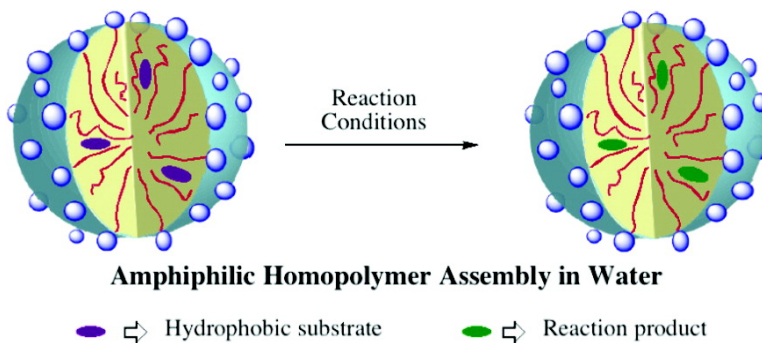


Amphiphilic Homopolymer as a Reaction Medium in Water: Product Selectivity within Polymeric Nanopockets

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Amphiphilic Homopolymer as a Reaction Medium in Water: Product Selectivity within Polymeric Nanopockets

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Abstract: A styrene-based water-soluble polymer has been explored for its use as a host for lipophilic substrates in aqueous medium. Unimolecular reactions, namely, photo-Fries rearrangement of naphthyl esters, α -cleavage reaction of 1-phenyl-3-*p*-tolyl-propan-2-one, and Norrish type I and type II reactions of benzoin alkyl ethers were examined. We find that the hydrophobic domains generated by the polymer not only restrict the mobility of the radicals but also modestly incarcerate the substrate, intermediates, and products during the time scale of the reactions. Comparative studies of the same photoreactions in micelles formed from small molecule surfactants and an amphiphilic diblock copolymer demonstrate that the styrene-based water-soluble polymer aggregates in aqueous medium offer better selectivity.

Introduction

Although today's environmental consciousness imposes use of water as a solvent¹ and despite the fact that water is cheap, organic solvents are still the primary choice. Most of the organic substrates are not soluble in water, and many reactive molecules are decomposed or deactivated by water. Surfactants,² water soluble dendrimers,³ and organic hosts⁴ have been used as reaction media to conduct reactions in an aqueous medium. Recently a new class of polymer superstructures having a hydrophilic carboxylic acid moiety and a hydrophobic benzyl moiety within its monomer unit was reported by one of our groups (Figure 1).⁵ In aqueous medium, this amphiphilic homopolymer (polymer-A) adopts a conformation in which the hydrophilic units are exposed to water and the hydrophobic units

are tucked inside to form nanosized-pockets (average size of about 50 nm) that are capable of sequestering hydrophobic guest molecules. This behavior opens up the possibility of utilizing such a polymer as a reaction medium in aqueous solutions. In this report, the potential of this polymer's hydrophobic domains to provide product selectivity was investigated with four unimolecular reactions. We show here that this amphiphilic polymer does indeed provide a unique hydrophobic environment providing selectivity better than conventional micelles based on small molecule surfactants and an amphiphilic diblock copolymer. The photoreactions reported here also serve as probes to understand the nature of hydrophobic pockets provided by the polymer.

Results and Discussion

In this study, the styrene-based amphiphilic polymer (Figure 1a; polymer-A) has been utilized as a host for carrying out

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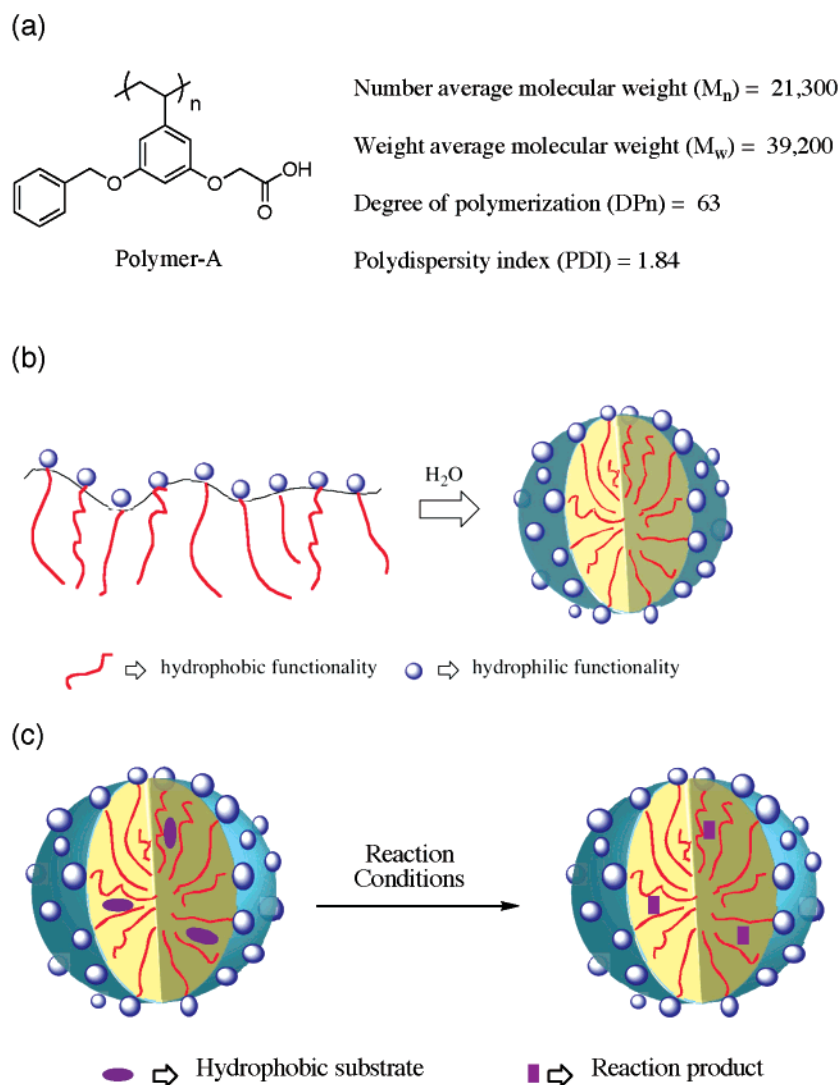


Figure 1. (a) Structure of the polymer used for the study. (b) Idealized view of the cross section of the micellar assembly. (c) Schematic representation of the micelle with the reaction within the polymer micelle-type nanocontainer.

photochemical reactions in aqueous medium. Polymer-A is water soluble in its salt form at pH 8.5. In aqueous solution, polymer-A self-organizes into spherical micellar type aggregates having a hydrophobic interior and a hydrophilic exterior (Figure 1b). To probe the micropolarity of these hydrophobic domains, we have employed pyrene as a probe.⁶ Fluorescence spectra were recorded for various host/guest ratios, and it was observed that the fluorescence intensity increases with the addition of a solution of polymer-A. In aqueous solution, some of the pyrene molecules exist as aggregates (excimer emission in the region 430–500 nm). But upon addition of the polymer to the aqueous solution, the emission consisted of only unimolecular fluorescence in the region 380–440 nm revealing that the pyrene molecules are held isolated by the hydrophobic domains of polymer-A.

The ratio of the intensities of vibrational peaks 1 and 3 (I_1/I_3) in the monomer fluorescence spectrum is a measure of the polarity of the environment around the pyrene moiety.⁶ It was observed that pyrene exhibited an I_1/I_3 ratio of 1.7 in an aqueous solution of pH 8.5. The ratio decreased from 1.7 to 1.47 upon

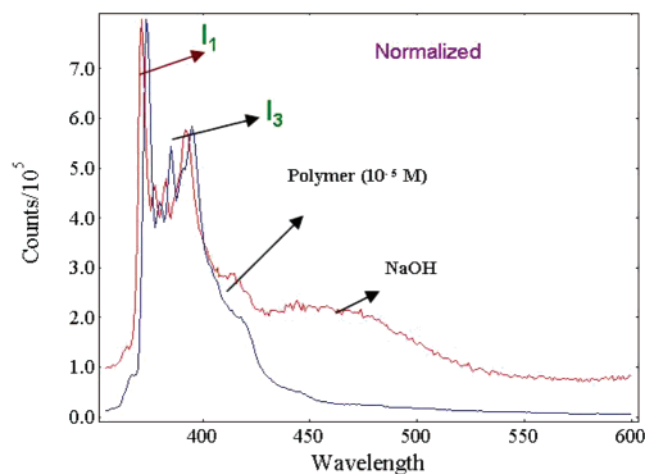
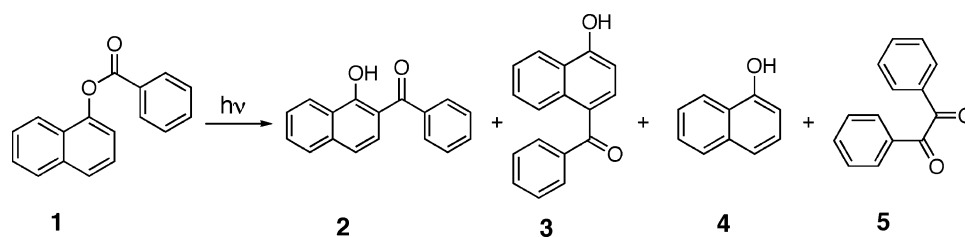


Figure 2. Fluorescence spectrum of pyrene (10^{-5} M) in aqueous NaOH and in aqueous polymer-A solution (1×10^{-5} M).

addition of polymer-A (Figure 2) which could be attributed to the presence of a slight hydrophobic environment around pyrene in the aqueous polymer-A solution. The critical micellar concentration of the polymer-A was calculated using pyrene as

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Scheme 1



the probe. The change in the intensity I_1 of monomer fluorescence spectrum of pyrene as a function of the concentration of the polymer-A was plotted. In this plot, the major change in the slope is related to the onset of micelle formation and thereby provides quantitative determination of critical micellar concentration of polymer-A. The critical micellar concentration was calculated to be 2.4×10^{-6} M from the point of intersection of extrapolated line segments as shown in Figure 3.⁷

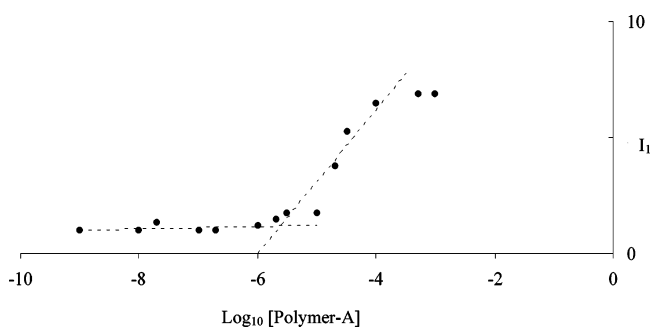


Figure 3. A Plot of pyrene (1×10^{-5} M) fluorescence intensity I_1 as function of homopolymer concentration.

To examine the usefulness of polymer-A as a reaction medium, four unimolecular photochemical reactions, namely, photo-Fries rearrangement of 1-naphthyl benzoate (1), photo-Fries rearrangement of 1-naphthyl phenyl acyl ester (6), Norrish type I reactions of 1-phenyl-3-*p*-tolyl-propan-2-one (14), and benzoin alkyl ethers (16a–c) were investigated. In all the above reactions, upon irradiation, a molecule from either its excited singlet or triplet state fragments to form a radical pair. Depending upon the mobility and confinement provided by the medium, the primary intermediates yield various products as discussed below.

The first reaction carried out was the photo-Fries rearrangement of 1-naphthyl benzoate (1). This molecule upon irradiation in hexane afforded four products, as shown Scheme 1.^{8,9}

Table 1. Products Distribution upon Irradiation of 1-Naphthyl Benzoate (1)^a

medium	product distribution ^b (%)				benzoic acid
	2	3	4	5	
hexane	60	30	7	3	
aq. NaOH (pH= 8.5) ^b	2		60		38
polymer-A ^c	>99				
CTAC ^d	87	12	1		
SDS ^e	83	14	2		
SDO ^f	75	21	3	1	
PS- <i>b</i> -PSA ^{b,g}	50	6	23		21

^a [1] = 2.4×10^{-4} M. ^b Product 4 and benzoic acid resulted from thermal hydrolysis. ^c [Polymer-A] = 1.1×10^{-4} M. ^d [CTAC] = 1×10^{-2} M. ^e [SDS] = 1×10^{-2} M. ^f [SDO] = 1×10^{-1} M. ^g [PS-*b*-PSA] = 1.1×10^{-4} M. ^h The percentage yield was kept $\sim 20\%$ in all reaction media and was calculated by gas chromatography using undecane as the internal standard. The mass balance was estimated to be 90–95%.

However in an aqueous solution in the absence of polymer-A at pH 8.5, 1 thermally underwent hydrolysis into 1-naphthol and benzoic acid. But in an aqueous polymer-A solution (1×10^{-4} M), hydrolysis was completely suppressed, and when irradiated, it yielded 2-benzoyl 1-naphthol (2) as the only photoproduct. The selectivity obtained within this polymer-A assembly is better than that obtained within micelles from classical surfactant small molecules such as cetyl trimethylammonium chloride [CTAC], sodium dodecyl sulfate [SDS], and sodium dodecanoate [SDO] where a significant amount of *para*-rearrangement product 3 (12–21%) was obtained. For comparison, photolysis was also conducted in an aqueous solution of the diblock copolymer, polystyrene-*b*-poly (sodium acrylate) [PS-*b*-PSA].¹⁰ In a 10^{-4} M aqueous solution of [PS-*b*-PSA] at pH 9.5, 1 underwent thermal hydrolysis to yield α -naphthol and benzoic acid, and when irradiated, *ortho*- and *para*-rearrangement products resulted in the ratio 1:8. The product distributions upon irradiation in various media are presented in Table 1. Absence of hydrolysis product suggests that the naphthyl ester is protected from the basic aqueous medium by homopolymer-A. Note that all photochemical reactions were kept at about 20% conversion, which is a standard operating procedure in mechanistic photochemistry.¹¹ This avoids complications in analysis due to secondary photoreactions from the products of the reaction under investigation.

(7) At first sight, this result seems inconsistent with our previous report,⁵ where we mention that the integrity of the micelles is intact even at 10^{-9} M concentration based on TEM. Note however that the CMC determination using pyrene is a measure of the partition coefficient of the hydrophobic probe in the micellar interior vs the bulk solvent (see: Zhao, J.; Allen, C.; Eisenberg, A. *Macromolecules* **1997**, *30*, 7143). Therefore, it is possible that the integrity of the micelle is intact at nanomolar concentration, but the partition coefficient of a molecule with polarity similar to that of pyrene into that micelle is low at this concentration. Moreover, note that the concentration (10^{-4} M) that we use for the photochemical reactions in this report is well above the CMC measured using pyrene as the hydrophobic probe. Therefore, the comparison of this polymer above its CMC with other micelle forming molecules above their respective CMCs is consistent and valid.

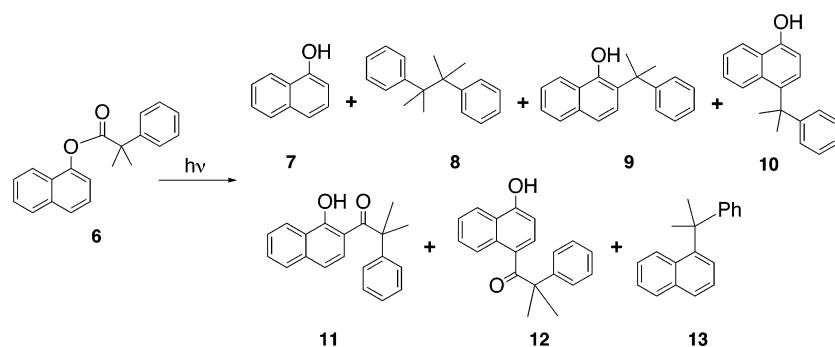
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(10) It has been previously reported that a 10^{-4} M aqueous solution of PS-*b*-PSA provides a micellar environment; see: (a) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7339. (b) Zhang, L.; Eisenberg, A. *Macromolecules* **1996**, *29*, 8805. To confirm this with the polymers purchased from commercial sources, we performed the pyrene-based CMC determination experiments with this polymer. We obtained a CMC value of 1×10^{-7} M, which is consistent with the values reported in the literature (data provided in the Supporting Information). Since we perform our experiments at 10^{-4} M concentration, we are indeed working well above the CMC of this polymer.

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Scheme 2

**Table 2.** Products Distribution upon Irradiation of 1-Naphthyl Phenyl Acetate (**6**)^a

medium	product distribution (%) ^a						
	7	8	9	10	11	12	13
hexane	18	11	2.5	9	39	19	1.5
aq NaOH (pH = 8.5)	2				74	24	
polymer-A ^b					>99		
CTAC ^c	2				86	12	
SDS ^d	2				83	15	
SDO ^e	2				81	17	
PS- <i>b</i> -PSA ^f	15				74	12	

^a [**6**] = 2.0×10^{-4} M. ^b [Polymer-A] = 1.1×10^{-4} M. ^c [CTAC] = 1×10^{-2} M. ^d [SDS] = 1×10^{-2} M. ^e [SDO] = 1×10^{-1} M. ^f [PS-*b*-PSA] = 1.1×10^{-4} M; Product **7** was resulted from thermal hydrolysis. ^g The percentage yield was kept $\sim 20\%$ in all reaction media and was calculated by gas chromatography using undecane as the internal standard. The mass balance was estimated to be 90–95%.

The second reaction investigated was the photo-Fries rearrangement of 1-naphthyl phenyl acyl ester (**6**).¹² Upon irradiation in hexane, this compound afforded seven products **7–13** (Scheme 2). Unlike naphthyl benzoate, when taken in an aqueous solution at pH 8.5, it remained stable against thermal hydrolysis and upon irradiation, 1-naphthol (**7**), 2-phenylacyl-1-naphthol (**11**), and 4-phenylacyl-1-naphthol (**12**) were obtained. The product distributions in various media are presented in Table 2. But when irradiated in an aqueous polymer-A solution of 1×10^{-4} M, 2-phenylacyl-1-naphthol was the only photoproduct observed. The selectivity increased with an increase in concentration of the polymer (Figure 4). The selectivity observed during photolysis of 1-naphthyl benzoate and 1-naphthyl phenyl acyl ester could be attributed to the restricted mobility of the radicals that are confined within the hydrophobic pockets. The photo-Fries rearrangement of **6** was also carried out in aqueous micellar solutions of CTAC, SDS, SDO, and PS-*b*-PSA. Reaction of **6** within surfactant micellar solution resulted in both *ortho*- and *para*-rearrangement products (**11** and **12**) in the ratio $\sim 6:1$ along with $\sim 2\%$ of 1-naphthol. Photolysis of **6** in an aqueous micellar solution of PS-*b*-PSA yielded *ortho*- and *para*-rearrangement products in the ratio 8:1 along with appreciable amount of α -naphthol ($\sim 15\%$) which resulted from thermal hydrolysis (pH of PS-*b*-PSA = 9.5). The difference in the formation of the hydrolysis product **7** could be attributed to the difference in the pH of the

solution. However, we have noticed significant differences in the formation of the photoproducts. The absence of *para*-rearrangement product (**12**) upon irradiation of **6** within polymer-A reveals the more confined nature of its hydrophobic domains compared to that of micelles formed by surfactants and block copolymer.

To address the question, whether the hydrophobic pockets of polymer-A can restrict the mobility of guest molecules even on a longer time scale, Norrish type I reactions of 1-phenyl-3-*p*-tolyl-propan-2-one (**14**)^{13,14} and benzoin alkyl ethers (**16a–c**)^{15,16} were investigated. These two systems cleave from their triplet excited states to yield triplet radical pairs. Under such conditions, coupling of radicals can take place only if the radical pair can intersystem cross to a singlet state or escape from the cage to form free radicals. Results discussed below on these two systems reveal that the hydrophobic reaction cavities of polymer-A confine the guest molecules even on a microsecond time scale.

Upon irradiation, 1-phenyl-3-*p*-tolyl-propan-2-one (**14**) undergoes α -cleavage to form the radical pairs **C** and **C'**, followed by the decarbonylation to yield the radicals **A** and **B** (Scheme 3). When the radicals **A** and **B** are held in a cage, the only expected product is the recombination product **AB**.¹⁷ The cage effect of the medium is given by the formula $[\mathbf{AB} - (\mathbf{AA} + \mathbf{BB})]/[\mathbf{AA} + \mathbf{AB} + \mathbf{BB}]$. It was also observed that in reaction media such as a dimerized cavitand, or water soluble dendrimers, the radical pair **C** and **C'** intersystem cross to a singlet state to yield the rearrangement products such as **15a** (Scheme 3).¹⁸ However, no rearrangement products were observed in the polymer-A medium. The cage effect in various reaction media are presented in Table 3.

About 80% cage effect was observed when the reaction was carried out in aqueous polymer-A solution (1.1×10^{-4} M). To understand the observed cage effect, the roles of the concentration of the polymer-A, the concentration of the substrate, and dilution were examined. The cage effect increased with an increase in the polymer concentration, as shown in Figure 5.

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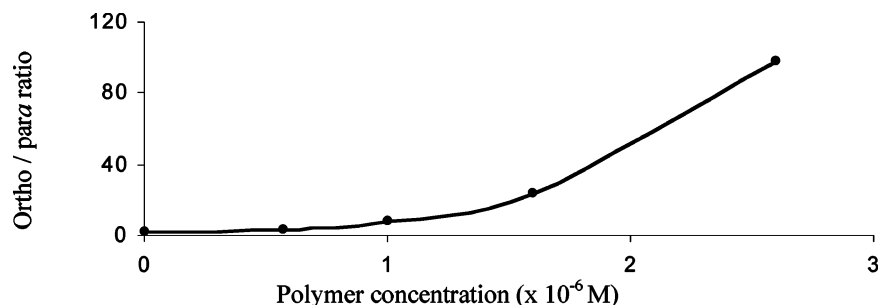


Figure 4. Concentration effect of polymer-A on the products distribution upon photolysis of 1-naphthyl phenyl acyl ester (6).

Scheme 3

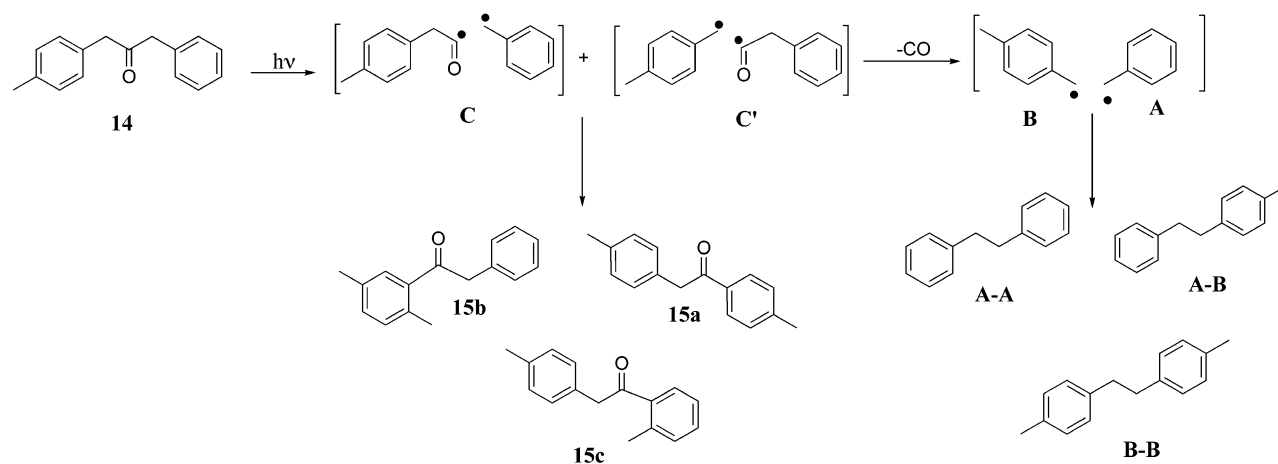


Table 3. Products Distribution upon Photolysis of 1-Phenyl-3-*p*-tolyl-propan-2-one (14)^a

medium	product distribution ^g (%)			cage effect
	AA	AB	BB	$F_c = \frac{AB - [AA + BB]}{AA + AB + BB}$
hexane	22	53	25	0.05
aq NaOH (pH = 8.5)	22	52	26	0.04
polymer-A ^b	4	90	6	0.80
CTAC ^c	16	61	18	0.27
SDS ^d	16	64	20	0.28
SDO ^e	18	61	21	0.22
PS- <i>b</i> -PSA ^f	15	66	19	0.32

^a [14] = 2.2×10^{-4} M. ^b [Polymer-A] = 1.1×10^{-4} M. ^c [CTAC] = 1×10^{-2} M; Rearrangement product 15a was observed in small amounts (~5%) upon photolysis of 14 within CTAC micelles. ^d [SDS] = 1×10^{-2} M. ^e [SDO] = 1×10^{-1} M. ^f [PS-*b*-PSA] = 1.1×10^{-4} M. ^g The percentage yield was kept ~ 20% in all reaction media and was calculated by gas chromatography using undecane as the internal standard. The mass balance was estimated to be 90–95%.

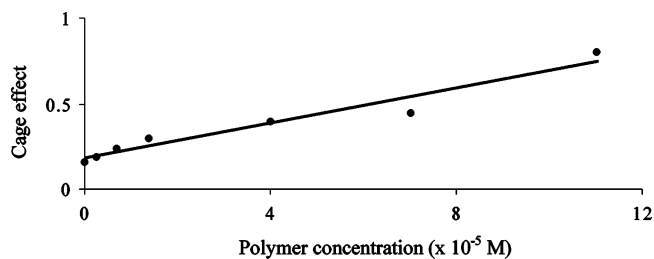


Figure 5. Cage effect as a function of polymer-A concentration in Norrish type I reaction of 1-phenyl-3-*p*-tolyl-propan-2-one (14).

This behavior could be attributed to two factors. The number of hydrophobic domains in the medium increases with an increase in polymer concentration, which would enhance the reactant uptake by the polymer matrix preventing reaction from

the aqueous exterior. Also the number of hydrophobic units will increase with an increase in polymer concentration, which enhances the solvophobic interaction of the hydrophobic domains with the aqueous phase. In other words, the hydrophobic pockets are more protected from an aqueous phase at a higher polymer concentration, and hence leaking of the radicals into bulk environment is minimized. The cage effect was constant up to 4.5×10^{-4} M concentration of the reactant ketone, and then it decreased as shown in Figure 6. Either multiple occupancy of guest molecules in a single cage or leaking to aqueous phase from the hydrophobic interior due to the saturation of the substrate should be causing the decrease in the cage effect with increased reactant concentration.

As a part of a control experiment, a 10 mL sample with the substrate concentration 2.2×10^{-4} M and the polymer concentration 1.1×10^{-4} M was prepared. The sample was then diluted to 25 mL, 50 mL, and 100 mL. Under these conditions the ratio of the polymer to reactant molecules remained constant. If there is strong binding between the reactant and the polymer, the cage effect should remain constant. However the cage effect decreased with dilution almost linearly as shown in Figure 7.

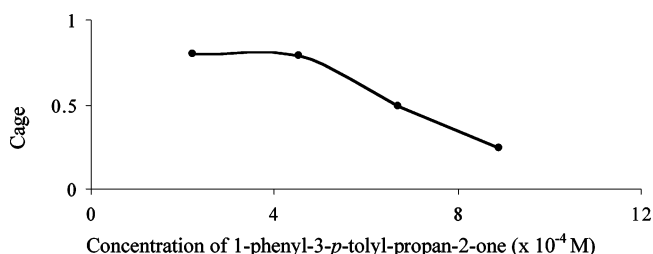
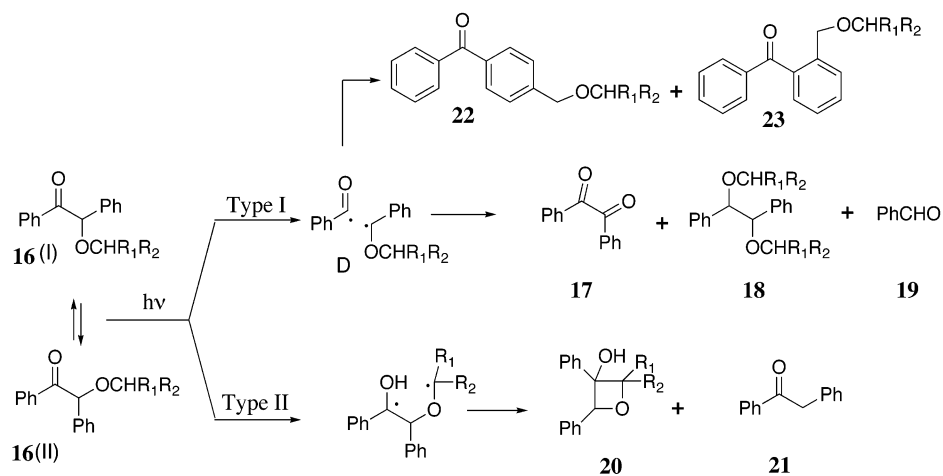


Figure 6. Cage effect dependence on the substrate concentration in Norrish type I reaction of 1-phenyl-3-*p*-tolyl-propan-2-one (14).

Scheme 4



We attribute this effect to both the solubility of the ketone in water and to a decrease in the concentration of the polymer aggregates. The decrease in cage effect upon dilution suggests that the complex between the substrate and the polymer aggregates is responsible for the cage effect rather than the complex between the reactant and a single polymer chain. The cage effect obtained within the aggregates of polymer-A was also compared with that of surfactant micelles and micelles obtained from PS-*b*-PSA, and the results are tabulated in Table 3. Moderate cage effect (22–32%) obtained within conventional micelles and micelles formed by PS-*b*-PSA suggests that the aggregates of polymer-A provide a better confining environment for the reactive intermediates.

The final unimolecular reaction examined was the Norrish type I and type II reactions of benzoin alkyl ethers (**16a–c**). The photochemical behavior of benzoin methyl ether, benzoin ethyl ether, and benzoin isopropyl ether in aqueous polymer-A solution was investigated. Irradiation of **16a**, **16b** and **16c** in benzene yields the corresponding radical pair **D**, which escapes to form benzil (**17**) and the respective pinacol ether (**18**) as shown in Scheme 4.¹⁹ However, benzaldehyde was observed only in trace amounts when the reaction was carried out in aqueous solution without the polymer (pH = 8.5). Only minor amounts of oxetenol (**20**) and deoxybenzoin (**21**) (Norrish type II products) via γ -hydrogen abstraction were obtained (Table

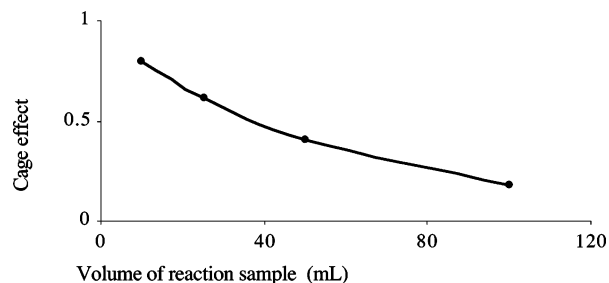


Figure 7. Cage effect as a function of volume of the reaction sample that contains 23 mg of the polymer and 0.5 mg of **14** in Norrish type I reaction of 1-phenyl-3-*p*-tolyl- propan-2-one (**14**).

Table 4. Products Distribution upon Photolysis of Benzoin Alkyl Ethers **16a**, **16b**, and **16c**

medium	type I products' (%)			type II products' (%)		type II / type I
	17	18	22	20	21	
Benzoin Methyl Ether (16a)^d						
benzene	33	64			3	32
aq NaOH (pH = 8.5)	trace	94			6	15
polymer-A ^b	trace	44			56	0.8
CTAC ^c	34	48			18	4.5
SDS ^d	18	38			44	0.9
SDO ^e	26	59			15	3.1
PS- <i>b</i> -PSA ^f		44			56	0.8
Benzoin Ethyl Ether (16b)^g						
benzene	32	63		5		32
aq NaOH (pH = 8.5)	trace	80		4	16	4
polymer-A ^b	trace	14	13	14	59	0.37
CTAC ^c	trace	54	4	23	19	1.4
SDS ^d	19	35		37	9	1.17
SDO ^e	8	47		21	24	1.22
PS- <i>b</i> -PSA ^f	8	46		11	35	1.17
Benzoin Isopropyl Ether (16c)^h						
benzene	33	64			3	32
aq NaOH (pH = 8.5)	12	84			2	48
polymer-A ^b	trace	10	23		67	0.5
CTAC ^c	29	35			36	1.8
SDS ^d	19	27			54	0.9
SDO ^e	25	51			24	3.2
PS- <i>b</i> -PSA ^f	10	40			50	1.0

^a [**16a**] = 2.3×10^{-4} M. ^b [Polymer-A] = 1.1×10^{-4} M. ^c [CTAC] = 1×10^{-2} M. ^d [SDS] = 1×10^{-2} M. ^e [SDO] = 1×10^{-1} M. ^f [PS-*b*-PSA] = 1×10^{-4} M. ^g [**16b**] = 2.3×10^{-4} M. ^h [**16c**] = 2.2×10^{-4} M. ⁱ The percentage yield was kept at $\sim 20\%$ in all reaction media and was calculated by gas chromatography using benzophenone as the internal standard. The mass balance was estimated to be 90–95%.

4). When taken in aqueous polymer-A solution, the photochemical behavior of these ethers was significantly different. It was observed that the hydrophobicity of the alkyl part of the ether also had an influence on the product distribution upon irradiation in an aqueous polymer-A solution. Irradiation of **16a** included

(19) (a) Turro, N. J.; Gould, I. R.; Baretz, H. B. *J. Phys. Chem.* **1983**, *87*, 531. (b) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529.

within the polymer matrix yielded pinacol ether **18** (type I) and deoxybenzoin **21** (type II) in the ratio 44:56, while irradiation in aqueous solution without polymer-A (pH 8.5) yielded pinacol ether and deoxybenzoin in the ratio 94:06. In the case of **16b**, irradiation within aggregates of polymer-A resulted in 73% of Norrish type II products **20** and **21** along with 13% of *para*-rearrangement product (**22b**) due to Norrish type I reaction, while irradiation in aqueous solution without polymer-A yielded ~80% of type I products as given in Table 4.²⁰ Similarly, irradiation of **16c** within polymer-A yielded 67% of deoxybenzoin along with 23% of *para*-rearrangement product (**22c**).

The above results suggest that the excited-state behavior of **16a–c** is altered by homopolymer-A. Two observations are important to note: (a) The type II reaction which is almost negligible becomes predominant in the presence of polymer-A. (b) The rearrangement products **22b** and **22c** that are not formed in solution are formed in minor amounts in the presence of polymer-A.

Both of these observations suggest that the hydrophobic pockets provided by polymer-A control the diffusion of the caged radical pair **D** (Scheme 4). In the absence of cage escape even if the type I cleavage occurs, the radical pair would be expected to recombine to yield the reactant under these conditions. The efficiency of type I products formation would be expected to be low. The type II process whose rate may be slow would eventually lead to the products in greater amount. This model fits the observed results. The yield of rearrangement products **22** increases with the hydrophobicity of the alkyl part of the ether. For example, while the most hydrophobic **16c** gives the highest amount of **22c**, the least hydrophobic **16a** gives no rearrangement product. This suggests that the escape of the primary radical **D** from the hydrophobic cage provided by the polymer depends on the alkyl chain. The photochemical behaviors of **16a–c** were also studied within surfactant micelles (CTAC, SDS, and SDO) and micelles obtained from PS-*b*-PSA. Photolysis of **16a–c** within conventional surfactant micelles yielded more type I products compared to photolysis within homopolymer aggregates. The rearrangement product **22** which was observed from the photoreaction in aqueous homopolymer solution was not obtained from the reaction within surfactant micelles. The photobehavior of **16a**, less hydrophobic among the other ethers, within PS-*b*-PSA micelles was very similar to that within homopolymer aggregates. However the photochemical behaviors of **16b** and **16c** were significantly different within

PS-*b*-PSA. Photoreaction of **16b** and **16c** within PS-*b*-PSA yielded more type I product relative to reaction within homopolymer. Also the rearrangement product **22** was absent from photolysis of **16b** and **16c** within PS-*b*-PSA micelles. All the above observations suggest that the homopolymer aggregates effectively incarcerate the relatively more hydrophobic ethers **16b** and **16c** compared to PS-*b*-PSA micelles, whereas the less hydrophobic ether **16a** resides at the interfacial region in both cases. Evidently homopolymer aggregates in aqueous medium are capable of providing a better confining hydrophobic reaction cavity for benzoin alkyl ethers compared to micelles obtained from conventional small molecule surfactants and PS-*b*-PSA.

Conclusion

In summary, we have demonstrated that the self-assembly of the styrene-based amphiphilic homopolymer can be used as a supramolecular reaction cavity to perform photochemical reactions in aqueous solution, giving rise to an environmentally friendly reaction system. Based on our investigation of four unimolecular reactions in polymer micelle solution, we have shown the following: (i) the amphiphilic polymer is capable of acting as an effective nanoscale container for carrying out reaction of lipophilic compounds in water. (ii) The polymer nanoparticle is capable of providing confined environments to provide products in a selective fashion despite the fact that these particles are about 50 nm in size. (iii) The environment provided by the amphiphilic homopolymer is more rigid and confined compared to that formed by conventional small molecule surfactant micelles (CTAC, SDS, and SDO) and micelles obtained from the diblock amphiphilic copolymer PS-*b*-PSA. With these comparisons, it is also clear that the charge on the surfactant has very little influence on the selectivities. Also, the amphiphilic diblock copolymer behavior seems to be more similar to the small molecule surfactants than our amphiphilic homopolymer. The significant differences between micelles obtained from homopolymer and block copolymer (PS-*b*-PSA) in terms of selectivities warrant further investigation on the polymer assembly itself.

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Supporting Information Available: Experimental Section. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) For thermal synthesis and characterization of the photoproducts of this reaction, see: Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* **1990**, *55*, 5269.