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Photophysics of Isomeric Poly(acetonaphthyl methacrylates), Polymers with High Yields of Long-Lived Triplet States

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ABSTRACT: Homopolymers from four isomeric acetonaphthyl methacrylates were synthesized. The polymers show no measurable fluorescence but are intensely phosphorescent in 1:1 THF/2-methyltetrahydrofuran glasses at 77 K. Triplet lifetimes at 77 K varied from 0.11 s for poly(4-aceto-1-naphthyl methacrylate) to 0.51 s for poly(1-aceto-2-naphthyl methacrylate). From analysis of the phosphorescence spectra of copolymers of 1-aceto-2-naphthyl methacrylate with 2,4-diaceto-1-naphthyl methacrylate on excitation of the donor, quantum efficiencies of triplet quenching were determined. At 1 mol % copolymerized quencher, the quantum yield of triplet quenching was 0.40. The reduction in the donor decay time with increasing mole fraction of 2,4-diaceto-1-naphthyl methacrylate established a dynamic quenching process under diffusion-free conditions. Experiments on copolymers containing 9-anthrylmethyl methacrylate traps eliminated the possibility of singlet quenching and established the involvement of triplet energy migration.

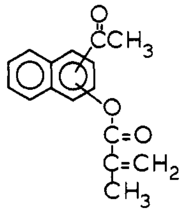
Introduction

In polymers containing high concentrations of light-absorbing groups, the separation between chromophores is so small that these chromophores interact significantly. One important form of interaction is electronic energy transfer to quenching groups,[1,2] a significant process in the degradation and stabilization of polymers. In addition such processes are under intensive study in their own right, with the two major lines of investigation being synthesis of new polymers in which the effects of energy migration are more pronounced[3,4] and theoretical modeling of energy migration and transfer in random-coil polymers.[5]

Much of the recent research has concentrated on singlet energy migration and transfer,[1,3-6] with less emphasis on the corresponding triplet processes. Among the experimental approaches to studying triplet energy migration are the investigation of delayed fluorescence resulting from triplet-triplet annihilation[7,8] and studies of the quenching of triplet states of chromophores on polymers by small molecules. Such studies may involve diffusive quenching, as in a fluid solution at room temperature,[9-15] or diffusion free quenching, as in a glass.[11,16-25] One approach that has proven particularly useful in establishing the range and mechanism of singlet energy migration and transfer involves quenching by copolymerized luminescent species.[1,6,26,27] Such an approach has not been widely used to study triplet phenomena, and this is unfortunate, because there is an enormous divergence of opinion regarding the time scale of triplet energy migration. For example, Scaiano and co-workers have concluded that in substituted poly(acrylophenones), the hopping frequency ω of the triplet excitation between chromophores may be as high as 10^{10}–10^{12} s^{-1}.[28,29] On the other hand, other authors have concluded that triplet migration is an insignificant process on the time scale of a triplet lifetime of from 10^{-7} to 10^{-6} s.[14,31] While the above experiments involve fluid solutions, similar discrepancies arise from studies on glassy solutions at low temperature.

Triplet states are generated by intersystem crossing from singlet states. In an experiment which shows enhanced quenching of the triplet, the question arises whether this is evidence for triplet migration or for migration of the singlet precursor. This question can be answered by studies on polymers containing chromophores with short-lived singlet states and very long-lived triplet states. While simple polymeric ketones such as poly(methyl vinyl ketone) and poly(acrylophenone) belong to this class, they suffer from the high photochemical reactivity of the n-π^* state. As a result, the triplet lifetime is considerably shortened and the photochemical products of the Norrish Type II reaction function as competing quenchers.

In the present publication, triplet processes were studied in new polymers from isomeric acetonaphthyl methacrylates 1 (aceto-NMA). The acetonaphthyl ester chromophore was found to have unit efficiency of $S_1 \rightarrow T_1$ intersystem crossing, a long triplet lifetime, and an unreactive π-π^* triplet state. These features make such polymers particularly well-suited to studies of triplet energy migration. Triplet migration was studied by determining the absolute efficiency of triplet quenching by copolymerized 2,4-diaceto-1-naphthyl methacrylate (2,4-diaceto-1-NMA, 2). This monomer has the advantage of a reactivity ratio very similar to 1, so that random copolymers are obtained with 1. In order to determine the role of singlet energy migration, copolymers with 9-anthrylmethyl methacrylate (9-AMMA) were also studied.



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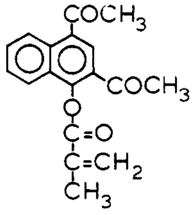

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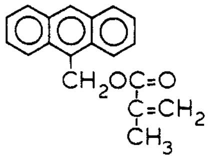

9-AMMA

Experimental Details

General. Melting points were recorded on a Fisher Mel-temp apparatus and are corrected. ^{1}H NMR spectra were recorded on a Bruker WP-80 instrument with Me_4Si as internal reference. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. All UV absorption spectra were recorded with a Cary 118 instrument. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario. Number-average molecular weights of polymers were determined with a Hewlett-Packard Model 502 membrane osmometer with dioxane or 1,2-dichloroethane as solvent. Polydispersities were estimated by size exclusion chromatography (SEC) of samples dissolved in 2-butanone, using a Waters Model 590 instrument with a Model R401 differential refractometer detector. In the case of the co-

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polymers of methyl methacrylate with 0.25–1.5% isomeric acetonaphthyl methacrylates, molecular weights were also obtained from SEC, by substituting the Mark–Houwink constants of pure poly(methyl methacrylate) for those of the copolymers.

Materials. The known compounds 2-aceto-1-naphthol, 1-aceto-2-naphthol, 4-aceto-1-naphthol, and 6-aceto-2-naphthol were prepared as described in an earlier publication.[32] These compounds were purified by a combination of vacuum distillation, multiple recrystallization, and vacuum sublimation. 9-Anthrylmethyl methacrylate was prepared following a published procedure and had mp 85–86 °C following recrystallization from methanol.[27] Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol at −10 °C. Benzene and toluene (J.T. Baker Photrex grade) were used as received. Tetrahydrofuran and 2-methyltetrahydrofuran were distilled from CuCl and then redistilled under nitrogen from $LiAlH_4$.

2,4-Diaceto-1-naphthol. To a solution of 15 g of anhydrous $ZnCl_2$ and 10 mL of acetyl chloride in 60 mL of dry $PhNO_2$ cooled to −5 °C, 10 g of 1-naphthol was added in small amounts. The mixture was allowed to warm to room temperature overnight. After addition of H_2O, the product was extracted into ether. The ether was then evaporated, and the $PhNO_2$ was distilled off at reduced pressure. The residue of product was extracted with hexanes, which removed residual $PhNO_2$ and 2-aceto-1-naphthol, and then with cold methanol, which removed a dark-brown impurity. After two recrystallizations from 125 mL of methanol, the product was sublimed in vacuo at 130 °C to give very pale-yellow crystals having mp 140–141 °C [lit.[33] mp 140 °C]: IR (Nujol) 3000 (br), 1660, 1627 cm^{-1}; NMR ($CDCl_3$) δ 2.75 (s, 3 H), 2.77 (s, 3 H), 7.57–8.99 (m, 5 aromatic ring H and 1 phenolic H).

1-Aceto-2-naphthyl Methacrylate. 1-Aceto-2-naphthol was distilled twice at reduced pressure and recrystallized twice from ACS hexanes. A solution of 5.0 g of 1-aceto-2-naphthol, 2.2 g of dry pyridine, and 0.01 g of 2,6-di-*tert*-butyl-4-methylphenol in 10 mL of dry CH_2Cl_2 was cooled to 0 °C, and 2.8 g of freshly distilled methacryloyl chloride was added gradually. The reaction mixture was diluted with 15 mL of CH_2Cl_2 and stirred at room temperature for 48 h. The large crystals of pyridinium hydrochloride were filtered off, and the solution was extracted with water and saturated NaCl solution and dried over Na_2SO_4. After the solvent was evaporated, the product was recrystallized twice from 2:1 cyclohexane–hexanes between 30 and 0 °C, and the warm solutions were treated with activated charcoal and filtered. The yield of monomer having mp 39–40.5 °C was 3.4 g: IR (Nujol) 1730, 1692, 1642 cm^{-1}; NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.60 (s, 3 H), 5.82 (s, 1 H), 6.39 (s, 1 H), 7.24–7.98 (m, 6 H); UV (CH_2Cl_2) λ_{max} 319 nm (ϵ 1310 M^{-1} cm^{-1}), 289 (5030), 282 (5350), 273 (5100), 273 (5100). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.31; H, 5.56. Other monomers were prepared similarly.

6-Aceto-2-naphthyl methacrylate: mp 99.5–100.5 °C (three recrystallizations from 1:5 benzene–hexanes); IR (Nujol) 1735, 1676, 1626 cm^{-1}; NMR ($CDCl_3$) δ 2.11 (s, 3 H), 2.72 (s, 3 H), 5.81 (s, 1 H), 6.43 (s, 1 H), 7.25–7.94 (m, 6 H); UV (THF) λ_{max} 339 nm (ϵ 1680 M^{-1} cm^{-1}), 323 (1980), 287.5 (11 230). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.57; H, 5.80.

2-Aceto-1-naphthyl methacrylate: mp 89–90 °C (recrystallized from cyclohexane); IR (Nujol) 1736, 1683, 1636 cm^{-1}; NMR ($CDCl_3$) δ 2.19 (s, 3 H), 2.63 (s, 3 H), 5.94 (s, 1 H), 6.55 (s, 1 H), 7.26–7.95 (m, 6 H); UV (THF) λ_{max} 331 nm (ϵ 1900 M^{-1} cm^{-1}), 296.5 (5950), 286.5 (7320), 250 (48 200), 242 (48 000). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.19; H, 5.69.

4-Aceto-1-naphthyl methacrylate: mp 127.5–128 °C (recrystallized from 1:8 benzene–cyclohexane); IR (Nujol) 1731, 1673, 1636 cm^{-1}; NMR ($CDCl_3$) δ 2.17 (s, 3 H), 2.75 (s, 3 H), 5.90 (s, 1 H), 6.54 (s, 1 H), 7.26–8.04 (m, 6 H); UV (THF) λ_{max} 327 nm (ϵ 5550 M^{-1}), 308 (9020), 240 sh (26 000), 225.5 (38 600). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.20; H, 5.76.

2,4-Diaceto-1-naphthyl methacrylate: mp 73.5–74 °C (recrystallization from 1:5 benzene–hexanes, followed by recrystallization from ethanol at −20 °C); IR (Nujol) 1737, 1682, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 2.65 (s, 3 H), 2.79 (s, 3 H), 5.98 (s, 1 H), 6.60 (s, 1 H), 7.25–8.86 (m, 5 H); ^{13}C NMR ($CDCl_3$) ester C=O at 164.34, 2 ketone C=O at 196.55, 200.64 ppm; UV (THF) λ_{max} 340 nm (ϵ 2960 M^{-1} cm^{-1}), 309 (11 500), 240.5 (44 200). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.56; H, 5.43.

Table I
Properties of Isomeric Poly(acetonaphthyl methacrylates)

polymer	IR C=O stretch,[a] cm^{-1}	$10^{-4}M_n$[b]
poly(1-aceto-2-NMA)	1752, 1703	12.1
poly(6-aceto-2-NMA)	1752, 1681	11.3
poly(2-aceto-1-NMA)	1754, 1696	1.2
poly(4-aceto-1-NMA)	1755, 1678	4.3

[a] Film cast on NaCl disk. [b] By membrane osmometry.

Table II
Properties of Copolymers of Isomeric Acetonaphthyl Methacrylates with Methyl Methacrylate

sample	isomer	mol % copolymer[a]	$10^{-5}M_n$	M_w/M_n[b]
1	1-aceto-2-NMA	0.51	4.8	1.94
2	6-aceto-2-NMA	0.25	5.6	1.58
3	2-aceto-1-NMA	0.44	1.8	1.74
4	4-aceto-1-NMA	1.52	12.6	1.45
5	2,4-diaceto-1-NMA	0.30	14.0	1.45

[a] By UV spectroscopy. [b] By SEC; 2-butanone solvent.

Preparation of Poly(1-aceto-2-naphthyl methacrylate). A solution of 0.93 g of 1-aceto-2-naphthyl methacrylate and 0.006 g of AIBN in 4.0 mL of toluene was degassed and sealed under high vacuum. Polymerization was carried out in a water bath at 60 °C for 6.5 h. The polymer began to precipitate after 10 min. At the end of the polymerization, the solution was cooled to 0 °C and the toluene was decanted. The polymer was dissolved in 10 mL of $CHCl_3$ and precipitated into ethanol. It was filtered, washed thoroughly with ethanol, and dried in vacuo to yield 0.65 g of a white powder, soluble in $CHCl_3$, CH_2Cl_2, DMF, pyridine, and THF and insoluble in benzene, toluene, acetone, or ethanol. The IR spectra of a film cast from $CHCl_3$ shows loss of the methacrylate C=C stretch at 1642 cm^{-1} and shift of the ester and aromatic ketone carbonyl bands to 1752 and 1703 cm^{-1}. Other homopolymers and copolymers were prepared similarly. Table I lists the properties of the four homopolymers. The isomeric poly(acetonaphthyl methacrylates) are remarkable in their tribocharging capability: they are best handled dampened with methanol, as the dry powders cannot easily be transferred or manipulated.

Copolymers were prepared by polymerization in toluene to 60% ± 5% conversion, except in experiments designed to test the effect of degree of conversion on polymer composition and luminescence properties. The compositions of copolymers with methyl methacrylate were determined by UV absorption spectroscopy by using the extinction coefficients of the monomeric acetonaphthyl methacrylates. Compositions of copolymers with 9-anthrylmethyl methacrylate were calculated based on the extinction coefficients of the corresponding homopolymers and 9-anthrylmethyl pivalate.[27] Compositions of copolymers of 1-aceto-2-NMA with 2,4-diaceto-1-NMA were determined from the extinction coefficients of poly(1-aceto-2-NMA) and 2,4-diaceto-1-NMA monomer at 282.5 and 360 nm, respectively. Allowance was made for the overlap of the absorption of 2,4-diaceto-1-NMA with that of 1-aceto-2-NMA at the lower wavelength. The properties of the copolymers prepared for use in the present luminescence study are listed in Tables II and III.

Luminescence Measurements. Fluorescence and phosphorescence spectra were recorded with a Perkin-Elmer MPF-2A spectrofluorimeter with low-temperature and phosphorescence accessories. Solutions of polymers in 1:1 THF/2-methyltetrahydrofuran (2-MeTHF) were prepared having an optical density of 0.1–0.2 in a 1-mm cell. They were transferred to 3-mm-diameter quartz tubes and deoxygenated with a stream of high-purity nitrogen before being cooled slowly to 77 K. Phosphorescence decay times were measured by leading the output from the spectrofluorimeter photomultiplier to a recording oscilloscope and cutting out the excitation beam by means of an electromechanical shutter. The lower limit of measurement of lifetimes by this technique was 30 ms. In order to minimize the possibility of distortion of the phosphorescence decay profile by triplet–triplet annihilation, the excitation slit widths were kept as narrow as possible, consistent with adequate signal-to-noise ratio.

Table III
Properties of Copolymers of Acetonaphthyl Methacrylates with Monomers Containing Quenching Chromophores

	monomer		mol % monomer 2		
sample	1	2	in feed	in copolymer[a]	$10^{-4}M_n$[b]
6	4-aceto-1-NMA	9-AMMA	1.22	1.0	3.1
7	1-aceto-2-NMA	9-AMMA	1.34	0.95	10.3
8	1-aceto-2-NMA	2,4-diaceto-1-NMA	1.15	1.0	8.4
9	1-aceto-2-NMA	2,4-diaceto-1-NMA	2.36	1.8	10.9
10	1-aceto-2-NMA	2,4-diaceto-1-NMA	4.80	3.9	11.9
11	1-aceto-2-NMA	2,4-diaceto-1-NMA	7.21	6.6	6.2
12	1-aceto-2-NMA	2,4-diaceto-1-NMA	9.74	8.7	7.5

[a] By UV spectroscopy. [b] By membrane osmometry.

Table IV
Absorption and Emission Properties of Homopolymers of Isomeric Acetonaphthyl Methacrylates

	absorption[a]	phosphoresence[b]	
polymer	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{max}, nm	τ, s
poly(1-aceto-2-NMA)	322 (sh, 750), 290 (sh, 4640), 282.5 (5050)	496, 534, 575 (sh)	0.51
poly(6-aceto-2-NMA)	340.5 (1640), 324 (sh, 1980), 289 (8500), 252 (29200), 244 (32600)	515, 546	0.29
poly(2-aceto-1-NMA)	333 (1620), 290.5 (5690), 244 (33100)	516, 555	0.31
poly(4-aceto-1-NMA)	310 (8640), 227 (30900)	518, 531, 560	0.11

[a] In CH_2Cl_2. [b] In nitrogenated 1:1 THF/2-MeTHF at 77 K.

Relative quantum efficiencies of phosphorescence were measured by comparing uncorrected spectra recorded under identical conditions of samples having the same optical density at the excitation wavelength. In this experiment, excitation bandwidths were kept narrow (2 nm) to avoid artifacts arising from differences in the absorption spectra around the excitation wavelength.

Results and Discussion

Spectroscopy of Isomeric Poly(acetonaphthyl methacrylate). Table IV lists the UV absorption maxima and extinction coefficients of the homopolymers of four isomeric acetonaphthyl methacrylates in dichloromethane. Pronounced differences in the UV spectra are observed between isomers, and these reflect the partial reinforcement or cancellation of the dipole moments of the two substituents on the naphthalene ring. For each isomer, the UV spectrum of the homopolymer is red-shifted by 1-2 nm from the corresponding monomer and has an extinction coefficient lower by 5-20%. The differences between the absorption maxima of homopolymers and copolymers with methyl methacrylate (Table V) are even smaller. Thus, the perturbation in the ground state of the acetonaphthyl ester group as a result of interactions with adjacent chromophores is small, a result consistent with other studies on naphthalene-containing polymers.[34]

Table V
Absorption and Emission Properties of Copolymers of Isomeric Acetonaphthyl Methacrylates with Methyl Methacrylate

		absorption	phosphorescence[c]	
sample	comonomer	λ_{max}, nm	λ_{max}, nm	τ, s
1	1-aceto-2-NMA	322 (sh), 290 (sh), 282[a]	485, 518, 560 (sh)	2.55
2	6-aceto-2-NMA	339, 324, 288[a]	480, 491, 515, 556 (sh)	1.04
3	2-aceto-1-NMA	332, 299 (sh), 289[b]	509, 546, 590 (sh)	0.56
4	4-aceto-1-NMA	328 (sh), 310[b]	509, 523 (sh), 549, 590 (sh)	0.18
5	2,4-diaceto-1-NMA	312, 249[b]	524, 564, 610 (sh)	0.23

[a] In CH_2Cl_2 at 25 °C. [b] In THF at 25 °C. [c] In 2-MeTHF at 77 K.

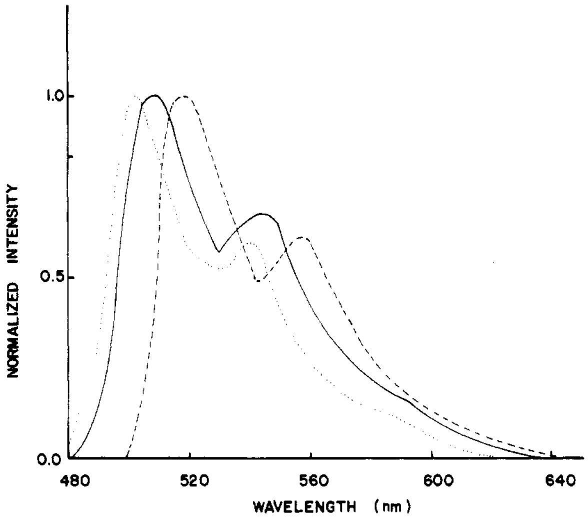

Figure 1. Phosphorescence spectra of solutions in THF/2-MeTHF glasses at 77 K: (---) poly(2-aceto-1-NMA), (—) poly(methyl methacrylate-*co*-0.44% 2-aceto-1-NMA), (···) 2-aceto-1-NMA monomer.

Homopolymers of the isomeric acetonaphthyl methacrylates show virtually no fluorescence, either in fluid solution at room temperature or in low-temperature glasses. At 77 K the phosphorescence of these polymers is intense, as shown in Figure 1. Identical spectra and lifetimes were obtained for solutions cooled slowly in liquid nitrogen or chilled rapidly in liquid propene at -185 °C. This result is significant, as it establishes that the polymers do not exist as partially precipitated collapsed coils in THF/2-MeTHF glasses at 77 K.[35] Tables IV and V compare the positions of the phosphorescence maxima of acetonaphthyl methacrylate homopolymers with those of copolymers with excess methyl methacrylate. In contrast with the absorption spectra, the phosphorescence spectra of the homopolymers are red-shifted by 7-30 nm from those of the corresponding copolymers. This result suggests substantial perturbation of the lowest triplet energy of the acetonaphthyl ester group by neighboring chromophores. The phosphorescence decays of the homopolymers and copolymers are exponential and independent of excitation intensity over a fourfold range of excitation intensities, a result which indicates the insignificance of triplet-triplet annihilation as a deactivation pathway at the low excitation intensities used. The decay times, listed in Tables IV and V, range from 0.11 to 0.51 s for the homopolymers and are somewhat longer for the isolated chromophores in methyl methacrylate copolymers. This

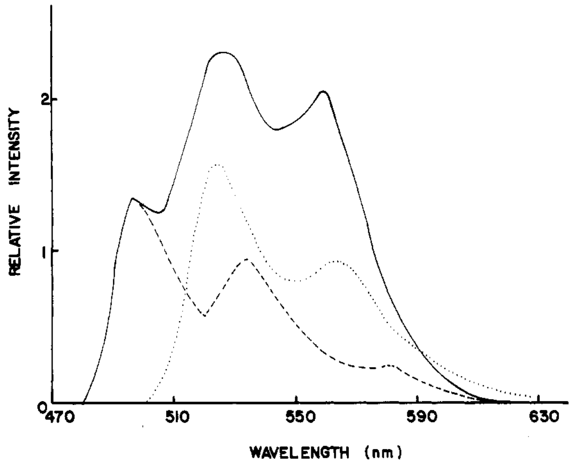

Figure 2. Phosphorescence spectrum of poly(1-aceto-2-NMA-*co*-3.9% 2,4-diaceto-1-NMA) in THF/2-MeTHF glass at 77 K: (—) Excitation at 282 nm, (···) excitation at 330 nm. Also shown is the separation of the spectrum into components of donor and acceptor emission.

shortening of decay times in going from copolymer to homopolymer is further evidence for perturbation of the triplet state by neighboring groups in the homopolymer. While it may reflect a self-quenching process, such self-quenching would have to be exceedingly inefficient; otherwise, the high triplet mobility in the homopolymers, to be discussed later, would result in much larger differences between the phosphorescence decay times of each copolymer and the corresponding homopolymer. The shorter decay times in the homopolymers do not arise solely from quenching by copolymerized impurities because the decay times of the monomers are much closer to those of the homopolymers than they are to the copolymer lifetimes. The decay times listed in Tables IV and V may be compared with phosphorescence lifetimes of 0.7 and 1.15 to 1.7 s for homopolymers of 1- and 2-naphthyl methacrylate.[27,36] These results show that while the aceto substituent increases the rate of $S_1 \rightarrow T_1$ intersystem crossing by at least 2 orders of magnitude, it has a much smaller effect on the rate of $T_1 \rightarrow S_0$ intersystem crossing. This behavior is typical of π–π^* triplet states, where the excitation resides primarily on the aromatic ring.[37]

Studies of Triplet Energy Migration and Transfer. Of the four acetonaphthyl methacrylates, the 1-aceto-2-naphthyl isomer was selected for studies of intramolecular quenching for several reasons, the most important being that its absorption and phosphorescence spectra are significantly different from those of the acceptor 2,4-diaceto-1-naphthyl methacrylate. In addition, its phosphorescence decay time is long, so that the effects of triplet energy migration would be expected to be more pronounced. In copolymers of 1-aceto-2-NMA with 2,4-diaceto-1-NMA, the phosphorescence spectrum on excitation at the maximum absorption wavelength of the donor shows overlapping emission bands of both chromophores, as illustrated in Figure 2. Direct excitation of the acceptor at 340 nm gives the same spectrum as a copolymer of 2,4-diaceto-1-NMA with methyl methacrylate. As the mole fraction of 2,4-diaceto-1-NMA in the copolymers increases, the relative intensity of the acceptor emission increases and becomes dominant.

Resolution of the spectra into the two components was achieved by using the spectra of the 2-aceto-1-NMA homopolymer and copolymerized 2,4-diaceto-1-NMA on direct excitation. The 496-nm band in Figure 2 arises solely from donor phosphorescence. While the relative intensity of acceptor phosphorescence is moderate at low acceptor mole fractions, this is deceptive, as the phosphorescence quantum yield of the acceptor is only about one-third that of the donor. Quantum yields of energy transfer were determined by using eq 1[27] where I_D and I_A are the uncor-

$$\frac{\phi_{DA}}{1 - \phi_{DA}} = \frac{I_A}{I_D}\frac{\phi_D}{\phi_A} \tag{1}$$

rected intensities of the donor and acceptor phosphorescence. The ratio $\phi_D/\phi_A = 3.27$ of the phosphorescence quantum yields of the donor and acceptor was obtained from measurement of the relative intensities of the phosphorescence of poly(1-aceto-2-naphthyl methacrylate) and poly(methyl methacrylate-*co*-0.30% 2,4-diaceto-1-NMA) samples having identical optical density at the excitation wavelength. The value of this ratio is also uncorrected for the wavelength dependence of the photomultiplier detector. The use of the methyl methacrylate copolymer with 2,4-diaceto-1-NMA as a "model compound" for copolymerized 2,4-diaceto-1-NMA surrounded by 1-aceto-2-NMA chromophores is a necessary approximation. One can expect the difference in ϕ_A between the two copolymers to correspond to the differences in the acceptor phosphorescence lifetimes. These are 0.23 s for the methyl methacrylate copolymer and 0.20 s for the 1-aceto-2-NMA copolymer, so that this approximation may result in an error in ϕ_A of 15%.

Table VI
Variation of Quantum Efficiency, ϕ_{DA}, of Triplet Energy Transfer and Donor Phosphorescence Decay Time, τ, with Trap Concentration in Copolymers of 1-Aceto-2-NMA with 2,4-Diaceto-1-NMA[a]

mol % 2,4-diaceto-1-NMA in copolymer	ϕ_{DA}	donor τ,[b] s
0		0.51
1.0	0.40	0.47
1.8	0.62	0.34
3.9	0.85	
6.6	0.88	0.25[c]
8.7	0.91	0.20

[a] Samples in 1:1 THF/2-MeTHF glasses at 77 K. [b] Measured at 496 nm. [c] In this sample, the acceptor τ is 0.20 s at 524 nm, following direct excitation at 330 nm.

Table VI shows the variation of ϕ_{DA} with copolymer composition. On excitation of these samples at 282 nm, the amount of direct excitation of the acceptor is too small to account for the observed values of ϕ_{DA}, since it contributes only about 6% to the trap phosphorescence intensity at the highest acceptor mole fraction. The data in Table VI show that while ϕ_{DA} is high at 1% acceptor, increasing the acceptor concentration increases ϕ_{DA} by decreasing amounts. Such behavior is typical for polymers with copolymerized traps and is attributed to the overlap of quenched regions which occurs in statistical copolymers.[27] The effect does not arise in the present system from the presence of a statistical fraction of polymer chains which do not contain any copolymerized traps. As proof of this, Table III shows that these copolymers all have number-average degrees of polymerization of over 300, so that the fraction of unlabeled chains is very small for all but the lowest concentrations of quenchers. Although conversions were typically 60%, the two monomers have almost identical reactivity, so that there is no depletion of 2,4-diaceto-1-NMA during the copolymerization and the samples do not contain unlabeled poly(1-aceto-2-NMA) formed in the later stages of polymerization. Additional copolymer samples were prepared at much lower degrees of conversion. Table VII summarizes the phosphorescence

Table VII
Effect of Conversion on Composition and Efficiency of Triplet Quenching in Copolymers of 1-Aceto-2-NMA with 2,4-Diaceto-1-NMA

mol % 2,4-diaceto-1-NMA			
in feed	in copolymer	conversion, %	ϕ_{DA}[a]
5.3	3.9	10	0.80
5.2	4.5	29	0.81
4.8	3.9	65	0.85

[a] In 1:1 THF/2-MeTHF at 77 K.

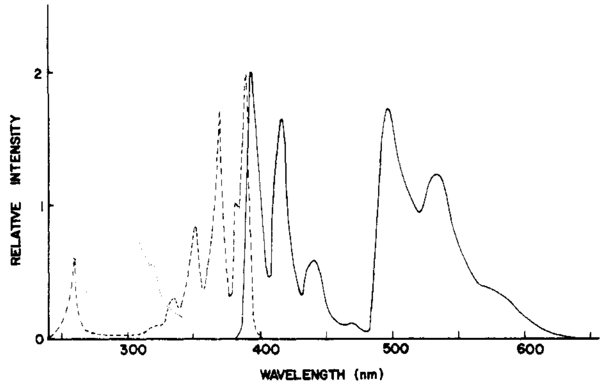

Figure 3. (—) Total emission spectrum of poly(1-aceto-2-NMA-*co*-1.0% 9-AMMA) in THF/2-MeTHF glass at 77 K on 300-nm excitation. (- - -) Excitation spectrum viewed at 416 nm. (···) Excitation spectrum viewed at 500 nm.

data for three samples of similar composition but taken to very different conversions. The values of ϕ_{DA} for the samples are nearly identical, a result which eliminates composition drift in this copolymer system as a significant factor in triplet behavior.

Once the efficiency of triplet quenching by a copolymerized acceptor has been established, the question of the roles of singlet and triplet energy migration must be settled. To do this, copolymers of the singlet quencher 9-anthrylmethyl methacrylate were prepared. Figure 3 shows that the total emission spectrum of a 1-aceto-2-NMA copolymer containing 1% 9-AMMA contains both anthracene fluorescence and acetonaphthyl ester phosphorescence on excitation at the absorption maximum of the naphthalene chromophore. That the anthracene fluorescence arises from direct excitation of anthracene is revealed by the excitation spectra. The excitation spectra of naphthalene phosphorescence and anthracene fluorescence are completely different and correspond to the absorption spectra of the two chromophores. The absence in the anthracene excitation spectrum of a component of acetonaphthyl ester absorption shows that the singlet excited state of the acetonaphthyl donor is too short-lived to allow significant singlet quenching by the anthracene acceptor. As a result, phosphorescence quenching by 2,4-diaceto-1-NMA can only occur by triplet energy migration and transfer. Figure 4 illustrates the two possible quenching mechanisms in an energy diagram. The energy-transfer pathway ruled out by the experiment with the fluorescent singlet quencher 9-AMMA is shown as a dashed line.

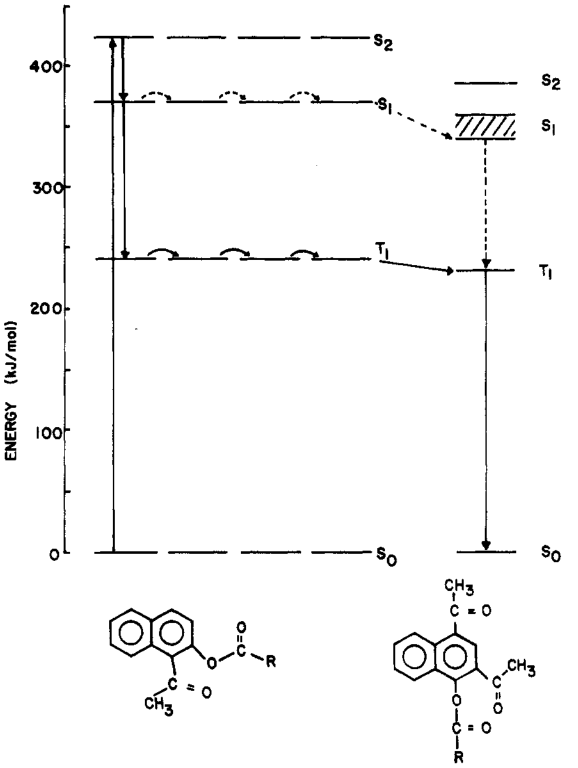

Figure 4. Energy level diagram for poly(1-aceto-2-NMA-*co*-2,4-diaceto-1-NMA): (—) proposed quenching pathway, (- - -) alternative singlet quenching pathway ruled out by experiments on anthracene-containing copolymers.

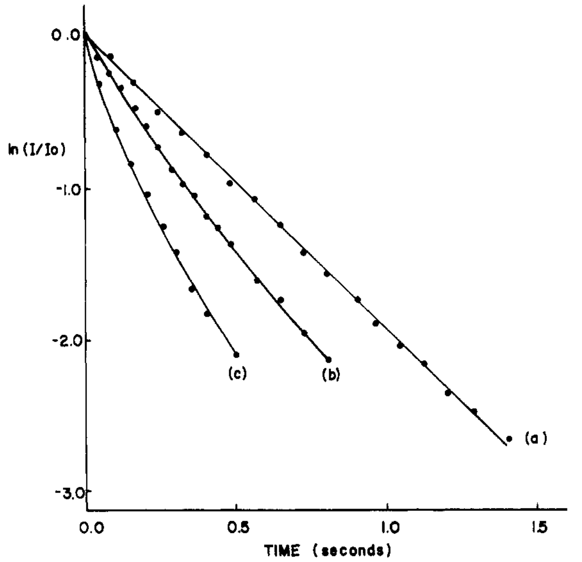

Figure 5. Donor phosphorescence decays at 496 nm on 282-nm excitation of poly(1-aceto-2-NMA-*co*-2,4-diaceto-1-NMA) samples in THF/2-MeTHF at 77 K: (a) homopolymer, (b) 1.8% 2,4-diaceto-1-NMA, (c) 8.7% 2,4-diaceto-1-NMA.

The phosphorescence decays of copolymers of 1-aceto-2-NMA with 2,4-aceto-1-NMA are wavelength-dependent. At 524 nm the emission is a superposition of the phosphorescence spectra of the two chromophores. The phosphorescence decays are therefore nonexponential at this wavelength, and the initial decay rate corresponds to the 0.20-s lifetime of the acceptor. Figure 5 shows phosphorescence decays observed at 496 nm, a region where only the donor emits. With increasing 2,4-diaceto-1-NMA content, the donor decay time shortens, as shown by the 1/*e* decay times listed in Table VI. Thus, while the relationship between decay time and quenching efficiency does not correspond to a homogeneous quenching process (eq 2, where τ_0 is the donor decay time in the absence of

$$\tau/\tau_0 = 1 - \phi_{DA} \qquad (2)$$

quencher), the shortening of the phosphorescence decay time nevertheless establishes a dynamic quenching process. This conclusion that the ensemble of triplets is mobile but

Table VIII
Triplet Migration Rates Expressed as Hopping Frequencies, ω, for Polymers in Low-Temperature Glasses

polymer	quencher	ω, s^{-1}	ref
poly(1-aceto-2-NMA)	copolymerized 2,4-diaceto-1-NMA	4×10^3	this work
poly(1-vinylnaphthalene)	1,3-pentadiene	128	20
poly(acenaphthylene)	1,3-pentadiene	128	20
poly(2-vinylnaphthalene)	1,3-pentadiene	58–183[a]	24
poly(1-NMA)	1,3-pentadiene	300	22
poly(styrene-*co*-4-vinylbenzophenone) film	naphthalene	7×10^4	17

[a] Varies with molecular weight.

decays inhomogeneously is in agreement with Pasch et al.'s study on the quenching of poly(2-vinylnaphthalene) phosphorescence and delayed fluorescence by piperylene.[24] Similar conclusions have been reached by other authors from studies of the relative decay rates of phosphorescence and delayed fluorescence in polymers.[7] A proposal for the origin of an inhomogeneous triplet population is that the excitation can remain for a much longer than average time on a donor chromophore a higher than average distance from its neighbors or on a chromophore which is lower in energy by virtue of some especially favorable alignment with its neighbors. This concept of shallow traps is familiar from studies of triplet migration in organic crystals.[7,8]

With several simplifying assumptions, it is possible to calculate a value for the rate of an individual transfer step between donor chromophores from the quenching data listed in Table VI. The final triplet transfer to the 2,4-diaceto-1-NMA acceptor occurs by a short-range interaction[38] with a characteristic interaction distance of 1.0–1.1 nm. This one-step transfer is therefore capable of deactivating only the three or four nearest-neighbor donor chromophores, so that the contribution from triplet energy migration is dominant. If one defines n as the average number of donors quenched per acceptor, then n is given by

$$n = \lim_{f \to 0} \phi_{DA}/f \qquad (3)$$

where f is the mole fraction of 2,4-diaceto-1-NMA in the copolymer. Extrapolation of the data of Table VI to $f = 0$ gives $n = 48 \pm 2$. If one inverts eq 3 and instead extrapolates a plot of $(f/\phi_{DA})^{1/2}$ vs. f to $f = 0$, the intercept gives a value of $n = 52 \pm 5$. The latter plot has the advantage of being almost linear out to much higher values of f. Allowing for the possibility of one-step transfer from the four nearest-neighbor donor chromophores, the mean displacement n of the triplet excitation in poly(1-aceto-2-NMA) is 45 donor chromophores in the limit of zero quencher concentration. If triplet energy migration is represented as a random-walk process, then eq 4 holds for

$$\omega = n^2/\tau_0 \qquad (4)$$

ω, the average transfer frequency between donor chromophores. For poly(1-aceto-2-naphthyl methacrylate) in THF/2-methyltetrahydrofuran glasses at 77 K, $\omega = 4 \times 10^3$ s^{-1}. This value is compared in Table VIII with literature values obtained for other polymers from analysis of phosphorescence quenching by small molecules. The value of ω for poly(1-aceto-2-NMA) falls between those obtained from quenching studies on naphthalene-containing polymers, and those inferred from the effects of molecular weight on the intensity of delayed fluorescence in naphthalene-containing polymers.[36,39] Together these results establish significant mobility of the triplet excitation under conditions where the triplet lifetime is long. In order for triplet migration to extend over many chromophores in fluid solution at room temperature, however, where rapid internal conversion and photochemical reaction decrease triplet lifetimes by a factor of 10^6–10^7 from their 77 K values, triplet migration would require a remarkably large temperature coefficient.

Conclusions

The photophysics of polymers from isomeric acetonaphthyl methacrylates is determined by the properties of their long-lived π–π^* lowest triplet states. Poly(1-aceto-2-naphthyl methacrylate) displays a significant triplet antenna effect at low temperature, where its T_1 lifetime approaches the limiting value for the acetonaphthyl ester chromophore. This research confirms that polymers containing copolymerized luminescent quenchers can be valuable probes of triplet energy migration and transfer, just as they have proven useful probes of the corresponding singlet processes.

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References and Notes

(1) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, UK, 1985.
(2) *Polymer Photophysics*, Phillips, D., Ed.; Chapman and Hall: London, 1985.
(3) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 1741.
(4) Ren, X. X.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2012.
(5) For a list of references to recent work by several authors, see: Holden, D. A.; Safarzadeh-Amiri, A.; Jordan, K. *Macromolecules* **1986**, *19*, 895.
(6) Ng, D.; Guillet, J. E. *Macromolecules* **1982**, *15*, 724.
(7) Klöpffer, W. *Spectrosc. Lett.* **1978**, *11*, 863.
(8) MacCallum, J. R. *Chem. Soc. (London), Ann. Rep. A* **1978**, 99.
(9) Faure, J.; Fouassier, J. P.; Lougnot, D. J.; Salvin, R. *Eur. Polym. J.* **1977**, *13*, 891.
(10) Salvin, R.; Meybeck, J.; Faure, J. *Makromol. Chem.* **1977**, *178*, 2275.
(11) Turro, N. J.; Kochevar, I. E.; Noguchi, Y.; Chow, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 3170.
(12) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815.
(13) Kilp, T.; Guillet, J. E. *Macromolecules* **1981**, *14*, 1680.
(14) Pratte, J. F.; Noyes, W. A., Jr.; Webber, S. E. *Polym. Photochem.* **1981**, *1*, 3.
(15) Scaiano, J. C.; Lissi, E. A.; Stewart, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 1539.
(16) Eisinger, J.; Schulman, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 1387.
(17) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 537.
(18) Cozzens, R. F.; Fox, R. B. *J. Chem. Phys.* **1969**, *50*, 1532.
(19) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 1405.
(20) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 417.
(21) Szerenyi, P.; Dearman, H. H. *J. Chem. Phys.* **1973**, *58*, 2467.
(22) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(23) Dan, E.; Somersall, A. C.; Guillet, J. E. *Macromolecules*, **1973**, *6*, 228.
(24) Pasch, N. F.; McKenzie, R. E.; Webber, S. E. *Macromolecules* **1978**, *11*, 733.
(25) Webber, S. E.; Avots-Avotins, P. E. *Macromolecules* **1979**, *12*, 708.
(26) Aspler, J. S.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1979**, *11*, 925.
(27) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.
(28) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 1167.
(29) Scaiano, J. C.; Selwyn, J. C. *Macromolecules* **1981**, *14*, 1723.

(30) Urruti, E.; Kilp, T. *Macromolecules* **1984**, *17*, 50.
(31) Sanchez, G.; Knoesel, R.; Weill, G. *Eur. Polym. J.* **1978**, *14*, 485.
(32) Merle-Aubry, L.; Holden, D. A.; Merle, Y.; Guillet, J. E. *Macromolecules* **1980**, *13*, 1138.
(33) Witt, O. N.; Braun, O. *Ber. Deutsch. Chem. Ges.* **1914**, *47*, 3216.
(34) Frank, C. W.; Semerak, S. N. *Adv. Polym. Sci.* **1984**, *54*, 31.
(35) Winnik, M. A.; Pekcan, O. *Macromolecules* **1983**, *16*, 1021.
(36) Pasch, N. F.; Webber, S. E. *Macromolecules* **1978**, *11*, 727.
(37) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.
(38) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
(39) Pasch, N. F.; Webber, S. E. *Chem. Phys.* **1976**, *16*, 361.

Poly(*N*-methylpyrrolylium) Poly(styrenesulfonate). A Conductive, Electrically Switchable Cation Exchanger That Cathodically Binds and Anodically Releases Dopamine

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ABSTRACT: A poly(*N*-methylpyrrolylium) poly(styrenesulfonate) composite was prepared by the anodic polymerization of *N*-methylpyrrole from an aqueous sodium poly(styrenesulfonate) solution. It was characterized by X-ray photoelectron spectroscopy, IR, electron microscopy, and combustion analysis. The polymer was conductive and had electrochemical properties superficially similar to those of poly(*N*-methylpyrrolylium) perchlorate. The polymer could be reduced at −0.4 V vs. SCE in aqueous NaCl, and it was shown that this process incorporated sodium ions. It was shown that reduction of the film in aqueous solutions of dopamine gave dopamine binding. The bound dopamine could be released by stepping the polymer film potential to +0.5 V.

Previous studies have shown that the properties of redox polymer films can be substantially changed by switching the film from one oxidation state to another. If the film is in an electrolyte solution and it is switched electrochemically, the process can be considered to be electrical switching of the film properties.[1] One property that will change during the redox process is the ability to bind ions. The change in the net charge on the redox polymer during reaction requires ions to flow into or out of the film and this allows the polymer film to bind and expel ions in response to the electrical signal. A particular application of interest is drug delivery, where control of the current would allow one to control the amount of ionic drug that was released from a polymer film on an electrode. This idea has, indeed, been reduced to practice for the binding and release of anions from the conducting polymers polypyrrole[2] and poly(3-methoxythiophene).[3] Conducting polymers are of particular interest because they can have a high density of redox states and their high conductivity can allow relatively thick films to be promptly switched. These factors can in principle allow binding and prompt release of relatively large quantities of the ion of interest. As an example,[2,4] a polymer film has been anodically synthesized which is composed of oxidized, cationic poly(pyrrolylium) that contains $Fe(CN)_6^{3-}$ to balance the charge. When this film (on a carbon electrode) is placed in aqueous NaCl solution the $Fe(CN)_6^{3-,4-}$ species remain strongly bound in the film unless the potential of the film is made as negative as −0.5 V. At −0.5 V $Fe(CN)_6^{4-}$ is flushed out. If the electrode potential is sequentially pulsed to −0.4 V for short times, each pulse gives release, providing increasing amounts of ferrocyanide. Thus, release can be controlled in time.

In the present study we set out to develop a new conducting polymer, which would act as a *cation* binder and releaser. Success was achieved by preparing a conducting, composite polymer, poly(*N*-methylpyrrolylium) poly(styrenesulfonate) (PMP^+PSS^-). Each component of this material was attractive for our purpose. The poly(styrenesulfonate) was expected to be strongly bound in the film and chemically inert. On the basis of literature reports of poly(*N*-methylpyrrolylium) "doped" with small anions, this polymer's electrochemical properties were appropriate, and considering the redox potentials, we expected reduced poly(*N*-methylpyrrole) to be somewhat more stable than polypyrrole in air. Importantly, a patent on poly(pyrrolylium) poly(styrenesulfonate)[6] reported reasonable stability and high conductivity for dry films. No electrochemical studies were reported.

For our drug delivery experiments, protonated dopamine was the ion of choice. Because it is a protonated amine, the binding and release of dopamine serve as a model for an extremely large class of pharmaceutically important amine and alkaloid compounds. Dopamine is a neurotransmitter and is itself of biological and medicinal interest. Furthermore, because we had previous experience with dopamine electrochemistry, this was a sensible starting point for a new venture. Previously, only two studies have described cation binding and release from electrodes. In one, several papers[8] from this laboratory described a method for covalently binding molecules (charged or neutral) into a polymer film and releasing them by cathodically cleaving the covalent bond. Dopamine was one of the molecules released that way. The other approach by Martin and co-workers[9] described cation binding and release from a poly(vinylferrocene) terpolymer based on principles very similar to those described here. The released cation was $Ru(NH_3)_6^{3+}$.

Experimental Section

Commercial samples were used without purification except for *N*-methylpyrrole, which was vacuum distilled at 30–40 mmHg. It was stored under argon in the dark, and samples were removed through a septum. The sodium poly(styrenesulfonate) (100% sulfonated) from Aldrich Chemical Co. was used except where noted. Its MW was determined as 100 000 (intrinsic viscosity). The 50% and 100% sulfonated, 500 000 MW PSS^-Na^+ was from Polysciences.

Electrochemical experiments were carried out with a Princeton

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