Amphiphilic Acenaphthylene−Maleic Acid Light-Harvesting Alternating Copolymers: Reversible Addition−Fragmentation Chain Transfer Synthesis and Fluorescence

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ABSTRACT: An amphiphilic alternating light-harvesting copolymer of narrow polydispersity containing an average of 38 acenaphthylene and maleic acid units with a terminal 9,10-diphenylanthryl energy acceptor has been synthesized by reversible addition−fragmentation chain transfer polymerization. Fluorescence and fluorescence anisotropy measurements of the polymer in methanol and aqueous solutions have been used to characterize energy transfer processes and conformational dynamics. The increased energy transfer efficiencies approaching 100% observed in low-pH aqueous solutions compared to those in more basic aqueous and methanol solutions can be attributed to the formation of a contracted polymer coil and reduced acenaphthenyl excimer formation.

Introduction

Macromolecular systems used to simulate the light-harvesting process of natural photosynthesis are known as “light-harvesting” or “antenna” polymers.[1] Since the first report of their synthesis and properties in 1981,[2] amphiphilic light-harvesting copolymers have attracted considerable interest.[3−6] Amphiphilic light-harvesting copolymers normally contain hydrophilic repeat units (conferring water solubility) and hydrophobic pendant aromatic chromophores (acting as light-absorbing antennae). Compared to light-harvesting homopolymers, amphiphilic light-harvesting copolymers exhibit modified photophysical properties as outlined below.

At low concentration in aqueous solution many amphiphilic polymers adopt a pseudomicellar (or “unimolecular micellar”) conformation. This has been confirmed by a number of experimental techniques including viscometry, light scattering, NMR, and fluorescence methods.[3−7] Such behavior can affect the polymer photophysics in the following ways: (i) Due to polymer coil collapse resulting in reduced interchromophore separations, the polymers often have higher efficiencies of energy migration and trapping in aqueous solution than in organic solution.[3] (ii) The hydrophobic microdomains formed in the pseudomicelle are capable of solubilizing sparingly water-soluble organic compounds, which can then act as an external energy trap.[4] When photoexcited, the energy absorbed by antenna chromophores of the polymer can be transferred to the solubilized molecules within the polymer coil, where a photochemical reaction may take place. These polymers were referred to as “photozymes” (photochemical enzymes) by Guillet.[4] (iii) The heterogeneous microenvironments of amphiphilic copolymers are also conducive to efficient electron transfer processes by retarding the electron recombination processes between incorporated electron donors and acceptors.[5]

In addition, external stimuli such as pH, temperature, ionic strength, or a combination of these can change the conformation of amphiphilic polymers in an aqueous solution, thus affecting the photophysics of light-harvesting polymers.[6]

Besides exhibiting unusual photophysical features, amphiphilic copolymers also show interesting rheology and self-assembly behavior, which suggest potential applications in water treatment, coatings, drug delivery, and other areas of biotechnology and nanotechnology.[8,9]

The synthesis of amphiphilic polymers of well-defined structure is difficult to achieve by conventional free radical polymerization methods. Controlled/living radical polymerization has, in recent years, emerged as one of the most effective synthetic routes to well-defined polymers.[10] Among them, nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition−fragmentation chain transfer (RAFT) polymerization appear to be the most efficient and can be successfully applied to a large number of monomers. However, a distinct advantage of the RAFT process over the others is that it is compatible with a wide range of hydrophilic functionalities (e.g., −OH, −COOH, $-CONR_2$, and $-SO_3Na$) and solvents (including water) under simple conditions.[11] RAFT polymerization has been used to successfully synthesize a number of amphiphilic copolymers with desired properties.[12]

The RAFT process involves performing a conventional free radical polymerization in the presence of certain thiocarbonylthio compounds (S=C(Z)−SR), the so-called RAFT agents.[11] The RAFT agents provide living characteristics during the polymerization via efficient reversible addition−fragmentation chain transfer processes. After RAFT polymerization, most polymer chains will carry the thiocarbonylthio group and the R group as terminals. RAFT polymerization thus provides a means of introducing specifically placed photoactive moieties into polymer chains using appropriately func-

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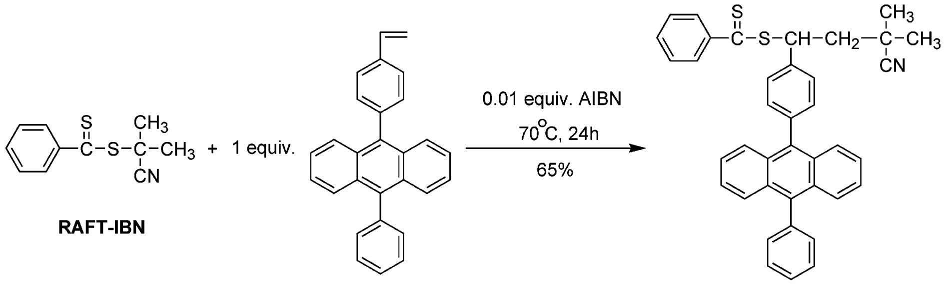
Scheme 1



tionalized RAFT agents. If an energy acceptor species is introduced into the R group and an energy donor into the monomer, a light-harvesting polymer can be made via RAFT polymerization.[13]

In the present work, an alternating light-harvesting copolymer of acenaphthylene and maleic anhydride with a terminal 9,10-diphenylanthryl group was prepared via RAFT polymerization. Acenaphthenyl and 9,10-diphenylanthryl chromophores were selected as the energy donor and acceptor, respectively, as they fulfill the spectral overlap requirements for excitation energy transfer, and acenaphthenyl can be preferentially excited with minimal direct excitation of the 9,10-diphenylanthryl chromophore using radiation between 290 and 320 nm. The high fluorescence quantum yield and relatively good photostability[14] of the 9,10-diphenylanthryl chromophore have made it an attractive choice as an energy acceptor previously in polymer studies.[15]

Results and Discussion

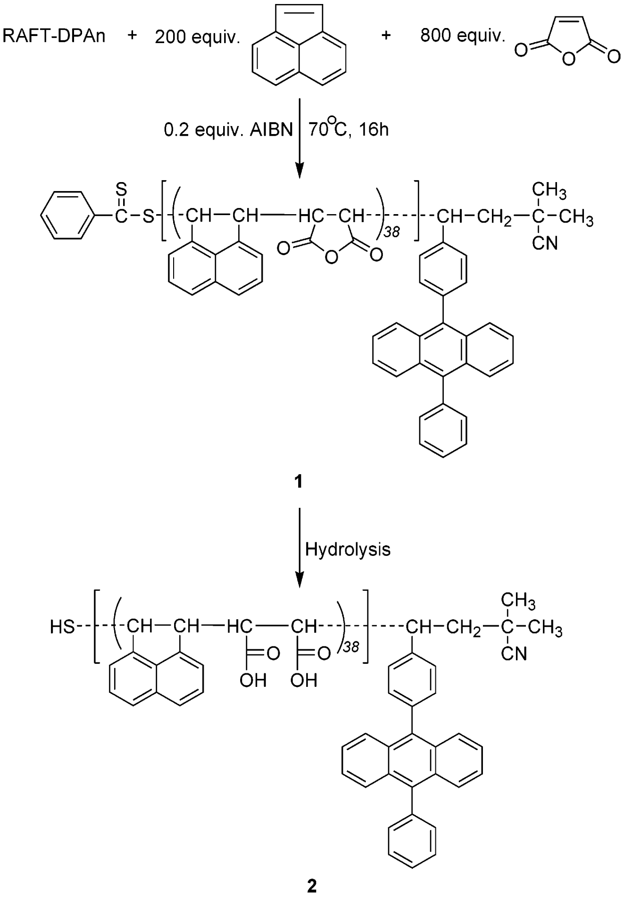
Synthesis of the Functional RAFT Agent and Polymers. The 9,10-diphenylanthryl moiety was introduced into the RAFT agent via a stable C−C linkage by a radical trapping reaction between 9-(*p*-vinylphenyl)-10-phenylanthracene and 2-cyanoprop-2-yl dithiobenzoate (RAFT-IBN) (Scheme 1).[13c] The resulting 9,10-diphenylanthryl-functionalized RAFT agent is denoted as RAFT-DPAn.

Fluorescence was not observed from RAFT-DPAn, indicating that the dithiobenzoyl group efficiently quenches the fluorescence of 9,10-diphenylanthryl as noted previously for other fluorophores.[13]

RAFT-DPAn was used as the chain transfer agent to control the copolymerization of acenaphthylene (AcN) and maleic anhydride (MaAN) (Scheme 2). The resulting polymer, **1**, had an average of 38 acenaphthenyl and maleic anhydride alternating units and one terminal 9,10-diphenylanthryl group. Its anhydride groups were then converted to acid groups by hydrolysis to give polymer **2**. Although the resulting thiol group could partially be oxidized in the presence of base to form a disulfide linkage,[16] this oxidation does not change the overall donor-to-acceptor ratio and did not affect the photophysical properties.

For comparative purposes, an alternating copolymer of acenaphthylene and maleic anhydride, **3**, with an average length of 20 acenaphthenyl and maleic anhydride alternating units, but without the terminal 9,10-diphenylanthryl group, was prepared similarly using RAFT-IBN as the RAFT agent (Scheme 3). This copolymer was hydrolyzed to give polymer **4**.

Scheme 2

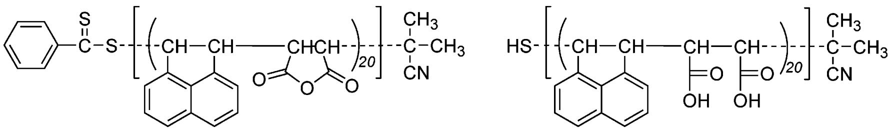


The strain in the unsaturated five-membered ring of the acenaphthylene monomer is partially relieved during polymerization. This accounts for the strong tendency of acenaphthylene to homopolymerize, even when copolymerized with maleic anhydride. Monomer reactivity ratios (R) for the copolymerization of acenaphthylene and maleic anhydride are reported to be $R_{\mathrm{AcN}} = 0.5$ and $R_{\mathrm{MaAN}} = 0$, respectively.[17] A molar feed ratio of [AcN]:[MaAN] = 1:4 was used here to ensure the polymer would have a high alternating tendency. Under the conditions used, the molar ratio of the two monomers (d[AcN]/d[MaAN]) in the resulting polymer is close to 1 according to eq 1.

$$\frac{\mathrm{d[AcN]}}{\mathrm{d[MaAN]}} = \frac{[\mathrm{AcN}](R_{\mathrm{AcN}}[\mathrm{AcN}] + [\mathrm{MaAN}])}{[\mathrm{MaAN}]([\mathrm{AcN}] + R_{\mathrm{MaAN}}[\mathrm{MaAN}])} = 1 + 0.5\frac{[\mathrm{AcN}]}{[\mathrm{MaAN}]} \quad (1)$$

The molecular weights of the alternating copolymers of acenaphthylene and maleic anhydride were determined by gel permeation chromatography (GPC) and UV−vis absorption spectroscopy (Table 1).

Scheme 3



3

4

The molecular weight distributions of the copolymers were quite narrow as determined by GPC. The chemical composition of the copolymers, determined from UV−vis absorption measurements, confirms that the average number of acenaphthenyl units, DP_{AcN}, is close to that of maleic anhydride units, DP_{MaAN}. As maleic anhydride does not homopolymerize during thermal radical polymerization,[18] it can be concluded that most of the maleic anhydride and acenaphthenyl repeat units of the resulting copolymers have a strong alternating tendency.

The two alternating copolymers of acenaphthylene and maleic acid, **2** and **4**, dissolve readily in alkaline aqueous solution and methanol, but not in dichloromethane or tetrahydrofuran.

Photophysics of the Amphiphilic Alternating Copolymers in Methanol. Energy transfer between an electronically excited donor and a ground-state acceptor is commonly described by the induced dipole−dipole (Förster) mechanism.[19] The strength of the electronic interaction is characterized by the Förster critical transfer distance, determined from the spectroscopic and photophysical properties of the donor and acceptor and defined as the distance at which the rate of energy transfer equals the rate of other excited-state relaxation processes of the donor.

Using the photophysical and spectroscopic properties of acenaphthylene and 9,10-diphenylanthracene as model compounds for the donor and acceptor, respectively, and assuming an orientation factor (κ^2) equal to 2/3 (corresponding to a random distribution of transition dipole orientations), the Förster critical distance between the acenaphthenyl and 9,10-diphenylanthryl chromophores was calculated to be 28.7 Å in methanol.

Comparison of the molar extinction coefficients of acenaphthene and RAFT-DPAn indicates that the absorbance at 295 nm is almost exclusively (>95%) due to the acenaphthenyl chromophores in polymer **2**.

The fluorescence spectra of the two copolymers **2** and **4** are presented in Figure 1. The fluorescence of **4** consists of a structured emission from monomeric acenaphthenyl chromophores (wavelength maximum at 340 nm) and a broad emission at 400 nm arising from acenaphthenyl excimers as noted previously.[20] In polymer **2** significant quenching of the acenaphthenyl donor fluorescence is observed, and the characteristic emission of the 9,10-diphenylanthryl acceptor appears from 400 to 550 nm. Furthermore, the fluorescence excitation spectrum of **2**, recorded by monitoring the 9,10-diphenylanthryl emission at 435 nm, contains a major contribution associated with the acenaphthenyl chromophore absorption around 295 nm (Figure 2). These observations show that in this polymer excitation energy is transferred from acenaphthenyl units to the 9,10-diphenylanthryl trap. By comparison of the corrected fluorescence excitation spectrum of the emitting trap and the corresponding absorption spectrum of the solution as described previously,[21] the energy transfer efficiency was determined to be 36%.

Table 1. Molecular Weights of Acenaphthylene−Maleic Anhydride Copolymers Determined by Different Methods

		M_n by UV[b]		GPC[d]	
	M_n(calcd)[a]	M_n	DP_{AcN}/DP_{MaAN}[c]	M_n	M_w/M_n
1	10 100	10 300	37/42	6500	1.22
3	5200	4100	16/15	4200	1.30

[a] Conversions were determined assuming that the two monomers were consumed at equal rates. Theoretical molecular weights were calculated using the expression M_n(calcd) = ([AcN]/[RAFT agent])(conversion yield)(MW of AcN + MW of MaAN) + MW of RAFT agent. [b] In the UV method, molar extinction coefficients of acenaphthene and the corresponding RAFT agent were used as references. The molar extinction coefficients (M^{-1} cm^{-1}) in dichloromethane are as follows: at 290 nm, acenaphthene (6.46×10^3), RAFT-IBN (1.08×10^4), RAFT-DPAn (1.30×10^4); at 395 nm, RAFT-DPAn (1.33×10^4); at 515 nm, RAFT-IBN (1.01×10^2). [c] DP_{AcN} and DP_{MaAN} are the average number of corresponding repeat units in a single polymer chain. [d] Molecular weights are reported as linear polystyrene equivalents.

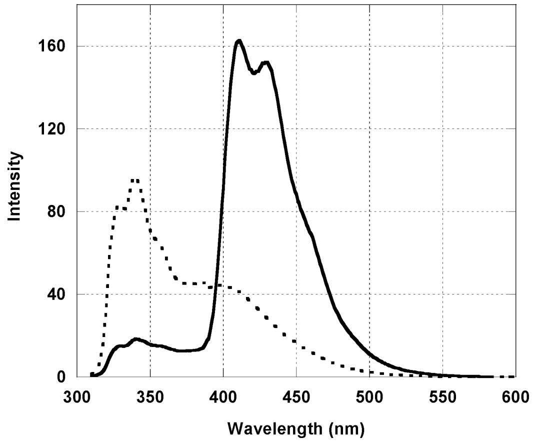


Figure 1. Fluorescence from degassed methanol solutions of **2** (—) and **4** (---). Both solutions have equal absorbance (A = 0.10) at the excitation wavelength of 295 nm.

Photophysics of Polymer 4 in Aqueous Solutions. The dissociation occurring in alternating copolymers of maleic acid and hydrophobic comonomers with pH is known to be complex, but it has been shown that the conformation of such polymers changes from a compact globule (lower pH) to an extended coil (higher pH) resulting from balancing the hydrophilic and hydrophobic interactions.[22]

The fluorescence of **4** in aqueous solution was studied over the pH range 12.5−4; below pH 4, the polymer began to precipitate from the solution. The fluorescence spectrum of **4** shows two major bands, one at shorter wavelength (monomer emission) and the other a broad structureless band at longer wavelengths (excimer emission). The relative intensity of excimer emission can be characterized by the excimer-to-monomer intensity ratio (I_E/I_M), which was obtained by measuring the intensities of the monomer emission at 330 nm and the excimer emission maxima at 400 nm. The relationship between pH and I_E/I_M is shown in Figure 3.

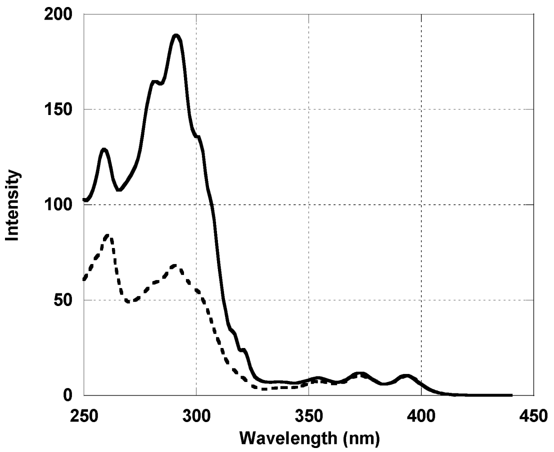


Figure 2. Corrected fluorescence excitation spectrum monitored at 435 nm (---), and the absorption spectrum (—) of **2** in methanol. Both spectra are normalized at 390 nm.

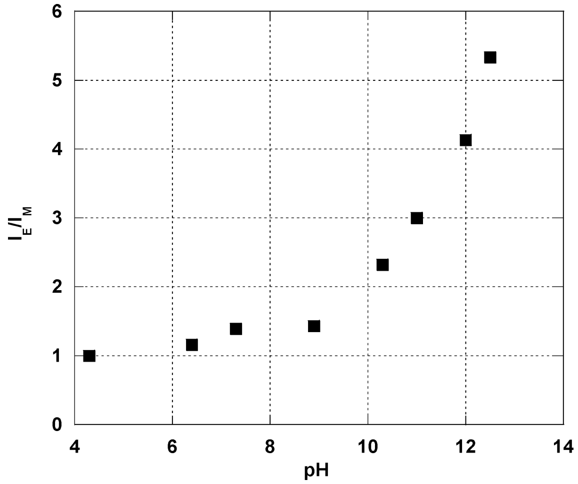


Figure 3. I_E/I_M ratios of **4** as a function of pH.

Compared to the excimer emission observed in methanol ($I_{400nm}/I_{330nm} = 0.53$), excimer emission was more intense in the aqueous solution, indicating that the hydrophobic acenaphthenyl units are likely to be in a more compact arrangement in aqueous solutions than in methanol.

The strongest excimer emission was observed in aqueous solution at pH 12.5. Under alkaline conditions, the polymer chain containing ionized carboxylate groups can be expected to adopt a relatively extended conformation due to the mutual repulsion of the negatively charged carboxylate groups. However, the high excimer emission observed indicates that the acenaphthenyl units are still in close proximity under these conditions. It is proposed that the alternating copolymer in dilute alkaline solution adopts a structure in which the hydrophobic acenaphthenyl units form the interior of the coil and the carboxylate groups form an outer "shell" (Figure 4). The hydrophobic character of the acenaphthenyl units, combined with the alternating characteristic of the amphiphilic polymer, might favor such a hypercoiled structure. A similar structure has also been proposed by other workers to explain high energy trapping efficiencies under basic conditions in other amphiphilic polymers.[23]

The relative intensity of excimer emission decreases with decreasing pH of the solution. This trend differs from previous observations of an alternating copolymer made from 2-vinylnaphthylene and maleic acid, where excimer emission was reported to be more intense at lower pH.[24] This can be attributed to differences in the chain conformation and the mobility of the aromatic units between these two polymers. As there are no (or minimal) adjacent chromophores in the alternating copolymers, the interactions between well-separated acenaphthenyl units are important for excimer formation. These well-separated acenaphthenyl units are brought together by the diffusional movements of chain segments during the excited-state lifetime. However, it has been shown that not only the proximity but also the relative orientations of interacting chromophores are important in controlling the formation of acenaphthenyl excimers.[25] Unlike 2-vinylnaphthyl units, the acenaphthenyl chromophores are attached rigidly to the polymer backbone through two C−C linkages. Therefore, the rotation of acenaphthenyl units to achieve the appropriate orientation for excimer formation is impossible, unless it is associated with movement of the "local" chain segments. When the pH is changed to a lower value, carboxylate groups are protonated, resulting in a compact chain conformation and restricted motion of the chain segments. Ultimately, this will result in less excimer formation at lower pH. The more restricted motion of acenaphthenyl units compared to their vinylnaphthalene analogues, when attached to a (meth)acrylic acid polymer at low pH, has been postulated in a previous study based on time-resolved anisotropy measurements.[26]

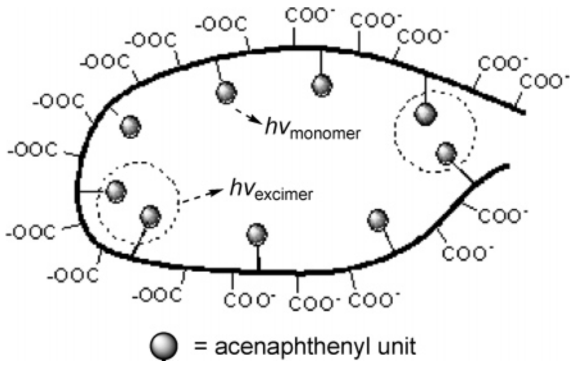


Figure 4. Schematic diagram of the proposed structure of polymer **4** in dilute alkaline solution.

It was also observed that when the pH of the solution is lower than 7, the overall fluorescence quantum yield of the solution decreases. This may be due to changes in the polarity of microenvironments surrounding the acenaphthenyl chromophores. In addition, the higher local concentration of the acenaphthenyl units in the collapsed polymer coils under such conditions (pH < 7) may enhance self-quenching processes as previously reported in other amphiphilic aromatic polymers.[27]

Photophysics of Polymer 2 in Aqueous Solutions. Figure 5 compares the fluorescence from equally absorbing aqueous solutions (pH 12.5) of **2** and **4** when excited at 295 nm. The predominance of 9,10-diphenylanthryl emission confirms efficient energy transfer from acenaphthenyl chromophores to the 9,10-diphenylanthryl trap.

The dependence of the energy transfer efficiency on pH in aqueous solution is shown in Figure 6. The efficiency of energy transfer increases with decreasing pH.

Using direct excitation of the 9,10-diphenylanthryl group at 375 nm, the fluorescence anisotropy (*r*) was

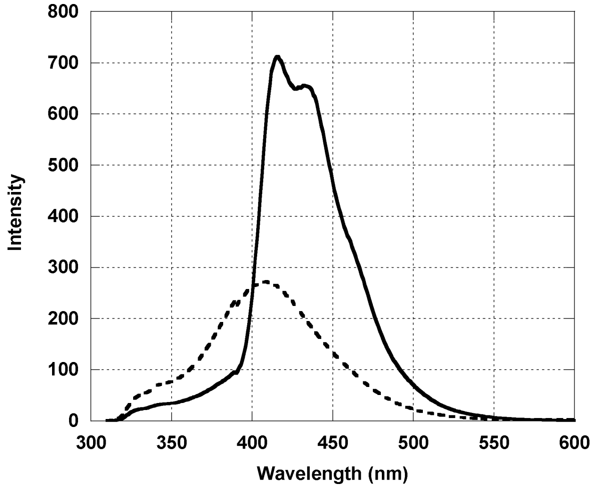


Figure 5. Fluorescence from aqueous solutions (pH 12.5) of **2** (—) and **4** (---). Both solutions have equal absorbance (A = 0.10) at the excitation wavelength of 295 nm.

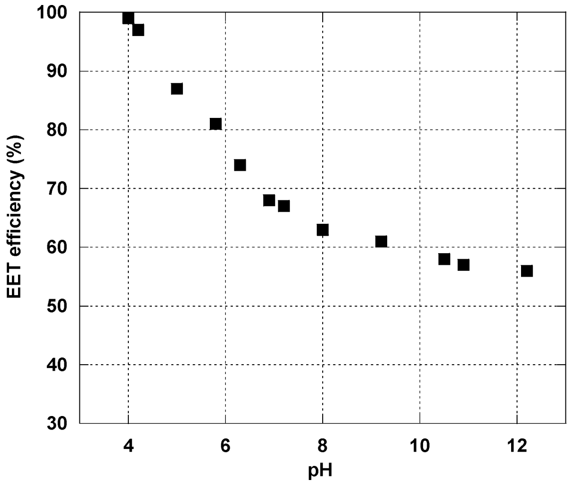


Figure 6. EET efficiencies of aqueous solutions of **2** at different pH values.

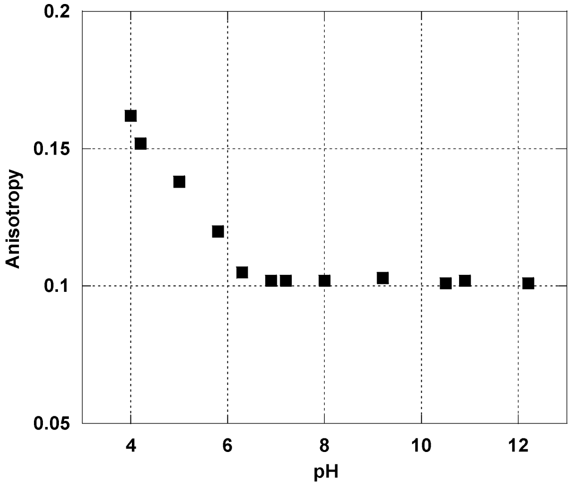


Figure 7. Fluorescence anisotropy (r) of the 9,10-diphenylanthryl group of polymer **2** excited at 375 nm as a function of pH.

also measured as a function of pH (Figure 7). The fluorescence anisotropy is obtained by measuring the polarization characteristics of the emission following excitation with polarized light.[28] A low value indicates rapid rotation of the lumophore during its excited-state lifetime, while higher values indicate more restricted motion.

Figures 6 and 7 show several noteworthy features. First, the energy transfer efficiencies are larger in the aqueous solutions than in methanol (36%), and 100% energy transfer efficiency is observed at pH 4. Similarly, the anisotropy values of 9,10-diphenylanthracence in aqueous solutions are larger than in methanol (0.07). These results indicate that the aromatic groups form hydrophobic microdomains in aqueous solutions, which consequently decreases interchromophore separations and the mobility of the terminal group. Second, both the energy transfer efficiency and anisotropy values of the aqueous solution increase with a decrease of pH, suggesting that a more compact coil is present at lower pH. In the range of pH 6−4, the conformation of the polymer undergoes a marked change; a relatively extended chain in a basic medium changes to a tight coil in an acidic medium, as a significant fraction of the carboxylic groups are protonated. This leads to an accelerated change in the energy transfer efficiency and anisotropy over this range.

The reduced excimer formation at lower pH may also be a further factor leading to the higher energy transfer efficiency in acidic conditions. As with **4**, the alternating copolymer without an energy trap, less excimer emission was observed at lower pH. Clearly, excimer formation acts as a competing energy-trapping process for the excitation energy in acenaphthenyl units. Because of poor spectral overlap of the corresponding emission and absorption, energy transfer from the acenaphthenyl excimer to the 9,10-diphenylanthryl trap is not favored. Therefore, reduced excimer formation at lower pH is expected to enhance the energy transfer efficiency from the acenaphthenyl units to the 9,10-diphenylanthryl trap.

Conclusions

An amphiphilic alternating light-harvesting copolymer of acenaphthylene and maleic acid with a terminal 9,10-diphenylanthryl trap has been synthesized by RAFT polymerization. Energy transfer was observed to be more efficient in aqueous solutions than in methanol. High energy transfer efficiencies at low pH have been attributed to the formation of a contracted polymer coil and reduced acenaphthenyl excimer formation. The structurally well-defined polymers described here provide templates for developing a wide range of amphiphilic light-harvesting macromolecules. Compared to previous studies, the RAFT process provides a means to synthesize light-harvesting polymers with predictable molecular weight, narrow polydispersity, and specifically placed energy acceptors.

Experimental Section

General Experimental Methods. Maleic anhydride (Fluka) was twice recrystallized from chloroform. Acenaphthene, anthracene, and 9,10-diphenylanthracene were obtained from Aldrich and purified by multiple recrystallizations from ethanol. Tetrahydrofuran was refluxed over sodium/benzophenone and then fractionally distilled. 9-(p-Vinylphenyl)-10-phenylanthracene[29] and 2-cyanopropan-2-yl dithiobenzoate[30] were prepared as reported previously.

Water was purified by passing deionized water through a Milli-Q water-purifying system, yielding water with a resistivity of 18 MΩ cm^{-1}. For photophysical measurements, an alkaline polymer solution with pH 12.5 and appropriate absorbance at the excitation wavelength was prepared first using a 0.1 N sodium hydroxide aqueous solution. Lower pH values were obtained by addition of the appropriate amount of a 0.1 N hydrochloric acid. The pH value of the solution was measured using an Activon digital pH meter (Cyberscan 1000). All aqueous solutions were deoxygenated by purging with N_2 bubbling for 10 min prior to use. Organic solvents used for absorption and fluorescence measurements were spectroscopic grade, and solutions were degassed by multiple freeze−pump−thaw cycles to 10^{-6} Torr prior to spectroscopic measurements. Fluorescence and excitation spectra were corrected for the wavelength dependence of detector sensitivity and excitation light source output. Steady-state fluorescence anisotropy measurements were performed by standard methods using a Varian Cary Eclipse fluorometer equipped with a polarization accessory.[28]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av400 spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.63 MHz) at 25 °C in deuterated solvents as stated. Positive ion electron impact (EI) mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000−10000 using PFK as the reference compound.

Molecular weights of the polymers were characterized by GPC performed in tetrahydrofuran (THF; 1.0 mL/min) at 25 °C using a Waters GPC instrument, with a Waters 2414 refractive index detector, a series of four Polymer Laboratories PLGel columns (3 × 5 μm Mixed-C and 1 × 3 μm Mixed-E), and Millennium software. The GPC was calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories EasiCal, MW from 264 to 256000), and molecular weights are reported as polystyrene equivalents.

Synthesis of RAFT-DPAn. A mixture of RAFT-IBN (0.424 g, 1.9 mmol), 9-*p*-vinylphenyl-10-phenylanthracene (0.678 g, 1.9 mmol), and AIBN (3 mg, 0.02 mmol) in chlorobenzene (2 mL) was degassed by three freeze−pump−thaw cycles, sealed under a vacuum, and heated at 70 °C for 24 h. Purification by column chromatography on silica gel (Kieselgel-60, 230−400 mesh) with ethyl acetate:*n*-hexane = 1:9 (v/v) as eluent gave the title compound as a red solid (0.720 g, 65%). ^{1}H NMR (400.13 Hz, $CDCl_3$, ppm): δ 1.43 (s, 3H), 1.59 (s, 3H), 2.48−2.63 (m, 2H), 5.54 (dd, 1H, J = 9.6 Hz, 5.2 Hz), 7.28−7.35 (m, 4H), 7.37−7.44 (m, 2H), 7.44−7.63 (m, 8H), 7.66−7.75 (m, 6H), 8.01−8.07 (m, 2H). ^{13}C (100.63 MHz, $CDCl_3$, ppm): δ 26.7, 28.6, 31.9, 45.3, 52.4, 124.2, 125.2, 125.4, 127.1, 127.2, 127.7, 128.60, 128.64, 129.0, 130.0, 131.5, 132.2, 132.9, 136.5, 137.5, 137.7, 139.2, 139.8, 144.9, 226.0. HRMS (EI): *m/z* calcd for $C_{39}H_{31}NS_2$ 577.1892, found 577.1890. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 302 nm (4.18), 355 nm (4.07), 375 nm (4.18), 395 nm (4.12), 495 nm (2.13).

Synthesis of 1. A mixture of RAFT-DPAn (0.010 g, 0.018 mmol), acenaphthylene (0.547 g, 3.599 mmol), maleic anhydride (1.411 g, 14.400 mmol), AIBN (0.6 mg, 0.004 mmol), and anhydrous THF (2.5 mL) was degassed through three freeze−pump−thaw cycles, sealed under a vacuum, and heated at 70 °C for 16 h. The polymerization was terminated by rapid cooling. The polymer was precipitated three times by addition into a rapidly stirred large excess of anhydrous diethyl ether (75 mL), filtered, and dried in a vacuum to give 180 mg of orange polymer (19%).

Synthesis of 3. Polymer **3** was prepared using RAFT-IBN (0.009 g, 0.039 mmol), acenaphthylene (0.598 g, 3.934 mmol), maleic anhydride (1.542 g, 15.737 mmol), AIBN (0.6 mg, 0.004 mmol), and anhydrous THF (2.5 mL) at 70 °C for 16 h. Yield: 205 mg of orange polymer (20%).

Hydrolysis of 1. An aqueous solution of sodium hydroxide (2 mL, 1 mol/L) was added dropwise into a THF solution (2 mL) of polymer **1** (100 mg) under nitrogen in the dark. After being stirred for 48 h, the solution turned to colorless. It was diluted with water (40 mL), and aqueous hydrochloric acid (5%) was added until the pH was lower than 2. After dialysis against deionized water for one week using a Pierce dialysis tube with MWCO equal to 3500, 90 mg of colorless polymer **2** was obtained after freeze-drying.

Hydrolysis of 3. Polymer **3** (150 mg) was similarly hydrolyzed to give 130 mg of colorless polymer **4**.

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