Annealing also promoted the phase separation by increasing the degree of hydrogen bonding, and therefore TL trap concentration (intensity), in the hard-segment domains. The TL results of the elongation of SPUU showed that the orientation, disintegration, and phase mixing of the hard-segment domains occurred in stages during elongation, and as a result, the intensity of the lower TL peak L increased considerably and the intensity of the higher peak H decreased accordingly in this process. The above TL results were well supported by those of the pulsed NMR measurements. In summary, the results reported in this paper show that TL promises to provide much detailed information about the phase separation in polyurethanes and other phase-separated polymers.

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Registry No. (PTMG)(BDO)(MDI) (block copolymer), 107678-92-2; (PTMG)(MDI)(PDA) (block copolymer), 111634-02-7.

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Studies of the Antenna Effect in Polymer Molecules. 11. Photochemical Reactions of 2-Undecanone Solubilized in an Aqueous Solution of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

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ABSTRACT: Photochemical reactions of 2-undecanone solubilized in a water solution of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) were studied by using monochromatic light at $\lambda = 280$ nm and solar-simulated radiation. Photoreactions of 2-undecanone were found to be photosensitized by the pendant naphthalene chromophores in the copolymer. Experimental evidence supports a mechanism in which singlet–singlet energy transfer occurs from the naphthalene groups to 2-undecanone by a diffusion-controlled collisional mechanism. The process was found to be efficient because of the high local concentration of ketone solubilized in the polymer microdomains. The photolysis of 2-undecanone solubilized in the copolymer occurs according to the Norrish type II process. Norrish type I reaction products were not formed in detectable amounts.

Introduction

Study of the photophysical phenomenon known as the "antenna effect" in synthetic polymers is important from both a scientific and practical point of view. The natural "antenna pigments", such as chlorophyll in green plants, have been found to act as photocatalysts in photosynthesis. The solar energy absorbed by the chlorophyll pigment is transferred via singlet energy migration to the active center where it is used in the primary steps of photosynthesis.[1] This process is also referred to as "photon harvesting". An

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example of where this process can be used to sensitize a classical organic photochemical reaction is reported in this paper.

Synthetic polymers displaying the antenna effect have consisted of a sequence of pendant aromatic groups with a small number of low-energy traps either located at the end of the polymer chain or randomly distributed along the backbone of the polymer.[2,3] The successful synthesis of antenna polymers soluble in organic solvents[4-8] has been followed by work on water-soluble polymers. Copolymers of 1-naphthylmethyl methacrylate and acrylic acid terminated with anthracene and of partially sulfonated poly(1-vinylnaphthalene) and poly(2-vinylnaphthalene) have shown very interesting physicochemical and photophysical behavior.[9-11] These polyelectrolytes, consisting of hydrophobic and hydrophilic groups, have been shown to form a "pseudomicellar" conformation in dilute aqueous solution. This conformation not only enhances the efficiency of energy transfer from the polymer to the covalently attached trap but also has been shown to solubilize hydrophobic organic compounds. The solubilized molecules can then act as energy traps. It is expected that the energy transferred to the solubilized molecule may induce photochemical reactions. Thus, the polyelectrolyte plays two important roles: (1) as a source of hydrophobic microdomains for the photochemical reactions of hydrophobic substances in water and (2) as a photocatalyst.

It has been shown that the physicochemical and photophysical properties of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) are quite promising for applications as antenna-type photocatalysts.[12] The PSSS-VN copolymer has been found to solubilize large hydrophobic organic molecules, i.e., 2-undecanone, 10-nonadecanone, perylene, 9,10-dimethylanthracene, and anthracene, as well as being able to absorb light from the near UV-visible spectral range.

This report deals with studies of the photochemical reactions of 2-undecanone solubilized in aqueous solutions of PSSS-VN. Because of the high catalytic efficiency and analogy to biological catalysts, which usually contain a hydrophobic reaction center, such polymer systems have been termed "photozymes".

Experimental Section

Materials. Commercial 2-vinylnaphthalene (2VN, Aldrich) was purified by adsorption chromatography, using cyclohexane as eluent and alumina as adsorbant. The ratio of length to the diameter of the column was 5:1. The purity of the compound (99.5%) was confirmed by gas chromatography.

Commercial sodium styrene sulfonate (SSS, Du Pont) was purified by recrystallization from a 9:1 (v/v) mixture of methanol and water, followed by two recrystallizations from pure methanol (Caledon, Spectro grade).

Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS-VN) was prepared by 2,2′-azobis(isobutyronitrile) (AIBN) initiated radical polymerization of SSS and 2VN monomers in degassed dimethyl sulfoxide (DMSO) solution at 60 °C. After polymerization (21 h) the sample was precipitated with 1-butanol, filtered, washed three times with diethyl ether, and dried in a vacuum oven at 40 °C. The resulting polymer was dissolved in water, exhaustively dialized (Fisher, cellulose tubing, cutoff 12 000–14 000 g mol^{-1}) against deionized water and freeze dried. Elemental analysis (Galbraith Laboratories Inc.) showed that the polymer consisted of 59 mol % VN and 41 mol % SSS (C, 66.3; H, 5.62; S, 7.34; O, 12.68; Na 8.07). Using the ultracentrifuge method the weight-average molecular weight, M_w, of the polymer was determined to be 310 000. The sedimentation equilibrium work was performed on a Beckman Model E analytical ultracentrifuge according to the high-speed meniscus depletion method of Yphantis.[13] The number-average molecular weight of the polymer was estimated by assuming a polydispersity of 2.0.

DMSO, 1-butanol, and diethyl ether (all Caledon, ACS reagent grade) were used without further purification. Distilled water was passed through a deionizer and subsequently filtered through a trace organic removal cartridge (Norganic, Millipore). Hexadecane (99%, Alpha Products, Venton Division) was purified by vacuum distillation. Nonane and *n*-dodecane (both Polysciences, Quant grade, gas chromatography standards) were used without further purification. 1-Octene (Eastman Organic Chemicals, practical grade), acetone (Caledon, ACS Spectro grade), and acetaldehyde (99%, Aldrich) were purified by distillation. 2-Undecanone (Eastman Organic Chemicals) was purified by vacuum distillation. The purity, 99.96%, was confirmed by gas chromatography. Naphthalene (Aldrich, 99+%, Gold label) was recrystallized three times from spectral grade methanol.

Procedures. *Solubilization of 2-Undecanone.* Microliter quantities of 2-undecanone were slowly added to the 25 mL of aqueous PSSS-VN (c_{pol} = 1.5 g dm^{-3}) solution. The mixture was shaken for 5 min, tumbled overnight, and filtered by using fine filter paper (Whatman no. 42). The technique used to calculate the concentration of 2-undecanone solubilized by polymer microdomains is discussed elsewhere.[12]

Irradiation was carried out by using a deep-UV constant intensity control system (Optical Associates Model 780). The light source was a 500-W xenon–mercury arc lamp equipped with an optical setup to produce a collimated beam (100 mm wide and 70 mm high). The system has electronic feedback circuitry that maintains a constant irradiation intensity throughout the experiment. A 280-nm intereference filter was used to obtain the monochromatic light. Incident light intensity was determined by using a ferrioxalate actinometer;[14] $I_0 = 6.86 \times 10^{-7}$ einstein dm^{-3} s^{-1}.

The solar-simulated irradiations were performed by using an apparatus designed by V. Foyle. The intensity in the spectral region 300–350 nm, determined by irradiation of 2-undecanone ($\phi = 0.240$) in hexadecane, was estimated to be $\sim 2 \times 10^{-7}$ einstein dm^{-3} s^{-1}.

Gas Chromatography Analysis. The quantitative and qualitative analysis of the systems studied were carried out by using a Varian Aerograph series 1700 gas chromatograph. The instrument contained a flame ionization detector (FID) and a 6 ft × 2 mm OV17 glass column (5% w/w Carbowax on Chromosorb G) fitted with a glass-wool precolumn. The function of the precolumn was to remove the polymer from the samples, thereby enabling direct analysis of the reaction products. Both programmed temperature (from 50 to 250 °C at 10 °C min^{-1}) and isothermal runs at 200 °C were used. The qualitative analyses were based on a comparison of the retention times of the products found with the corresponding pure substances. Absolute calibration and internal standardization methods were used for quantitative analysis of the reaction substrate and products formed during photolysis in photozyme and hydrocarbon solution, respectively. In the internal standardization method the concentrations of the substrate and products were determined by comparing their peak areas to the peak area of a standard added to the system before irradiation. The relative responses of the products and of the standard were obtained from standard solutions containing known concentrations of the substances. Dodecane was used as an internal standard as it is photochemically stable under the irradiation conditions. The peak areas were measured by a disk integrating unit attached to the chromatograph recorder.

Ultraviolet Spectra Measurement. The UV absorption spectra of the samples were measured by using a Hewlett-Packard 8451A diode-array spectrophotometer.

Fluorescence Spectra Measurements. Steady-state fluorescence spectra of the polymer solution were recorded at room temperature on a Spex Fluorolog-2 fluorescence spectrometer. Emission spectra were corrected for the wavelength dependence of the detector response by using an internal correction function provided by the manufacturer. Deconvolution of the monomer and excimer emission bands of PSSS-VN was carried out by using the novel block polymer poly(2-isopropylnaphthalene-*co*-methacrylic acid) (poly(2-IPN-MAA)).[15] The fluorescence profile of poly(2-IPN-MMA) seems to be mostly due to monomer emission.

Transient Measurements of Fluorescence Decay. Fluorescence decay curves were measured with a single-photon-counting apparatus. The solutions were degassed with five

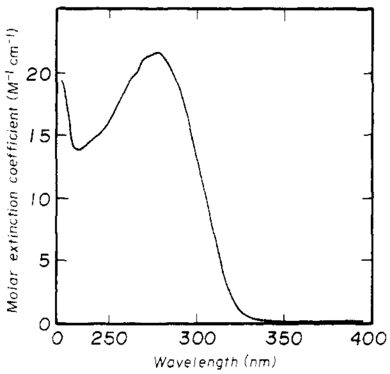


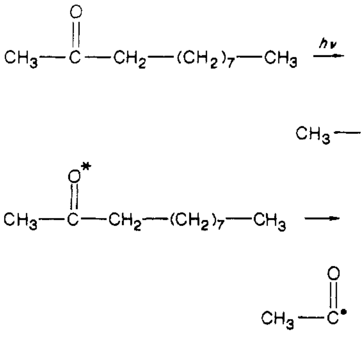
Figure 1. UV absorption spectrum of 2-undecanone in hexadecane solution.

freeze–pump–thaw cycles before being sealed in quartz test tubes. Two 10-μm slits were used at both the entrance and exit of the monochromator for reduction of scattered light. The samples were excited at 283 nm, and emission at 330 nm for monomer and 450 nm for excimer was measured. The lamp profiles for monomer and excimer decay were obtained by using reference compounds with a lifetime of 1.10 and 1.47 ns, respectively. Analysis was performed using the same initial and final channel number. The nonlinear iterative deconvolution technique was used to fit the decay curves.

Results and Discussion

Photochemical Reaction of 2-Undecanone in Hexadecane Solution: Model Studies. Before attempting to investigate the photochemical reactions of 2-undecanone solubilized in the polymer core, we performed model studies in hydrocarbon solvent. Hexadecane was chosen as a solvent because of its relatively high viscosity, and ease of separation from the 2-undecanone, and expected photoproducts.

Figure 1 shows the UV absorption spectrum of 2-undecanone in hexadecane solution for the spectral range 220–400 nm. The absorption band connected with the n→π* transition of the carbonyl group shows a maximum at 278 nm with a corresponding extinction coefficient of 21.6 M^{-1} cm^{-1}. The system consisting of 2-undecanone ($c_U^{init} = 3.0 \times 10^{-3}$ M) was irradiated with monochromatic light at 280 nm in air at room temperature. Gas chromatographic analysis of the initial and irradiated samples was then used to monitor the concentration of the products formed. Figure 2 shows the dependence of the 2-undecanone conversion on the intensity of light absorbed by the sample and irradiation time. The analysis of the products formed during photolysis of 2-undecanone showed the presence of acetaldehyde, nonane, 1-octene, acetone, and 1-methyl-2-hexylcyclobutanol-1. This result indicated that both the Norrish type I and type II reactions occur for 2-undecanone in hexadecane. The Norrish type I reaction results in the formation of two free radicals through cleavage of the bond between the carbonyl group and the α-carbon atom:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-(CH_2)_7-CH_3 \xrightarrow{h\nu} CH_3-\overset{\overset{O^*}{\|}}{C}-CH_2-(CH_2)_7-CH_3 \tag{1}$$

$$CH_3-\overset{\overset{O^*}{\|}}{C}-CH_2-(CH_2)_7-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}{}^\bullet + {}^\bullet CH_2-(CH_2)_7-CH_3 \tag{2}$$

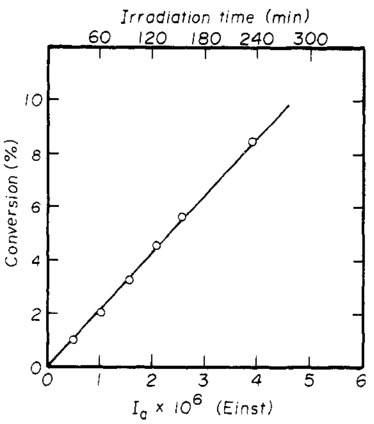
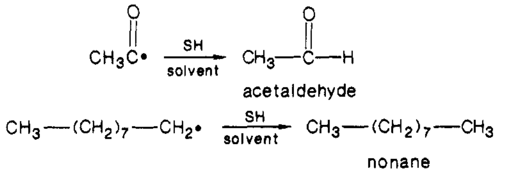


Figure 2. Dependence of the percent conversion of 2-undecanone on the intensity of light absorbed and irradiation time for photolysis in hexadecane solution (λ_{ex} = 280 nm).

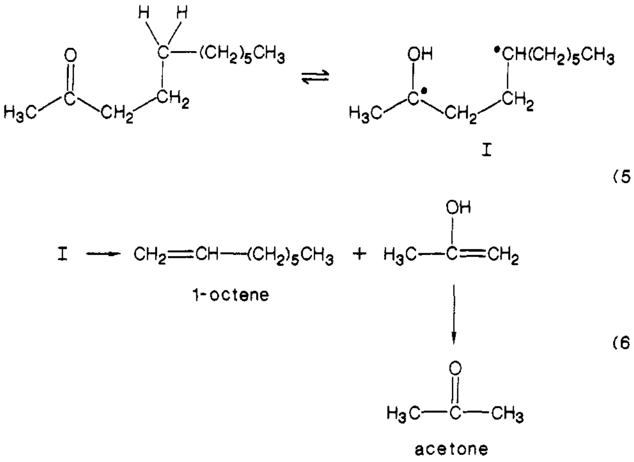
The reaction of the free radicals with solvent results in the formation of the following molecular products:



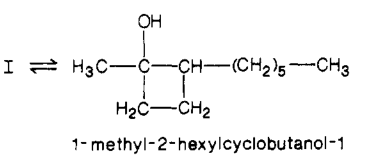
$$CH_3\overset{\overset{O}{\|}}{C}{}^\bullet \xrightarrow[\text{solvent}]{SH} \underset{\text{acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \tag{3}$$

$$CH_3-(CH_2)_7-CH_2{}^\bullet \xrightarrow[\text{solvent}]{SH} \underset{\text{nonane}}{CH_3-(CH_2)_7-CH_3} \tag{4}$$

The Norrish type II process originates from a six-membered cyclic intermediate. Formation of the biradical occurs through H-abstraction on the carbon γ to the carbonyl group, followed by the cleavage of the α–β C–C bond resulting in the formation of acetone and 1-octene:



The photocyclization process results in the formation of a cyclobutanol derivative:



$$\mathrm{I} \rightleftharpoons \underset{\text{1-methyl-2-hexylcyclobutanol-1}}{H_3C-\overset{\overset{OH}{|}}{\underset{\underset{H_2C}{|}}{C}}-\underset{\underset{CH_2}{|}}{CH}-(CH_2)_5-CH_3} \tag{7}$$

The values of the overall quantum yield of photolysis of 2-undecanone in hexadecane as well as the quantum yields of the Norrish type I and II processes are summarized in Table I. The values previously determined by Golemba and Guillet[16] in dodecane and hexane solution at 313 nm are given for comparison. The results of the photolysis of 2-undecanone in dodecane and hexane indicate that the quantum yield of the Norrish type II reaction is independent of temperature and solvent viscosity and is comparable to the value obtained in hexadecane. The slightly

Table I
Overall Quantum Yields (ϕ_R^U) and Quantum Yields for Norrish Type I (ϕ_I) and Type II (ϕ_{II}) Processes for 2-Undecanone Photolysis

solv	viscosity of solv, cP	temp, °C	λ, nm	ϕ_R^U	ϕ_I	ϕ_{II}	% conversn
hexadecane[a]	3.47	25	280	0.240 ± 0.02	0.007 ± 0.001	0.230 ± 0.02	3
dodecane[b]	1.35	35	313	0.197 ± 0.02	0.0003 ± 0.0001	0.196 ± 0.02	2
hexane[b]	0.29	26	313	0.211 ± 0.02	0.0006 ± 0.0001	0.210 ± 0.002	3

[a] This work. [b] Reference 16.

higher value of the quantum yield of the Norrish type I reaction observed in the present work is probably due to the higher energy of excitation (280 nm) used to irradiate the samples. It has been shown that the quantum yield of the Norrish type II reaction for several 2-alkanones is independent of the initial concentration of ketone and is not influenced by the presence of air in the system.[16] The reaction has been observed to occur from both the singlet and triplet excited states of the ketone molecule. Using *cis*-1,3-cyclooctadiene as an excited triplet state quencher, it was found that about 35% of the Norrish type II events for 2-undecanone occur via the excited singlet state.[16]

Naphthalene-Sensitized Photoreactions of 2-Undecanone in Hexadecane Solution. The hexadecane solution of 2-undecanone (3.0×10^{-3} M) and naphthalene (1.8×10^{-4} M) was irradiated in the presence of air with light at 280 nm. It was observed that naphthalene sensitized the photodecomposition of 2-undecanone. (Ninety-three percent of the light absorbed by the system was absorbed by naphthalene.) The value of the quantum efficiency of the sensitized photoreactions of 2-undecanone at 3% conversion was found to be 0.04 ± 0.005.

The following kinetic scheme for the naphthalene-sensitized photoreactions of 2-undecanone can be proposed:

$$^1N_0 + h\nu \rightarrow {}^1N^* \qquad \text{(i)}$$

$$^1N^* \xrightarrow{k_f^N} {}^1N_0 \qquad \text{(ii)}$$

$$^1N^* \xrightarrow{k_{isc}^N} {}^3N^* \qquad \text{(iii)}$$

$$^1N^* \xrightarrow{k_{nr}^N} {}^1N_0 \qquad \text{(iv)}$$

$$^1N^* + {}^3O_2 \xrightarrow{k_q[O_2]} {}^1N_0 + {}^1O_2^* \qquad \text{(v)}$$

$$^1N^* + {}^1U_0 \xrightarrow{k_{ET}[U]} {}^1N_0 + {}^1U^* \qquad \text{(vi)}$$

$$^1U^* \xrightarrow[k_{nr}^U]{k_f^U} {}^1U_0 \qquad \text{(vii)}$$

$$^1U^* \xrightarrow{k_{isc}^U} {}^3U^* \qquad \text{(viii)}$$

$$^1U^* \rightarrow \text{products} \qquad \text{(ix)}$$

$$^3U^* \rightarrow \text{products} \qquad \text{(x)}$$

where $^1N_0$, $^1N^*$, and $^3N^*$ represent the naphthalene molecule in the ground, excited singlet, and excited triplet states, respectively, $^1U_0$, $^1U^*$, and $^3U^*$ are 2-undecanone in the ground, excited singlet, and excited triplet states, respectively, and $^3O_2$ and $^1O_2$ are oxygen in the ground triplet and excited singlet states, respectively.

On the basis of the above proposed kinetic scheme, the overall quantum efficiency of the sensitized photochemical reactions can be expressed as

$$\phi_R^{sens} = \phi_{ET}\phi_R^U \qquad (8)$$

where ϕ_{ET} is the quantum yield of energy transfer from naphthalene to 2-undecanone and ϕ_R^U is the quantum yield of the photochemical reaction for 2-undecanone. Taking into account that the photochemical reactions of 2-undecanone occur from both the excited singlet (35%) and excited triplet (65%) states, eq 8 can be rewritten as follows:

$$\phi_R^{sens} = \phi_{ET}(\phi_R^S + \phi_{isc}^U\phi_R^T) \qquad (9)$$

where ϕ_R^S and ϕ_R^T are the quantum yields of 2-undecanone photoreactions originating from the singlet (step ix) and triplet (step x) excited states, respectively, and ϕ_{isc}^U is the quantum yield of intersystem crossing for 2-undecanone.

In order to establish whether the energy-transfer process in the system is efficient, information regarding the mechanism of the ET process is needed. Dubois and Cox[17] and Heskins and Guillet[18] studied the fluorescence quenching of naphthalene by various ketones and suggested that the dipole–dipole interaction can be neglected for such systems. It was suggested that the ET process occurred by a collisional or exchange mechanism. Dubois and Cox[17] also observed that the rate constant of energy transfer from naphthalene in its singlet excited state to biacetyl was dependent on the solvent viscosity. Calculations of the possibility of long-range transfer by the Förster mechanism confirm that a collisional diffusion-controlled mechanism is more likely.

The radius of interaction (R_0) between naphthalene in its excited singlet state and 2-undecanone can be obtained from the Förster equation:[2]

$$R_0^6 = \frac{8.8 \times 10^{-25} k^2 \phi_D}{n^4} \int_0^\infty F_D(\bar{\nu})\epsilon_A(\bar{\nu})\,(d\nu/\bar{\nu}^4) \qquad (10)$$

where ϵ_A is the extinction coefficient of the acceptor, F_D is the relative fluorescence intensity of the donor at $\bar{\nu}$ satisfying $\int_0^\infty F_D(\bar{\nu})\,d\bar{\nu} = 1$, $\int_0^\infty F_D(\bar{\nu})\epsilon_A(\bar{\nu})\,d\bar{\nu}$ is the overlap integral between the emission profile of the donor and the absorption spectrum of the acceptor, ϕ_D is the fluorescence quantum yield of the donor in the absence of acceptor, n is the refractive index, and k^2 is the molecular orientation factor. If the transition dipole moments are averaged over a random distribution of orientation, k^2 takes a value of $^2/_3$. The values for ϕ_D and n used in this calculation are 0.19 and 1.44, respectively.[19,20] A critical radius of 4.9 Å was obtained for the interaction of naphthalene in its excited state and 2-undecanone. This value is in good agreement with that of Dubois and Cox[17] who obtained a radius of interaction of 4 Å when biacetyl was used as the energy acceptor and phenanthrene or chrysene as the energy donor. The low value of the radius of interaction indicates that energy transfer from naphthalene to the ketone takes place over a short range, i.e., more likely in a collisional process. If it is assumed that the energy-transfer process is diffusion-controlled, the rate constant of this process can be determined by using the equation[21]

$$k_{ET} = pk_{diff} = p(8RT/2000\eta) \qquad (11)$$

where R is the gas constant, T is the absolute temperature, η is the viscosity of the solvent, and p is an efficiency factor ($p = 0.34$).[18] A value of 9.9×10^8 M^{-1} s^{-1} was obtained for

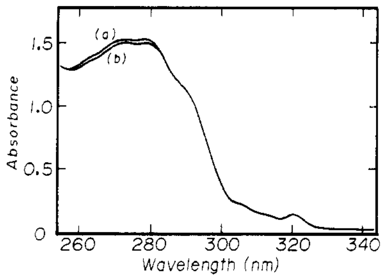


Figure 3. UV–visible absorption spectrum of PSSS-VN water solution (a) before and (b) after saturation with 2-undecanone.

the bimolecular energy-transfer process between naphthalene in excited singlet state and 2-undecanone.

Using the kinetic scheme, reactions i through x, and assuming photostationary conditions, the quantum yield of energy transfer from naphthalene in its excited singlet state to 2-undecanone can be expressed as

$$\phi_{\mathrm{ET}} = \frac{k_{\mathrm{ET}}[\mathrm{U}]}{k_{\mathrm{ET}}[\mathrm{U}] + k_{\mathrm{q}}[\mathrm{O_2}] + k_{\mathrm{f}}^{\mathrm{N}} + k_{\mathrm{nr}}^{\mathrm{N}} + k_{\mathrm{isc}}^{\mathrm{N}}} \qquad (12)$$

where k_{ET} is the rate constant of the energy-transfer process (9.9×10^8 M^{-1} s^{-1}), k_{q} is the rate constant for the naphthalene excited singlet state quenched by oxygen, $k_{\mathrm{q}} = k_{\mathrm{diff}} = 2.9 \times 10^9$ M^{-1} s^{-1}, [O$_2$] is the equilibrium concentration of oxygen dissolved in the solvent at atmospheric pressure (1.44×10^{-3} M),[20] [U] is the concentration of 2-undecanone, and the sum of $k_{\mathrm{f}} + k_{\mathrm{nr}} + k_{\mathrm{isc}}$ was calculated by using the value of 96 ns for the lifetime of the singlet excited state of naphthalene.[19] Using eq 12 a value of 0.17 was obtained for the quantum yield of energy transfer from the excited singlet state of naphthalene molecules to 2-undecanone.

On the basis of the model study, it can be concluded that (1) naphthalene sensitizes photoreactions of 2-undecanone, (2) the process of ET occurs via the short-range collisional mechanism, (3) the energy-transfer process is efficient at relatively high ketone concentration, and (4) the ET process is expected to be efficient in polymer systems in which solubilization leads to an increase of the local concentration of ketone in proximity to the naphthalene chromophores (energy donors).

Photochemical Reactions of 2-Undecanone Solubilized in an Aqueous Solution of PSSS-VN. Figure 3 shows the absorption spectrum of an aqueous solution of PSSS-VN ($c_{\mathrm{pol}} = 0.13$ g dm^{-3}) before (curve a) and after (curve b) saturation with 2-undecanone ($c_{\mathrm{U}}^{\mathrm{tot}} = 8 \times 10^{-4}$ M). It can be seen that saturation of the aqueous polymer solution with 2-undecanone leads to only a small change in the absorption spectrum which is primarily due to the absorbance of the naphthalene chromophore.

Irradiation of the photozyme was carried out by using monochromatic light at $\lambda = 280$ nm, with virtually all (99.9%) of the incident light being absorbed by naphthalene groups in the polymer. The low value of the extinction coefficient and the large screening effect of the polymer all contribute to the small extent of direct excitation of 2-undecanone.

Irradiation of the photozyme induced the photochemical reaction of 2-undecanone. Gas chromatographic analysis of the products formed after photolysis showed that Norrish type I reaction products were not formed in detectable amounts (i.e., a quantum yield of $<1 \times 10^{-4}$). This result suggests that the free radicals formed during photolysis of the solubilized ketone molecules easily recombine before they can escape from the polymer core. It is envisaged that the translational freedom of the free radical is restricted to the hydrophobic microdomains. This results in a high local concentration of free radicals and greatly enhances the probability of recombination.

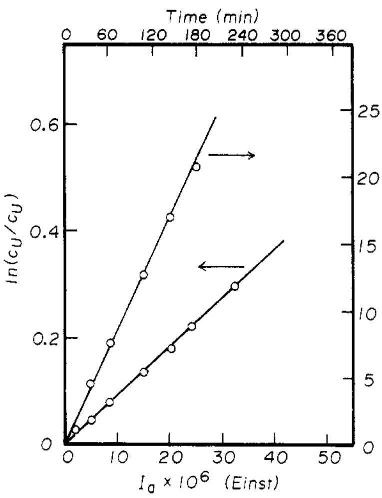


Figure 4. Dependence of the ln ($c_{\mathrm{U}}^0/c_{\mathrm{U}}$) and percent conversion of 2-undecanone on the intensity of light absorbed by the photozyme and on the irradiation time.

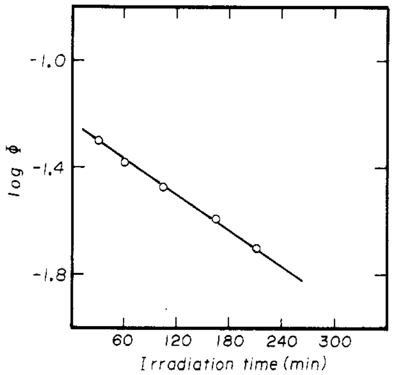


Figure 5. Dependence of the log ϕ (where ϕ is the quantum efficiency of 2-undecanone photolysis) on irradiation time in the photozyme.

Figure 4 shows the dependence of the percent conversion and ln ($c_{\mathrm{U}}^0/c_{\mathrm{U}}$) on irradiation time and light absorbed by the system where c_{U}^0 is the initial concentration of 2-undecanone and c_{U} is the concentration of 2-undecanone at time t. Comparison of these data with the data obtained during the experiment with direct excitation of the ketone (Figure 2) indicates that the polymer sensitized the photochemical reaction of 2-undecanone. The values of the quantum efficiency for the photolysis of 2-undecanone were observed to decrease with prolonged irradiation times, as shown in Figure 5. Since, the photolysis of 2-undecanone is a photosensitized process, its quantum efficiency is dependent on the quantum yield of energy transfer, which is a function of the concentration of the energy acceptor. As 2-undecanone is converted to products, this efficiency decreases.

In order to determine the mechanism of the energy-transfer process from the pendant naphthalene groups to the ketone molecules, the effect of 2-undecanone on the steady-state fluorescence of PSSS-VN was studied.

Effect of 2-Undecanone on the Fluorescence of PSSS-VN Copolymer in Aqueous Solution. The steady-state fluorescence spectrum of an aqueous solution of PSSS-VN at room temperature ($\lambda_{\mathrm{ex}} = 280$ nm) is shown in Figure 6 (curve a). The emission profile consists of two bands. The shorter wavelength structured band with a maximum at 335 nm is due to monomer emission while the

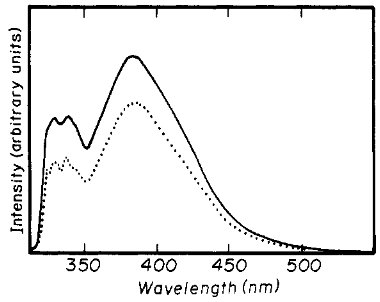


Figure 6. Steady-state fluorescence emission of PSSS-VN copolymer in water solution in (a) the absence and (b) presence of 2-undecanone (c_U^{tot} = 6.6 × 10^{-4} M).

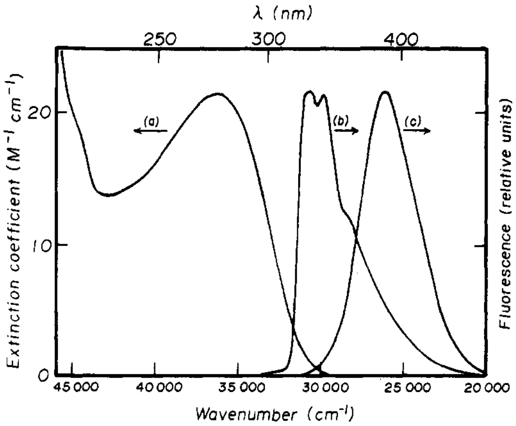


Figure 7. Comparison of (a) the UV absorption spectra of 2-undecanone, (b) monomer, and (c) excimer emission in PSSS-VN copolymer.

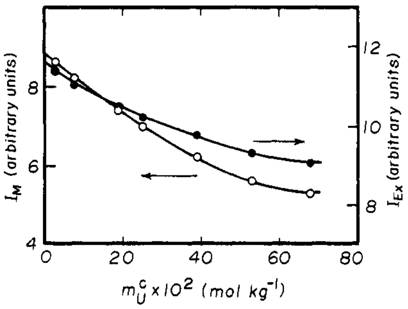


Figure 8. Plot of the monomer I_M and excimer fluorescence intensity I_{Ex} on the molal concentration of ketone in the polymer microphase.

broad, more intense band at 400 nm originates from excimer fluorescence. The steady-state emission profile of PSSS-VN in the presence of 2-undecanone (c_U^{tot} = 6.5 × 10^{-3} M, c_p = 0.05 g dm^{-3}) is shown in Figure 6 (curve b). It can be seen that 2-undecanone solubilized in the aqueous polymer solution quenches the luminescence of PSSS-VN. A comparison of the absorption spectrum of 2-undecanone with the monomer and excimer bands of PSSS-VN indicated that 2-undecanone quenches almost exclusively the monomer fluorescence (Figure 7). The decrease of the excimer intensity appears to be due to the quenching of monomer excitation which leads to a lower efficiency of excimer emission. The overlap of monomer and excimer emission also contributes to lowering of the excimer intensity. Figure 8 shows the change in the monomer and excimer intensity with increasing amounts of 2-undecanone solubilized in the polymer microphase. It can be seen that the decrease in the excimer intensity is much less than the monomer intensity. Thus, the ratio of excimer to monomer fluorescence increases with an increase in the concentration of solubilized ketone (Figure 9).

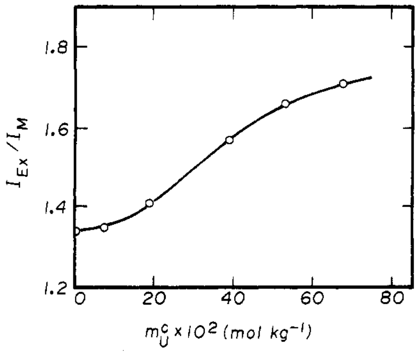


Figure 9. Dependence of the ratio of excimer fluorescence intensity to monomer fluorescence intensity of PSSS-VN on molal concentration of 2-undecanone in the polymer microphase.

Table II
Monomer Fluorescence Decay Parameters for PSSS-VN in Water Solution^a in the Absence and Presence of 2-Undecanone

lifetime, ns	fractn F, %	ΔF, %
Polymer Solution ($I = I_0$)		
16.8	26.0	
43.4	66.0	
91.6	8.0	
Polymer Solution + 2-Undecanone ($I = 0.7I_0$)		
4.9	43.6	+17.5
27.3	18.2	−47.8
62.2	8.2	+0.2

^{a} λ_{ex} = 283 nm; λ_{em} = 330 nm.

Transient decay studies of the monomer fluorescence intensity seem to support the results obtained from the steady-state measurements. Decay curves could not be fitted to a double exponential of the type used in the Birks kinetic scheme.[21] The application of a triple-exponential function[11]

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \qquad (13)$$

gave a relatively good fit with the coefficient χ^2 = 1.10 and χ^2 = 1.20. The monomer fluorescence decay in the absence and in the presence of 2-undecanone is given by eq 14 and 15, respectively. Table II summarizes the fluorescence

$$I(t) = 2.22 \times 10^{-1} \exp(-t/16.8) + 2.18 \times 10^{-1} \exp(-t/43.4) + 1.27 \times 10^{-2} \exp(-t/91.5) \qquad (14)$$

$$I(t) = 5.05 \times 10^{-1} \exp(-t/4.9) + 3.78 \times 10^{-2} \exp(-t/27.3) + 7.5 \times 10^{-3} \exp(-t/62.2) \qquad (15)$$

decay parameters and relative fractions of the respective components, $F = (A_i\tau_i/\sum_i A_i\tau_i)$ (100%), of PSSS-VN in the presence and in the absence of 2-undecanone.

It can be seen that in the presence of 2-undecanone the lifetimes of all three components were shortened; however, only the fraction characterized by the lifetime τ = 43 ns decreased considerably. The fraction connected with the longest lifetime remained unchanged. From a comparison of the fluorescence decay of the monomer and excimer bands the longest lifetime has been assigned to the overlap of monomer–excimer emission.[12] Thus the constancy in the magnitude of the fraction associated with the longest decay component is consistent with the steady-state spectra, which showed that 2-undecanone almost exclusively quenches the monomer emission.

The results of steady-state and transient fluorescence measurements indicated that the singlet–singlet energy transfer from excited pendant naphthalene groups to 2-

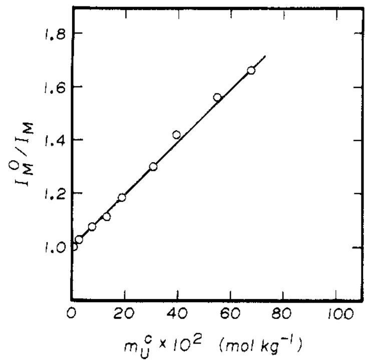


Figure 10. Stern–Volmer plot of the ratio of monomer fluorescence intensities (I_M^0/I_M^Q) in the absence (I_M^0) and in the presence of quencher (I_M^Q) versus 2-undecanone molal concentration in the polymer core microphase.

undecanone occurs in the photozyme. Two main mechanisms can thus be considered as probable for this type of energy transfer: (1) the long-range resonance Förster mechanism and (2) the diffusion-controlled process described by Stern–Volmer kinetics. Using the Förster equation (10) and substituting the refractive index of water (n = 1.36), the fluorescence quantum yield for 2-methylnaphthalene, $\phi_D = 0.32$,[22] and the experimentally determined J integral for overlap between monomer emission and the absorption spectrum of 2-undecanone, the radius of interaction was found to be $R_0 = 5.6$ Å. At this distance collisional interactions would be expected to dominate the energy-transfer process. Figure 10 shows the plot I_M^0/I_M^Q for monomer fluorescence quenching versus concentration of 2-undecanone in photozyme. Hence, the quenching process does fit the Stern–Volmer kinetic equation

$$I_M^0/I_M^Q = 1 + k_q\tau[Q] \qquad (16)$$

where I_M^0 and I_M^Q are the monomer fluorescence intensities in the absence and presence of 2-undecanone, respectively, τ is the lifetime of the energy donor species, and [Q] is the concentration of quencher (energy acceptor). This supports the thesis of a collisional energy transfer mechanism for the PSSS-VN + 2-undecanone photozyme. From the slope of the Stern–Volmer plot, assuming a density of unity for the polymer microphase and using the value of 43 ns for the lifetime of the naphthalene chromophore quenched by ketone, the rate constant for the energy-transfer process was estimated to be 2.3×10^7 M^{-1} s^{-1}. Because of the complex nature of the monomer fluorescence decay of the polymer and the uncertainty of the lifetime of the energy donor, the above rate constant should be treated as a rough estimate. The value of the quantum yield of energy transfer was determined from steady-state data by using eq 17,

$$\phi_{ET} = 1 - (\phi_M^Q/\phi_M^0) \qquad (17)$$

where ϕ_M^Q and ϕ_M^0 are the absolute fluorescence quantum yields of naphthalene monomer in the presence and absence of 2-undecanone. Figure 11 shows the dependence of the quantum yield of energy transfer on the concentration of ketone in the polymer microphase.

Effect of Oxygen on the Photochemical Reactions of 2-Undecanone in the Photozyme. Oxygen is known to be a very efficient quencher of organic molecules in their electronically excited states. Thus, it is expected to affect the photosensitized photochemical reactions of 2-undecanone assuming that a reasonable amount of oxygen is present in the polymer core. There is some controversy in the literature concerning the solubility of oxygen in micellar and polyelectrolyte systems.[23-27] In the opinion of some authors the concentration of oxygen is negligible, while others have suggested that the solubility of oxygen is even greater than in hydrocarbon solvents for such systems under identical conditions.

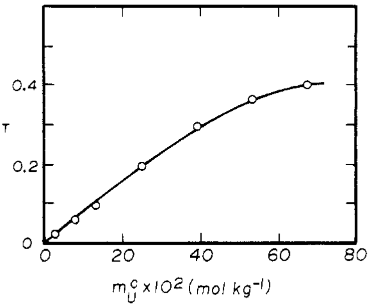


Figure 11. Plot of the dependence of the quantum yield of energy transfer on the 2-undecanone concentration in the polymer core.

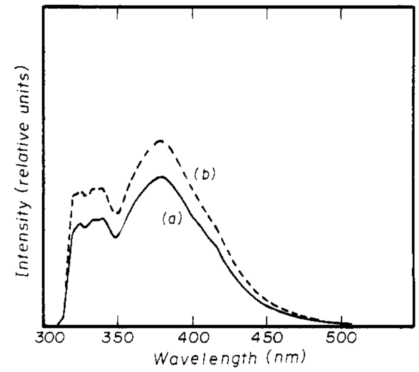


Figure 12. Steady-state fluorescence emission of PSSS-VN in water solution (a) in the absence and (b) in the presence of air.

The steady-state fluorescence spectrum of an aqueous solution of PSSS-VN in the presence and absence of oxygen is shown in Figure 12. It can be seen that oxygen present in the system does quench the polymer fluorescence. The ratio of the quantum yield of naphthyl fluorescence in the presence of argon and air, respectively, was found to be $\phi_f^{Ar}/\phi_f^{air} = 1.3$.

The effect of oxygen on photochemical reactions in the photozyme was studied by comparing the quantum efficiencies of photolysis of 2-undecanone ($c_U^{tot} = 6.6 \times 10^{-4}$ M) in two samples. One sample was bubbled with argon and the other with air for 30 min and then irradiated for a period of 30 min. The quantum efficiency of photodecomposition of 2-undecanone was higher in the argon atmosphere than in the presence of air

$$\phi_U^{Ar} = 0.177 \pm 0.01 \qquad (18)$$

while

$$\phi_U^{Ox} = 0.150 \pm 0.01 \qquad (19)$$

Since it is known that oxygen does not seriously affect the photochemical reactions of 2-undecanone,[16] it can be assumed that the quantum yield of photolysis is identical in both cases and the following expression can be written:

$$(\phi_U^{Ar}/\phi_U^{Ox}) = (\phi_{ET}^{Ar}/\phi_{ET}^{Ox})(\phi_r/\phi_n) = (\phi_{ET}^{Ar}/\phi_{ET}^{Ox}) = 1.18 \qquad (20)$$

Taking into account the values of the overall quantum yield of 2-undecanone photolysis ($\phi_U^{Ar} = 0.177$) and energy transfer in the oxygen-free solution under experimental conditions ($\phi_{ET} = 0.30$), the quantum yield of the process (ϕ_r) has been estimated to be 0.59 ± 0.1. This value of the quantum yield of photolysis of 2-undecanone solubilized in the polymer microphase is considerably higher than that

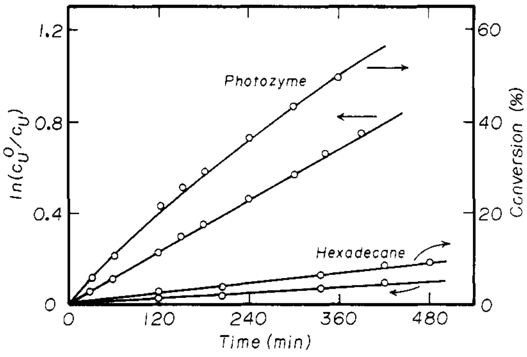


Figure 13. Plot of the ln (c_U^0/c_U) (where c_U^0 and c_U are the concentration of 2-undecanone at irradiation time $t = 0$ and $t = t$) and 2-undecanone conversion versus irradiation time of the photozyme with solar-simulated radiation.

observed in hydrocarbon solvents. As was mentioned above, the photolysis of 2-undecanone in the polymer system occurs according to the Norrish type II process. The considerable increase in the quantum yield of this process may indicate that the polymer core microenvironment is more polar than that of a hydrocarbon solvent. A similar increase in the relative quantum yield of the Norrish type II reaction of valerophenone and octanophenone in a micellar solution of hexadecyl tetramethylammonium chloride compared to benzene was reported by Turro et al.[28] (The relative quantum yields increase from 0.33 to 1.06 for valerophenone and from 0.21 to 0.71 for octanophenone.) Wagner et al.[29] attributed this to hydrogen-bond formation between the biradical intermediate and a molecule of a polar solvent which favors the formation of the reaction products relative to reversion of the biradical to the initial ketone molecule.

Photochemical Reactions of 2-Undecanone in Aqueous Solutions of PSSS-VN Initiated with Solar-Simulated Radiation. The possible practical application of PSSS-VN as a photocatalyst for photochemical reactions of hydrophobic substances in aqueous solution was studied by using simulated solar light. It was found that the photolysis of 2-undecanone leads to the formation of the expected Norrish type II products. In order to compare the efficiency of the photoreaction in the photozyme to that in organic solvent, an aqueous polymer solution and a hexadecane solution, containing identical amounts of 2-undecanone ($c_U^{tot} = 6 \times 10^{-4}$ M), were irradiated. As can be seen from Figure 13, the photoreaction can be described by the first-order kinetic equation up to 50% conversion. The values of the rate constants were found to be 1.9×10^{-3} and 2.1×10^{-4} min^{-1} in aqueous polymer solution and hexadecane solution, respectively. Hence, the photoreaction in the photozyme is about 9 times faster than that in organic solvent. It should be stressed that PSSS-VN was photostable under the experimental conditions. Both the polymer photostability and relatively high efficiency of photolysis of 2-undecanone suggest that PSSS-VN may have practical applications in the solar synthesis of organic compounds.

Conclusions

From photophysical and photochemical studies of the poly(sodium styrenesulfonate-*co*-vinylnaphthalene)-2-undecanone system the following can be concluded. (1) The PSSS-VN copolymer in water solution sensitized photolysis of 2-undecanone. (2) Energy transfer from excited pendant naphthalene chromophores to the ketone is a diffusion-controlled collisional process. (3) The high local concentration of 2-undecanone in hydrophobic polymeric microdomains increases the efficiency of the energy transfer process. (4) The 2-undecanone photolysis occurs primarily by the Norrish type II process. (5) The notable lack of Norrish type I products is an important feature of these systems. This may be attributed to the enhancement of radical–radical recombination following α-cleavage in the small polymer microdomains, although the higher polarity of the surrounding medium may also play a role. (6) The polymer is photostable under the experimental conditions which makes possible its repeated usage in a cyclic process, i.e., solubilization of probe–photochemical reaction–extraction–resolubilization.

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Registry No. PSSS-VN, 115468-37-6; O_2, 7782-44-7; 2-undecanone, 112-12-9.

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