Studies of the Antenna Effect in Polymer Systems. 18. Photochemical Reactions of Styrene Solubilized in an Aqueous Solution of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

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ABSTRACT: Photochemical reactions of styrene solubilized in an aqueous solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) were studied using monochromatic light at 280- and 313-nm wavelength and using solar-simulated radiation. In an oxygen-free atmosphere, photohydration of styrene was observed, and in the presence of oxygen, photosensitized oxidation of styrene occurs. The comparison of the photochemical processes occurring in an aqueous polymeric solution with those observed during direct irradiation of styrene in water as well as with those in photosensitized oxidation in low molecular weight model systems supports the mechanism of styrene oxidation involving participation of singlet oxygen. Styrene photooxidation was found to be much more efficient when styrene was solubilized in an aqueous solution of PSSS-VN than when styrene was dissolved in water. PSSS-VN displays considerably higher photosensitizing ability than the low molecular weight model compound, sodium 2-naphthalenesulfonate (NSA).

Introduction

There are both scientific and practical reasons for studying the antenna effect in synthetic polymers. This phenomenon, occurring in polyelectrolytes, is of special and growing interest because of the unique properties of such systems. In previous studies in this series it was shown that the novel polyelectrolyte poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) efficiently solubilized large, sparingly water-soluble hydrophobic compounds.[1-6] It was also shown that PSSS-VN displays very interesting photocatalytic activity by sensitizing photochemical reactions of the solubilized molecules. Direct energy transfer to solubilized molecules such as 2-undecanone resulted in their photochemical reaction. In the presence of oxygen, singlet oxygen was formed and subsequently oxidized various polynuclear aromatic compounds or 1,3-diphenylisobenzofuran. Both reactions have been shown to be quite efficient.[1,2,4]

Styrene is one of the compounds whose presence in the environment is of real concern. Because it is widely used, quite soluble in water (2.88×10^{-3} M at 20 °C),[7] and volatile, the search for a method of removing it from polluted water is of great interest.

This paper reports studies of the solubilization and photochemical reactions of styrene in dilute aqueous solutions of PSSS-VN. The results are compared with those obtained during irradiation of styrene dissolved in water in the presence and in the absence of model photosensitizers.

Experimental Section

Materials. Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) was synthesized and purified according to the method described previously.[1] The polymer consists of 60 mol % vinylnaphthalene and 40 mol % sodium styrenesulfonate. The weight-average molecular weight, $\bar{M}_w$, was determined by the ultracentrifuge method to be 310 000. The number-average molecular weight of the polymer was estimated by assuming a polydispersity of 2.0.

Sodium 2-naphthalenesulfonate (NSA) (Aldrich, technical grade) was purified by two recrystallizations from water. Rose Bengal (RB) (97%, Aldrich) was used as received. Styrene (99%, Aldrich) was purified by vacuum distillation.

The compounds used for product determinations, benzaldehyde, formaldehyde, and acetophenone, were commercially available. 1-Phenylethanol was obtained by lithium aluminum hydride reduction of acetophenone.

Polymer solutions were prepared with deionized water. Methanol (Caledon, ACS spectrograde) was used without further purification.

Solubilization of Styrene. Microliter quantities of styrene were slowly added to 25 mL of aqueous PSSS-VN ($c_p = 1.5$ g dm^{-3}) solution. The mixture was shaken for 5 min, tumbled overnight, and filtered through fine filter paper (Whatman no. 42). Alternatively, a known amount of solid polymer was added to the styrene-saturated aqueous solution.

Irradiation of Samples. Irradiations were carried out with a deep-UV constant-intensity control system (Optical Associates Inc. Model 780) described previously.[1] Interference filters (280 and 313 nm) were used to obtain monochromatic light in the particular wavelengths of interest. Incident light intensities were determined with a ferrioxalate actinometer:[8] $I_0 = 3.81 \times 10^{-7}$ einstein dm^{-3} s^{-1} at 280 nm and $I_0 = 4.11 \times 10^{-7}$ einstein dm^{-3} s^{-1} at 313 nm.

The solar-simulated irradiations were performed with an apparatus described earlier in detail.[1]

Product Studies. An aqueous solution of PSSS-VN containing solubilized styrene ($c_p = 1.5$ g dm^{-3}, $c_S = 5 \times 10^{-3}$ M) was degassed with nitrogen or saturated with oxygen and then irradiated with solar-simulated radiation. The progress of the reaction was followed by gas chromatography measurements. After 20 h of irradiation the solution was extracted with chloroform. The aqueous phase and the organic phase were then analyzed separately. The solvents were removed on a rotary evaporator, and the residues were dissolved in methanol. The components of the mixture were separated by preparative-layer chromatography (PLC). Analysis of the products was performed by using gas chromatography, spectroscopic measurements, and chemical tests. The presence of aldehydes in the reaction mixture was confirmed by using the fuchsin–sulfurous acid test.[9]

Ultraviolet Absorption Spectra. The absorption spectra of the samples in the UV–visible spectral region were recorded on a Hewlett-Packard 8451A diode array spectrophotometer.

IR Spectra. The IR spectra of the products formed were recorded on a Fourier transform infrared spectrophotometer (Nicolet).

Gas Chromatography Analysis. The quantitative and qualitative analyses of the systems studied were carried out with a Varian Aerograph Series 1700 gas chromatograph with a temperature program from 50 to 280 °C at 10 °C min^{-1}). The

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Table I
Summary of Analytical Results for Photochemical Reactions of Styrene in the Systems Studied

system	atmosphere	λ_{ex}, nm	$c_S^0 \times 10^4$, M	t_{irr}, min	$I_a \times 10^4$, einstein	products, mol × 10^6	
						1-phenylethanol	benzaldehyde
1. styrene in water	N_2	280	5.0	30	4.42	1.32 ± 0.05	
				60	8.74	2.64 ± 0.05	
2. styrene in water	O_2	280	5.0	120	17.61	1.95 ± 0.05	1.06 ± 0.05
				240	34.01	3.74 ± 0.05	2.04 ± 0.05
3. styrene + NSA in water	O_2	280	5.0	120	27.38	5.48 ± 0.10	1.65 ± 0.05
		313	20.0	60	14.56		2.91 ± 0.05
4. styrene in aq PSSS-VN solution	N_2	280	5.0	120	27.38	8.49 ± 0.10	
				240	54.75	17.00 ± 0.10	
5. styrene in aq PSSS-VN solution	O_2	280	5.0	480	109.50	1.10 ± 0.10	136.50
		313	20.0	60	14.56	64.1 ± 0.5	

Table II
Quantum Yields of Styrene Photohydration (ϕ_{ph}), Quantum Efficiencies of Styrene Photooxidation (γ_{MO_2}), and Products Formed in the Systems Studied

system	atmosphere	$\phi_{ph} \times 10^2$	$\gamma_{MO_2} \times 10^2$	products
1. styrene in water	N_2	3.0 ± 0.5		ArCH(OH)(CH_3)
2. styrene in water	O_2	0.11 ± 0.04	0.060 ± 0.005	ArCHO, HCHO ArCH(OH)(CH_3), ArC(O)CH_3
3. styrene + NSA in water	O_2	2.0 ± 0.5	0.20 ± 0.03	ArCHO, HCHO ArCH(OH)(CH_3), ArC(O)CH_3
4. styrene in aq PSSS-VN solution	N_2	0.31 ± 0.05		ArCH(OH)(CH_3)
5. styrene in aq PSSS-VN solution	O_2	0.01 ± 0.005	4.4 ± 0.5	ArCHO, HCHO ArCH(OH)(CH_3), ArC(O)CH_3

instrument contained a flame ionization detector and an OV 17 glass column (5% w/w OV 17 on Chromosorb G). The qualitative analyses were based on a comparison of the retention times of the products found with those of the corresponding pure substances.

Quantum Yield Determination. The quantum yields of the reaction have been determined based on the amount of the products formed and styrene consumed. Each analysis was repeated three times, and the results are estimated to be precise to ±1% and accurate to ±5%.

Results and Discussion

The results will be presented in two major parts. The first deals with photochemical processes of styrene in water and with photosensitized oxidation of styrene by low molecular weight sensitizers such as RB and NSA. The aim of this part is to evaluate the photochemical reactivity of styrene in water as well as to determine the mechanism of photosensitized oxidation of styrene in model-type studies. The second part is devoted to studies of solubilization and sensitized photochemical reactions of styrene in aqueous solutions of PSSS-VN.

The analytical results for the photochemical reactions of styrene in all systems studied are summarized in Table I, and the quantum yields of the respective processes are given in Table II.

1. Photochemical Reactions of Styrene in Aqueous Solution. Irradiation of styrene in degassed aqueous solution with light at λ = 280 nm results in photohydration of styrene. 1-Phenylethanol is formed in the process. The mechanism of photohydration of aromatic alkenes has been the subject of detailed studies.[10-12] It has been shown that in the case of styrene the reaction consists of Markovnikov addition of water. The process involves a rate-limiting protonation step of the first excited singlet state:

$$\mathrm{ArCH{=}CH_2} \xrightarrow[\mathrm{H^+}]{h\nu} \mathrm{Ar\overset{+}{C}HCH_3} \xrightarrow{\mathrm{H_2O}} \mathrm{ArCH(OH)CH_3} \quad (1)$$

The reported lifetime of the styrene excited singlet state is short (τ = 7.5 ns) and the photoprotonation rate constant is relatively low ($k_H = 2.3 \times 10^6$ M^{-1} s^{-1}).[10] In this work the quantum yield of styrene photohydration has been found to be equal to $(3.0 \pm 0.5) \times 10^{-2}$ under experimental conditions. The value is in good agreement with that previously published: 2.5×10^{-2}.[10]

The photochemistry of styrene in aqueous solution changes in the presence of oxygen. Irradiation of an oxygen-saturated aqueous solution of styrene with monochromatic light at 280 nm results in formation of photooxidation products, benzaldehyde and formaldehyde, along with the photohydration product 1-phenylethanol. This indicates that both processes, photooxidation and photohydration, occur in the system (compare eq 2). The

$$\mathrm{ArCH{=}CH_2} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{ArCH(OH)(CH_3)} \xrightarrow{\mathrm{O_2}} \mathrm{ArC(O)CH_3} \quad (2a)$$

$$\mathrm{ArCH{=}CH_2} \xrightarrow[\mathrm{O_2}]{h\nu} \mathrm{ArCHO + HCHO} \quad (2b)$$

quantum yields of styrene consumption, photooxidation, and photohydration have been found to be equal to $(3.5 \pm 0.3) \times 10^{-2}$, $(6.0 \pm 0.5) \times 10^{-4}$, and $(1.1 \pm 0.4) \times 10^{-3}$, respectively. It has been also observed that prolongation of the irradiation results in additional appearance of acetophenone. Acetophenone might be considered to be a secondary product formed during oxidation of 1-phenylethanol.

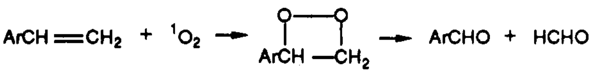
On the basis of the experimental results presented above, one can postulate two different mechanisms for styrene photooxidation: (1) reaction between excited singlet- or triplet-state styrene and molecular oxygen in the ground state, and (2) reaction between ground-state styrene and singlet oxygen formed during the quenching of electronically excited styrene by oxygen (see eq 3).

$$\begin{tikzcd} \mathrm{ArCH{=}CH_2} + {}^3\mathrm{O_2} \arrow[r, "h\nu"] & (\mathrm{ArCH{=}CH_2})^* + {}^3\mathrm{O_2} \arrow[r, "k_r'"] \arrow[d, "k_q"] & \text{products} \\ & \mathrm{ArCH{=}CH_2} + {}^1\mathrm{O_2} \arrow[r, "k_r^*"] & \text{products} \end{tikzcd} \quad (3)$$

In order to elucidate the mechanism of photooxidation of styrene, the photosensitized oxidation of the compound was studied.

Photosensitized Oxidation of Styrene. The photosensitized oxidation of styrene has been studied in two different systems, organic solvent (methanol) using RB as the photosensitizer and in aqueous solution, applying NSA as the sensitizer.

Irradiation of a mixture of RB and styrene in oxygen-saturated methanol solution with solar-simulated radiation resulted in the formation of benzaldehyde and formaldehyde. RB is known to generate singlet oxygen. The same products have also been detected during photosensitized oxidation of styrene using other sensitizers known to produce singlet oxygen.[13] Thus, it seems that the styrene photooxidation occurs with participation of singlet oxygen. The reaction between singlet oxygen and monoolefins, such as ethylene or styrene, consists of 1,2-cycloaddition with formation of 1,2-dioxetane intermediates.[13,14] In the case of styrene, the decomposition of dioxetanes occurs via homolytic cleavage and results in the generation of stable molecular products such as benzaldehyde and formaldehyde[13] (see eq 4).



$$\mathrm{ArCH{=}CH_2} + {}^1\mathrm{O_2} \longrightarrow \begin{array}{c}\mathrm{O{-}O}\\ |\quad\ |\\ \mathrm{ArCH{-}CH_2}\end{array} \longrightarrow \mathrm{ArCHO} + \mathrm{HCHO} \qquad (4)$$

In the next step of the present studies, the photosensitizing ability of NSA with respect to oxidation of styrene in aqueous solution was investigated. NSA was chosen as a photosensitizer because it is soluble in water and can be regarded as a model compound for the naphthalene chromophores present in PSSS-VN. It has been observed that during NSA-photosensitized oxidation of styrene the same products are formed as those detected during oxidation sensitized by RB. This suggests that in the case when NSA is chosen as a sensitizer, the reaction also involves the participation of singlet oxygen. Singlet oxygen can be formed in the quenching of electrically excited states, mainly he triplet state of the NSA molecule with oxygen. The quantum efficiency of styrene photooxidation (γ_{MO_2}) is given as a product of the efficiency of singlet oxygen formation (γ_Δ) and styrene addition efficiency (ϕ_{MO_2}):[15]

$$\gamma_{MO_2} = \gamma_\Delta \phi_{MO_2} \qquad (5)$$

where

$$\phi_{MO_2} = [M]/([M] + \beta) \qquad (6)$$

In eq 6 [M] is the concentration of styrene, and β is the styrene reactivity index, $\beta = k_d/k_r$, where k_r is the rate constant of the reaction between singlet oxygen and the styrene molecule and k_d is the rate constant for singlet oxygen decay, $k_d = 1/\tau_\Delta$; τ_Δ is the singlet oxygen lifetime. The quantum efficiency of styrene photooxidation (γ_{MO_2}) at a total styrene concentration of 2×10^{-3} M was determined to be equal to $(2 \pm 0.3) \times 10^{-3}$. The oxidation process was accompanied by photohydration. The overall quantum yield of the photohydration calculated based on the total light absorbed by the system at the wavelength of irradiation was found to be $(1.5 \pm 0.5) \times 10^{-3}$. It should be pointed out that the photohydration process is initiated by direct absorption of light by styrene. Energy transfer from excited naphthalene chromophores to styrene cannot be expected because the energy levels for styrene singlet and triplet are both higher than the corresending levels for naphthalene.[15] The calculations in which the fraction of light absorbed by the styrene present in the system is taken into account gave the value of the quantum yield for the photohydration reaction as $(2.0 \pm 0.5) \times 10^{-2}$. The value is slightly lower than that determined for the reaction occurring in water in the absence of photosensitizer.

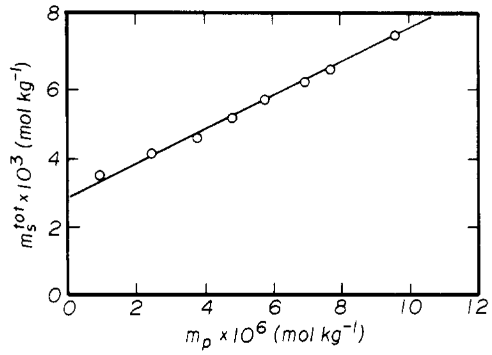


Figure 1. Dependence of the total concentration of solubilized styrene on the concentration of PSSS-VN in aqueous solution.

2. Studies of the Photosensitized Reactions of Styrene Solubilized in Aqueous Solutions of PSSS-VN. The investigation of the photochemistry in aqueous solutions of PSSS-VN was preceded by studies of the solubilization of styrene in this system. It has been shown that the solubility of styrene increases with an increase in the concentration of the polymer. In the concentration range $(0\text{–}1) \times 10^{-5}$ M, the concentration of styrene solubilized depends linearly on the concentration of PSSS-VN (see Figure 1). The solubilized styrene is distributed between the aqueous phase and the polymeric pseudophase. A distribution coefficient K can be calculated based on experimental data and using an analytical form of the dependence between the concentration of solubilized styrene and polymer concentration in the form[6]

$$m_S^{tot} = (x^c/K)(10^3/M_{H_2O}) + [x^c/(1 - x^c)]m_p \qquad (7)$$

where x^c is the mole fraction of styrene in the polymeric pseudophase, K is the distribution coefficient, m_S^{tot} is the total molal concentration of styrene in the system, and m_p is the molal concentration of the copolymer. On the basis of the experimental data presented in Figure 1 and using eq 7, we found the value of the distribution coefficient for styrene to be $(1.92 \pm 0.50) \times 10^4$. It should be stressed that although the thermodynamic treatment presented above is quite useful in understanding chemical reactions that can occur in the core of PSSS-VN, it is nevertheless sensitive to the precision of the molecular weight determination for the polymer used. The alternative approach in which the distribution coefficient (K^*) is defined as a ratio of weight fractions of styrene in the polymer pseudophase and the aqueous phase was also applied. The value of the distribution coefficient K^* was determined to be $(1.45 \pm 0.50) \times 10^3$. Both the relatively high values for the solubility of styrene in water[7] and the distribution coefficient result in a high local concentration of styrene in the polymeric pseudophase. This phenomenon may influence the photochemical processes occurring in the system.

Irradiation of degassed aqueous solutions of PSSS-VN containing solubilized styrene with light at 280 nm results in the formation of 1-phenylethanol. This indicates that photohydration occurs in the system. The overall quantum yield of the process determined for this styrene-containing system at a total initial concentration of 2×10^{-3} M was equal to $(1 \pm 0.2) \times 10^{-4}$. Taking into account that the reaction is initiated by direct excitation of styrene in the system (no energy transfer occurs), the low efficiency observed may be connected with the existence of a large screening effect caused by the large fraction of light absorbed by the copolymer at the excitation wavelengths. When the fraction of light actually absorbed by styrene is taken into account, the value for the quantum yield of styrene photohydration in an aqueous solution of PSSS-VN is (3.1 ± 0.5) × 10^{-3}. One can notice that the value is an order of magnitude lower than that found for the reaction occurring in water. This may indicate that not all of the styrene present in the system actually participates in the reaction. As water is one of the reagents in the process, it is reasonable to assume that only styrene present in water undergoes photohydration. The calculations performed based on this assumption resulted, however, in a value of the quantum yield above unity. This suggests that the observed phenomenon cannot be treated by using such a simple model.

Two possibilities can be considered to explain the above observations. The first is that the reaction takes place only in water and that the amount of styrene present in water during the course of the process is higher than that determined at equilibrium based on the distribution coefficient. The distribution of the styrene between the aqueous phase and the polymeric pseudophase changes during the reaction. The migration of styrene from the polymeric to the aqueous phase is induced by the concentration gradient that results from the consumption of styrene during the photoreaction.

The second possibility is that the photohydration process involves the participation not only of molecules of styrene present in the aqueous phase but also of those solubilized by the copolymer but located in a certain intermediate region, in which they are still in contact with water. Interestingly, the overall quantum yield of styrene consumption in the system was found to be (8 ± 0.2) × 10^{-2}, a value considerably higher than that for photohydration. As 1-phenylethanol was the only low molecular weight product detected, the additional consumption of styrene may be connected with formation of products of higher molecular weight such as styrene oligomers.

Irradiation of oxygen-saturated aqueous solutions of PSSS-VN containing solubilized styrene results mainly in the photooxidation of styrene. The formation of the same primary oxidation products, benzaldehyde and formaldehyde, detected in the model studies was observed. The photosensitized oxidation was also accompanied by the photohydration of styrene. The quantum yield of the latter process is, however, highly limited. It was found to be ca. 350 times lower than the quantum efficiency of styrene photooxidation. The quantum efficiency of photooxidation of styrene (γ_{MO_2}) determined at a styrene concentration of 2 × 10^{-3} M is equal to (4.4 ± 0.5) × 10^{-2}. It should be pointed out that at the same concentration of styrene and the same total absorption of the system at the excitation wavelength, the efficiency of the photooxidation in the polymeric system is ca. 20 times higher than observed in the low molecular weight system using NSA as a photosensitizer. This may be connected with differences in quantum yield of singlet oxygen formation (γ_Δ) in these two systems as well as with differences in the reactivity indices of styrene with singlet oxygen (β). The latter may reflect a difference in singlet oxygen lifetime which is very short (ca. 2 μs) in water but which should be considerably longer in the polymeric hydrophobic phase[17] where the oxidation reaction is expected to occur.

Table I summarizes the results of photochemical processes of styrene observed in all of the systems studied. Values of the quantum yield of styrene hydration ϕ_{ph} and quantum efficiency of its photooxidation were determined at the same initial concentration of styrene equal to 2 × 10^{-3} M.

In the next stage of the studies, attempts to describe the photosensitized oxidation of styrene in aqueous solutions of PSSS-VN in a more quantitative way were undertaken. One can expect that the studies of the relationship between quantum efficiency of styrene photooxidation and initial concentration of styrene should provide the information needed. Equation 8, a rearranged form of eq 6, predicts a linear relationship between $1/\gamma_{MO_2}$ and 1/[M]:

$$1/\gamma_{MO_2} = 1/\gamma_\Delta + (\beta/\gamma_\Delta)(1/[M]) \qquad (8)$$

Figure 2 shows the experimental data plotted according to eq 8. The highest possible concentration of styrene in the system is limited by its solubility in the aqueous copolymer solution. From the extrapolation of the straight line drawn through the experimental points, the values of the quantum efficiency of singlet oxygen formation and the styrene reactivity index in the system were estimated to be equal to 0.25 ± 0.05 and (1.1 ± 0.2) × 10^{-2} M, respectively. The value of the quantum efficiency of singlet oxygen formation in aqueous polymer solution is relatively high. It should also be noted that singlet oxygen can be produced in this system even when low-energy radiation, e.g., solar light, is applied.

Figure 3 (lines a and b) gives a comparision of the rates of styrene consumption during solar-simulated irradiation of an oxygen-saturated aqueous solution of styrene with that of an aqueous solution of PSSS-VN containing styrene at the same total initial concentration. The comparison was based on the saturation limit of styrene in water at room temperature. It should be noted that the consumption of styrene in oxygen-saturated systems is ca. 4 times faster in an aqueous solution of PSSS-VN. The reaction

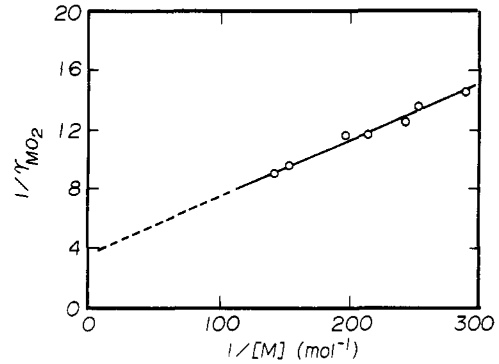


Figure 2. Plot of $1/\gamma_{MO_2}$ versus 1/[M] (γ_{MO_2} = quantum efficiency of styrene photooxidation; [M] = styrene concentration).

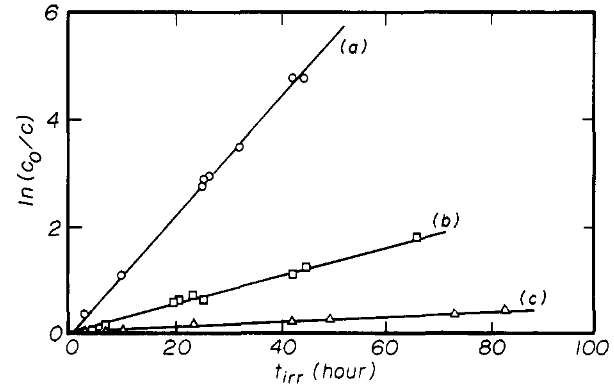


Figure 3. Plot of ln (c_S^0/c_S) (c_S^0 and c_S are the concentrations of styrene at irradiation time t = 0 and t = t, respectively) versus irradiation time with solar-simulated radiation of (a) oxygen-saturated aqueous PSSS-VN solution containing solubilized styrene, (b) oxygen-saturated solution of styrene in water, and (c) aqueous styrene solution being in equilibrium with air.

of styrene in aqueous solution in equilibrium with air is considerably slower (compare Figure 3, line c). It should be pointed out that the rate of styrene consumption is important considering that the phototransformation of styrene is a potential solution of environmental problems. The high volatility of the styrene results in its relatively fast evaporation from polluted water. It seems thus that an increase in the rate of photochemical reactions is important. It is also worth noting that the products formed during styrene photooxidation can undergo further photochemical reactions as they absorb light in the UV-visible region and are photolabile under these conditions.

Conclusions

On the basis of the experimental results presented one can conclude that styrene dissolved in water undergoes photochemical reactions such as photohydration and photooxidation. However, the quantum yield of these processes is low. Styrene was shown to be efficiently solubilized in aqueous solutions of PSSS-VN. Irradiation of the system in the presence of oxygen led to photosensitized oxidation of styrene. It was found that the process can be initiated not only with highly energetic radiation from the UV spectral region but also with low-energy solar light. This is due to the absorption of the naphthalene "antenna chromophores" present in the polymer and may be important in a possible practical application of PSSS-VN.

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Registry No. (SSS)(VN) (copolymer), 115468-37-6; RB, 11121-48-5; NSA, 532-02-5; styrene, 100-42-5; 1-phenylethanol, 98-85-1; benzaldehyde, 100-52-7; formaldehyde, 50-00-0.