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Synthesis and Photophysical Properties of a Novel Water-Soluble, Calixarene-Containing Polymer

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ABSTRACT: The synthesis of a novel calixarene-containing monomer has been reported. Free radical polymerization of this monomer with 2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS) resulted in a water-soluble polymer. Despite the presence of the ionic sulfonate groups on the naphthalene groups of the polymer, excimer emission was still observed. Solvent and ionic strength studies demonstrated that the excimer emission was predominantly from cross-chain contacts rather than from nearest-neighbor sites. Steady state fluorescence emission studies showed that the polymer had the ability to solubilize perylene efficiently and that the calixarene units were primarily responsible for the solubilization of the perylene. Energy migration among the naphthalene sulfonate groups and energy transfer from the naphthalene sulfonate groups to the solubilized perylene were observed.

Introduction

Photon-harvesting or antenna polymers have proved interesting in attempts to mimic the processes involved in photosynthesis.[1−5] Antenna polymers usually consist of a hydrophobic chromophore and a hydrophilic component which gives the polymer overall water solubility. These antenna polymers have been shown to solubilize various organic probe molecules, while the presence of the chromophores gives them the ability to transfer energy absorbed by the polymer to the solubilized probe molecules which can lead to the sensitized photochemical reaction of these solubilized probe molecules. A copolymer of sodium styrenesulfonate and 2-vinylnaphthalene, for example, has been shown to sensitize the photodechlorination of polychlorinated biphenyls (PCBs),[6,7] the photocleavage of 2-undecanone,[8] and also the photo-oxidation of various polynuclear aromatic hydrocarbons (PAHs).[9,1]10

The solubilization of probe molecules is considered to be due to the pseudomicellar conformation that these polymers are believed to adopt in aqueous solution.[11−13] A recent conformational study proposed that the polymer behaves as a random coil with a proposed "blob-polyion" type conformation in aqueous solution.[14] The exact location of the solubilized probe molecules within the polymer is still undetermined. The synthesis of a polymeric system which would contain well-defined hydrophobic cavities for solubilization of probe molecules would eliminate this problem.

The hydrophobic cavity required for such a system should possess the following properties: (1) "bind" the probe molecule with a high association constant to ensure that the other components in the polymer did not compete with the cavity for solubilization of the probe molecules, (2) be readily synthesized with relatively high yields, and (3) be readily derivatized to allow incorporation into an antenna polymer.

Shinkai et al.[15] showed that a suitably derivatized calix[4]arene could solubilize pyrene with an association constant of 3×10^6 M^{-1}, which is about 3 orders of magnitude greater[16] than that for cyclodextrins, another type of hydrophobic cavity often used in the complexation of organic probe molecules.[17] Calixarenes[18,19] are synthetic cyclic molecules which are usually synthesized by the reaction of 4-substituted phenols and formaldehyde under basic conditions. The most common and readily synthesized calixarenes are the cyclic tetramer, the cyclic hexamer, and the cyclic octamer. Due to the ease of synthesis, the number of known subsequent derivatization reactions, and the previous complexation studies, the cyclic tetramer calix[4]arene was chosen as the basis of the hydrophobic cavity for an antenna polymer system. Incorporation of such a hydrophobic cavity was made possible due to the synthesis of the hydrophilic chromophore 2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS).[20] This paper reports the syntheses of a novel calixarene-containing monomer and a novel water-soluble, calixarene-containing polymer as well as some of its photophysical properties.

Experimental Section

Reagents. Anhydrous dimethyl sulfoxide (DMSO; Aldrich), acetone (Caledon; spectrograde), methanol (Caledon; spectrograde), perylene (Aldrich; 99.9%), lithium bromide (Fisher), dimethylformamide (DMF; BDH), pyridine (BDH), acetonitrile (Aldrich; HPLC grade), ethyl acetate (Aldrich), formaldehyde (Fisher; 37%, w/w), diphenyl ether (Aldrich; 99%), *N*,*N*-diethylaniline (Aldrich; 99+%), allyl bromide (Aldrich; 99%), benzoyl chloride (Aldrich; 99+%), BH_3·THF (Aldrich; 1 M in THF), *p*-toluenesulfonyl chloride (BDH), *p*-*tert*-butylphenol (Aldrich; 99%), and 1-bromobutane (Aldrich) were used without further purification.

2-Hydroxyethyl methacrylate (Aldrich) was purified by vacuum distillation. 2,2′-Azobis(isobutryonitrile) (AIBN; Kodak) was recrystallized from spectrograde methanol. 2-Naphthol (Aldrich) was recrystallized from toluene. *p*-*tert*-Butylcalix[4]arene and calix[4]arene were synthesized using the methods of Gutsche and co-workers.[21,22] 2-(6-Sulfo-2-naphthoxy)ethyl methacrylate sodium salt was synthesized according to previously published methods.[20] Merck silica gel (Aldrich; grade 60, 230−400 mesh, 60 Å) was used for column chromatography. Thin layer chromatography (TLC) was performed using silica gel on polyester TLC plates (Sigma; 254 nm fluorescence indicator, 60 Å, 5−25 μm particle size). Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8−12 mesh). Tetrahydrofuran (THF; BDH) and toluene (BDH) were dried by refluxing over sodium/benzophenone and then fractionally distilled. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The pH of solutions was adjusted with either stock HCl or NaOH solutions, while the ionic strength of solutions was adjusted with stock NaCl solutions.

25,26,27-Tris(benzoyloxy)-28-hydroxycalix[4]arene (1).[22] Calix[4]arene (4.24 g) was dissolved in 50 mL of pyridine and

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cooled in an ice bath. Benzoyl chloride (9.4 mL) was added, and the mixture was stirred at 0 °C for 1 h and then allowed to warm slowly to room temperature over another hour. Water (300 mL) was added. The insoluble material was filtered, washed thoroughly with methanol, and then recrystallized from methanol/$CHCl_3$ to yield 5.75 g (78%) thin colorless plates: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 8.1−6.5 (m, 27H, Ar-H), 5.44 (s, 1H, Ar-OH), 3.92−3.46 (2 pair d, 8H, Ar-H).

25-(Allyloxy)-26,27,28-tris(benzoyloxy)calix[4]arene (2).[22] 25,26,27-Tris(benzoyloxy)-28-hydroxycalix[4]arene (**1**) (13.44 g), 2.18 g of NaH (80% in oil), 9.6 mL of allyl bromide in 30 mL of DMF, and 400 mL of THF were refluxed for 6 h which resulted in a cream-colored solution. The solvent was removed under vacuum. Methanol was added, and the insoluble material was filtered and recrystallized from methanol/$CHCl_3$ to yield 9.0 g (63%) of product: ^{1}H-NMR ($CDCl_3$) δ 7.9−6.4 (m, 27H, Ar-H), 6.0−6.2 (m, 1H, C-CH=C), 5.5−5.3 (m, 2H, C=CH_2), 4.4−4.3 (d, 2H, O-CH_2-C=C), 3.9−3.5 (pair d + s, 8H, Ar-CH_2-Ar).

5-Allyl-25-hydroxy-26,27,28-tris(benzoyloxy)calix[4]arene (3).[22] 25-(Allyloxy)-26,27,28-tris(benzoyloxy)calix[4]arene (**2**) (5.0 g) in 30 mL of *N*,*N*-diethylaniline was refluxed for 2 h under a nitrogen atmosphere. After cooling, the resultant solution was added dropwise to a rapidly stirring 1 M HCl (400 mL) solution. The solid material was filtered and then recrystallized from methanol/$CHCl_3$ to yield 3.95 g (79%) of a cream-colored solid: ^{1}H-NMR ($CDCl_3$) δ 8.06−6.58 (m, 26H, Ar-H), 5.88−5.54 (m, 1H, -CH=C), 5.13 (s, 1H, -OH), 4.98−4.87 (m, 2H, CH_2=C-), 3.87−3.48 (m, 8H, Ar-CH_2-Ar) 3.13 (d, 2H, Ar-CH_2-C).

5-Allyl-25,26,27,28-tetrahydroxycalix[4]arene (4).[22] 5-Allyl-25-hydroxy-26,27,28-tris(benzoyloxy)calix[4]arene (**3**) (6.0 g), 14.0 g of NaOH, 75 mL of water, 170 mL of ethanol, and 500 mL of THF were stirred rapidly and heated at 70 °C for 18 h, after which the solvent was removed under vacuum. Methanol (20 mL) was added followed by 200 mL of 1 M HCl. The pH was adjusted to 2 using concentrated HCl, and the resultant solution was stirred for 1 h. The solid product was filtered and recrystallized from methanol/CH_2Cl_2 to yield 2.95 g (82%) of small, colorless plates: ^{1}H-NMR ($CDCl_3$) δ 10.20 (s, 4H, -OH), 7.55 (d, 6H, Ar-H), 6.86 (s, 2H, Ar-H), 6.73 (t, 3H, Ar-H), 6.0−5.8 (m, 1H, -CH=C), 5.09−4.99 (m, 2H, CH_2=C-), 4.2 (br s, 4H, Ar-CH_2-Ar), 3.5 (br s, 4H, Ar-CH_2-Ar), 3.17 (d, 2H, Ar-CH_2-).

5-Allyl-25,26,27,28-tetrabutoxycalix[4]arene (5). NaH (4.0 g, 80% in mineral oil) was added to a solution of 4.0 g of 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene (**4**) in 50 mL of THF and 5 mL of DMF. The mixture was stirred for 10 min, which resulted in a purple-colored solution. 1-Bromobutane (24 mL) was then added, and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then refluxed for 24 h to yield a yellow-brown solution. The solvent was removed under vacuum, and the excess NaH was destroyed by adding H_2O dropwise. The aqueous layer was then neutralized with concentrated HCl, and the product was extracted with $CHCl_3$. The solvent was removed under vacuum, and the product was isolated by flash chromatography using 1% acetone/99% hexane as eluent. The chromatographic process was repeated to obtain a colorless oil (4.75 g, 80%) that produced a single spot on TLC (R_f = 0.79): ^{1}H-NMR ($CDCl_3$) δ 7.24−5.6 (m, 12H, Ar-H, -CH=C), 5.21−2.95 (m, 20H, Ar-CH_2-Ar, -O-CH_2-, Ar-CH_2-C, CH_2=C-), 1.92−1.95 (m, 28H, CH_3-CH_2-CH_2-); MS (EI+) 688 (M^+). Anal. Calcd for $C_{47}H_{60}O_4 \cdot {}^1/_4CH_3COCH_3$: C, 80.61; H, 8.71. Found: 80.51; H, 8.61.

5-(3-Hydroxypropyl)-25,26,27,28-tetrabutoxycalix[4]arene (6). $BH_3 \cdot$THF (14.7 mL, 1 M in THF) was added dropwise to a solution of 2.0 g of 5-allyl-25,26,27,28-tetrabutoxycalix[4]arene (**5**) in dry THF at 0 °C. The reaction mixture was stirred for 1 h while warming to room temperature and then stirred for a further 2 h at room temperature. H_2O (2 mL) was then added dropwise to destroy the remaining BH_3. NaOH (16 mL, 2 M) was added followed by 8 mL of 30% H_2O_2. The mixture was stirred at room temperature for 1 h, after which it was heated for 2 h at 40 °C. A saturated NaCl solution (20 mL) was added, upon which the aqueous and organic components separated into two layers. The organic portion was separated off, and the solvent was removed under vacuum to leave a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 7.3−6.1 (m, 11H, Ar-H), 4.5−2.2 (m, 21H, Ar-CH_2-Ar, -O-CH_2-, Ar-CH_2-C, -C-OH), 2.0−0.96 (m, 30H, CH_3-CH_2-CH_2-, Ar-C-CH_2-); MS(EI+) 706 (M^+). Anal. Calcd for $C_{47}H_{62}O_5$: C, 79.85; H, 8.84. Found: C, 79.53; H, 9.11.

5-[3-(Methacryloyloxy)propyl]-25,26,27,28-tetrabutoxycalix[4]arene (7). Methacryloyl chloride[23] was prepared by stirring methacrylic acid with thionyl chloride in the presence of cuprous chloride. After the gas evolution had ceased, the reaction mixture was refluxed for 1 h followed by fractional distillation. Methacryloyl chloride (3.2 mL) was added dropwise to a solution of 2.0 g of 5-(3-hydroxypropyl)-25,26,27,28-tetrabutoxycalix[4]arene (**6**) in 20 mL of $CHCl_3$ and 2 mL of pyridine at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then for an additional 1.5 h at room temperature. The reaction mixture was then extracted with $CHCl_3/H_2O$. The $CHCl_3$ layer was washed twice with a NaOH solution and then three times with H_2O. The $CHCl_3$ layer was dried with Na_2SO_4 (anhydrous) and filtered, and the solvent was removed under vacuum. The resultant viscous oil was chromatographed on a flash column using 1% acetone/99% hexane as eluent. The process was repeated to yield 1.05 g (48%) of a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 7.3−6.0 (m, 12H, Ar-H, CH_2=CH-), 5.55 (m, 1H, CH_2=C-), 4.5−2.3 (m, 20H, Ar-CH_2-Ar, -O-CH_2-, Ar-CH_2-C), 2.0−0.9 (m, 33H, CH_3-C=C, CH_3-CH_2-CH_2-, Ar-C-CH_2-); MS (EI+) 774 (M^+). Anal. Calcd for $C_{47}H_{60}O_4 \cdot {}^1/_4CH_3COCH_3$: C, 77.93; H, 8.53. Found: C, 77.93; H, 8.51.

Poly[(2-(6-sulfo-2-naphthoxy)ethyl methylacrylate)-*co*-(5-(3-(methacryloyloxy)propyl)-25,26,27,28-tetrabutoxycalix[4]arene)] (NS−CAL). 2-(6-Sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS; 0.73 g, 79.8 mol %), 0.40 g (19.9 mol %) of 5-[3-(methacryloyloxy)propyl]-25,26,27,28-tetrabutoxycalix[4]arene (CAL), and 1 mL (0.33 mol %) of 0.014 g of AIBN in 10 mL of DMSO stock solution were dissolved in a solvent mixture of 10 mL of DMSO and 4 mL of toluene. The solution was transferred into a glass polymerization ampule, after which it was degassed by three freeze−pump−thaw cycles. The ampule was sealed and placed in a water bath at 60 °C for 24 h. The resultant viscous solution was added dropwise into 350 mL of acetone. The fluffy white precipitate was filtered and washed with acetone and then ether. The polymer was then dissolved in the minimum volume of water, exhaustively dialyzed (Fisher; cellulose tubing, cutoff 12 000−14 000 g mol^{-1}) against deionized water, and freeze-dried.

A second polymer was made in a similar manner using 1.02 g (89.9 mol %) of NS, 0.24 g (9.8 mol %) of CAL, and 1 mL (0.25 mol %) of 0.013 g of AIBN in 10 mL of DMSO. In the remainder of this paper, the polymer which had the starting composition of ≈80% NS and ≈20% CAL will be referred to as 80−20 NS−CAL. Similarly, the polymer which had the starting composition of ≈90% NS and ≈10% CAL will be referred to as 90−10 NS−CAL. Elemental analysis (Galbraith Laboratories) showed that the final compositions (mol %) of the 80−20 NS−CAL and 90−10 NS−CAL polymers were 80.0:20.0 NS:CAL and 88.7:11.3 NS:CAL, respectively. All studies were performed on both polymer compositions, but only the data for 90−10 NS−CAL will be displayed unless otherwise stated.

Poly[2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt]. 2-(6-Sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS; 1.00 g) and 1 mL (0.25 mol %) of a stock solution of AIBN (0.012 g of AIBN in 10 mL of DMSO) were dissolved in 14 mL of DMSO. The solution was transferred into a glass polymerization ampule, after which it was degassed by three freeze−pump−thaw cycles. The ampule was sealed and placed in a water bath at 65 °C for 24 h. The resultant viscous solution was added dropwise into 300 mL of acetone. The fluffy white precipitate was filtered and washed with acetone and then ether. The polymer was dried overnight under vacuum. The polymer was dissolved in the minimum volume of water, exhaustively dialyzed (Fisher; cellulose tubing, cutoff

12 000−14 000 g mol^{-1}) against deionized water, and then freeze-dried.

Steady State Fluorescence Measurements. Steady state fluorescence spectra were recoreded at room temperature using an SLM 4800S fluorescence spectrophotometer. All fluorescence emission spectra are uncorrected. For solutions having an absorbance >0.5 at the excitation wavelength, front-face measurements were made, while for quantitative mesurements, absorbances at the excitation wavelengths were kept below 0.05 to minimize self-absorption. For energy transfer studies, the excitation wavelength was chosen such that most of the incident light was absorbed by the donor species.

Steady State Fluorescence Depolarization Measurements. The degree of polarization, *P*, of the samples was determined using eq 1:[24]

$$P = I_{\parallel} - GI_{\perp}/I_{\parallel} + \mathrm{GI}_{\perp} \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities observed through a polarizer oriented parallel and perpendicular to a vertically polarized excitation beam. *G*, an instrumental correction factor for depolarization effects arising from the instrument, is given by

$$P = I'_{\perp}/I'_{\parallel} \tag{2}$$

where $I'_{\perp}$ and $I'_{\parallel}$ are the fluorescence intensities observed through a polarizer oriented perpendicular and parallel to a horizontally polarized excitation beam.

The steady state fluorescence depolarization measurements were made using an SLM 4800S fluorescence spectrophotometer equipped with 10 mm Glan-Thompson calcite prism polarizers. The samples for fluorescence polarization measurements were prepared by introducing microliter quantities of the required stock solutions into 10 mL of water. The samples were placed in a quartz cell, and the fluorescence intensity reading was averaged over 30 s.

Ultraviolet Spectral Measurements. The ultraviolet (UV) absorption spectra of samples were measured using a Hewlett-Packard 8451A diode array spectrophotometer.

NMR Spectral Measurements. General ^{1}H- and ^{13}C-NMR spectra were obtained using a Varian Gemini-200 spectrometer, while the ^{1}H-NMR temperature studies were measured on a Varian 400 spectrometer.

Mass Spectral Measurements. Mass spectra were obtained using a VG Analytical 70-250S mass spectrometer.

Solubilization of Polynuclear Aromatic Hydrocarbons. The solubilization of the PAH probes was achieved by slow injection of microliter volumes of a stock solution of the PAH dissolved in acetonitrile. The solution was shaken vigorously for 5 min and then allowed to equilibrate for 12−24 h in the dark.

Distribution Coefficient Determination. Aqueous polymer solutions were treated as a two-phase system consisting of an aqueous phase and a polymer core pseudophase.[25] The distribution coefficient, *K*, is defined as

$$K = x_{\mathrm{p}}/x_{\mathrm{aq}} \tag{3}$$

where x_{p} and x_{aq} represent the weight fraction of the probe molecule solubilized in the polymer and water, respectively. The quantity of probe required to saturate a polymer system was determined by sequentially adding microliter aliquots of a probe stock solution and then measuring the fluorescence emission intensity. The saturation point was taken to be the intercept of the initial linear region and the final plateau region.

The concentration of the probe molecule solubilized by the polymer systems was measured by initially saturating the polymer system with the desired probe and then measuring the fluorescence emission intensity of the sample. Since the probe used was virtually insoluble in water, the fluorescence emission would be dominated by emission from the probe in the organic-like environment of the hydrophobic region of the polymer, and thus the fluorescence emission intensity was quantified from the slope of a calibration plot fluorescence emission intensity versus the probe concentration in an organic solvent. This was repeated using different initial polymer concentrations.

Results and Discussion

Synthesis. Having chosen the calix[4]arene as the basis for a derivative which contains a hydrophobic cavity, a synthetic scheme had to be developed to enable derivatization of the molecule in such a manner as to allow its incorporation into an antenna system. Such a synthetic route is shown in Scheme 1. The syntheses of calix[4]arene and compounds **1**−**4** were based on the procedures developed by Gutsche and co-workers,[21,22] while reaction steps leading from **4** to the final product **7** are reported for the first time.

The first reaction step developed in this work was the butylation of **4**. Shinkai et al.[15] synthesized a sulfonated calixarene derivative which was capable of complexing pyrene efficiently. This derivative was synthesized by sulfonation of the aromatic rings of the calix[4]arene followed by butylation of the hydroxyl groups. The butylation was required since the basic calix[4]arene cavity has a diameter of ca. 2 Å[26] and would be too narrow to complex a large organic molecule. The addition of the butyl groups extended the cavity, thereby allowing complexation of larger molecules such as pyrene. A similar rationale was followed in this work.

It has been shown[27] that attachment of methyl groups to the phenolic part may not result in conformational rigidity. If, however, larger groups such as allyl or butyl are used, then steric hindrance results in the locking in of a particular conformation.

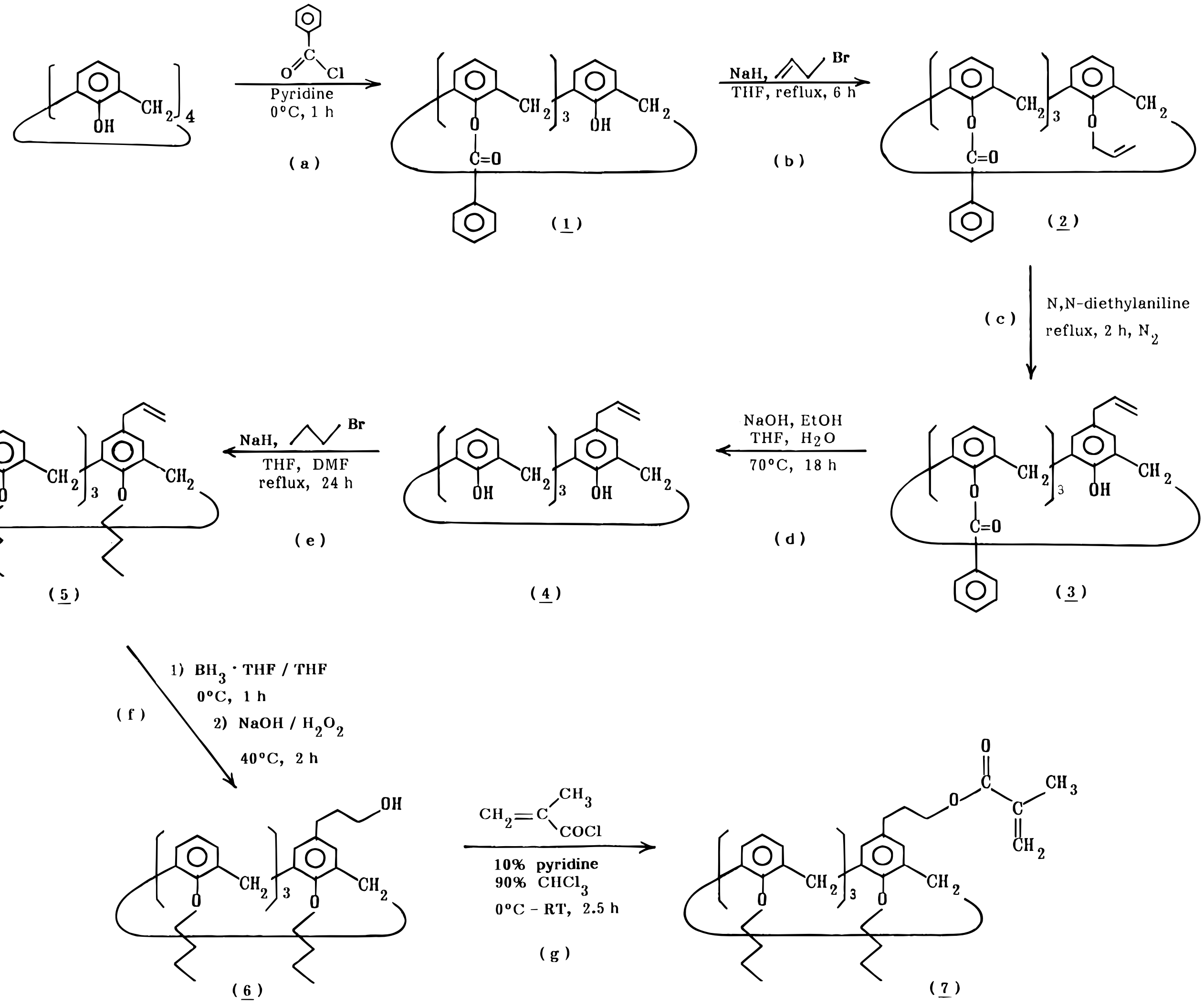
Shinkai and co-workers[28,29] have shown that the attachment of butyl groups to *tert*-butylcalix[4]arene results in 47% partial cone, 50% cone, and 3% 1,3-alternate isomers. They found that refluxing the samples at 147 °C for 3 days did not result in isomerization of any of the isomers thereby showing that they were in fact fixed in conformation. ^{1}H-NMR can be used to identify the different conformational isomers since each different conformation results in the methylene protons between the aromatic rings experiencing a different environment to each other. Calixarene can generally have four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate.[18] In addition to these basic types of conformational isomers, there can also be cases where the substituents are either “inside” or “outside”.[27]

Most calix[4]arene derivatives synthesized usually contained the same substituents at the 4-position of all four phenol groups. For **5** however there is a single substituent at the para position of only one of the phenol groups. This means that there can be additional isomers for the partial cone conformation.

Thus, on converting **4** to the tetrabutyl derivative **5** (reaction e, Scheme 1), one can expect a number of different conformational isomers that should have similar properties. Column chromatography did not result in separation of the various isomers, and thus all further reactions were performed on samples which contained all the different isomers. Even though exact NMR peak assignments for each particular conformation could not be made, generalized assignments were made, and the various changes in the NMR spectra could be clearly seen on each derivatization step.

In order to determine whether the isomers were locked in a particular conformation, ^{1}H-NMR spectra were run at various temperatures[18] to determine whether peak broadening or coalescence could be observed

Scheme 1



(Figure 1). From these spectra, it can be seen that on going from 40 to 80 °C, there are no significant changes in the spectra in the 3–4.5 ppm region which shows that the various isomers are in fact conformationally rigid as would be expected from other similar derivatives.

Having extended the cavity by attachment of the butyl groups, the next step was to convert the double bond of the allyl group to a primary alcohol (reaction f, Scheme 1). This conversion was achieved by using a hydroboration–oxidation process which results in the anti-Markovnikov hydration of the double bond.

The final reaction step was the attachment of the methacrylate group to **6** to produce the final desired monomer. The ^{1}H-NMR spectrum of **7** (Figure 2) clearly shows the methacrylate group by the presence of the peaks at 5.5–5.6 ppm ($CH_2{=}C<$) and 2 ppm (CH_3-$C{=}C$). Thus Scheme 1 resulted in the successful synthesis of a calixarene derivative which could then be incorporated into an antenna system by copolymerization with NS.

Photophysical Studies. Having synthesized poly[(2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt)-*co*-(5-(3-(methacryloyloxy)propyl)-25,26,27,28-tetrabutoxycalix[4]arene)] (NS–CAL), it had to be seen whether it would behave as an antenna polymer and have the capability of solubilizing an organic probe molecule. The fluorescence emission spectrum of NS–CAL shows peaks at 372 and 395 nm (Figure 3a) which were assigned as emission from individual naphthalene sulfonate groups (monomer) and from naphthalene sulfonate excimer, respectively. A comparison of the UV absorption spectrum of NS and the fluorescence excitation spectrum of NS–CAL showed that they were virtually identical and that there was no ground state dimer formation (Figure 3b).

A plot of the monomer and excimer fluorescence emission intensity versus increasing polymer concentration (Figure 4) shows a steady increase with increasing polymer concentration. Changes in the amount of excimer formation were monitored by using the ratio of the fluorescence emission intensity at 395 nm (I_{ex}) to that at 372 nm (I_m). I_{ex}/I_m remains constant over the polymer concentrations used which is indicative that there is no aggregation of the polymer coils and that they remain as individual entities. If there were aggregation of the polymer coils, I_{ex}/I_m would increase with increasing polymer concentration since the aggregation would bring the naphthalene sulfonate groups closer together, thereby increasing the probability of excimer formation. From this data it can be concluded that excimer formation is intramolecular and not intermolecular.

The effect of solvent composition on I_{ex}/I_m was then studied. Figure 5 shows that I_{ex}/I_m decreased steadily as the DMSO content of the solution was increased. At 90% DMSO, the fluorescence emission spectrum of NS–CAL (curve d, Figure 6) is virtually identical with that

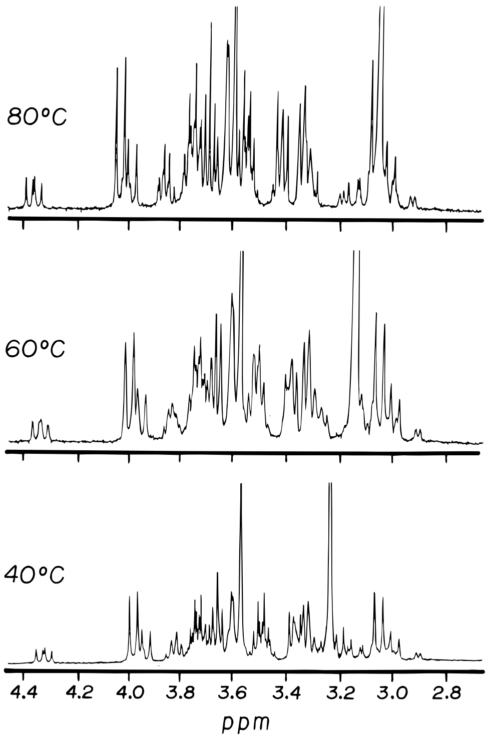


Figure 1. Effect of temperature on the ^{1}H-NMR spectrum (400 MHz) of 5-allyl-25,26,27,28-tetrabutoxycalix[4]arene (**5**).

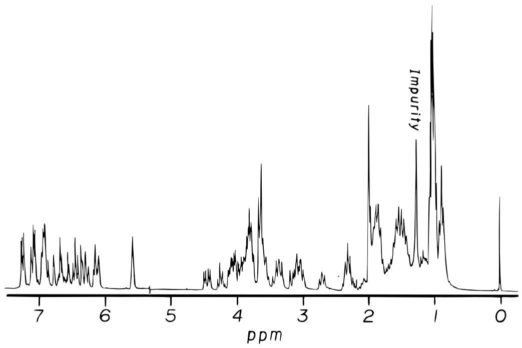


Figure 2. ^{1}H-NMR spectrum (200 MHz) of 5-[3-(methacryloyloxy)propyl]-25,26,27,28-tetrabutoxycalix[4]arene (**7**).

of NS (curve e, Figure 6), thereby showing that under such solvent conditions, virtually all excimer is eliminated. This leads to the conclusion that in the presence of DMSO, a better solvent for the polymer, NS−CAL adopts a more expanded conformation so that the probability of excimer formation is reduced.

Increases in the ionic strength of a polyelectrolyte solution can result in decreases in the coil dimensions.[1] For NS−CAL such changes could influence the amount of excimer emission. From Figure 7 it can be seen that I_{ex}/I_m increases steadily as the ionic strength of the solution increases. Increased ionic strength of the solution will result in increased screening effects which would reduce the electrostatic repulsion between the naphthalene sulfonate groups, and thus the polymer is expected to adopt a more compact conformation. This would then bring the naphthalene sulfonate groups closer together thereby increasing the probability of excimer formation. It is interesting to note that even though the ionic strength of the solution is increased by 5 orders of magnitude, the change in I_{ex}/I_m is rather small which shows that the additional amount of excimer formation is rather low.

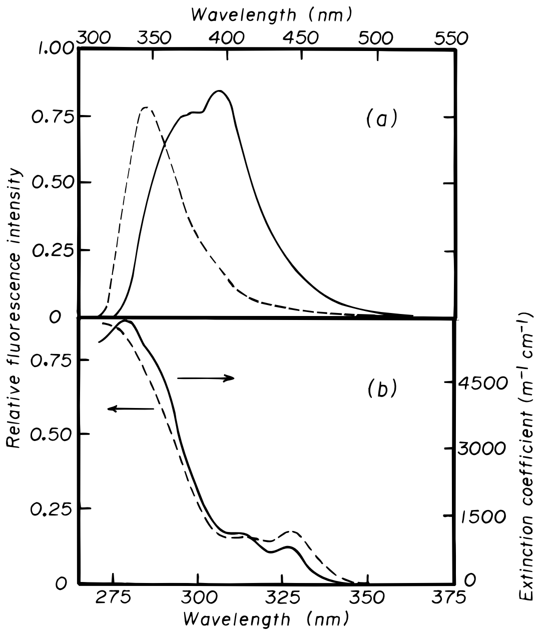


Figure 3. (a) Fluorescence emission spectra of (– –) NS (5.0×10^{-5} M) and (—) NS−CAL (0.01 g dm^{-3}; $\lambda_{ex} = 280$ nm). (b) Comparison of (—) the absorption spectrum of NS (5.0×10^{-5} M) and (– –) the fluorescence excitation spectrum of NS−CAL (0.01 g dm^{-3}; $\lambda_{em} = 430$ nm).

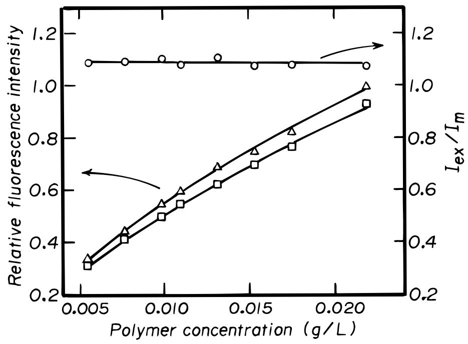


Figure 4. Dependence of the (□) monomer (I_m) and (△) excimer (I_{ex}) fluorescence intensity and (○) the ratio of the excimer-to-monomer emission intensity (I_{ex}/I_m) on NS−CAL concentration in aqueous solution ($\lambda_{ex} = 280$ nm).

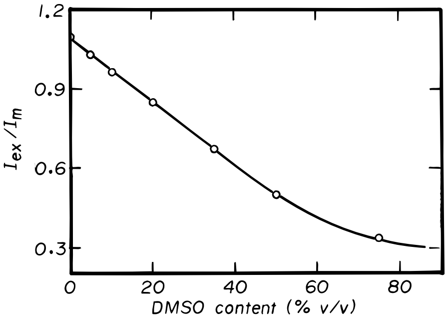


Figure 5. Dependence of the excimer-to-monomer emission intensity (I_{ex}/I_m) of NS−CAL (0.01 g dm^{-3}) on the DMSO content (v/v) of the aqueous solution ($\lambda_{ex} = 280$ nm).

Nakahira et al.[30] showed that the probability of excimer formation decreased significantly as the number of atoms separating nearest neighbors increased. Since the adjacent naphthalene sulfonate groups are separated by 11 atoms, the probability of achieving the correct configuration for excimer formation between nearest neighbors is rather low. This, together with these solvent studies and ionic strength studies, sug-

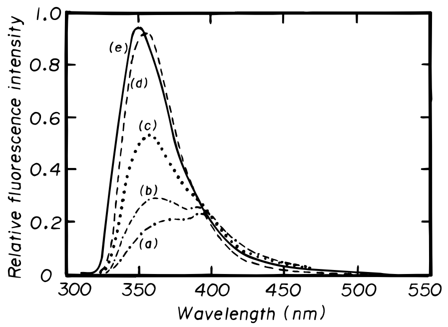


Figure 6. Fluorescence emission spectra of NS−CAL (0.01 g dm^{-3}) in (a) aqueous solution, (b) 80:20 H_2O:DMSO, (c) 50:50 H_2O:DMSO, (d) 10:90 H_2O:DMSO, and (e) NS in aqueous solution.

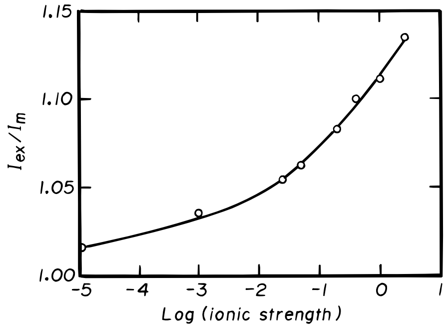


Figure 7. Dependence of the excimer-to-monomer emission intensity (I_{ex}/I_m) of NS−CAL (0.01 g dm^{-3}) on the ionic strength of the aqueous solution (λ_{ex} = 280 nm).

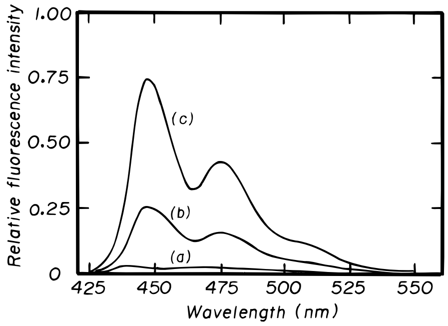


Figure 8. Steady state fluorescence emission spectra (λ_{ex} = 415 nm) of perylene in (a) water, (b) 0.02 g dm^{-3} NS−CAL (90−10), and (c) 0.02 g dm^{-3} NS−CAL (80−20).

gests that excimer formation occurs predominantly via cross-chain contacts rather than from nearest-neighbor contacts.

Solubilization of a Probe Molecule. Having synthesized a novel calixarene monomer and then copolymerized it with NS to produce a water-soluble polymer with a specific hydrophobic site, the next step was to determine whether this polymer had the ability to solubilize an organic probe molecule. Perylene was chosen as the probe molecule since it had low solubility[31] as well as a low fluorescence emission[32] in water. Figure 8 shows the effect of the presence of NS−CAL on the fluorescence emission of an aqueous solution of perylene. As expected, the perylene emission from water (curve a) was low but drastically enhanced upon the addition of NS−CAL (curves b and c). This enhanced emission can be attributed to an increase in the perylene solubility by its transfer from the water to the hydrophobic environment of the calixarene. This shows that the polymer has the ability to solubilize perylene. Figure 8 also shows that the 80−20 composition can solubilize more perylene than the 90−10 composition. Figure 9 shows that the amount of solubilized perylene increases linearly with increasing polymer concentration, as observed with other photozymes.

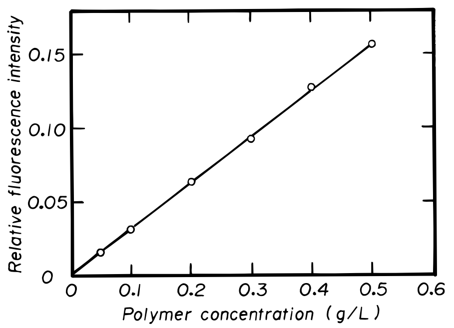


Figure 9. Dependence of the perylene fluorescence intensity as a function of NS−CAL concentration (λ_{ex} = 415 nm, λ_{em} = 446 nm).

Table 1. Comparison of Distribution Coefficients (K) for Perylene and Various Antenna Polymers

polymer	K ($\times 10^{-6}$)
NS−CAL (80−20)	4.56
NS−CAL (90−10)	1.94
NS−LM (70−30)[a]	6.03[b]
NS−LM (80−20)[a]	2.58[b]
PSSS−VN[c]	4.4[d,e]
PSSS−AHCz[f]	2.93[e]

[a] Poly[(2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt)-*co*-(lauryl methacrylate)]. [b] Gravett, D. M.; Guillet, J. E. *Macromolecules* **1995**, *28*, 274. [c] Poly[(sodium styrenesulfonate)-*co*-(2-vinylnaphthalene)]. [d] White, B. Ph.D. Thesis, University of Toronto, 1989. [e] Nowakowska, M.; White, B.; Vogt, S.; Guillet, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 271. [f] Poly[(sodium styrenesulfonate)-*co*-(*N*-((acryloyloxy)hexyl)carbazole)].

In order to quantify the solubilizing ability of the polymer, the distribution coefficient (K) between perylene and the polymer was measured. Distribution coefficients of (1.94 ± 0.03) × 10^6 and (4.56 ± 0.17) × 10^6 were obtained for the 90−10 and 80−20 compositions of NS−CAL, respectively. These values compare favorably with those obtained for other antenna polymers (Table 1).

Comparison of the distribution coefficients for the two different NS−CAL compositions showed that as the calixarene content of the polymer was increased, the amount of perylene that could be solubilized by the polymer increased. This indicates that the hydrophobic calixarene units are primarily responsible for the solubilization of the perylene.

Figure 10a shows the effect of the ionic strength of the solution on the solubilization of perylene. As the ionic strength increases, the amount of perylene solubilized also increases. This was unexpected since, if the perylene was solubilized by the individual calixarene units only, changes in the polymer coil size brought about by the increased ionic strength should not be expected to change the amount of perylene solubilized. Since this was not the case, there must be other factors contributing to the ability of the polymer to solubilize perylene. The only other component present in the system was NS, and thus it had to be determined whether an NS homopolymer had the ability to solubilize perylene. Figure 11 shows that the presence of NS homopolymer (curve b) results in an enhancement of the perylene fluorescence emission compared to perylene in water (curve a), thereby showing that the NS homopolymer does have the ability to solubilize perylene. A

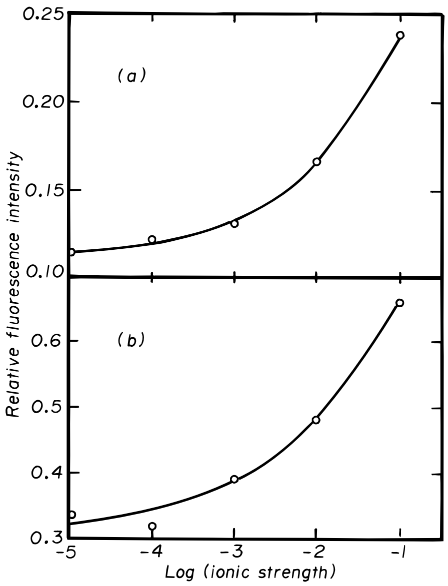


Figure 10. Dependence of the perylene fluorescence intensity as a function of the ionic strength (λ_{ex} = 415 nm, λ_{em} = 446 nm): (a) NS−CAL (0.4 g dm^{-3}) solution and (b) NS homopolymer (0.4 g dm^{-3}) solution.

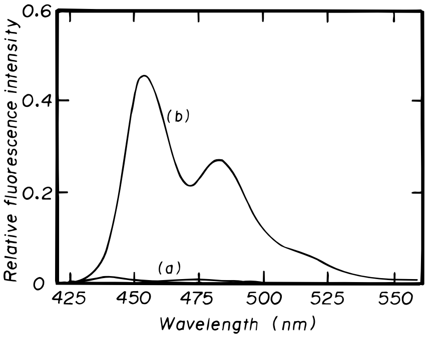


Figure 11. Steady state fluorescence emission spectra of perylene (4.6 × 10^{-6} M) in (a) water and (b) 0.5 g dm^{-3} NS homopolymer solution (λ_{ex} = 415 nm, λ_{em} = 446 nm).

distribution coefficient of (3.88 ± 0.20) × 10^5 was measured for the perylene/NS homopolymer system. From this and the distribution coefficients measured for the two compositions of NS−CAL (Table 1), it was calculated that 92% of the perylene would be solubilized by the calixarene groups for the 80−20 composition, while 80% of the perylene would be solubilized by the calixarene groups for the 90−10 composition. Thus, even though the NS components of the polymer have the ability to solubilize perylene, most of the perylene would be solubilized by the calixarene units of the polymer.

Figure 10b shows that as the ionic strength increases, the amount of perylene solubilized by the NS homopolymer increases in a similar manner to that of NS−CAL. This would indicate that changes in the ionic strength result in changes in the ability of the NS components to solubilize perylene.

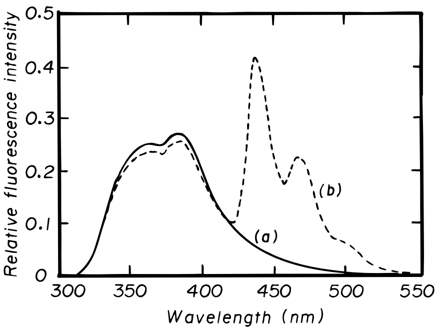


Figure 12. Fluorescence emission spectra (λ_{ex} = 280 nm) of (a) NS−CAL (0.01 g dm^{-3}) in aqueous solution and (b) NS−CAL (0.01 g dm^{-3}) containing solubilized perylene (7.6 × 10^{-7} M).

Table 2. Fluorescence Depolarization Measurements for Perylene via Direct and Indirect Excitation (λ_{em} = 446 nm)

excitation wavelength (nm)	degree of polarization (*P*)
313[a]	0.0245 ± 0.0006
415[b]	0.3293 ± 0.0002

[a] Excitation of antenna. [b] Direct excitation of perylene.

Energy Transfer and Energy Migration. Having demonstrated that NS−CAL had the ability to solubilize an organic probe molecule, the next step was to determine whether energy transfer from the NS groups to the solubilized perylene was possible. The Förster radius for energy transfer between NS and perylene was determined to be 27.4 Å.[20] Figure 12 compares the fluorescence emission spectra of NS−CAL in the absence and presence of perylene. Under the experimental conditions used, all of the incident light at the 280 nm excitation wavelength was absorbed by the polymer. Comparison of curves a and b shows that the addition of perylene results in a decrease in the fluorescence emission in the 320−400 nm region as well as an increase in fluorescence emission in the 420−500 nm region. The decreased emission in the 320−400 nm region is evidence that the naphthalene emission is being quenched by the presence of the solubilized perylene. The new fluorescence emission in the 420−500 nm region is characteristic of the fluorescence emission of perylene. The quenching of the naphthalene and the appearance of the perylene emission demonstrate that energy transfer from the naphthalene sulfonate groups to the solubilized perylene is occurring.

Although direct evidence for singlet energy migration is difficult to obtain, Soutar et al.[33] showed that energy migration can be observed by monitoring the degree of polarization, *P*, of a directly and indirectly excited probe molecule that has been solubilized by the polymer. Perylene was used as the probe molecules for these fluorescence depolarization studies.

Table 2 shows that the degree of polarization for the directly excited perylene is 0.329. This is not too far off from the value of 0.46 obtained for perylene[24] in propylene glycol at −50 °C, under which conditions the rotational motion of perylene is eliminated. This small difference suggests that the perylene solubilized in the polymer does not undergo significant rotational motion over the time scale of the perylene fluorescence lifetime. This would indicate that the perylene is held fairly rigidly in the polymer, and the small amount of depolarization is more likely the result of the entire polymer coil undergoing some rotational motion. Comparison of the values of *P* shows that there is almost complete depolarization of the perylene emission for the indirectly excited perylene. If energy migration between the NS groups did not occur in the system prior to the final energy transfer step from NS to the solubilized perylene, then similar values of *P* would be expected for the directly and indirectly excited perylene, which is not observed. Depolarization effects that can be brought about as a result of excimer formation and dissociation are expected to be minimal since the amount of excimer formation for this system is rather small. Therefore, from these data, it can be seen that energy migration does occur prior to the final energy transfer step from the naphthalene sulfonate to the solubilized perylene.

These studies confirms that NS−CAL exhibits energy migration among the naphthalene sulfonate groups and that energy transfer from the excited naphthalene sulfonate groups to a solubilized probe molecule can occur.

Conclusion

Scheme 1 led to the successful synthesis of 5-[3-(methacryloyloxy)propyl]-25,26,27,28-tetrabutoxycalix[4]arene (**7**), a calixarene derivative that was capable of undergoing polymerization. Copolymerization of **7** with NS gave a water-soluble polymer that contained specific hydrophobic groups. The presence of the sulfonate groups did not lead to the elimination of excimer emission. Solvent and ionic strength studies showed that the excimer formation was probably due to cross-chain contacts rather than from nearest-neighbor chromophores. Fluorescence studies showed that NS−CAL solubilized an organic probe molecule (perylene) and that the solubilizing ability of NS−CAL was dependent on the calixarene content. The calixarene component, however, was not the only component capable of contributing to the probe solubilization since studies with the NS homopolymer showed that the NS groups were capable of making a small contribution to the solubilization of the probe. Fluorescence emission and depolarization studies showed that energy transfer from the naphthalene sulfonate to the solubilized probe occurred and that energy migration among the naphthalene sulfonate groups preceded the final energy transfer step. This novel polymer exhibits all of the criteria needed to behave as an efficient antenna polymer while also possessing the ability to solubilize probe molecules in specific self-contained hydrophobic components. The use of NS−CAL to sensitize photochemical reactions will be the subject of a future paper in this series.

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