

# A styrene based water soluble polymer as a reaction medium for photodimerization of aromatic hydrocarbons in water

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## Abstract

A styrene based water soluble polymer (polymer-A) has been explored as a host for solubilizing otherwise insoluble aromatic hydrocarbons in water. The increased local concentration of encapsulated aromatic hydrocarbons within the hydrophobic pockets of polymer-A was utilized for performing efficient photodimerization of acenaphthylene (**1**) and six 9-substituted anthracenes [AnCOOH, AnCHO, AnCH<sub>2</sub>OH, AnCH<sub>3</sub>, AnBr and AnCN] in water. Photodimerization of these aromatic hydrocarbons were more efficient than in water and yielded dimers even at low concentrations ( $\sim 10^{-4}$  M). At the same concentration of anthracenes in organic solvents such as benzene and methanol, no dimers were formed even after 48 h of irradiation. Although the polymer-A was able to increase the local concentration of the reactant aromatics it was unable to orient them towards a single dimer.

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## 1. Introduction

Water soluble polymers have attracted attention in recent times, owing to their application in areas ranging from material science to biology [1–5]. These amphiphilic polymers undergo self-organization in aqueous media resulting in assemblies such as micelles, vesicles, fibers, helical superstructures and macroscopic tubes [6–12]. A new class of polymer superstructures having a hydrophobic styrene unit and a hydrophilic carboxylic group has been reported recently by one of our groups [13]. In aqueous medium, this polymer (polymer-A; Fig. 1) can adopt a conformation in which the hydrophilic units are exposed to water and the hydrophobic units are tucked inside to form nanosized-pockets that are capable of sequestering hydrophobic guest molecules. We have recently demonstrated the utility of polymer-A as a reaction medium to achieve selectivity in unimolecular photoreactions [14]. In the current study we have extended the investigation to bimolecular photoreactions. At the

concentrations used in this study, aggregation number and average size of polymer-A in water are estimated to be 60 and 50 nm, respectively [13,14]. With the help of polymer-A we have solubilized  $6 \times 10^{-4}$  M of acenaphthylene in  $1.1 \times 10^{-4}$  M aqueous polymer solution. We presume that the solubilized acenaphthylene molecules (327) are distributed in the hydrophobic domains present within the polymer-A micelle.

Encapsulation of water insoluble organic substrates within water soluble hosts has been an area of active interest [15–22]. Herein we demonstrate the ability of polymer-A to solubilize higher concentrations of aromatic hydrocarbons in aqueous medium and present our results on photodimerization of acenaphthylene (**1**) and 9-substituted anthracenes **4a–f** included within polymer-A. Results of this study allow us to compare the effectiveness of polymer-A with other established reaction media such as micelles, dendrimers and organic hosts.

## 2. Results and discussion

Polymer-A is water soluble in its salt form at pH 8.5. In aqueous solution, the polymer self-organizes into spherical micellar type aggregates having a hydrophobic interior and a hydrophilic exterior at concentration above its CMC

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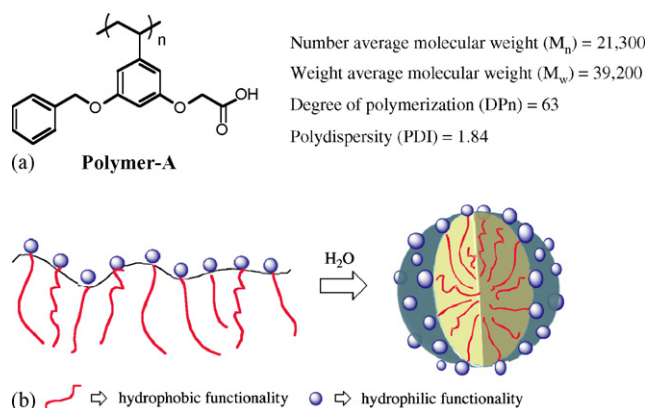
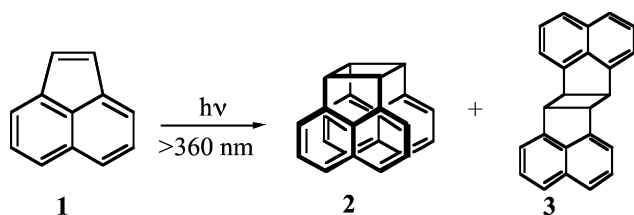


Fig. 1. (a) Structure of the polymer used in this the study. (b) Idealized view of the cross section of the polymeric micellar assembly.

( $2.6 \times 10^{-5}$  M) (Fig. 1b) [14]. The hydrophobic interior of polymer-A was probed with pyrene [14]. It was observed that the solubility of pyrene increases in the presence of polymer-A. The ratio of vibrational peaks 1 and 3 ( $I_1/I_3$ ) in the fluorescence spectrum of pyrene in an aqueous solution of polymer-A, the measure of polarity of its immediate environment, was calculated to be 1.47, which indicated the hydrophobic nature of the polymer interior ( $I_1/I_3$  is 1.87 in water; 1.35 in methanol; 1.05 in benzene). We did not monitor the interior polarity with any other probes.

The first bimolecular reaction we have investigated is the photodimerization of acenaphthylene [23–26]. Acenaphthylene upon irradiation is known to photodimerize to yield *syn* and *anti* dimers as shown in Scheme 1. The ratio of *syn* to *anti* dimer depends upon the nature of the excited state from which the reaction takes place and the concentration of acenaphthylene. Singlet excited state yields predominantly the *syn* dimer (90%) while the triplet gives both *syn* and *anti* dimers in the ratio 1:2.3 [27]. Although the solubility of acenaphthylene in water is very low ( $<1 \times 10^{-5}$  M) [28], it is enhanced ( $6 \times 10^{-4}$  M) in the presence of polymer-A ( $1.1 \times 10^{-4}$  M). Photolysis of acenaphthylene ( $6 \times 10^{-4}$  M) in an aqueous polymer solution ( $1.1 \times 10^{-4}$  M) under  $N_2$  atmosphere, resulted in  $>90\%$  conversion within 30 min. The conversions were estimated by GC analysis using docosane as the internal standard (Fig. 2). It is important to note that at the same concentration of acenaphthylene in organic solvents such as benzene and cyclohexane, no dimers were formed even after 48 h of irradiation. Even higher concentration of acenaphthylene (0.6 M) in benzene and cyclohexane yielded only 10% of photodimers after 24 h of irradiation. The remarkable enhancement of photoreactivity in aqueous



Scheme 1. Photodimerization of acenaphthylene.

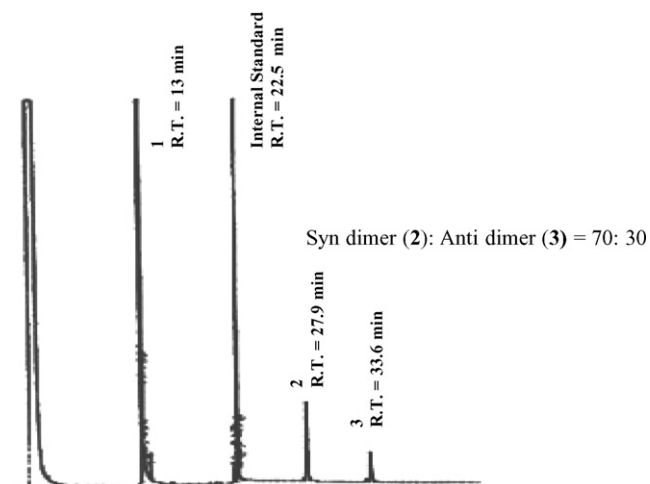


Fig. 2. A GC trace showing the product distribution upon photolysis of acenaphthylene (1) in benzene (SE-30 capillary column with dodecane as the internal standard).

polymer-A solution is most likely due to the increased local concentration within hydrophobic pockets of polymer-A. The above results are consistent with the previously reported micellar effects on photodimerization of acenaphthylene in aqueous solutions of surfactants and dendrimers [29,30]. The *syn* to *anti* dimer ratio obtained during direct irradiation within polymer-A is very similar to that obtained in benzene at 0.6 M of acenaphthylene (Table 1). Dimerization results obtained upon irradiating acenaphthylene in organic solvents and in aqueous polymer-A solution are summarized in Table 1. Triplet sensitization of 1 within polymer-A using the triplet sensitizer, eosin-Y was also performed. Considering the high solubility of eosin-Y in water (400 mg/mL), the sensitizer most likely remains in the aqueous phase and the energy transfer is presumed to take place at the interface between the polymeric micelle and water. The *syn* to *anti* dimer ratio decreased from 2.3 upon direct excitation to 1 upon triplet sensitization. It was previously demonstrated by Cowan and Drisko [27] that triplet photochemistry of acenaphthylene yielded dimers with *syn/anti* ratio of 0.44 in organic solvents such as methanol and acetonitrile, where the media do not impose any restriction on the acenaphthylene molecules. We expected the same *syn/anti* ratio from the triplet state of acenaphthylene in aqueous polymer-A solution, provided there is no restriction on the acenaphthylene molecules imposed by the

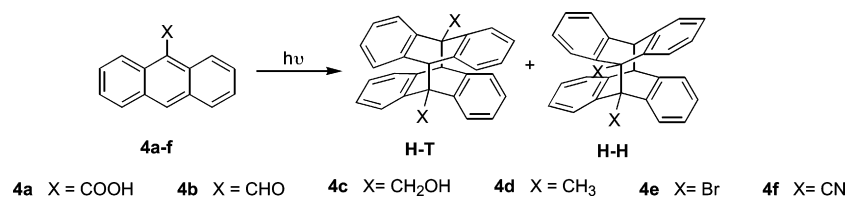
Table 1  
Product distribution of acenaphthylene (1)<sup>a</sup> upon irradiation in solution and within polymer-A

Medium	Irradiation wavelength (nm)	2 (%) <sup>a</sup>	3 (%) <sup>a</sup>	2/3 [ <i>syn/anti</i> ] ratio
Benzene <sup>b</sup>	360	70	30	2.3
Cyclohexane <sup>b</sup>	360	83	17	4.8
Polymer-A <sup>c</sup>	360	70	30	2.3
Methanol/eosin-Y <sup>b</sup>	510	30	70	0.44
Polymer-A/eosin-Y <sup>c</sup>	510	50	50	1

<sup>a</sup> For structures see Scheme 1.

<sup>b</sup> [1] = 0.6 M.

<sup>c</sup> [1] =  $6 \times 10^{-4}$  M, [polymer-A] =  $1.1 \times 10^{-4}$  M.



Scheme 2. Photodimerization of 9-substituted anthracenes.

polymer media. However, the observed low *anti* dimer yield in aqueous polymer-A solution suggests that the rotation of acenaphthylene molecules might be hindered within polymer-A aggregates.

The dimerizations of 9-substituted anthracenes (**4a–f**) in an aqueous polymer solution ( $1.1 \times 10^{-4}$  M) were investigated next (Scheme 2). Photodimerization of 9-substituted anthracenes has been extensively studied in various reaction media [31–40] and has been demonstrated previously that encapsulating them into micelles and vesicles can increase the yield of H–H dimers [41–45]. We envisaged such a possibility in the case of polymer-A. Irradiation of most anthracene-9-derivatives in organic solutions resulted head–tail dimer as the major product due to electrostatic and steric factors [46].

Irradiation of 9-substituted anthracenes **4a** and **4c–f** ( $9 \times 10^{-4}$  M) in an aqueous solution of the polymer for 2 h, yielded photodimers in  $\sim 30\%$  conversion. In the case of **4b**, 40% conversion was observed within 15 min of irradiation. It is of interest to note that irradiation of 9-substituted anthracenes **4a–f** at such concentrations ( $9 \times 10^{-4}$  M) in methanol resulted in no dimers even after 24 h. The increased reactivity of 9-substituted anthracenes within polymer-A could once again be attributable to localization effect within the hydrophobic pockets of polymer-A. The product distributions and the conversion of various anthracene-9-derivatives in solution and within the polymer-A aggregates are presented in Table 2.

The photochemical behaviors of 9-substituted anthracene within polymer-A aggregates were very similar to their solution behaviors in terms of regio-selectivity, in contrary to what was previously observed in conventional micelles and vesicles. The difference in the regio-selectivity within the micelles of polymer-A, compared to conventional micelles, suggests that the encapsulated anthracene molecules are located in the core of hydrophobic domains and not at the interface. Whereas, in the case of surfactant micelles and vesicles, they prefer to be at the interface in a head–head fashion [41–45]. Our previously reported results on unimolecular reactions within polymer-A also support the encapsulation of guest molecules in the deep hydrophobic core rather than at the interface [14].

In conclusion, we have demonstrated that the polymer-A aggregates can be utilized to solubilize water insoluble aromatic molecules in aqueous solution and thus perform photodimerization of aromatic hydrocarbons in an environmentally friendly solvent. The polyaromatic hydrocarbons that are used in our studies are soluble to less than  $10^{-5}$  M in water and presence of polymer-A increases their solubility to more than  $10^{-3}$  M. Remarkably, the efficiency of photodimerization enhanced upon photolysis within polymer-A. Ability of polymer-A to solubilize

Table 2

Product distribution upon irradiation of anthracene-9-derivatives (**4a–f**) in various media

Anthracene-9-derivatives <sup>a</sup>	Medium	Irradiation time (h)	Conversion (%)	Dimers (HT/HH)
<b>4a</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	20	100/0
	Polymer-A <sup>d</sup>	2	30	100/0
<b>4b</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	10	100/0
	Polymer-A <sup>d</sup>	0.25	40	100/0
<b>4c</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	10	80/20
	Polymer-A <sup>d</sup>	2	30	60/40
<b>4d</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	20	66/33
	Polymer-A <sup>d</sup>	2	30	70/30
<b>4e</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	20	100/0
	Polymer-A <sup>d</sup>	2	30	100/0
<b>4f</b>	Methanol <sup>b</sup>	24	–	–
	Methanol <sup>c</sup>	8	20	100/0
	Polymer-A <sup>d</sup>	2	30	100/0

<sup>a</sup> For structures see Scheme 2.

<sup>b</sup> [**4a–f**] =  $9 \times 10^{-4}$  M.

<sup>c</sup> [**4a–f**] =  $4.5 \times 10^{-3}$  M.

<sup>d</sup> [Polymer-A] =  $1.1 \times 10^{-4}$  M, [**4a–f**] =  $9 \times 10^{-4}$  M.

and thus increase the local concentration of aromatic hydrocarbons in a confined space within itself has been demonstrated. The aromatic hydrocarbons must reside deep within the polymer as no regiocontrol on product dimers could be observed.

### 3. Experimental

#### 3.1. Materials

The styrene based polymer used for the study was synthesized and characterized following the literature procedure [13]. Acenaphthylene (**1**) and anthracene-9-derivatives (**4a–f**) were purchased from Sigma–Aldrich. Acenaphthylene (**1**) was purified by sublimation and anthracene-9-derivatives were used as received.

#### 3.2. Preparation of polymer stock solution

The aqueous polymer solutions of different concentration were prepared by adding the desired amount of the poly-

mer in aqueous NaOH solution which contains 1.3 equivalents of NaOH corresponding to the equivalent weight of the polymer. The resulting solution was then sonicated for 1 h at room temperature to get a clear solution suitable for photolysis.

### 3.3. Inclusion and photolysis procedure in aqueous polymer solution

The procedure followed for all the substrates were similar and one of them is described as below. Substrate **1** (1 mg,  $6.4 \times 10^{-4}$  M) was added to a stirred solution of the polymer of concentration  $1.1 \times 10^{-4}$  M (10 mL). After the solution was stirred for 12 h, it was filtered using Whatmann filter paper to remove any substrates that were not included. The clear solution was then purged with nitrogen for 20 min and then irradiated under nitrogen atmosphere with a 450 W medium-pressure Hg lamp.

### 3.4. Extraction and analysis procedures

After photolysis, the products and the unreacted starting material were extracted with a mixture of ethyl acetate and acetonitrile (10:1), dried over  $\text{MgSO}_4$  and concentrated. Photodimerization of **1** was analyzed on a Shimadzu 17 A series gas chromatography fitted with SE-30 column. Product distributions of anthracene-9-derivatives (**4a–f**) upon irradiation were analyzed by  $^1\text{H NMR}$ . Spectral data for all the anthracene derivatives were compared with literature values [31,38]. Photodimers of acenaphthylene were identified from solution reaction and the spectral data were matched with previously reported values [23–26].

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