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References and Notes

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(2) Eidgenossische Technische Hochschule.

(3) Fendler, J. H.; Tundo, P. *Acc. Chem. Res.* **1984**, *17*, 3-7.

(4) Fendler, J. H. In "Surfactants in Solution"; Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984.

(5) Gros, L.; Ringsdorf, H.; Schupp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 305-325.

(6) Fendler, J. H. *Science (Washington, D.C.)* **1984**, *223*, 888-894.

(7) Fuhrhop, J. H.; Mathieu, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 100-113.

(8) Reed, W.; Guterman, L.; Tundo, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 1897-1907.

(9) Hauser, H.; Gains, N.; Semerra, G.; Spress, M. *Biochemistry* **1982**, *21*, 5621-5628.

(10) Hauser, H.; Palfrauf, F.; Shipley, G. G. *Biochemistry* **1982**, *21*, 1061-1067.

(11) Austin, R. H.; Karohl, J.; Jovin, T. M. *Biochemistry* **1983**, *22*, 3082-3090.

(12) Reed, W. Dissertation, Clarkson University, Potsdam, NY, 1984.

(13) Robbins, R. J.; Fleming, G. K.; Beddard, G. S.; Robinson, G. W.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 6271-6279. VonJena, A.; Lessing, H. E. *Chem. Phys. Lett.* **1981**, *78*, 187-193.

(14) Reed, W.; Politi, M. J.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 4591-4593.

(15) David, C.; Baeyans-Volant, D. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 341-355.

(16) Peak temperatures in the excess heat capacity curves were taken as the transition temperature.

Studies of the Antenna Effect in Polymer Molecules. 9. Energy Transfer, Migration, and Photoreactivity of Copolymers of 1-Naphthylmethyl Methacrylate and [2-(9,10-Anthraquinonyl)]methyl Methacrylate

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ABSTRACT: Energy migration and transfer were investigated in 1-naphthylmethyl methacrylate polymers containing anthraquinone chromophores. The naphthalene singlet state is quenched by singlet energy migration and transfer to anthraquinone. Energy-transfer efficiencies of ca. 80% were obtained at acceptor mole fractions of 2%. These molecular antenna successfully mimic the energy-harvesting function of the antenna pigments of natural photosynthetic systems. The effect of copolymer composition on the efficiency of energy transfer, the quenching mechanism of the singlet, and the mechanism of the delayed fluorescence were studied. After their formation the anthraquinone triplet states are in turn quenched by triplet energy transfer to naphthalene, a process that leads to enhanced naphthalene phosphorescence intensity. The occurrence of cyclic energy transfer shows that both singlet and triplet migration and transfer occur in the same polymer chain. In THF solution at 25 °C the anthraquinone traps undergo rapid photoreduction to the corresponding hydroquinone.

The analogy between "antenna polymers", which consist of sequences of aromatic donor chromophores such as naphthalene or phenanthrene, and the "antenna pigments" in natural photosynthesis has been discussed in previous papers in this series.[1-10] In the latter system it is postulated that a regular arrangement of the chlorophyll molecules in the plant thylakoid membrane promotes rapid singlet energy migration to the active center where the excitation energy is used to drive a sequence of reactions leading to charge separation and the ultimate formation of high-energy products that are used as fuels by both plants and animals.[11] In previous work it has been shown that singlet energy migration can also take place within a single macromolecule in solution at high dilution and that the excitation can be trapped with efficiencies exceeding 80%, which is comparable to that estimated for the antenna pigments in plant chloroplasts. It has also been shown that the process takes place rapidly—on the order of 5-20 ns, a time scale that precludes any large movement of either the polymer chain or its side groups—and appears to be nearly as efficient in a solid organic glass at 77 K as in fluid solution at ambient temperature. Although triplet energy migration also occurs in aromatic polymers[12-14] by a mechanism now generally accepted, in this work the term "antenna effect" is restricted, by analogy with the natural photosynthetic system, to the migration and trapping of singlet excitons.[15]

In previous studies, anthracene was used as a trap, because its fluorescence emission could be used as a probe of the photophysics of the processes involved. Three studies in which phenyl ketone traps were used did not show enhanced reactivity of the ketone because of the rapid occurrence of "cyclic energy transfer" in which the singlet excitation transferred to the trap, after rapid intersystem crossing to the triplet, was efficiently quenched by the adjacent naphthalene groups.[7,10,16]

In the present work anthraquinone traps were used in a typical antenna polymer, poly(1-naphthylmethyl methacrylate) (P1NMMA). The traps were introduced by copolymerization with [2-(9,10-anthraquinonyl)]methyl methacrylate (2AQMMA). Copolymers of 2AQMMA with 2-naphthylmethyl methacrylate (2NMMA) had been prepared earlier by Nakahira et al.,[17] who showed that

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direct irradiation of the anthraquinone units could result in efficient photoredox reactions with L-ascorbic acid and the dye Fast Red A. The slightly higher efficiencies of the polymeric sensitizers were ascribed to a mechanism involving the migration of triplet energy among the naphthalene units in the polymers. However, no attempt was made to study singlet energy migration in these systems, and the concentrations of 2AQMMA used were such that the effect would be minimal in any case.

The ability of quinones to undergo reversible photooxidation and photoreduction makes them of special interest as traps in an antenna polymer system. In higher plants, large amounts of vitamin K–naphthoquinone were found in chloroplasts.[18] In addition, some new classes of quinoidal substances, grouped under the generic terms "coenzyme Q" and "ubiquinone" (now termed "plastoquinone"), appear to be important constituents of plant and algal chloroplasts.[19,20] The characteristic structures for these substances are substituted benzoquinones.[21–23] A current view holds that there are two acceptor quinones, Q_1 and Q_2, that accumulate electrons and transfer them pairwise to a larger pool of plastoquinone in photosystem II, which is associated with water splitting and oxygen evolution in higher plants.[24] Anthraquinones are another group of natural products occurring in plants,[25] and 2-(hydroxymethyl)anthraquinone has been found in the bark and leaves of certain plants in concentrations up to 1%.[26]

In the present work, polymers of 1NMMA with anthraquinone chromophores were synthesized for the investigation of electronic energy migration and transfer. The effects of polymer composition on the efficiency of energy transfer have been evaluated quantitatively. In addition, delayed fluorescence and phosphorescence measurements have been used to explore a cyclic energy-transfer process in this system. The photochemical activity of the anthraquinone trap was also examined.

Experimental Section

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride[27] and was fractionally distilled before use. 1NMMA was synthesized from 1-naphthalenemethanol (Aldrich) and methacryloyl chloride. The purified monomer was stored at −20 °C over a small amount of inhibitor. It was chromatographed on alumina again just before use. The first band off the column was collected and used immediately.

2-(Hydroxymethyl)anthraquinone.[28] 2-(Chloromethyl)anthraquinone was synthesized by heating a mixture of 2-methylanthraquinone, CCl_4, and AIBN with SO_2Cl_2 at 90–100 °C: yield, 76%; mp 162–163 °C (EtOAc). 2-(Chloromethyl)anthraquinone was refluxed with 600 mL of $(CH_3)_2SO$ containing 30% H_2O by volume. The progress of the reaction was followed by measuring the melting point of the sample obtained by precipitating small aliquots of the reaction mixture into water. In the present case, the melting point, which was initially 163 °C, rose to 185 °C and became constant after 40 h of reflux. At that point, the reaction mixture was cooled, washed repeatedly with H_2O to remove $(CH_3)_2SO$, and dried under vacuum. The crude product was recrystallized from benzene: yield, 70%; mp 193–194 °C; NMR ($CDCl_3$) δ 4.86 (s, 2 H), 7.2–8.3 (m, 7 H).

[2-(9,10-Anthraquinonyl)]methyl Methacrylate (2AQMMA). To a solution of 0.3 g of 2-(hydroxymethyl)anthraquinone, 0.5 mL of dry Et_3N, and 30 mL of dry THF cooled to 0 °C, was added 1 mL of methacryloyl chloride over 1 h with stirring. After the solution was stirred an additional 8 h at 0 °C, 31 mL of H_2O was added to dissolve the amine salt. The product was extracted with ether, and the combined extracts were washed with 0.1 M HCl, 5% aqueous $NaHCO_3$, and saturated NaCl and dried over Na_2SO_4. After removal of the ether solvent, the product was purified by recrystallization from ethanol as yellow crystals: NMR ($CDCl_3$) δ 1.98 (s, 3 H), 5.3 (s, 1 H, =CH), 5.6 (s, 2 H, $ArCH_2O$), 6.17 (s, 1 H, =CH), 7.2–8.3 (m, 7 H, aromatic ring H). It was stored at −20 °C in the dark.

Table I
Properties of the Anthraquinone-Containing Samples

sample no.	monomer 1	monomer 2	mol of anthraquinone in copolymer	$M_n \times 10^{-3}$ [a]
R1	1NMMA		0	94
R2	1NMMA	2AQMMA	0.022	73
R3	1NMMA	2AQMMA	0.059	71
R4	1NMMA	2AQMMA	0.095	65
R5	1NMMA	2AQMMA	0.37	57
R6	1NMMA	2AQMMA	1.13	60
R7	1NMMA	2AQMMA	1.81	62
R8	1NMMA	methacryloyl chloride + 2-(hydroxymethyl)anthraquinone	2.14	

[a] By membrane osmometry in dioxane.

Polymer Preparation. The anthraquinone-containing polymers were prepared in two ways. The first method involved reaction on a preformed polymer. A copolymer of 1NMMA with methacryloyl chloride was synthesized by decanoyl peroxide initiated radical polymerization in degassed benzene at 60 °C. The copolymer was precipitated with cyclohexane, separated by filtration, and washed with dry pentane. A new copolymer having anthraquinone chromophores was obtained by refluxing a solution of 2-(hydroxymethyl)anthraquinone, dry Et_3N, and dry benzene with the copolymer. All of the reagents and equipment used for these synthetic processes were dried thoroughly.

A set of random copolymers having different compositions was made by AIBN-initiated copolymerization of 1NMMA with 2AQMMA monomer in degassed dimethylformimide at 70 °C.[17] In this way the concentration of anthraquinone in the polymer can be controlled more accurately.

The copolymers were purified by three precipitations from solution into methanol, washed thoroughly with methanol and with spectroscopic grade *n*-pentane, dried in vacuo, and stored at −20 °C in the dark. The mole fraction of anthraquinone in these copolymers was determined by UV spectroscopy, using the measured extinction coefficient of 2-methylanthraquinone to approximate that of the polymer-bound anthraquinone. Number-average molecular weights were measured by membrane osmometry in dioxane for these copolymers. The compositions and molecular weights of these copolymers are listed in Table I.

The solvents used for fluorescence spectroscopy were purified carefully. Benzene was refluxed with P_2O_5 overnight and fractionated over P_2O_5 under nitrogen. Tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2MeTHF) were refluxed over $LiAlH_4$ for 24 h and fractionally distilled under nitrogen. The samples were dried again in vacuo before use. All spectroscopic samples were prepared at room temperature at a concentration of 10^{-4} M in naphthalene chromophores.

The steady-state fluorescence spectra of the polymers in deoxygenated solution were recorded with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. All of the sample solutions were prepared freshly and used only in a single steady-state experiment. In order to minimize the effects of fluctuations in the intensity of the excitation source, each experiment on a copolymer sample was followed immediately by the same measurement on a 1NMMA homopolymer for calibration.

The prompt fluorescence and delayed fluorescence at 77 K were measured in 2MeTHF glass with liquid nitrogen as a coolant. Sample cells were 2-mm quartz tubes that fitted into a liquid nitrogen Dewar. The sample cells used in fluorescence measurements at room temperature were 10-mm quartz cells. The spectrofluorimeter was fitted with a phosphorescence accessory including a chopper used at a frequency of 1 kHz to eliminate prompt signals to the photomultiplier for delayed fluorescence measurements.

Results and Discussion

Steady-State Fluorescence Quenching. The quenching of naphthalene luminescence in polymers by

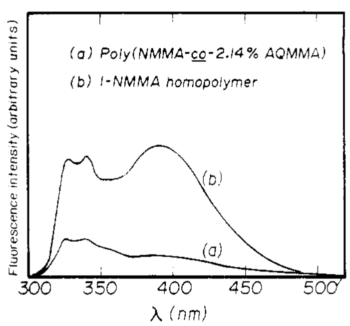


Figure 1. Fluorescence emission spectra from (a) copolymer R8 (2.14 mol % 2AQMMA) and (b) poly(1NMMA) in deoxygenated benzene at 25 °C, λ_{ex} = 290 nm (10^{-4} M in naphthalene chromophores).

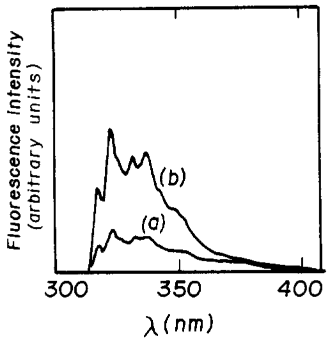


Figure 2. Fluorescence emission spectra from (a) copolymer R7 (1.81 mol % 2AQMMA) and (b) poly(1NMMA) in deoxygenated 2MeTHF at 77 K, λ_{ex} = 280 nm (10^{-4} M in naphthalene).

Table II
Efficiency χ of Quenching of Naphthalene[a] Fluorescence by Anthraquinone in Anthraquinone-Containing 1NMMA Copolymers in 2MeTHF at 77 K (λ_{ex} = 280 nm)

anthraquinone in polymer, mol %	no. of traps per molecule	χ, %
0	0	0
0.022	0.07	6
0.059	0.18	9
0.095	0.27	15
0.37	0.93	29
1.13	3.0	56
1.81	4.0	72
2.14		79.5[b]

[a] In benzene solution at 25 °C. [b] λ_{ex} = 290 nm.

copolymerized ketone groups has been reported previously[7,29] and was recently studied quantitatively in 2-vinylnaphthalene–phenyl vinyl ketone copolymer systems.[10] The fluorescence of naphthalene chromophores can also be quenched by the anthraquinone group in the 1NMMA–2AQMMA copolymer system studied in this paper. Figure 1 shows the fluorescence spectrum of a copolymer of 1NMMA containing 2.14 mol % 2AQMMA compared with that of 1NMMA homopolymer at the same concentration (10^{-4} M) in deoxygenated benzene at 25 °C. The naphthalene chromophores were excited at 290 nm, where the direct absorption of anthraquinone is low. From the reduction in naphthalene fluorescence shown in Figure 1, it is evident that singlet electronic energy transfer occurs from the naphthalene to anthraquinone in the polymer chain.

Solutions of 1NMMA–2AQMMA copolymer dissolved in 2MeTHF form a clear glass at 77 K. No emission from the naphthalene excimer is observed in the fluorescence spectra of the 1NMMA homopolymer and its copolymers at this temperature. For example, Figure 2 shows the fluorescence spectrum of a 1NMMA copolymer containing 1.81 mol % 2AQMMA on excitation of the naphthalene chromophores at 280 nm in deoxygenated 2MeTHF at 77 K. The spectrum of 1NMMA homopolymer is shown in the same figure on the same scale. The occurrence of energy transfer is again indicated by the reduction in fluorescence intensity of the copolymer.

Alkyl-substituted anthraquinones normally do not fluoresce, so it is not surprising that there is no observable emission from the anthraquinone chromophores in the fluorescence spectra of any of these copolymers. Values of the efficiency of energy transfer from the naphthalene to the anthraquinone χ can be calculated from the fluorescence intensity I_F of copolymers and homopolymer at constant excitation intensity by means of eq 1.[38] The relative areas of the fluorescence bands for the copolymers and the homopolymer were measured with a planimeter to determine I_F.

$$\chi = 1 - [(I_F)_{\text{copolymer}}/(I_F)_{\text{homopolymer}}] \qquad (1)$$

Table II shows the variation of χ with anthraquinone content for 1NMMA–2AQMMA copolymer solutions in 2MeTHF at 77 K. From Table II it is evident that the efficiency χ of energy transfer from the naphthalene to the anthraquinone increases with anthraquinone content. High efficiencies of energy transfer are achieved at relatively low mole fractions of the bound acceptor. By raising the anthraquinone content of the polymer to about 2%, one can obtain approximately 80% efficiency of energy transfer, even in benzene, which is a good solvent for the 1NMMA polymers. The value of χ of about 80% in a synthetic macromolecule containing 2% acceptor may be compared with estimated efficiencies of from 75%[30] to 96%[31] for transfer from the antenna pigments to the reaction centers of natural photosystems. The results show that it is possible to create a single polymer molecule that absorbs UV light and transfers the energy to a trap nearly as efficiently as in natural photosynthetic systems.

Similar high efficiencies of energy transfer can also be obtained for bound anthraquinone copolymers at room temperature, implying that energy transfer is as efficient in a rigid glass as it is in fluid solution. That efficient energy transfer occurs in a polymer glass is particularly significant. In fluid solutions, energy transfer could result from segmental diffusion and collisional processes by the Dexter mechanism. However, in a polymer glass, where segmental diffusion is suppressed, the quenching of naphthalene fluorescence by bound anthraquinone seems to imply the occurrence of long-range Förster transfer. It appears that efficient migration of the singlet excitation energy between naphthalene chromophores on the copolymer in the solid phase plays a predominant role in the mechanism of energy transfer and that segmental diffusion contributes a comparatively small effect. Furthermore, energy transfer to anthraquinone from the naphthalene excimer is not the major mechanism of transfer, because the values of χ are very similar under conditions where no excimer is present.

In a previous paper,[32] a mechanism was proposed for the antenna effect in an individual aromatic polymer molecule containing a trap for singlet excitation. This consists of two processes: (i) direct single-step Förster transfer from donor chromophores with distance R_0 of the trap and (ii) energy migration among donors located outside the spherical volume defined by R_0 until the exciton reaches a location within R_0 where single-step transfer to the trap becomes favored. A more detailed treatment has been given by Guillet.[33]

An important problem is to distinguish the relative contribution of these two processes to the observed ener-

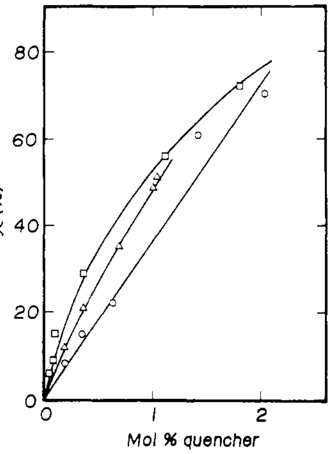


Figure 3. Efficiency of energy transfer χ as a function of mol % trap for (○) 2NMMA-9AMMA, (△) 2VN-PVK, and (□) 1NMMA-2AQMMA in 2MeTHF at 77 K (~4 × 10^{-4} M in naphthalene).

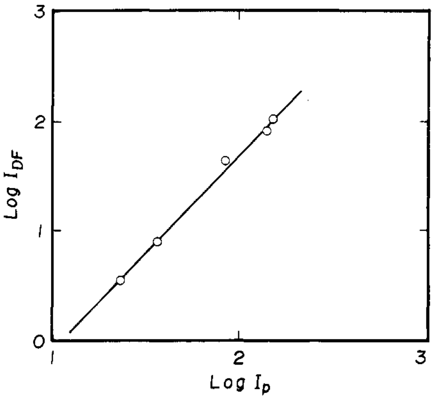


Figure 4. Relation between the intensity of delayed fluorescence (I_{DF}) and phosphorescence (I_P) at various slit widths for copolymer R6 in 2MeTHF at 77 K, λ_{ex} = 280 nm.

gy-transfer efficiency. In order to elucidate this problem, the data of Table II are plotted in Figure 3, along with values of χ for copolymers of 9-anthrylmethyl methacrylate and 2NMMA[34] and for copolymers of 2-vinylnaphthalene and phenyl vinyl ketone.[10] All of the data were obtained under similar conditions of concentration and temperature.

It is evident that both the anthraquinone and ketone traps quench the naphthalene emission with greater efficiency than the anthracene trap, which has a significantly higher Förster radius for single-step transfer. This is strong evidence for the importance of singlet migration in P1NMMA. It seems likely that the efficiency of singlet energy migration depends mainly on the nature of donor chromophore and the spatial relationships between donor chromophores attached along the polymer chain.

Studies of Delayed Fluorescence. Fox and Cozzens first demonstrated triplet–triplet annihilation in poly(1-vinylnaphthalene) which resulted from intramolecular triplet energy migration between the naphthalene groups, leading to delayed fluorescence emission.[12,13,35] Somersall and Guillet[36] prepared 2-naphthyl methacrylate polymers and also observed triplet–triplet annihilation leading to delayed fluorescence.

Delayed fluorescence was also observed in P1NMMA and the copolymers studied in this work. Measurements were made in 2MeTHF at 77 K in a solid matrix. Figure 4 shows a log–log plot of the area under the delayed fluorescence and phosphorescence peaks obtained by varying the excitation slit width for the copolymer having an anthraquinone content of 2.14 mol %. The plot is linear and has an average slope of 1.80. The slope is 1.98 when the excitation slit width ≤10. However, the I_{DF} of polymers of 1NMMA decreases with excitation time, even with a narrow excitation slit width, but much faster when the excitation slit width is >10. Possibly, photoproducts of the copolymers have the ability to quench the delayed fluorescence. At narrow slit widths the slope of the line in Figure 4 is 2.0 ± 0.1, indicating that the process leading to the delayed fluorescence is second order with respect to the intensity of the exciting light. This is consistent with a bimolecular triplet–triplet annihilation process for delayed fluorescence from the naphthalene chromophore.[36]

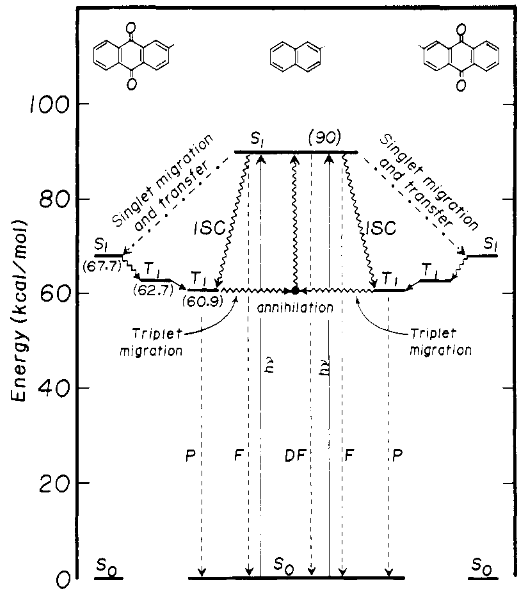


Figure 5. Energy level diagram showing photophysical processes in polymers containing naphthalene and anthraquinone groups in dilute solution. (Energy levels are given in kcal·mol^{-1}.)

These results can be explained by reference to the energy level diagram shown in Figure 5. The absorption of two photons by two different naphthalene chromophores on the same polymer molecule forms excited singlet states that intersystem cross to the triplet manifold. The triplet excitation energy migrates by a series of hopping events along the polymer chain by way of the naphthalene rings until the two triplets come close enough to undergo triplet–triplet annihilation with the formation of a ground singlet and an excited singlet, which then fluoresces. The process takes place not only in 1NMMA homopolymer but also in 1NMMA–2AQMMA copolymers. In the absence of triplet migration, the triplet energy would be completely localized on the segment that initially absorbed the photon, and the possibility of encountering a second triplet in a neighboring position for annihilation within the lifetime of the first triplet would be very small. The triplets that do not encounter a second triplet will lose their energy by emission of phosphorescence or by a radiationless transformation to the singlet ground state.

Figure 6 shows a plot of the ratio I_{DF}/I_P as a function of concentration for 1NMMA–2AQMMA copolymer having an anthraquinone content of 1.13 mol %. I_{DF} and I_P represent the intensities of delayed fluorescence and phosphorescence, respectively, determined from the relative peak area. It is evident that the I_{DF}/I_P ratio is almost independent of copolymer concentration in dilute solution. This is consistent with the occurrence of intramolecular energy migration and transfer along single polymer chains in the rigid matrix. A relatively high concentration of chromophores exists in the cylindrical volume surrounding the polymer main chain in a highly dilute polymer solution,

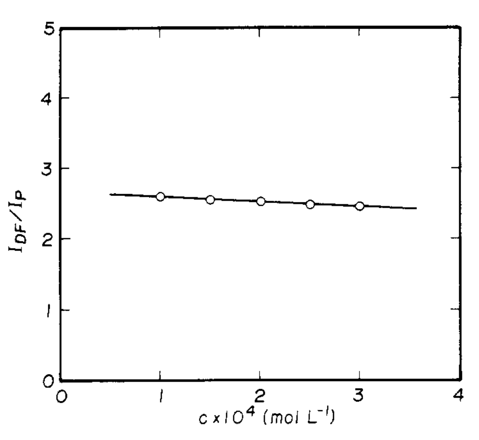


Figure 6. Ratio I_{DF}/I_P as a function of polymer concentration for copolymer R6 in 2MeTHF at 77 K.

Table III
Relative Intensities of Naphthalene Phosphorescence $I_p{}^0$ and the Intensity Ratios of Fluorescence to Phosphorescence I_F/I_P Related to the 1NMMA-2AQMMA Copolymer Compositions

anthraquinone in polymer, mol %	$I_P{}^0$	I_F/I_P
0	1	268.9
0.022	1.29	197.2
0.059	1.44	170.7
0.095	1.56	146.7
0.37	1.75	109.2
1.13	2.25	52.3
1.81	4.25	18.0
2.14		17.2

even though the polymer coils occupy only a small fraction of the total solution volume.[37] As a consequence, polymers exhibit effects characteristic of concentrated solutions such as energy transfer between chromophores.

Naqvi[38] has proposed that the triplet energy migrates by electron-exchange interaction over distances up to 15 Å, to sites at which two triplets can interact by another electron-exchange interaction process.

$$\text{migration} \quad {}^3\text{N} + \text{N}_0 \rightarrow \text{N}_0 + {}^3\text{N} \tag{2}$$

$$\text{annihilation} \quad {}^3\text{N} + {}^3\text{N} \rightarrow {}^1\text{N} + \text{N}_0 \tag{3}$$

Many observations in rigid solution have confirmed this mechanism for small molecules and all the results on polymers are consistent with a scheme involving intramolecular triplet migration among the naphthalene chromophores in the polymer.

Cyclic Energy Transfer in a Polymer Chain. Table III lists the relative intensities of naphthalene phosphorescence I_P and the intensity ratios of fluorescence to phosphorescence I_F/I_P, related to the 1NMMA-2AQMMA copolymer compositions in 2MeTHF at 77 K. The data were taken from total emission spectra at constant excitation intensity. No quinone phosphorescence was observed in any copolymers, a result which indicates efficient triplet energy transfer from the excited carbonyl group to the naphthalene chromophores. It is consistent with Lamola's result that the transfer of triplet excitation energy from a benzophenone group to a naphthalene group within the same molecule was 100% efficient.[39] Nakahira et al.[40] have also demonstrated that the anthraquinone triplet can be quenched efficiently by naphthalene in the same molecule and the data fitted the Perrin model for static quenching.

The results in Table III show that as the fluorescence of naphthalene is quenched by increasing amounts of copolymerized anthraquinone, a parallel increase in naphthalene phosphorescence is observed. Thus the anthraquinone group functions as a sensitizer of the naphthalene triplet. Furthermore, the higher intersystem crossing rate in the anthraquinone trap leads to a more efficient mechanism for the creation of naphthalene triplets, thus leading to a significant increase in the phosphorescence of the copolymers as compared to the P1NMMA homopolymer. However, the intensity of delayed fluorescence from naphthalene decreases in spite of the increase in triplet naphthalene concentration, as shown in Figure 7. This is because of the rapid quenching of the naphthalene singlet produced by triplet–triplet annihilation, as a result of energy migration to the anthraquinone traps.

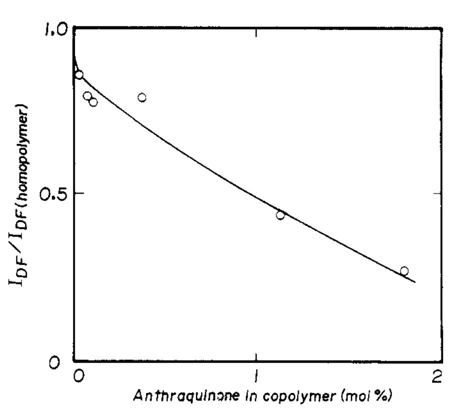


Figure 7. Relative intensity of delayed fluorescence. I_{DF}/I_{DF}(homopolymer) as a function of trap concentration for 1NMMA-2AQMMA copolymers.

This mechanism of cyclic energy conversion in antenna polymers has been discussed in previous papers in this series.[7,16] The process is illustrated for the NMMA-2AQMMA copolymers by the energy level diagram shown in Figure 5 and is explained by the following sequence of photophysical steps.

Excitation and fluorescence emission of naphthalene chromophores

$${}^1\text{Naph}^0 \xrightarrow{h\nu} {}^1\text{Naph}^* \tag{4}$$

$${}^1\text{Naph}^* \rightarrow h\nu_F + {}^1\text{Naph}^0 \tag{5}$$

Singlet energy migration and transfer from naphthalene to anthraquinone

$${}^1\text{Naph}^* + {}^1\text{Naph}^0 \rightarrow {}^1\text{Naph}^0 + {}^1\text{Naph}^* \tag{6}$$

$${}^1\text{Naph}^* + \text{AQ} \rightarrow {}^1\text{AQ}^* + {}^1\text{Naph}^0 \tag{7}$$

Intersystem crossing

$${}^1\text{AQ}^* \rightarrow {}^3\text{AQ}^* \tag{8}$$

Triplet energy transfer from anthraquinone to naphthalene

$${}^3\text{AQ}^* + {}^1\text{Naph}^0 \rightarrow \text{AQ} + {}^3\text{Naph}^* \tag{9}$$

Phosphorescence emission

$${}^3\text{Naph}^* \xrightarrow[\text{emission}]{} h\nu + {}^1\text{Naph}^0 \tag{10}$$

Triplet annihilation and delayed emission

$${}^3\text{Naph}^* + {}^3\text{Naph}^* \rightarrow {}^1\text{Naph}^* + {}^1\text{Naph}^0$$

$${}^1\text{Naph}^* \xrightarrow{\text{emission}} \text{delayed fluorescence} \tag{11}$$

Additional data on the delayed fluorescence of the copolymers are summarized in Table IV along with various molecular parameters, including the average number of anthraquinone traps per polymer molecule, n, and the sequence length, s, between traps. At low concentrations

Table IV
Luminescence Characteristics of Copolymers[a]

copolymer	AQ, mol %	$\bar{P}_n$	n	s	I_P	I_{DF}/I_P	q	χ
R1	0	416	0	416	1.0	9.9	1.0	0
R2	0.022	323	0.07	301	1.04	7.2	0.80	6
R3	0.059	314	0.18	265	1.06	6.5	0.76	9
R4	0.095	288	0.27	266	1.09	5.8	0.76	15
R5	0.37	252	0.93	130	1.22	5.0	0.86	29
R6	1.13	265	3.0	66	1.39	2.5	0.78	56
R7	1.81	274	4.0	46	2.27	1.0	0.79	72

[a] $\bar{P}_n$ = number-average degree of polymerization; n = average number of anthraquinone traps per molecule; s = average sequence length between traps; q = relative efficiency of formation of delayed singlets, corrected for singlet quenching by anthraquinone.

Table V
Number of Naphthalene Donors Quenched per Anthraquinone Trap, $\bar{n}$

f_A, %	χ, %	n	$\bar{n}$
0.022	6	0.07	272
0.059	9	0.18	152
0.095	15	0.27	157
0.37	29	0.93	78
1.13	56	3.0	50
1.81	72	4.0	40

of 2AQMMA, there will be less than one trap per molecule, and hence the effects will be masked by the presence of large amounts of P1NMMA homopolymer. Samples R-5, R-6, and R-7 contain from one to four traps per molecule, and also show significant increases in phosphorescence. The relative efficiency of formation of delayed singlets q can be determined from the relation[10]

$$q = (I_{DF}/I_{DF}^0)(1/(1-\chi)) \tag{12}$$

where I_{DF} and I_{DF}^0 are the intensities of delayed fluorescence for the copolymer and homopolymer, respectively, and χ is the singlet energy transfer efficiency. This corrects for the rapid quenching of the delayed singlet by the adjacent anthraquinone trap. The values of q calculated in this way are nearly constant at ~0.8 for the copolymer series, which illustrates the high efficiency of anthraquinone as a trap for migrating singlet excitons.

Additional information regarding the efficiency of anthraquinone as a singlet energy trap can be obtained by calculating the number of naphthalene donors $\bar{n}$ quenched per anthraquinone trap. This is given by

$$\bar{n} = \chi/f_{AQ} \tag{13}$$

where f_{AQ} is the mole fraction of anthraquinone in the copolymer. Values of n, the number of traps per molecule, and $\bar{n}$ are shown in Table V and are plotted in Figure 8 along with similar values of $\bar{n}$ calculated for anthracene in P1NMMA[3] and phenyl vinyl ketone in poly(2-vinylnaphthalene).[10] The value of $\bar{n}$ gives an upper limit for the singlet migration distance, since it includes those donors quenched by a single-step Förster transfer to the trap. The value is only significant for low trap concentrations, where it is unlikely that chains carry more than one trap per molecule. In this series that corresponds to a value of $f_A \leq 0.2\%$. Unfortunately, this is also where the maximum error occurs in the determination of the concentration of traps. Furthermore, there will be a significant number of chains that do not contain traps. Nevertheless it is clear from Figure 8 that anthraquinone is significantly more efficient than phenyl ketone, which is more efficient than anthracene. In addition, it is clear that even at mole fractions of 1% anthraquinone, more than 50 naphthalene donors are quenched by each trap.

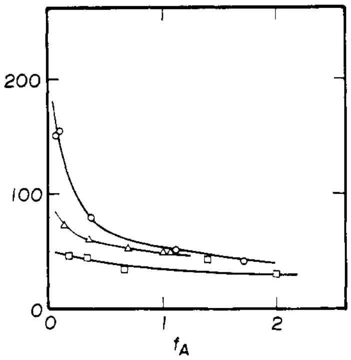


Figure 8. Number of naphthalene donors quenched per trap $\bar{n}$ as a function of trap concentration for (○) 1NMMA-2AQMMA, (△) 2VN-PVK, and (□) 2NMMA-9AMMA in 2MeTHF at 77 K (~4 × 10^{-4} M in naphthalene).

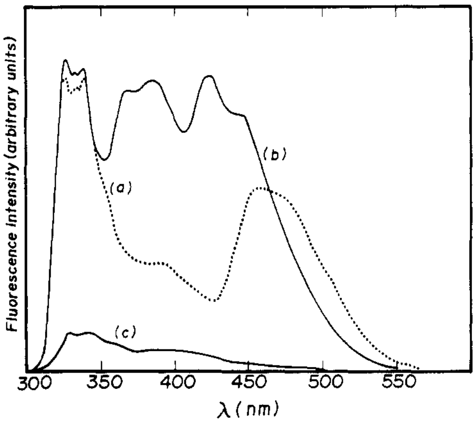


Figure 9. Fluorescence emission spectra from copolymer R8 after exposure to room light (a) in dry THF, (b) in moist THF, and (c) in dry benzene. (Intensities not to scale; c ~ 10^{-4} M.)

Photochemical Activity of the Anthraquinone Trap. It was found experimentally that solutions of 1NMMA-2AQMMA copolymers in THF at 25 °C were remarkably photoactive. Even at narrow excitation slit widths the fluorescence spectra changed rapidly with time. This was not true when the polymer was dissolved in anhydrous benzene. Curve a in Figure 9 shows the fluorescence spectrum of the copolymer containing 2.14% anthraquinone in deoxygenated THF at room temperature. In this case, the THF solvent was refluxed with $LiAlH_4$ for 24 h and used immediately. Curve b shows the spectrum of the same copolymer in deoxygenated THF containing some water, also at 25 °C. The monomer and excimer fluorescence of naphthalene chromophores was quenched partially by anthraquinone in all of these spectra. New fluorescent peaks appeared during the measurement, but the peak positions depended on moisture content of the THF and were similar to those obtained from 2-methylanthraquinone excited directly at 360 nm in the same THF solvents. No new peaks appeared in the steady-state fluorescence spectra of the copolymer in dried benzene (Figure 9c).

It is evident that some photoreaction occurs at the anthraquinone trap in THF solutions. The new fluorescence peak in dry THF is about 460–480 nm, which corresponds to that of 9,10-anthrahydroquinone. For example, Carlson and Hercules[41] showed that the fluorescence spectrum of 9,10-dihydroxyanthracene had a λ_{max} at 460 nm in hexane, but λ_{max} was shifted to 480–497 nm in ethanol solution. The quantum yield for this photoreduction was 0.98 ± 0.05 in ethanol solution, which dropped to 0.11 in hexane.

Based on the mechanism first proposed by Wilkinson[42] for the anaerobic photoreduction of 2-propanol, the following mechanism for the formation of 2,10-dihydroxyanthracene at the trap site is suggested:

$$ {}^1\mathrm{Naph}^0 \xrightarrow{h\nu} {}^1\mathrm{Naph}^* \tag{14} $$

$$ {}^1\mathrm{Naph}^* \underset{\mathrm{AQ}}{\overset{\text{migration}}{\rightsquigarrow}} ({}^1\mathrm{Naph}^* + \mathrm{AQ}) \xrightarrow{\text{energy transfer}} {}^1\mathrm{Naph}^0 + {}^1\mathrm{AQ}^* \tag{15} $$

$$ {}^1\mathrm{AQ}^* \overset{\text{isc}}{\rightsquigarrow} {}^3\mathrm{AQ}^* \tag{16} $$

$$ {}^3\mathrm{AQ}^* + \mathrm{RH} \rightarrow \mathrm{AQH}\cdot + \mathrm{R}\cdot \tag{17} $$

$$ \mathrm{AQH}\cdot + \mathrm{RH} \rightarrow \mathrm{AQH_2} + \mathrm{R}\cdot \tag{18} $$

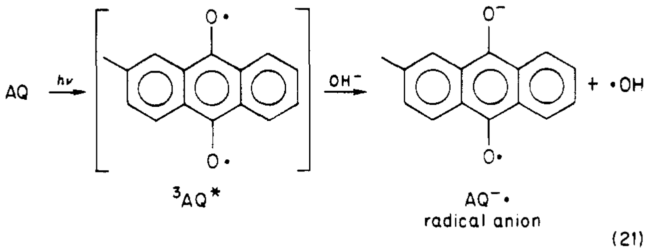
$$ 2\mathrm{R}\cdot \rightarrow \mathrm{RR} + \text{other products} \tag{19} $$

where AQ represents anthraquinone in the polymer chain and RH is 2MeTHF. In the Wilkinson mechanism, AQH_2 is formed by the disproportionation of two AQH· radicals; thus

$$ 2\mathrm{AQH}\cdot \rightarrow \mathrm{AQH_2} + \mathrm{AQ} \tag{20} $$

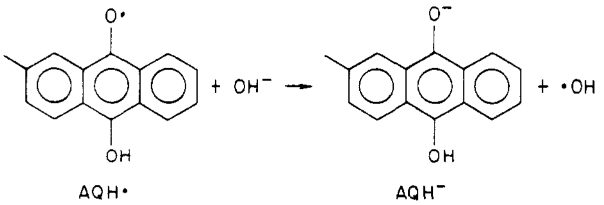
However, we find this process to be unlikely in our systems because the concentration of anthraquinone is very low, and since the traps are on widely separated polymer molecules, the possibility of a bimolecular process of this type competing with the pseudounimolecular reaction with solvent (eq 18) seems remote.

Two possibilities exist for the fluorescent species with λ_{max} = 385 and 425 nm. In the absence of more definitive spectral data one can only speculate on possible intermediates. For example, it is known that in aqueous alkaline media, excitation of anthraquinone and its derivatives can lead to the formation of OH radicals and the anthraquinone radical ion



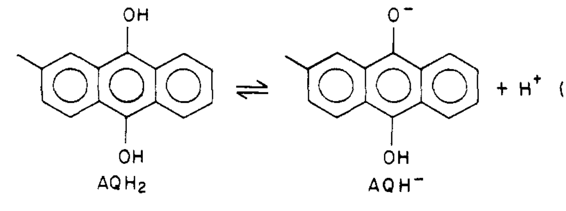
(21)

The semiquinone radical anion so formed is reported to be stable in the absence of oxygen.[41] A further possibility for the emitting state in the presence of water is the anthrahydroquinone monoion AQH^-, which can be formed either by reaction of the ketyl radical with OH^- by the scheme



(22)

or by dissociation of AQH_2



(23)

Due to the sensitivity of the fluorescence measurement, even very low concentrations of either AQH^- or $AQ^{-}\cdot$ would be detectable. Other procedures for identifying the exact origin of the fluorescence in $THF-H_2O$ systems are currently being evaluated.

In these experiments about 98% of the light energy was absorbed by the naphthalene chromophores while only about 2% was absorbed directly by the anthraquinone traps. Thus most of the excitation energy for the anthraquinone photoreaction came from the naphthalene chromophores in the same polymer chain. The excited anthraquinone is very photoreactive and rapidly abstracts hydrogen from dry THF or possibly from water. The intensity of fluorescence of the photoreduction products of the anthraquinone traps increases with time of exposure to light in the spectrometer or to external UV from laboratory sources. However, the products of the reaction depend on the solvent. In dry benzene, no fluorescence is observed from either the anthraquinone trap or its photoreduction products. On the other hand, in ordinary dried THF there is clear evidence for the formation of the reduced form of the trap (AQH_2). When the THF contains water, the reduction appears to go only part way, possibly to the semiquinone ion or radical ion.

The ability of the quininoid structure to undergo reversible oxidation and reduction is well-known, and polymers similar to those reported here have been used as redox catalysts by Nakahira et al.[17] for the oxidation/reduction of ascorbic acid and other substrates. In the presence of oxygen the anthrahydroquinone derivatives are autoxidized back to the quinone with remarkable efficiency.

$$ \mathrm{P}\!\rightsquigarrow\!\mathrm{AQH_2} + \mathrm{O_2} \rightarrow \mathrm{P}\!\rightsquigarrow\!\mathrm{AQ} + \mathrm{H_2O_2} \tag{24} $$

The hydrogen peroxide so produced is a fuel that represents the storage of a portion of the original energy of the light absorbed.

In conclusion, copolymers of 1NMMA containing minor amounts of 2AQMMA appear to mimic several of the essential steps in natural photosynthesis, namely the absorption of photon energy followed by migration of singlet excitons in an array of antenna chromophores to a trap where the excitation is converted into a photochemical product. In this case, the result is the reduction of the quinonoid moiety to the corresponding anthrahydroquinone. This reaction does not occur in dry benzene but does so in dry THF, which is presumably the source of the hydrogen acquired in the photoreduction. It is believed that this is the first example of an energy storage reaction induced in a single polymer chain utilizing the antenna effect to harvest the photon energy.

The copolymers also provide a further example of "cyclic energy transfer" in which the migrating singlet excitons on naphthalene are efficiently converted to naphthalene triplets through the intermediacy of the quinonoid trap. As demonstrated in previous publications from this laboratory,[7,16] this process can be significantly more rapid and efficient than direct intersystem crossing in the naphthalene groups themselves. The consequences of this interesting effect remain to be exploited.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. 2AQMMA, 47281-81-2; (1NMMA)·(2AQMMA) copolymer, 98105-00-1; 2-(hydroxymethyl)anthraquinone, 17241-59-7; (methacryloyl chloride)·(1-naphthylmethy(methacrylate) copolymer 2-(hydroxymethyl)anthraquinone ester, 98216-95-6; methacryloyl chloride, 920-46-7.

References and Notes

(1) Guillet, J. E. *Pure Appl. Chem.* 1977, *49*, 249.
(2) Aspler, J. S.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* 1978, *11*, 925.

(3) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.
(4) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11.
(5) Ng, D.; Guillet, J. E. *Macromolecules* **1982**, *15*, 724, 728.
(6) Holden, D. A.; Guillet, J. E. *Macromolecules* **1982**, *15*, 1475.
(7) Holden, D. A.; Shephard, S. E.; Guillet, J. E. *Macromolecules* **1982**, *15*, 1481.
(8) Holden, D. A.; Ng, D.; Guillet, J. E. *Br. Polym. J.* **1982**, *14*, 159.
(9) Ng, D.; Yoshiki, K.; Guillet, J. E. *Macromolecules* **1983**, *16*, 568.
(10) Holden, D. A.; Ren, X.-X.; Guillet, J. E. *Macromolecules* **1984**, *17*, 1500.
(11) Porter, G.; Archer, M. *ISR, Interdiscip. Sci. Rev.* **1976**, *1*, 119.
(12) Cozzens, R. F.; Fox, R. B. *J. Chem. Phys.* **1969**, *50*, 1532.
(13) Fox, R. B.; Cozzens, R. F. *Macromolecules* **1969**, *2*, 181.
(14) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(15) Guillet, J. E. "Polymer Photophysics and Photochemistry"; Cambridge University Press, 1985.
(16) Merle-Aubry, L.; Holden, D. A.; Merle, Y.; Guillet, J. E. *Macromolecules* **1980**, *13*, 1138.
(17) Nakahira, T.; Shinomiya, E.; Fukumoto, T.; Iwabuchi, S.; Kojima, K. *Eur. Polym. J.* **1978**, *14*, 317.
(18) Dam, H.; Glarind, J.; Nielsen, N. *Hoppe-Seyler's Z. Physiol. Chem.* **1940**, *265*, 86.
(19) Lester, R. L.; Crane, F. L. *J. Biol. Chem.* **1959**, *234*, 2169.
(20) Morton, R. A. *Nature (London)* **1958**, *182*, 1784.
(21) Trenner, N. R.; Arison, B. H.; Erickson, R. E.; Shunk, C. H.; Wolf, D. E.; Folkers, K. *J. Am. Chem. Soc.* **1959**, *81*, 2026.
(22) Kofler, M.; Langemann, I.; Rüegg, R.; Gloor, U.; Schwieter, U.; Würsch, J.; Wiss, O.; Isler, O. *Helv. Chim. Acta* **1959**, *42* (2), 2252.
(23) Linn, B. O.; Folkers, K. *J. Am. Chem. Soc.* **1959**, *81*, 1263.
(24) Sauer, K. *Annu. Rev. Phys. Chem.* **1979**, *30*, 155.
(25) Rudman, P. *Chem. Ind. (London)* **1960**, 1356.
(26) Olaechea, P. *Rev. Fac. Cienc. Quim. Univ. Nac. La Plata* **1945**, *20*, 229.
(27) Stempel, H. Jr.; Cross, R. P.; Mariella, R. P. *J. Am. Chem. Soc.* **1950**, *72*, 2299.
(28) Izovet, G. *Ann. Chim. (Paris)* **1962**, *7*, 151.
(29) Heskins, M.; Guillet, J. E. *Macromolecules* **1970**, *3*, 224.
(30) Tomita, G.; Rabinovitch, E. *Biophys. J.* **1962**, *2*, 483.
(31) Porter, G.; Treadwell, C. J.; Searle, G. F. W.; Barber, J. *Biophys. Acta* **1978**, *501*, 232.
(32) Guillet, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20* (*1*), 395.
(33) Reference 15.
(34) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11.
(35) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.
(36) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(37) Holden, D. A.; Guillet, J. E. In "Developments in Polymer Photochemistry"; Allen, N. S., Ed.; Applied Science Publishers: Barking, 1980; Vol. 1.
(38) Naqvi, K. R. *Chem. Phys. Lett.* **1968**, *1*, 497.
(39) Lamola, A. A.; Leermakers, P. A.; Byers, G. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 2322.
(40) Nakahira, T.; Maruyama, H.; Iwabuchi, S.; Kojima, K. *J. Macromol. Sci., Chem.* **1980**, *A14*, 779.
(41) Carlson, S. A.; Hercules, D. M. *Photochem. Photobiol.* **1973**, *17*, 123.
(42) Tickle, K.; Wilkinson, F. *Trans. Faraday Soc.* **1965**, *61*, 1981.

Dilute-Solution Dynamic Viscoelastic Properties of Schizophyllan Polysaccharide[†]

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ABSTRACT: The frequency dependences of the storage and loss shear moduli, G' and G'', of dilute solutions of the three-stranded helical rodlike polysaccharide schizophyllan were measured at 25.0 °C by the Birnboim–Schrag multiple-lumped resonator. The frequency range was 100–8000 Hz and the concentration range usually 0.6–3 g/L. The solvents were water, glycerol–water mixtures, dimethyl sulfoxide (Me_2SO), and Me_2SO–water mixtures. The hybrid model previously used to interpret viscoelastic properties of solutions of semiflexible rodlike macromolecules and the Yamakawa–Yoshizaki and Hagerman–Zimm theories for relating the intrinsic viscosity $[\eta]$ and rotational relaxation time τ_0, respectively, to the persistence length q were modified to take into account a moderate degree of molecular weight heterogeneity with assumption of a Schulz–Flory distribution. Data in water and glycerol–water (in which the only function of glycerol was to increase the effective frequency range by changing solvent viscosity) could be fitted by the hybrid model with a persistence length (based on number-average molecular length) of 116 nm, as compared with 140 nm calculated from $[\eta]$. In Me_2SO, the viscoelastic data could be fitted to the Zimm theory for flexible coils as expected from evidence of Fujita and collaborators that the helix is dissociated into single strands with random coil configuration. In a water–Me_2SO mixture with water weight fraction $w_H = 0.155$, the viscoelastic properties and intrinsic viscosity could be interpreted as indicating either a slight softening of the helix in a solvent composition with water content just above the critical composition for helix dissociation or else a mixture of coils and semiflexible rods, the latter having the same partial flexibility as in pure water. In a mixture with $w_H = 0.150$, the viscoelastic properties appeared more consistent with a very soft undissociated helix.

Introduction

Schizophyllan is an extracellular polysaccharide secreted by the bacterium *Schizophyllan commune*. It consists of linear chains of β-1, 3-D-glucose residues with one β-1,6-D-glucose side chain for every three backbone chain residues.[1,2] Extensive studies of light scattering and intrinsic viscosity by Fujita and collaborators[3-5] have shown that in aqueous solution the molecule contains three linear chains wound in a rodlike triple helix. The natural product can be sonicated and fractionated to obtain samples of different molecular weights. When dissolved in dimethyl sulfoxide (Me_2SO), the helix dissociates and the individual chains assume random coil configurations.[3-5] In Me_2SO–water mixtures, with increasing Me_2SO concentration, the dissociation occurs almost discontinuously at a water weight fraction w_H of about 0.13.

Measurements of the frequency dependence of viscoelastic properties in dilute solution, extrapolated to infinite dilution, can distinguish clearly between completely rigid

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[†] This paper is dedicated to Dr. Pierre Thirion on the occasion of his retirement.

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