/CH at $f_{CH} = 64\%$. This suggests the extreme effectiveness of the Hawker strategy for our system.

Figure 3 compares the proton NMR spectra of P1 and P1 tadpoles at an equal concentration of 2.70 mg/mL in $CDCl_3$, a solvent that solubilized both PtBA and un-cross-linked PCEMA. A CH_2Cl_2 peak is seen in both of the spectra because an equal amount of it was added to the samples as an internal standard. At a mere 25% PCEMA double bond conversion, the PCEMA peaks were already very broad. This confirmed the SEC conclusion that the PCEMA block was locked in a collapsed state in the tadpoles. The fact that the PtBA peak at 1.43 ppm for the two samples was unchanged in position and shape and was comparable in intensity supported the hypothesis that the PtBA block was essentially unperturbed by the cross-linking reaction.

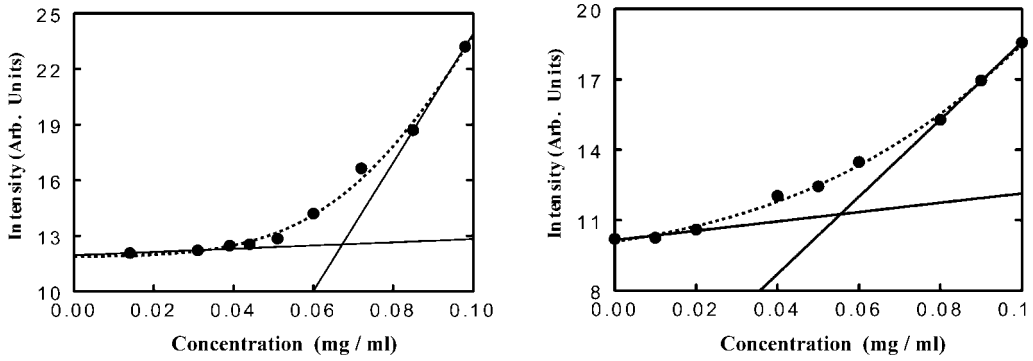


Figure 4. Variation in the scattered intensity from a P1 sample (left) and a P1 tadpole sample (right) in CF/CH at $f_{CH} = 64\%$ as a function of sample concentration.

Table 2. Effect of Changing f_{CH} on Tadpole Preparation from P1 by Using the Same f_{CH} for the Polymer Solution and Solvent

entry	f_{CH} (%)	solution conc (mg/mL)	CEMA conv (%)	tadpole purity (%)	SEC M_p red. (%)	vol red. (%)
1[a]	0	1.0	26	0	0	0
2	64	1.0	27	100	20	32
3	72	1.0	26	6	18	31
4	64	3.0	24	>93	21	33

[a] For all entries, the solution and solvent volumes were maintained at 20.0 and 13.3 mL, and the solution pumping speed was maintained at 0.22 mL/min.

Table 3. Effect of Changing hCEMA Content on Tadpole Preparation

sample	x (%)	CEMA conv[b] (%)	tadpole purity[c] (%)	SEC M_w red. (%)	vol red. (%)
P1[a]	0	31	100	24	37
P2	18	33	100	7	11
P3	34	34	100	2	4

[a] For all entries, the concentration, volume, f_{CH}, and pumping rate for the polymer solution were 2.0 mg/mL, 5.00 mL, 25%, and 0.22 mL/min, respectively. The volume and f_{CH} for the solvent were 95.0 mL and 66%, respectively. [b] Determined from UV absorbance decrease at 274 nm for PCEMA. [c] The higher molecular weight shoulder resulting from dimer was deemed absent based on visual inspection. No decovolution was performed.

Critical Micellar Concentrations. The scattered intensity of P1 and P1 tadpoles in CF/CH with $f_{CH} = 64\%$ was plotted as a function of their concentrations in Figure 4. The cmc of each sample was determined from the concentration at the cross-point between the two tangential lines drawn through the low and high concentration data. The values were 0.067 and 0.056 mg/mL for the diblock copolymer and tadpoles, respectively. Thus, the intramolecular cross-linking of the PCEMA block did not seem to change the cmc of the diblock copolymer significantly.

A closer examination of Figure 4 revealed that the slopes of the straight lines at the high concentration end in the two plots were different. This might be due to formation of micelles with different aggregation numbers or even shapes. However, the data should not be overinterpreted because the experimental errors involving measurements at such low polymer concentrations and low polymer scattering intensities could have been large.

Factors Affecting Tadpole Preparation. The tadpoles discussed so far were prepared under conditions that were optimized after many trials including those summarized in Table 1 of the Supporting Information and Tables 2 and 3.

Table 2 compares properties of tadpoles prepared at different f_{CH}'s. No tadpole formation was reported for entry 1 at $f_{CH} = 0\%$ because the reduction in the V_p of the irradiated sample was 0.12%, which was the same as 0% within experimental error. On the contrary, the V_p reduction was 20% and 18% at $f_{CH} = 64\%$ and $f_{CH} = 72\%$, respectively. These results suggest the necessity for the precollapsing of the cross-linkable PCEMA block. Entry 4 shows results reported in Figure 1 already, and the experiment was performed to show the possibility to produce tadpoles in large quantities.

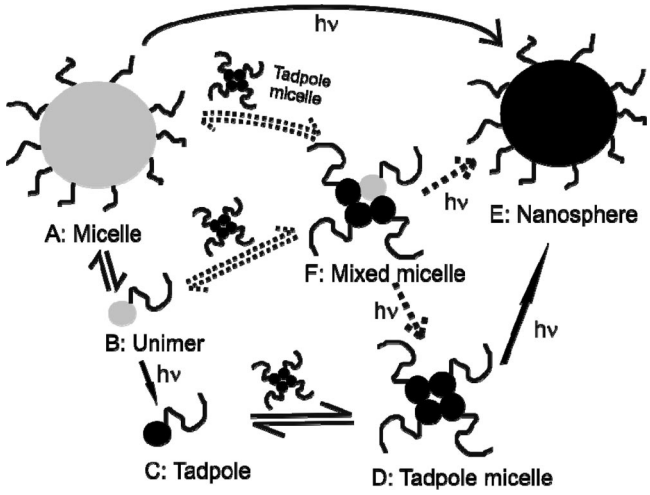
The data of Table 2 further show that an optimal f_{CH} existed for tadpole preparation. Under our preparation conditions, the optimal f_{CH} occurred ~64%. For entry 2 at $f_{CH} = 64\%$, the tadpoles were reported to have a 32% volume collapse and a 100% purity. At $f_{CH} = 72\%$ for entry 3, the tadpoles did not undergo further size collapse and were produced at a much reduced purity of 6%. The major product in this case was the cross-linked micelles.

The small size reduction of the irradiated copolymers in CF/CH with $f_{CH} = 0\%$ or in CF was not for lack of CEMA dimerization. For entry 1 of Table 2, the CEMA double bond conversion was 26%, which was the same as those for entries 2 and 3. The lack of a size reduction and the normal CEMA double bond conversion suggest that most of the CEMA dimerization occurred between adjacent CEMA units along the chain sequence in this sample rather than between CEMA units that were separated by several or more units along the chain sequence. The latter reaction helped increase tadpole compactness and required the folding of the cross-linkable block on itself. It should be favored in a solvent mixture poor for the PCEMA block.

The necessity for the precollapsing of the cross-linkable block here is in stark contrast to the observation of Hawker et al.,[8] who prepared tadpoles in a good solvent for the cross-linkable block. The different chemistry was probably the main cause for the different behaviors. The dimerization of VBCB occurred thermally, and the dimerization of CEMA occurred photochemically. The thermal reaction may occur whenever two VBCB groups collide with each other in the right orientation. The requirements for the photochemical reaction are more stringent. It not only requires the double bonds of two CEMA units to find one another within 4 Å and aligned[30] but also requires this configuration to be achieved within the triplet lifetime of CEMA.[31] Evidently, the precollapsing of the PCEMA block helped position the CEMA groups in proximity to facilitate the occurrence of the dimerization within the PCEMA triplet lifetime.

Another major difference between the Hawker system and our system was the different molar fractions used for the cross-linking groups. The VBCB molar fraction never exceeded 30% in the Hawker case. At such low VBCB molar fractions, even the closest VBCB neighbors in a chain sequence were on the average separated by several styrene units. Dimerization of such VBCB neighbors still helped compact the tadpoles. Furthermore,

Scheme 3. Processes Involved in Tadpole Preparation



the large distance between the closest VBCB neighbors in a chain sequence helped increase the competitiveness of dimerization between VBCB units far apart in a chain sequence.

Table 3 compares results of tadpole preparation from P1, P2, and P3 under identical conditions. As the CEMA content decreased from 100% for P1 to 66% for P3, the volume collapse of the tadpoles relative to their copolymer precursors decreased from an impressive 37% to a mere 4%. Some obvious effects of introducing hCEMA into the PCEMA block included the dilution of the CEMA groups and a possible solubility change to the original PCEMA block. Evidently, one or both of these factors helped decrease the efficiency of the dimerization of CEMA groups well separated in a chain sequence.

At a CEMA molar fraction of 66%, there should be still many CEMA−CEMA immediate neighbors in a P(CEMA-*ran*-hCEMA) chain sequence. The rate of dimerization for such neighbors should thus not change from that in a PCEMA chain. The rate of dimerization for CEMA groups well separated in a P(CEMA-*ran*-hCEMA) chain sequence should decrease relative to that in a PCEMA chain because of the global CEMA concentration decrease in the former polymer. It is thus easy to understand how this dilution effect helped produce less compact tadpoles. If P(CEMA-*ran*-hCEMA) is more soluble than PCEMA in CF/CH, the former will produce a unimer with a more swollen P(CEMA-*ran*-hCEMA) block. This will also help produce less compact tadpoles.

Processes Involved in Tadpole Formation. An explanation of the existence of an optimal f_{CH} for tadpole formation required a detailed analysis of all the possible processes occurring in the system during tadpole formation. Scheme 3 depicts the possible processes occurring for entries 2−4 of Table 2. Here the diblock copolymer was added into the solvent as micelles (A) for the high P1 concentrations in the initial solutions. After P1 addition into the solvent, the micelles should dissociate either fully or partially into unimers (A → B) in the photolysis cell. The extent of micelle dissociation depends on the copolymer mobility and cmc, which are in turn governed by the f_{CH} value. The photolysis of the unimers and micelles leads to tadpoles (B → C) and cross-linked micelles or nanospheres (A → E), respectively. If the reaction has been proceeding for quite some time, the tadpoles already formed should exist mostly as micelles. The newly produced tadpoles may incorporate into the existing tadpole micelles, or they may aggregate to form new tadpole micelles (C → D). Scheme 3 suggests that tadpoles are produced in high purity only if the formation of cross-linked diblock copolymer micelles (A → E) and cross-linked tadpole micelles (D → E) is avoided.

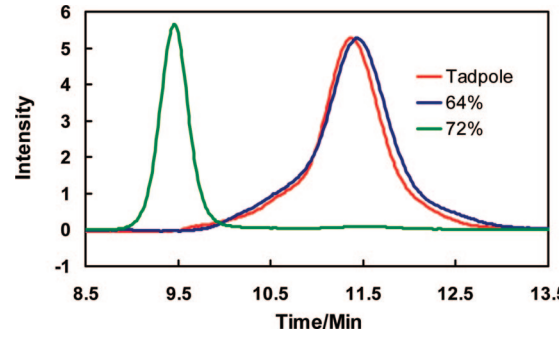


Figure 5. Comparison of SEC traces of a P1 tadpole sample (red) after its further irradiation in CF/CH with f_{CH} = 64% (blue) and f_{CH} =72% (green).

One may argue for the possible fusion of the copolymer micelles and tadpole micelles (A → F) or for the incorporation of the unimers into the tadpole micelles (B → F) to yield tadpole/copolymer mixed micelles. The cross-linking of the tadpoles in such mixed micelles may yield tadpole micelles (F → D) and cross-linked tadpole micelles (F → E). However, the tadpoles and their precursory diblock copolymers are different thermodynamic identities, and the mixing of these different polymers should be unfavorable thermodynamically. For this, we will not discuss further the effect on tadpole formation of these processes denoted by the dashed arrows in Scheme 3.

Optimal f_{CH} for Tadpole Formation. The existence of an optimal f_{CH} for tadpole preparation can be easily understood based on Scheme 3. First, the dissociation of the copolymer micelles into unimers or process A → B needs to be fast in the reaction flask to avoid process A → E. Our past experiments have demonstrated that the rate of PS-*b*-PCEMA micelle disintegration decreased as f_{CH} increased.[32] This trend should be obeyed by the PtBA-*b*-PCEMA micelles as well. Thus, f_{CH} should be sufficiently low to facilitate fast micelle disintegration. Then, the efficiency for process D → E should be f_{CH} dependent as well. The cross-linking of two tadpole heads requires the dimerization of at least two CEMA units from the different tadpoles. This dimerization occurs only if the double bonds of the two CEMA units are aligned and are within 4 Å.[30] As f_{CH} increases, the tadpole micelle cores become less solvent-swollen and the intertadpole dimerization or cross-linking efficiency should increase.

We have confirmed the effect of f_{CH} variation on tadpole micelle cross-linking or process D → E experimentally. The tadpoles of entry 4 of Table 2 were redispersed at 1.0 mg/mL in CF/CH with f_{CH} = 64% and f_{CH} = 72%. The resultant tadpole micelles were then irradiated with UV light for 1 h. Our UV absorbance analyses of the micelles before and after the photolysis indicated that the CEMA double bond concentration decreased by another 20% and 34% in CF/CH with f_{CH} = 64% and f_{CH} = 72%, respectively. This suggests the more facile CEMA dimerization in the latter sample with a less swollen micellar core. After solvent evaporation, the samples were redispersed in THF for SEC analyses with results shown in Figure 5. The data show that 97% of the tadpoles were converted at f_{CH} = 72% into nanospheres. In contrast, no significant peak shape change or tadpole cross-linking was observed for the sample irradiated in CF/CH with f_{CH} = 64%, except a further shift in its peak position to a longer retention time or a further increase in the tadpole head compactness.

IV. Conclusions

One PtBA-*b*-PCEMA sample and two PtBA-*b*-P(CEMA-*ran*-hCEMA) samples were prepared and characterized. All of the three samples were derived from the same PtBA-*b*-PHEMA

sample with 510 tBA units and 420 HEMA units, and the hCEMA molar fraction was varied from 0% to 18% and 34%. Tadpoles were prepared by pumping diblock copolymer solutions in CF/CH at f_{CH} into a CF/CH solvent at a different or the same f_{CH} under constant UV irradiation and stirring. Based on the criteria of high purity, a high final concentration, and a maximal volume collapse for the tadpoles, our systematic study revealed that the tadpoles were best prepared by using a low diblock copolymer addition rate and using copolymer solutions and solvents with the same f_{CH}. The precollapsing of the photocross-linkable block in a solvent with a sufficiently high f_{CH} was essential. Low f_{CH} values led to tadpoles with low degrees of volume collapsing. Too high f_{CH} values led to production of tadpoles containing cross-linked micelles. The optimal f_{CH} occurred ~64%. Tadpoles with the most volume collapsing were produced from PtBA-*b*-PCEMA which had the highest CEMA content among the three diblocks used. Using PtBA-*b*-PCEMA and $f_{CH} = 64\%$, tadpoles were prepared free of cross-linked micelles at a final tadpole concentration that was 27 times the cmc of the copolymer. Such tadpoles had a volume reduction of 33% relative to their precursory copolymer. Such a success renders the production of tadpoles in large quantities possible for potential applications mentioned already in the Introduction.

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Supporting Information Available: Results for the optimization of tadpole preparation from P2 and a discussion of the results. This material is available free of charge via the Internet at http://pubs.acs.org.

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