Studies of the antenna effect in polymer molecules. 28. Photo-Fries rearrangement of 1-naphthyl acetate in aqueous solutions of poly(sodium styrenesulfonate-co-2-vinylfluorene)[‡]

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Received (in Göttingen, Germany) 1st February 1999, Accepted 26th February 1999

The photo-Fries rearrangement of 1-naphthyl acetate (NA) in aqueous solutions of the novel antenna polyelectrolyte, poly(sodium styrenesulfonate-co-2-vinylfluorene) (PSSS-VF), was studied. Three copolymers with different fluorene (Fl) chromophore contents were synthesized. The solubilizing abilities of the PSSS-VF copolymers in aqueous solution were tested using perylene as a probe. The polarity of the polymeric medium was shown to be lower than that of the interior of typical surfactant micelles. It was demonstrated that electronic excitation energy can migrate along the polymer chain before being transferred to the solubilized probe molecule. The reaction of NA is sensitized efficiently by light absorbed by the polymeric fluorene chromophores. It was found that the product distribution of the reaction strongly depends on the content of fluorene in the copolymer. The reaction in aqueous solutions of PSSS-VF rich in Fl chromophores occurs with high selectivity to form the cage product, 2-acetonaphthol (2-AN) in 95% yield. Polymeric sensitizers with low fluorene content (~5%) gave 90% yields of the non-cage product 1-naphthol. Both are more selective than when the Fries reaction is carried out in methanol solution.

A new family of antenna polyelectrolytes has recently been synthesized and studied. The copolymers of sodium styrenesulfonate or methacrylic acid with 2-vinylnaphthalene,[1–5] 9-phenylanthracene,[6] *N*-vinylcarbazole, *N*-acryloxyhexyl carbazole,[7] and 9-vinylphenanthrene[8] have all been shown to display photocatalytic activity. In aqueous solutions they solubilize molecules of sparingly water-soluble hydrophobic organic compounds (probes). The aromatic polymeric units act as antennas, absorbing light from the near UV-visible spectral region and transferring the excitation to the probe molecules, often inducing photochemical reactions of the probe.[1–10]

Light scattering[11] and ultracentrifuge[12] experiments confirm that in neutral aqueous solutions of low ionic strength, these polyelectrolytes adopt spherical shapes with hydrodynamic volumes somewhat greater than that of a random polymer coil. However, based on luminescence studies involving energy transfer experiments, it seems clear that the polymer conformation is not random, but involves significant "clustering" of the hydrophobic monomeric units in the interior of the coil.[13,14]

In this work, the photo-Fries rearrangement of 1-naphthyl acetate (NA) was chosen to test the photocatalytic activity of vinylfluorene (VF) antenna units. The reaction has been widely studied for different substrates and in many systems such as: the vapour phase,[15] solutions,[16,17] polymer films,[16c,18] the ordered phase of alkyl alkanoates,[19] zeolites,[20] micelles[21] and supercritical fluids.[22] The distribution of the products of the reaction strongly depends on the type of reaction medium. The reaction cavity parameters, such as size, polarity, viscosity can influence both the proportion and the quantum yields of the products.[18–22]

Results and discussion

Polymer characterization

Three PSSS-VF copolymers were sythesized and used for further studies. The polymers obtained were very soluble in water and soluble in DMSO and methanol. The intrinsic viscosity of polymer B in DMSO solution at 40 °C was 1.81 ± 0.05 dl g^{-1}. The polymers were analyzed by NMR, UV and fluorescence spectroscopy. The UV absorption spectra in aqueous solution display the bands characteristic for the fluorene chromophore with a maximum at 306 nm. The compositions (Table 1) of the copolymers were determined based on their electronic absorption spectra and the respective spectra for PSSS in aqueous solution ($\varepsilon_{262} = 403$ dm^3 mol^{-1} cm^{-1})[23] and the fluorene spectrum measured in methanol solution ($\varepsilon_{262} = 19\,700$ dm^3 mol^{-1} cm^{-1} and $\varepsilon_{300} = 8400$ dm^3 mol^{-1} cm^{-1}).

Fig. 1(*A*) shows the steady-state fluorescence and excitation spectra of PSSS-VF(B) in aqueous solution. The excitation spectrum is in good agreement with the absorption spectrum and does not display any additional bands. The emission spectrum is broad but displays a distinct maximum at 323 nm. A comparison of the emission spectra of fluorene in methanol

Table 1 The composition of the polymerization mixtures and the copolymers

Sample	Feed ratio SSS : VF/mol%	Polymer composition SSS : VF/mol%
PSSS-VF(A)	90 : 10	95 : 5
PSSS-VF(B)	80 : 20	88 : 12
PSSS-VF(C)	70 : 30	77 : 23

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[‡] Part 27, see M. Nowakowska and J. E. Guillet, *J. Photochem. Photobiol.*, 1997 **112**, 285.

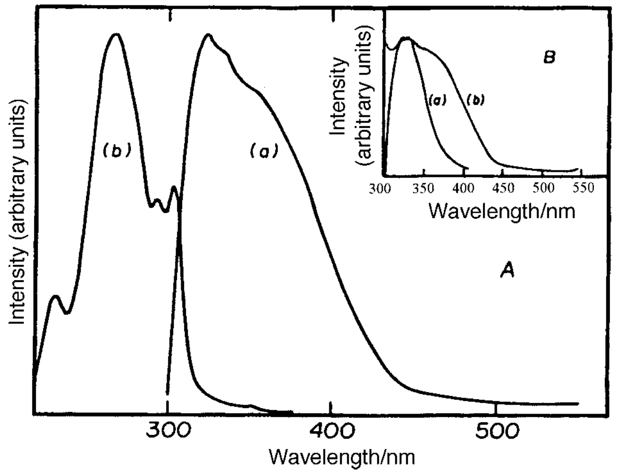


Fig. 1 (*A*) Fluorescence spectra of PSSS-VF(B) in aqueous solution. Curve a: steady-state fluorescence spectrum ($\lambda_{ex} = 280$ nm, $c_{pol} = 0.5$ g dm^{-3}); curve *b*: excitation spectrum ($\lambda_{em} = 390$ nm, $c_{pol} = 0.5$ g dm^{-3}). (*B*) Curve *a*: steady-state emission spectra of fluorene in methanol solution; curve *b*: PSSS-VF(B) in aqueous solution, $\lambda_{ex} = 280$ nm.

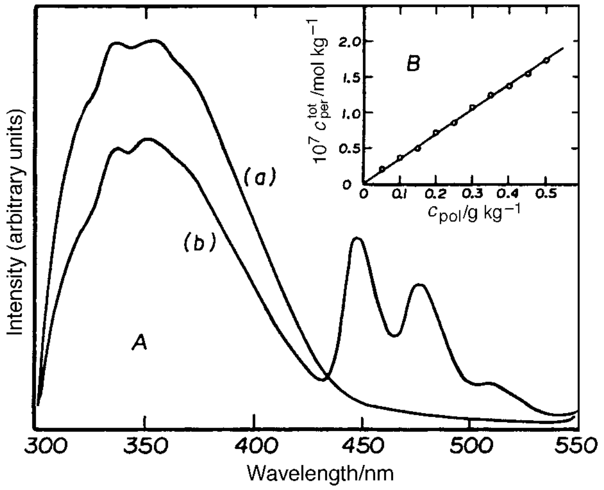


Fig. 2 (*A*) Steady-state fluorescence spectra of PSSS-VF(B) in aqueous solution. Curve *a*: $c_{pol} = 0.5$ g dm^{-3}, $\lambda_{ex} = 280$ nm; curve *b*: with solubilized perylene, $c_{per}^{tot} = 3.6 \times 10^{-7}$ M. (*B*) Dependence of the total concentration of perylene solubilized in an aqueous solution of PSSS-VF(B) on the polymer concentration.

solution and of PSSS-VF(B) in aqueous solution [Fig. 1(*B*)] suggests that the broadening in the long-wavelength spectral region for PSSS-VF can be attributed to the fluorene excimer. The appearance of the emission from the fluorene excimer was previously reported but only at a very high concentration of fluorene (0.24 M) in toluene solution at low temperatures.[24]

Formation of the excimer in aqueous solutions of PSSS-VF at room temperature requires proximity of the chromophores and stabilization of the excimer formed. One can expect that the VF chromophores will be close enough to form an excimer if VF exists in sequences in a copolymer chain, or if the macromolecule adopts a conformation in which the VF chromophores are forced to be in close proximity. An attempt to determine the sequence distribution from the NMR spectra of the PSSS-VF copolymers was unsuccessful. The spectra of all polymers in D_2O as well as in DMSO solutions were broad and did not provide sufficient resolution for sequence calculations. This indicates the existence of strong interactions between the aromatic polymeric units, possibly due to the clustering of polymeric hydrophobic chromophores in water. This observation is consistent with the conclusions reached from fluorescence data, and indicates that PSSS-VF behaves in aqueous solution in a manner similar to that shown by other antenna polyelectrolytes.[3,6,8] Clustering of the fluorene polymeric units results in the formation of hydrophobic microdomains with a high local concentration of fluorene chromophores in a restricted volume of the domain. This explains the broadening observed in the NMR spectra and the high fluorene excimer emission in a copolymer containing only 12 mol% VF units [Fig. 1(*B*)].

The presence of hydrophobic microdomains in aqueous solutions of PSSS-VF(B) was confirmed by the solubilization of pyrene as a polarity-sensitive probe. It is well-established that the intensity of the vibronic fine structure in pyrene monomer fluorescence is strongly dependent on solvent polarity. The ratio of the intensities of peak III to peak I is generally used as a sensitive measure of the environmental micropolarity.[25,26] Using this method, the relative polarity of the solubilizing microdomains in PSSS-VF(B) was determined. It was found that the ratio of the emission intensities III/I is equal to 0.75. This value is slightly higher than that for typical micelles (in a hexadecyltriethylammonium bromide micelle the III/I ratio is 0.72[26]) but lower than that determined earlier for the copolymers of methacrylic acid with 9-vinylphenanthrene.[8]

The solubilizing abilities of the PSSS-VF copolymers in aqueous solution were tested using perylene as a probe. Fig. 2(*A*) shows the steady-state emission spectra of an aqueous solution of PSSS-VF(B) and of the same solution containing solubilized perylene, excited within the fluorene absorption band ($\lambda = 280$ nm). In a system containing perylene, the excitation energy is transferred from fluorene to perylene, resulting in a decrease in fluorene emission and in the appearance of perylene fluorescence. The quantum yields of the energy transfer (φ_{ET}) in perylene-saturated aqueous solutions of PSSS-VF copolymers were determined as described earlier[1] (see Table 2).

Based on the experimental data [see Fig. 2(*B*)] and using the method described earlier, the distribution coefficients of perylene between the polymeric pseudophase and the aqueous phase can be determined.[27] The values of the distribution coefficient *K* (defined as the ratio of the weight fractions of perylene in the polymeric pseudophase and aqueous phase) were found (see Table 2). The values are in the same range as those found earlier for other antenna polyelectrolytes, which were characterized by a similar ratio of hydrophobic and hydrophilic units.[6,8]

The measurements of the degree of fluorescence polarization for solubilized perylene were carried out to confirm the energy migration between fluorene chromophores in the polymer chain. Soutar and Philips[28] showed that energy migration in polymers can be monitored by determining the degree of polarization, *P*, of a directly and indirectly (*via* energy transfer) excited probe molecule that has been solubilized by the polymer. The degrees of polarization for the directly excited perylene ($\lambda_{ex} = 415$ nm) solubilized in the PSSS-VF polymers are significant (see Table 3), although much lower than the value of 0.46 obtained for perylene under conditions that eliminate its rotational motion (propylene glycol at −50 °C).[29] Very significant depolarization of indirectly excited perylene ($\lambda_{ex} = 280$ nm) was observed for all three polymers (see Table 3). These data suggest that energy

Table 2 Quantum yields of energy transfer from fluorene chromophores to solubilized perylene in aqueous solutions of PSSS-VF copolymers and distribution coefficients of perylene between polymer pseudophase and aqueous phase

Sample	$\varphi_{ET}(\pm 0.05)$	$K \times 10^5(\pm 5\%)$
PSSS-VF(A)	0.20	0.8
PSSS-VF(B)	0.27	2.9
PSSS-VF(C)	0.32	5.5

Table 3 Fluorescence depolarization measurements for perylene *via* direct and indirect excitation (λ_{em} = 450 nm)

Sample	P_{280} [a]	P_{415} [b]
PSSS-VF(A)	0.060 ± 0.005	0.158 ± 0.008
PSSS-VF(B)	0.048 ± 0.003	0.160 ± 0.005
PSSS-VF(C)	0.034 ± 0.002	0.176 ± 0.005

[a] Excitation of fluorene chromophores with λ_{ex} = 280 nm. [b] Direct excitation of perylene with λ_{ex} = 415 nm.

migration between Fl groups occurs in the PSSS-VF polymers prior to the final energy transfer from Fl to the solubilized perylene. Energy migration is likely to be more efficient in the polymer containing more Fl chromophores and containing longer fluorene sequences. This is in agreement with the observation of decrease in the value of P_{280} for the polymers richest in fluorene [compare values for PSSS-VF(A) and PSSS-VF(C) in Table 3].

Photochemical reaction in aqueous solutions of PSSS-VF

In order to test the photocatalytic activity of the synthesized copolymers the photo-Fries rearrangement of NA in aqueous solutions of PSSS-VF copolymers was studied. Based on the energy diagram (Fig. 3) it can be expected that the reaction can be induced by both singlet–singlet and triplet–triplet energy transfer from Fl chromophores to NA. However, the participation of the NA triplet state in the reaction is believed to be negligible.[17] Gritsan *et al.*[17] have shown that decomposition of NA to acetyl and naphthoxyl radicals occurs mainly (>90%) in the singlet state. The subsequent steps of the reaction can occur both within and outside of a solvent cage, leading to the formation of different products (Scheme 1).[17] The ratio of "the escape product" to the "rearrangement products" can be used to probe the efficiency of cage escape.[22] The mobility of the phenoxyl and acyl radicals in a cage can additionally influence the ratio of the *ortho* to *para* isomers.

In our experiments, NA was solubilized in aqueous solutions of PSSS-VF containing 5, 12 and 23 mol% of VF. Fig. 4 shows that the solubilized NA quenches the fluorescence of fluorene polymeric chromophores. For all photochemical experiments the concentration of fluorene chromophores in solution was the same ([Fl] = 4.8×10^{-4} M) and a constant amount of NA was solubilized ($[\mathrm{NA}]_{tot} = 2.7 \times 10^{-5}$ M). Due to the low total concentration of NA and the low extinction coefficient of NA at the excitation wavelength (313 nm), the majority of incident radiation (>99.5%) was absorbed by the polymer. The irradiation was carried out to *ca.* 5% NA conversion in order to avoid reaction of the products.[17] After irradiation the solutions were extracted with chloroform and analyzed by gas chromatography. The products were identified using a preparative chromatographic method.‡ The results (see Table 4) indicate that the ratios of the products formed during the rearrangement of NA are strongly dependent on the content of Fl in the polymeric chain. In an aqueous solution of PSSS-VF(A) the major product of the reaction was 1-N. Macromolecules with such a low Fl content form loosely packed micelles and the radicals produced in the first step of the reaction (see Scheme 1) can easily separate and leave the polymeric microdomain. If the rate of cage escape is greater than the rate of radical recombination, 1-naphthoxyl radicals can abstract hydrogen atoms from the solvent to yield 1-naphthol.

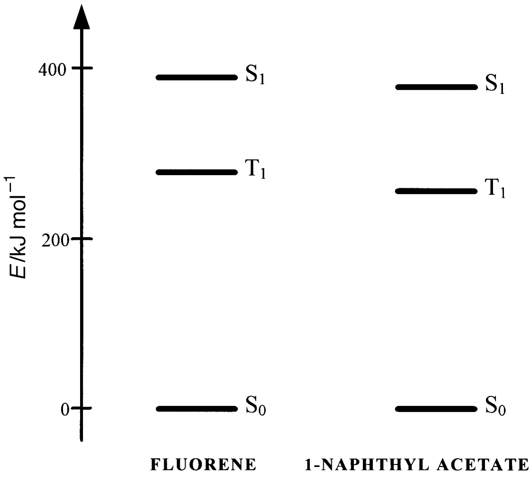
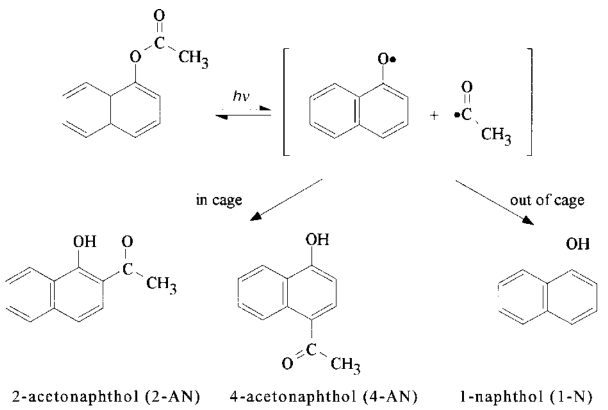


Fig. 3 The energy diagrams for the lowest electronically excited states of fluorene[30] and 1-naphthyl acetate.[17]



Scheme 1

The results obtained for PSSS-VF(C) indicate that both steps of the photo-Fries rearrangement of NA can occur in the polymeric microdomain. The absence of 1-N among the products suggests that the reaction occurs within condensed polymeric microdomains, where the escape of the initially formed radicals to the aqueous phase is very inefficient. The *ortho*

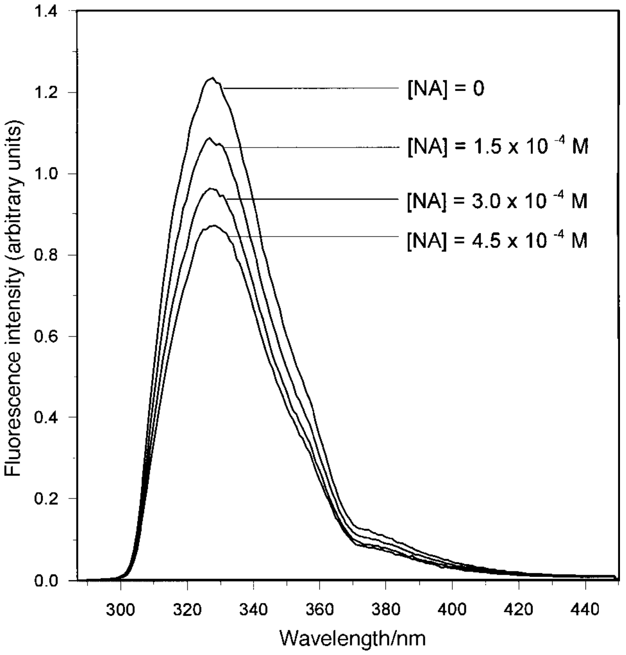


Fig. 4 Steady-state fluorescence spectra of aqueous solutions of PSSS-VF(B) (λ_{ex} = 280 nm, c_{pol} = 0.5 g dm^{-3}) in the absence and presence of solubilized NA at various total concentrations.

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‡ The reaction mixture of NA in methanol was separated after irradiation on the preparative chromatograph and the peak identification was based on the UV/Vis spectra of the products.[17]

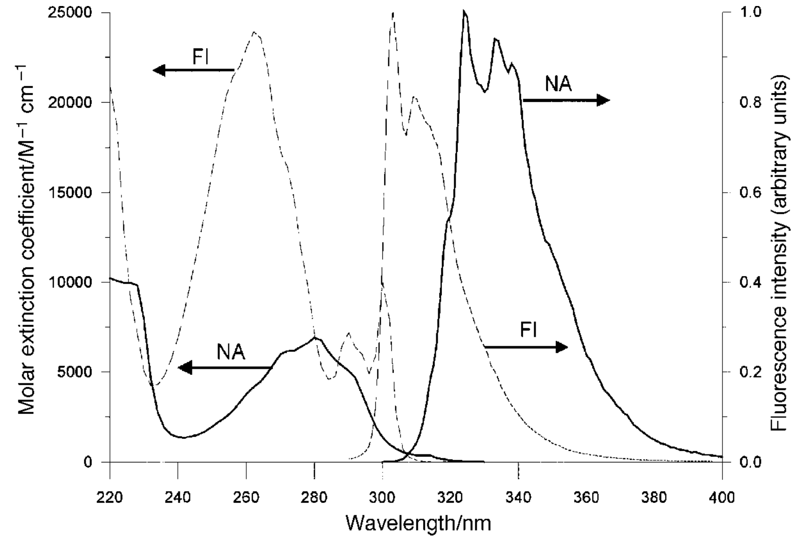


Fig. 5 Absorption and emission (λ_{ex} = 280 nm) spectra of Fl and NA measured at room temperature in heptane solution.

Table 4 Quantum yields of the photo-Fries rearrangement of NA and product distributions of the reaction in aqueous solutions of PSSS-VF copolymers[a] and in organic solvents

Sample	Polymer concentration/ g dm^{-3}	Relative quantum yields of consumption of NA γ_{NA}($\pm$10%)	Products/%		
			2-AV	4-AN	1-N
PSSS-VF(A)	2.05	1.0	5	5	90
PSSS-VF(B)	0.85	2.8	80	10	10
PSSS-VF(C)	0.44	3.0	95	5	0
Acetonitrile[b]	—	—	64	29	7
Acetonitrile[c]	—	—	59	29	12
Methanol[c]	—	—	50	17	33

[a] All measurements were carried out for solutions with the same concentration of polymeric fluorene chromophores ([Fl] = 4.8 × 10^{-4} M). [b] According to Ref. 21. [c] According to Ref. 17.

selectivity of the reaction can be explained in terms of the relatively high microviscosity,[21] which restricts the rotation necessary to form 4-AN. Quantum chemical calculations for the 1-naphthoxyl radical indicate that the spin density in the 4-position is higher than in the 2-position[17] and formation of the *para* isomer should be favored in non-restrictive systems.

In the case of PSSS-VF(B) both in-cage and out-of-cage products were observed because the compactness of the PSSS-VF(B) pseudomicelle is lower than that of PSSS-VF(C). Additionally, more 4-AN is formed as expected because of the less restricted mobility of radicals within this polymeric microenvironment in comparison with that in PSSS-VF(C).

The results obtained for the photo-Fries rearrangement of NA carried out in systems of restricted geometry such as zeolites,[20] polyethylene films,[18] typical micelles[21] or in highly viscous solvents[18,21] also show an *ortho* selectivity. Comparable literature values for the photo-Fries rearrangement of NA that were carried out in acetonitrile and methanol solutions monitored by GC and UV/Vis spectrophotometry are included in Table 4.

Model studies on the fluorene-photosensitized rearrangement of NA

Determination of the rate constants and quantum yields of the energy transfer from the electronically excited Fl to NA is difficult due to the spectral and photophysical characteristics of the system. The difference in the position of the energy levels of the excited singlet states for these compounds is quite small (ΔE = 14.5 kJ mol^{-1}, see Fig. 3). This leads to a substantial overlap between their absorption and fluorescence spectra (see Fig. 5). Moreover, the Fl fluorescence quantum yield is quite high, $\varphi_f = 0.66$.[30] Thus it is difficult to avoid interferences, (such as inner filter effect, reabsorption of the light emitted by Fl by both Fl and NA) during the measurements of the fluorescence quenching of Fl by NA. In order to diminish these problems the studies on Fl quenching by NA were carried out using the front-face geometry.

Measurements of the steady-state fluorescence spectra of Fl in heptane or hexadecane solution in the absence and in the presence of NA have shown that NA efficiently quenches the emission of Fl (see Fig. 6 for heptane solution). The absorption and excitation spectra recorded for Fl in the presence of NA do not display any additional bands even at high concentrations of components. The rate constants for the quenching of Fl by NA (k_q) in heptane and hexadecane were determined using the Stern–Volmer kinetic equation and based on measurements of the fluorescence intensities of Fl in the presence of NA at different concentrations (Fig. 7). The literature value of the fluorescence lifetime for Fl, τ = 10 ns,[30] was used in these calculations. The values of k_q are similar in heptane and

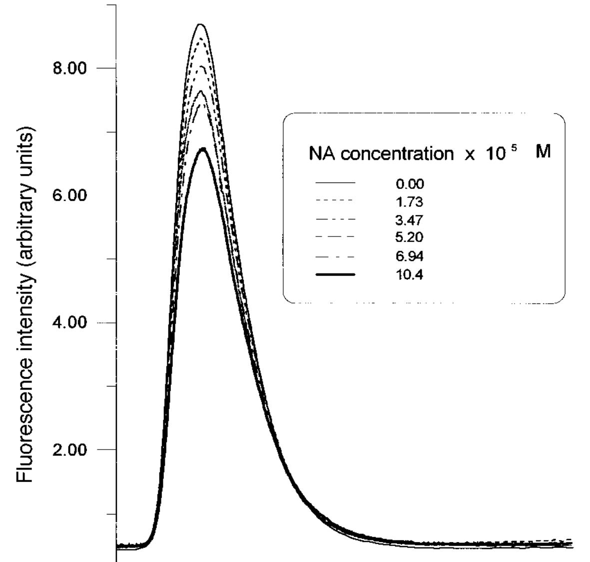


Fig. 6 Steady-state fluorescence spectra of Fl in heptane (c_{Fl} = 1.27 × 10^{-4} M, λ_{ex} = 300 nm) in the absence and presence of NA at various concentrations.

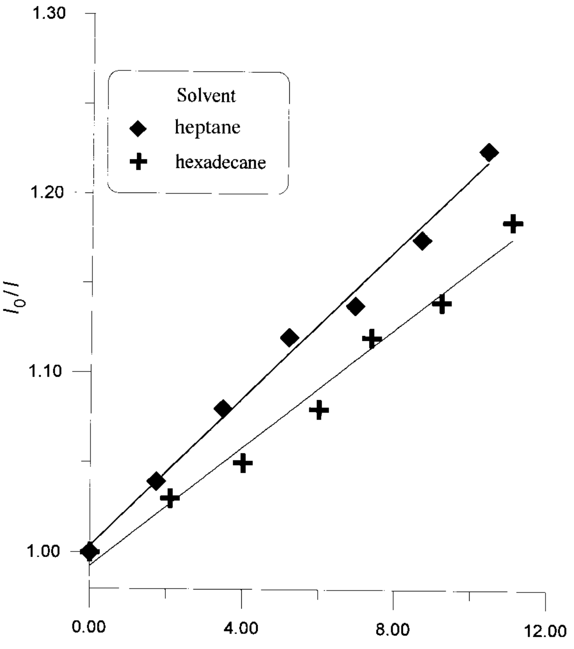


Fig. 7 Stern–Volmer plots of Fl fluorescence quenching by NA in heptane and hexadecane solutions ($c_{Fl} = 1.27 \times 10^{-4}$ M). I_0/I is the ratio of Fl fluorescence intensities measured at $\lambda = 315$ nm in the absence (I_0) and presence (I) of NA.

hexadecane solutions although the viscosities of the solvents differ considerably (see Table 5). Both values of k_q are significantly higher than a diffusion-controlled limit in the respective solvents. Although, as disscused above, these values should be taken with precaution, the fact that the viscosity of the solvent seems to have very little effect on the kinetics of energy transfer is indicative of a mechanism for that process. It seems that the long-range resonance mechanism markedly contributes to the energy transfer. The values of the critical radius [R_0, the separation of donor (D) and acceptor (A) for which energy transfer from D* to A and emission from D* are equally probable] for the system were calculated according to the equation given by Förster:[32]

$$R_0{}^6 = \frac{9000 \cdot (\ln 10) \cdot \kappa^2 \cdot \varphi_D}{128 \cdot \pi^5 \cdot n^4 \cdot N} \int_0^\infty F_D(\bar{\nu}) \cdot \varepsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (1)$$

where κ^2 is an orientation factor (equals 2/3 for a random distribution of the donor and acceptor molecules), φ_D is the quantum yield of the donor fluorescence, n is the refractive index of the solvent, N is Avogadro's number, $F_D(\bar{\nu})$ is the spectral distribution of the donor emission normalized so that $\int_0^\infty F_D(\bar{\nu})\, d\bar{\nu} = 1$, and $\varepsilon_A(\bar{\nu})$ is the molar extinction coefficient of the acceptor absorption. The values of R_0 are almost identical for both solvents (see Table 5) and large compared to molecular diameters.

Conclusions

The novel antenna polyelectrolyte, poly(sodium styrene-sulfonate-co-2-vinylfluorene), was synthesized and characterized. The solubilizing microdomains have higher hydrophobicities than the interior of typical micelles. Energy migration between polymeric fluorene chromophores and energy transfer to a solubilized probe molecule in aqueous solutions of PSSS-VF were demonstrated. The photocatalytic selectivity of the new photozyme was demonstrated using the photo-Fries rearrangement of 1-naphthyl acetate as an example. It was shown that PSSS-VF efficiently sensitizes the rearrangement of NA, solubilized in the polymer microdomain, with tunable selectivity of the products. It can be concluded that by increasing the content of Fl in PSSS-VF copolymers used as the photosensitizers, the ratio of the "in-cage" to the "out-of-cage" products increases and the *ortho* product predominates.

Table 5 Rate constants for the quenching of Fl fluorescence by NA in heptane and hexadecane solutions, critical radius for energy transfer from Fl to NA and the physicochemical parameters (viscosities and refractive indices) of the solvents[31]

Solvent	$k_q \times 10^{11}$/mol^{-1} s^{-1}	R_0/Å (±5%)	η/mPa s at 20 °C	n at 20 °C
Heptane	2.0	20.0	0.42	1.388
Hexadecane	1.6	19.6	3.34	1.434

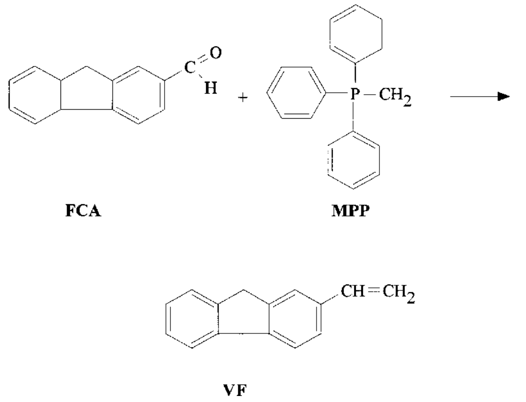
Experimental

Materials

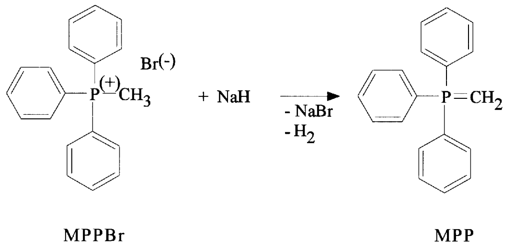
Dimethyl sulfoxide (DMSO, Caledon, ACS reagent) was refluxed for 2 h over CaH_2 and distilled in a nitrogen atmosphere under reduced pressure. Distilled water was passed through a deionizer and subsequently filtered through a trace organics removal cartridge (Norganic, Millipore). Pentane, chloroform, acetone, isooctane, methanol (all Caledon, spectro grade), tetrahydrofuran (Caledon, distilled in glass), 1-butanol (Caledon, ACS reagent), heptane (Aldrich, 99%, spectro grade) were used without further purification. Hexadecane (Reachim, pure) was distilled. Methyltriphenylphosphonium bromide (MPPBr, 98%, Aldrich), 2-fluorenecarboxaldehyde (FCA, 99%, Aldrich), perylene (99+%, Aldrich), 1-naphthyl acetate (NA, 98%, Aldrich) and fluorene (Fl, 99%, UCB) were used as received.

Commercial sodium styrenesulfonate (SSS, Monomer-Polymer and Dajac Laboratories) 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). Pyrene (99+%, Aldrich) was recrystallized twice from ethanol.

2-Vinylfluorene (VF) was synthesized using the Wittig reaction between fluorenecarboxaldehyde (FCA) and methylenetriphenylphosphorane (MPP) (Scheme 2). MPP was prepared by reacting MPPBr with sodium hydride (Scheme 3). The reactions were performed under nitrogen using the following procedures. Sodium hydride (60 wt% suspension in oil,



Scheme 2



Scheme 3

1.03 g) was washed twice with pentane and placed in a three-necked 100-ml flask with magnetic stir bar. A condenser and two pressure-equalized dropping funnels were attached to the flask. The setup was evacuated and filled with nitrogen three times. Dry DMSO (13 ml) was added to the NaH. The mixture was heated at 80 °C for 35 min and then cooled in an ice bath. A solution of MPPBr (25.7 mmol) in DMSO (25 ml) was added and the reaction mixture was stirred at room temperature for 10 min. The suspended sodium hydride slowly disappeared. A solution of 2-fluorenecarboxyaldehyde (25.7 mmol) in DMSO (20 ml) was added dropwise with ice cooling. The mixture quickly changed color from green to yellow. The ice bath was removed and the mixture was stirred for 2 h at room temperature and then for 5 h at 60 °C. The reaction was terminated by pouring the mixture into 40 ml of water. The yellow product was extracted four times with 200 ml of pentane. The organic phase was collected, washed twice with distilled water and dried over sodium sulfate. Pentane was removed under reduced pressure and the crude product dissolved in 5 ml of chloroform and purified by column chromatography (column: 15 cm length and 2 cm diameter) using $A1_2O_3$ as the stationary phase and chloroform as the eluent. The purified product was characterized by spectroscopic methods. A UV spectrum of the product measured in methanol solution shows a structured absorption band in the 240–360 nm spectral region with maxima at 292 and 308 nm, characteristic for the fluorene chromophore. The IR spectrum measured in chloroform solution displays a band with a maximum at 1628 cm^{-1}, typical for the C=C stretching mode in a vinyl group. The ^{1}H NMR in $CDCl_3$ solution confirmed that VF was synthesized [7 arom H, 7.24–7.9 (m); 1 vinyl H^a, 5.77–5.82 (dd); 1 vinyl H^b, 5.23–5.26 (dd); 1 vinyl H^c, 6.76–6.83 (m); 2 H (CH_2), 3.89; $J_{ac} = 11.3$ Hz, $J_{bc} = 17.6$ Hz, $J_{ab} = 0.95$ Hz].

Polymerization

PSSS-VF copolymers were prepared by free-radical polymerization using the starting mixtures containing various amounts of monomers (see Table 1). 2,2′-Azobis(isobutyronitrile) (AIBN) (0.25 mol%) was used as initiator. The required amounts of monomers and AIBN were dissolved in DMSO (40 ml). The solutions were placed in ampoules and deareated with nitrogen. The polymerization was carried out for 19 h at 68 °C. The resulting polymers were then precipitated with 1-butanol, filtered, washed four times with diethyl ether, and dried in a vacuum oven at 40 °C. The polymers were dissolved in water, exhaustively dialyzed (Fisher, cellulose tubing, cutoff 12 000–14 000 g mol^{-1}) against deionized water, and freeze-dried. The polymers were characterized using spectroscopic methods. All data are collected in Table 1.

Apparatus

UV/Vis absorption spectra were measured using a Hewlett-Packard 8452A diode-array spectrophotometer. IR spectra were recorded on a Nicolet FTIR spectrophotometer. NMR spectra were measured using a Varian Gemini 400 NMR spectrometer.

Steady-state fluorescence spectra of the polymer solutions were recorded at room temperature on Spex Fluorolog-2 and SLM AMINCO fluorescence spectrometers. Spectra were corrected for the wavelength dependence of the detector response. Steady-state fluorescence depolarization measurements were made using an SLM-AMINCO 8100 spectrofluorometer equipped with Glan–Thompson calcite prism polarizers.

Quantitative and qualitative analyses of the systems studied were carried out by using a Hewlett-Packard 6890 series gas chromatograph. Both the instrument and method used have been described earlier.[9]

Viscosities of the polymer solutions were measured using the automatic viscometer described elsewhere.[33]

Procedures

Perylene, pyrene and 1-naphthyl acetate were solubilized in aqueous polymer solutions by slowly injecting microliter (μl) quantities of probe (1×10^{-3} or 1×10^{-2} M) dissolved in THF into millilitre (ml) quantities of polymer solution. The mixture was shaken for 5 min and equilibrated in the dark for 2–4 h.

Rearrangement of NA was studied at 20 °C in deareated solutions. The solutions were thermostatted and stirred during irradiation. A medium-pressure mercury lamp with a 313 nm interference filter was used to obtain monochromatic light. Incident light intensity was determined by using a ferrioxalate actinometer[34] ($I_0 = 2.9 \times 10^{-10}$ Einstein s^{-1}).

For the GC analyses the aqueous solutions were shaken with chloroform to extract reagents into organic solvent.

Acknowledgements

The financial support of the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research is gratefully acknowledged. M.N. and Sz.Z. are grateful to the Polish State Committee for Scientific Research for support in the form of research grant Nr 3 T09A 095 15. J.S. thanks the Deutscher Akademischer Austauschdienst for the support of his studies at the University of Toronto.

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Paper 9/01026B