$\times 10^{-8}$ and J_s(sucrose) = 3.77×10^{-10} mol cm^{-2} s^{-1}. Note here that the value of J_s(NaCl) is several hundred times that of a conventional ion-exchange membrane. The ratio of J_s(NaCl) to J_s(sucrose) is 70.4.[10] This high value of solute flux ratio also cannot be attained by the conventional ion-exchange and semipermeable membranes.

Concluding Remarks

It has been shown that a charge-mosaic membrane can be prepared by introducing cationic and anionic groups in a cross-linked two-phase polymer system with a modulated structure. The high level of salt permeability J_s of the membrane is of interest. It is close to that of the membrane from a block copolymer.[4,5] According to theory,[1] the larger (periodic) distance between cationic and anionic elements induces a higher resistivity to current flow, resulting in a lower J_s. The periodic distance in our membrane from a polymer blend is 1.8 μm, while that in the membrane from a block copolymer is on the order of several hundred angstroms. Despite the large difference in the periodic distance, both membranes show comparable J_s values. We believe that the high J_s in our membrane originates from the co-continuous nature of the modulated structure: both elements penetrate from one surface to the other.

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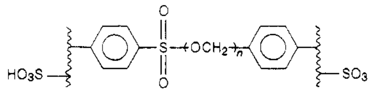
(8) TMDA is expected to elevate the cross-link density through interchain quaternization.
(9) Paraformaldehyde is added to elevate the cross-link density via the structure



(10) It has recently been found that a charge-mosaic membrane with J_s(NaCl)/J_s(sucrose) = 350 could be obtained by increasing the cross-link density.

Photophysics of Alternating Copolymers of Acenaphthylene and Methacrylic Acid and Maleic Acid

Fenglian Bai[†] **and S. E. Webber***

Department of Chemistry and Center for Polymer Research, University of Texas at Austin, Austin, Texas 78712.
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ABSTRACT: Copolymers of acenaphthylene and methacrylic acid or maleic acid were prepared, along with methoxy or ethoxy esters. On the basis of the method of preparation, these polymers are believed to be substantially alternating. All these systems display stronger excimer fluorescence in organic solvents than the corresponding 2-vinylnaphthalene polymers. While the excimer fluorescence decay shows a distinct buildup at early times, the rate of this buildup tends to be faster than the decay of the monomer precursor state. This implies that a significant fraction of excimers are formed by a very rapid (static) process. For PAcN-*alt*-MA (methacrylic acid) ca. 1 mol % of anthracene was covalently attached to the polymer to act as a long-range energy trap (Förster $R_0 \simeq 24$ Å). Sensitization of the anthracene via naphthalene excitation was reasonably efficient (ca. 30%) as measured from steady-state spectra and the shortening of the naphthalene fluorescence lifetime in the anthracene doped polymer. Fluorescence quenching by CCl_4 in organic solvents implied that there is essentially no energy transfer down the chain. In aqueous solutions (pH ≥ 7) excimer fluorescence dominated the steady-state spectrum and all fluorescence lifetimes were shortened. Fluorescence quenching effected by Cu^{2+} was quite efficient and operates primarily as a static process (the fluorescence lifetimes are changed only slightly). It is proposed that this high quenching rate is the joint result of electrostatic attraction of Cu^{2+} for the polyanion and energy migration between naphthalene groups that have collapsed into a micellar type structure. This structure also enhances excimer trapping of the singlet state.

Introduction

The photophysics and photochemistry of polymers has been the subject of several recent books and/or symposia recently.[1] One interesting class of polymers that has been the subject of only a few publications are alternating polymers. Those containing alternating hydrophilic–hydrophobic groups are amphiphilic and have very different properties in aqueous solution than random copolymers with the same pendent groups. A structural model for these polymers in water has not yet been proposed to our knowledge.

This paper describes fluorescence experiments on two members of this class containing the acenaphthylene chromophore. The polymer based on methacrylic acid and maleic acid respectively are denoted PAcN-*alt*-MA and PAcN-*alt*-MAA. There exists earlier work published for

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[†] Permanent address: Institute of Chemistry, Academia Sinica, Beijing, China.

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2-vinylnaphthalene chromophores with the same acid groups,[2-4] which allows one to compare the effect of rotational flexibility of the pendent chromophore on the photophysics. Qualitatively the results for the two naphthalenic polymers are comparable: (1) excimer fluorescence is more important in water than organic solvents; (2) maleic acid based polymers show more excimer formation than those of methacrylic acid; (3) fluorescence quenching by Cu^{2+} is extremely efficient, in part because of binding to the polymer, but also because of singlet energy migration along the coil. Acenaphthylene (AcN) alternating polymers differ from 2-vinylnaphthalene (2VN) in the following: (1) in organic solution the apparent energy migration rate is approximately zero for AcN while for P2VN-*alt*-MA this is not the case; (2) excimer formation is more important for AcN polymers than 2VN, especially for P2VN-*alt*-MA compared to PAcN-*alt*-MA; (3) the efficiency of sensitization of covalently bound anthracene is approximately 1.7 as large in P2VN-*alt*-MA-*co*-Anth (1%) than PAcN-*alt*-MA-*co*-Anth (1%) (50% and 30%, respectively) which we ascribe to the reduced importance of down-chain electronic energy transfer in the latter polymer.

No clear relationship has been found between chemical structure and photophysical properties for these naphthalenic polymers. In fact, it is surprising that AcN is more able to form excimers than 2VN, although this is suggested by the earlier work of Wang and Morawetz.[5] The kinds of structures formed by these polymers in aqueous solution is at present an open question. However, as a purely experimental observation, these systems demonstrate how one may construct polymers that have extremely efficient "photon harvesting" properties as measured by sensitized fluorescence and fluorescence quenching.

Experimental Section

(a) Preparation of Polymers. Alternating copolymers of methacrylic acid and acenaphthylene (PAcN-*alt*-MA) were prepared similarly to our earlier work on alternating copolymers of 2-vinylnaphthalene and methacrylic acid.[6] Acenaphthylene (Aldrich) was puried by recrystallization from methanol. The complex between ethylaluminum sesquichloride (8.4×10^{-3} mol) and trimethylsilyl methacrylate (8.4×10^{-3} mol (both from Aldrich)) was prepared at 0 °C under carefully anhydrous conditions in toluene (4 mL). A solution of acenaphthylene (4.2×10^{-3} mol) in toluene (M) was added slowly by injection through a septum and the reaction mixture allowed to react for 6 h at 0 °C. The reaction was quenched by addition to methanol/HCl, which produced the acid by hydrolysis of the silane. The polymer was purified by reprecipitation three times. In this procedure a THF solution of the polymer was added to a large excess of methanol with vigorous stirring.

The copolymer of acenaphthylene (AcN) and maleic anhydride (MAn) (PAcN-*alt*-MAn) was obtained by AIBN (recrystallized from ether) initiated polymerization in dioxane at 70 °C for 24 h. Amounts of each were as follows: AcN, 2.6×10^{-3} mol; MAn, 1.3×10^{-2} mol; AIBN, 0.5 mol %. The polymer was hydrolyzed to the acid (PAcN-*alt*-MAA) by reacting with $NaOH/H_2O$ (10%) under reflux for 10 h and then HCl was added to acidify the solution, followed by reefluxing for another 2 h. Reprecipitation (3X) was effected by addition of H_2O to a methanol solution of the polymer.

For NMR and GPC characterization PAcN-*alt*-MA was esterified by reaction with diazomethane (produced in a reactor by addition of concentrated $NaOH/H_2O$ (50%) to *N*-methyl-*N*-nitro-*N*-nitrosoquanidine (MNNG)). The ester of the maleic anhydride polymer was prepared by refluxing a THF solution of PAcN-*alt*-MAn with a molar excess of absolute ethanol with a small amount of concentrated H_2SO_4 (ca. 12 h). This polymer was precipitated by addition of H_2O, washed several times, and then dried at room temperature under vacuum. The NMR of this polymer was consistent with a monoethoxy ester; i.e., for each diacid group only one is esterified. However, uncertainty as to the completeness of esterification prevents an accurate determination of AcN mole fraction. These esters were also used in photophysical experiments to be described later, for comparison of the effect of the replacement of the acid proton by an alkyl group. These polymers will be denoted PAcN-*alt*-MMA and PAcN-*alt*-MAE, respectively.

The GPC traces of PAcN-*alt*-MMA showed a single peak with an average molecular weight of ca. 50 000 and polydispersity of ca. 2 (determined from a polystyrene-based calibration curve and Waters 10^3–10^5 Å^3 μstyragel columns, mobile phase THF). (GPC traces of the acid are broader and skewed to higher elution volumes, implying some interaction with the column material). The mole fraction of AcN was determined by UV absorption spectroscopy (~0.55) and the ^1H NMR relative areas of aromatic to aliphatic protons (~0.45 ± 0.02). Because the extinction coefficient of the naphthalene moiety may be perturbed in the polymer environment, the confidence level of the NMR results is higher. Since maleic anhydride does not polymerize with itself, one would expect that any nonalternation would manifest a mole percent of naphthalene greater than 50%.[7]

The solubility properties of the polyacids and polyesters were completely different, as would be expected. PAcN-*alt*-MA was soluble in THF, methanol, and (with care) basic H_2O. PAcN-*alt*-MAA was soluble in methanol and was more readily soluble in basic H_2O but was not soluble in THF. Both esters were readily soluble in THF or toluene.

As with our earlier studies on P2VN-*alt*-MA, aqueous solutions were prepared by adding a DMF stock solution to rapid stirred basic H_2O (pH ~10). The pH was then lowered (if desired) by dropwise addition of HCl. The highest concentration of PAcN-*alt*-MA and PAcN-*alt*-MAA that could be achieved at pH ~8 was 4×10^{-5} M in naphthalene moiety for both. The former was particularly unstable in aqueous solution with obvious aggregation in several days.

Anthryl-tagged polymers were prepared by direct reaction of 9-anthrylmethanol with the polyacid (heating 40:3:3 (v/v) $THF/CHCl_3$/acetone solution with small amount of H_2SO_4 added under reflux with removal of H_2O by distillation). The maximum mole fraction of anthryl group (ca. 1%) was similar to the previously studied P2VN-*alt*-MA-*co*-Anth system and may be limited by steric hindrance or the extent of nonalternation (i.e., attachment might occur at neighboring methacrylic acid groups).

Model polymers were prepared by either free radical reaction of acenaphthylene, styrene, and methacrylic acid or maleic acid. The composition of the former is styrene (24 mol %) and AcN (0.4 mol %) and the latter styrene (22 mol %) and AcN (0.4 mol %). Inclusion of styrene in the model was thought advisable to make the local polarity of the model more like the alternating copolymer. Certainly these model polymers displayed no excimer fluorescence although the fluorescence decay was not strictly monoexponential (see later).

(b) Fluorescence Methods. All steady-state fluorescence studies were carried out on a SPEX Fluorolog 2 with a 450W xenon lamp and a cooled Hammamatsu R508 photomultiplier. All spectra presented are uncorrected. Solutions were bubbled with N_2 unless stated otherwise.

The fluorescence decay was measured by using a synch-pumped, cavity-dumped dye laser pumped by a Nd:YAG mode-locked laser. This produces an instrumental response function of about 400-ps width. In some cases the fluorescence decay was analyzed by reconvolution of a multiexponential decay function with the instrumental response function using a nonlinear least-squares method.[8] The weighted residual vs. time was also examined to ascertain if deviations of the fit were random. In cases in which the time dependence over a wide range of time scales was thought to be of special interest a best fit to both time scales was obtained simultaneously. An example of this type of "global" fit is presented in the Results.

Results

(a) Steady-State and Time-Dependent Fluorescence in Organic Solvents. Because acenaphthylene is covalently bound to the polymer backbone at two positions on the aromatic system, no rotation of naphthalene moieties

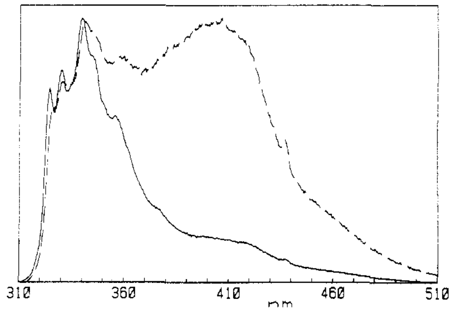

Figure 1. Fluorescence of PAcN-*alt*-MMA (—) and PAcN-*alt*-MAE (- - -) (THF, N_2 bubbled).

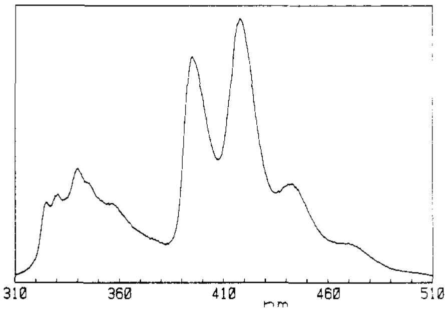

Figure 2. Fluorescence of PAcN-*alt*-MA-*co*-Anth (1.1%) excited at 294 nm (THF, N_2 bubbled).

Table I
Fluorescence Decay Parameters of Alternating Copolymers in THF

polymer	τ_i/a_i 340 nm	τ_i/a_i 400 nm
PAcN-*alt*-MAE	4.0/0.08[a] 13.3/0.92	4.6/−0.47[a] 23.5/1.00
PAcN-*alt*-MMA	11.4/0.362[b] 17.7/0.638	3.4/−0.660[b] 25.4/1.000
PAcN-*alt*-MA	12.6/0.493[b] 18.5/0.507	2.3/−0.632[b,c] 25.0/1.000
PAcN-alt-MA-*co*-Anth (1.1%)	4.6/0.490[b] 15.4/0.510	0.8/−0.778[b] 7.9/1.000 19.6/.084
P2VN-*alt*-MA[d]	3.2/0.218 2.2/0.047 56.2/0.735	*e*
P2VN-*alt*-MA-*co*-Anth (1.2%)[d]	1.1/0.381 9.7/0.207 42.2/0.418	0.9/−0.949 12.1/1.000 39.3/0.203

[a] Biexponential fit at CFKR without reconvolution. [b] Fit by reconvolution. [c] This rise time may be as short as ca. 1 ns based on the precision of the fit. [d] From ref 2 (for purposes of comparison). [e] Fluorescence intensity too low for reliable lifetime measurement.

into a classical excimer-forming configuration is possible. Despite this rigidity, David et al.[9] demonstrated that polyacenaphthylene shows strong excimer fluorescence, although not so strong as poly(2-vinylnaphthalene)[10] or poly(1-vinylnaphthalene). Wang and Morawetz[5] have shown that the presumably alternating copolymer P-(AcN-*co*-MAn) forms excimers, and we find the same result for both the PAcN-*alt*-MAA and PAcN-*alt*-MAE. We compare the fluorescence spectra of PAcN-*alt*-MMA and PAcN-*alt*-MAE in Figure 1. The fluorescence lifetimes measured at 340 and 400 nm are biexponential, and the excimer region displays a clear buildup of fluorescence (Table I). We note that PAcN-*alt*-MAA does not obey a classical Birks kinetics scheme since the two lifetimes of the monomer are not identical with those of the excimer. However for PAcN-*alt*-MAE the buildup time of the excimer is within ca. 10% of the fast component of the monomer decay. Thus we tentatively conclude that this latter polymer system approaches a classical scheme in which a *significant fraction of the emitting ensemble* of monomer states is also the precursor state of the excimer. It is much more common in our experience to observe essentially "static" formation of the excimer state, which implies very rapid energy trapping via energy migration and/or pendent group motion.

One further observation concerning PAcN-*alt*-MAn: in THF/diethyl ether at room temperature a very strong excimer band is observed (similar to Figure 1) while in a glass at 77 K the excimer is almost completely absent. It is common to quench excimer formation in naphthalenic polymers in low-temperature glasses and further demonstrates that excimer formation in this acenaphthylene polymer is not the result of a crowded polymer structure that can persist to low temperatures.

Excimer fluorescence is much weaker in the PAcN-*alt*-MA or PAcN-*alt*-MMA polymer in THF (Figure 1), and there is essentially no difference between the fluorescence spectra of these two polymers. Interestingly, there is more excimer for this acenaphthylene copolymer than the corresponding polymer with 2-vinylnaphthalene. There is very little difference in the fluorescence decay of the acid or ester in THF (see Table I), and in fact the general character of the time-dependent fluorescence is also very similar to the maleic ethoxy ester. The excimer component shows buildup time which is much shorter than the short lifetime component in the monomer fluorescence. Since the time dependence of monomer decay and excimer formation is so similar for the methacrylic acid/ester polymer and the maleic ester polymer, the vastly different monomer/excimer ratios imply that there is an undetected rapid sensitization of the excimer state for the maleic ester polymer, since the fluorescence quantum yields of these two polymers are quite similar.

These results demonstrate that the concept of steric hinderence of excimer fluorescence can be counterintuitive. it seems that placing a methyl group on the same carbon as the carboxylate or methyl ester is much more hindering than having two carboxylates on adjacent carbons (for the maleic acid system). For a similar observation see the recent paper by Galli et al.[11] Furthermore the rigidly held acenaphthylene moiety seems to be more able to form excimers than the presumed relatively mobile 2-vinylnaphthalene in these alternating copolymers. In the homopolymer P2VN has a more dominant excimer band than PAcN by a factor of ca. 3–4. While deferred to a later section, the same trend is observed for aqueous solutions of these copolymers.

(b) Intracoil Energy Transfer to an Anthryl Trap: PAcN-*alt*-MA-*co*-Anth (1.1%). Anthracene (1.1 mol %) was covalently bound to PAcN-*alt*-MA by direct esterification as discussed in the Experimental Section. Excitation of the AcN moiety at 290 nm (negligible direct absorption by anthracene) yields a mixed naphthalene–anthracene fluorescence spectrum (Figure 2). On the basis of the anthracene fluorescence intensity upon direct or indirect excitation (365 and 290 nm, respectively), we estimate the quantum efficiency (χ) to be ca. 0.29 ± 0.04 in THF, which is significantly smaller than the previously studied P2VN-*alt*-MA-*co*-Anth system.[2] Energy transfer to the anthryl trap shortens the average lifetime of the AcN monomer by approximately a factor of 0.6–0.7 and replaces the excimer fluorescence by a rapidly growing-in fluorescence which then decays with a lifetime close to that expected of anthracene (see Figure 3 and Table I). It is interesting that the buildup time for the anthracene is

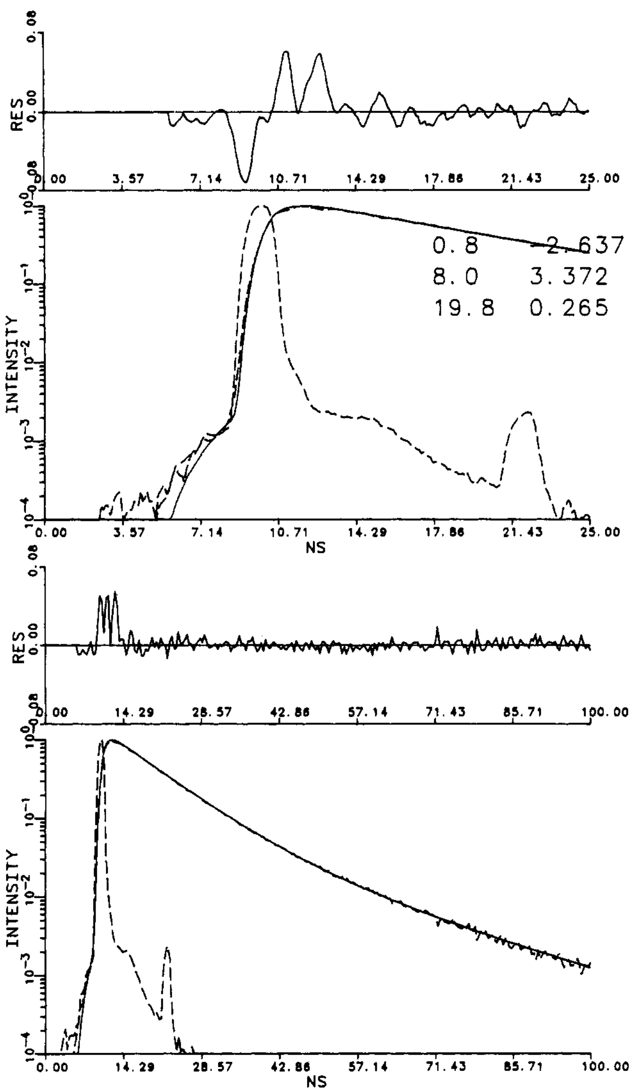

Figure 3. Fluorescence decay of PAcN-*alt*-MA-*co*-Anth (1.1%) (excitation 290 nm).

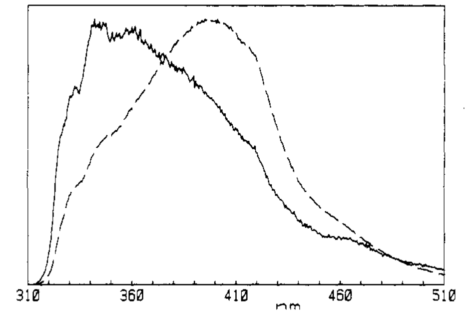

Figure 4. Fluorescence of PAcN-*alt*-MA (pH 7.8) (—) and PAcN-*alt*-MAA (pH 7.1) (- - -).

Table II
Fluorescence Decay Parameters of Alternating Copolymers in H_2O

polymer	340 nm	400 nm
PAcN-*alt*-MA (pH 7.7)	0.8/0.842[b] 4.4/0.158	1.5/0.812[b] 9.5/0.188
PAcN-*alt*-MA (pH 11.7)	4.2/0.40[a] 16.0/0.60	5.8/−1.0[c] 3.3/+1.0
PAcN-*alt*-MAA (pH 7.9)	1.7/0.69[a] 13.3/0.31	3.7/0.34[a] 28.1/0.66

[a] Biexponential fit at CFKR without reconvolution. [b] Fit by reconvolution. [c] Preexponential factor of growing-in component not determined very accurately by fit.

Table III
Monomer[a] Quenching Constants for CCl_4

polymer (solvt)	$10^{-10}k_q^{ss}$, $M^{-1}\ s^{-1}$ ($\bar{\tau}_0$[b])	$10^{-10}k_q^{\tau}$,[c] $M^{-1}\ s^{-1}$
PAcN-*alt*-MA (THF)	1.3 (16 ns)	1.3
PAcN-*alt*-MMA (THF)	1.3 (16 ns)	0.8
PS-*co*-AcN-*alt*-MA (THF)	1.3 (17 ns)	
PAcN-*alt*-MAA (MeOH)	1.4 (7.4 ns)	
PAcN-*alt*-MAE (MeOH)	1.1 (12.6 ns)	1.5
PS-*co*-AcN-*alt*-MAA (MeOH)	1.0 (18.5 ns)[d]	

[a] Observed at 340 nm. [b] $k_q^{ss} = K_{SV}/\bar{\tau}_0$, where $\bar{\tau}_0 = \sum a_i\tau_i$ (average lifetime) and $I_0/I - 1 = K_{SV}[CCl_4]$. [c] k_q^{τ} derived from $\bar{\tau}_0/\bar{\tau} - 1 = k_q^{\tau}\bar{\tau}_0[CCl_4]$ (lifetime quenching). [d] SV plot nonlinear – initial slope used.

much faster than that of the excimer (but similar to that of P2VN-*alt*-MA-*co*-Anth). For excimer formation there must be down-chain energy migration to excimer-forming sites and/or pendent group motion. Contrarily there is a significant probability for single-step transfer from an acenaphthylene moiety to anthracene ($R_0 \cong 24$ Å). Note that the efficiency of energy transfer as measured by the lifetime shortening is roughly commensurate with the value of χ as measured by steady-state spectra ($\chi_t = 1 - \bar{\tau}/\bar{\tau}_0 = 0.35$).[12] This agrees with the previously studied P2VN-*alt*-MA-*co*-Anth systems (at room temperature).

The anthracene groups replace the polar –COOH with a much larger moiety such that it is possible that some effect on coil density might be observed. To check this possibility the hydrodynamic radii of PAcN-*alt*-MA and PAcN-*alt*-MA-*co*-Anth (1.1%) in THF were estimated by time-correlated light scattering and the values were ca. 25 and 34 nm, respectively (several dilutions were used, from ca. 1 to ca. 0.25 mg/mL of polymer). While these results are far from definitive, they do suggest that relatively small loadings of a bulky chromophore onto a polymer may significantly modify the coil dimension.

(c) Steady-State and Time-Dependence Fluorescence in Aqueous Solutions. Both PAcN-*alt*-MA and PAcN-*alt*-MAA form metastable aqueous solution (turbidity may occur after several days at pH's lower than 10). The fluorescence of ca. 4 × 10^{-5} M solutions is dominated by the excimer (Figure 4). PAcN-*alt*-MA fluorescence is sensitive to pH (increased excimer component at lower pH) while that of PAcN-*alt*-MAA is essentially unchanged. The fluorescence decay of the monomer and excimer is much faster than in the organic phase, and for lower pH's the excimer time-dependent signal for PMA-*alt*-MA does not contain a buildup (Table II), which is consistent with very rapid (static) excimer formation.

For PAcN-*alt*-MA the fluorescence decay behavior (Table II) is dependent on pH in a systematic fashion. In particular the monomer lifetime increases at higher pH as would be expected as excimer formation becomes less important. At the highest pH studied there is a clear growing in of the excimer fluorescence. We presume this is a consequence of the less compact form of the polymer at high pH such that for many excimers either segmental motion or (see next section) energy migration to an excimer forming site may be required.

(d) Fluorescence Quenching and Energy Transfer. Organic Solvents and CCl_4 Quenching. THF or methanol solutions of the polyacids or polyesters were used in these quenching studies. The solutions were not deaerated, and microliter amounts of CCl_4 were added directly to the solution in a fluorescence cuvette (a maximum of 15 μL added to 3 mL solution). The I_0/I plots for the monomer fluorescence were linear for all the results

Table IV
Monomer[a] Quenching Constants for Cu^{2+}

polymer (pH)	K_{SV}, M^{-1}	$\bar{\tau}_0$,[d] ns
PAcN-*alt*-MA (7.5)	$3.5 \times 10^{+6}$	2.2
PAcN-*alt*-MAA (7.5)	$1.7 \times 10^{+6}$	5.3
P2VN-*alt*-MA (8)[b]	$1.05 \times 10^{+7}$	15.3
P2VN-*alt*-MAA (8)[c]	$9.4 \times 10^{+4}$	20.0

[a] λ_{obsd} = 331 nm. [b] From ref 3. [c] From ref 4. The lifetime and quenching results are for the excimer fluorescence, which completely dominate the fluorescence spectrum. [d] $\bar{\tau}_0 = \sum a_i \tau_i$.

presented in Table III (except for the PAcN–maleic acid model polymer). k_q^{SS} was determined from $K_{SV}/\bar{\tau}_0$ where $\bar{\tau}_0$ is the average lifetime defined in Table III. In a few cases k_q^{τ} was determined from the shortening of $\bar{\tau}_0$ upon the addition of CCl_4. In general these latter data represent only a few CCl_4 concentrations and consequently have a much lower confidence level. In all cases k_q is on the order of $(1.0–1.4) \times 10^{10}$ M^{-1} s^{-1}, which is essentially the diffusion-controlled limit. More importantly in the present context, there is no significant difference in k_q between the model polymers and the alternating polymers. We have previously used the relationship[6]

$$\Lambda_S/D_Q \simeq (k_q^{polym} - k_q^{model})/k_q^{model} \qquad (1)$$

to estimate the singlet energy migration rate Λ_S (D_Q is the quencher diffusion constant). In the present case $k_q^{model} \sim k_q^{polym}$ so $\Lambda_S \sim 0$. As noted above, the formation of the excimer state is more important in the AcN systems than 2-vinylnaphthalene alternating copolymers. Thus we speculate that the apparent energy-transfer rate is decreased because of excimer trapping (i.e., a short mean path for exciton hopping). Unlike P2VN, the excimer displays a clear buildup in these AcN polymers (see Table I), which implies that excimer formation is relatively slow. Since Λ_S is estimated to be small, the buildup time could reflect the time required for segmental diffusion into an excimer-forming configuration. However, we should emphasize that there is no a priori way to distinguish relatively slow down-chain exciton hopping to an excimer-forming site from segmental diffusion.

Aqueous Solution and Cu^{2+} Quenching. For P2VN-*alt*-MA polymers in aqueous solution we have previously found Cu^{2+} to be an extremely efficient fluorescence quencher[3] ($K_{SV} \approx 9 \times 10^6$ M^{-1}, $k_q \approx 4 \times 10^{14}$ M^{-1} s^{-1}). The same is true in the present case although K_{SV} is lower by a factor of 3–4 (Table IV).[13] For P2VN-*alt*-MA we found the lifetime quenching rate to be essentially the same as that for intensity quenching, while for the present systems there is little or no lifetime quenching; i.e., the fluorescence quenching by Cu^{2+} must be largely static. The very large values of the apparent k_q values implies that quenching occurs by a combination of electrostatic binding of the Cu^{2+} to the polyelectrolyte (a high local concentration) and either facile energy migration or rapid diffusion of Cu^{2+} ions along the coil (or both). Rapid energy migration for PAcN-*alt*-MA/MAA in aqueous solution might be the result of a "packed structure" formed between the hydrophobic AcN groups. Precisely the same excimer-forming site observed in organic solutions must not be present in large concentration in this structure since the excimer fluorescence observed in pH 7.5 aqueous solution is blue-shifted relative to that observed in organic solvents.

Summary

In this paper we have reported a number of photophysical properties of two alternating naphthalenic copolymers, PAcN-*alt*-MA (and the methyl ester) and PAcN-*alt*-MAA (and the monoethoxy ester). We have found the fluorescence in these polymers to display a stronger excimer component than the corresponding 2-vinylnaphthalene polymer and maleic acid copolymers form excimers more readily than methacrylic acid copolymers. This latter observation is consistent with the observations in 2-vinylnaphthalene copolymers.[4]

PAcN-*alt*-MA with a small mole percent of covalently bound anthryl group was studied. The quantum efficiency of anthryl sensitization via naphthalene excitation was estimated to be of the order 0.3. This is approximately 60% the value in the corresponding P2VN-*alt*-MA-*co*-Anth polymer.[2] Since the rate of down chain singlet energy transfer is estimated to be nearly zero in organic solvents, this quantum efficiency must correspond primarily to single-step Förster transfer ($R_0 \simeq 24$ Å).

The properties of the polyacids in basic aqueous solutions are complicated by aggregation of the hydrophobic naphthalene groups. Excimer fluorescence dominates the emission and tends to decrease with increased pH as the coil density responds to the electrostatic repulsion between $-CO_2^-$ groups. The monomer fluorescence decay in aqueous solution is much faster than in organic solvents presumably because of very rapid energy trapping at excimer forming sites. Fluorescence quenching by Cu^{2+} is extremely efficient, which is certainly due in large measure to electrostatic binding of Cu^{2+} to the polyelectrolyte. It is possible that down chain singlet energy migration occurs in the aqueous environment by virtue of the crowded structure of the aggregated naphthalenes. It is intriguing that there is almost 2 orders of magnitude difference in K_{SV} values for Cu^{2+} quenching for different alternating naphthalenic polymers (Table IV) and that they are so large. At the present time we have no direct information about the structure of these polymers in aqueous solution, which certainly must represent an interesting balance of electrostatic and hydrophobic interactions.

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Registry No. (AcN)(MAn) (alternating copolymer, ethyl ester), 112654-00-9; CCl_4, 56-23-5; Cu^{2+}, 7440-50-8.

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Nematic Order of Semiflexible Thermotropic Polymers from NMR Data. Further Developments of a Previous Analysis

Sergio Brückner[†]

Dipartimento di Chimica, Politecnico di Milano, P.zza L. da Vinci 32, 20133 Milano.

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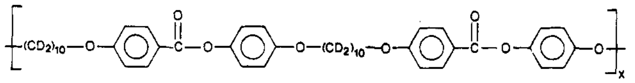
ABSTRACT: The approach, adopted in a previous paper for interpreting the observed ^{2}H NMR spectra of poly(oxyphenylenecarbonyloxyphenyleneoxydodecanediyl-d_{20}) in the nematic state is developed in order to take into account the different time scales affecting conformational jumps and uniaxial reorientations of the chain around the director. Results show that by decoupling these two kinds of motion, the model is no longer critical to geometry. A very local additional order parameter is in fact required and it accounts for all geometrical features which describe the connection of the spacer to the mesogen unit while the structure of the ^{2}H NMR spectrum is solely determined by the conformational mobility of CD$_2$ groups.

Introduction

Recently a paper (hereafter referred to as paper 1) has been published on the NMR study of nematic order of semiflexible thermotropic polymers[1] where it was shown that a proper choice of the conformer population which survives upon the phase transition from the isotropic to the nematic state can explain the ^{2}H NMR observed spectrum of poly(oxyphenyleneoxycarbonyloxyphenyleneoxydodecanediyl-d_{20}) (PDCB-d_{20}) with perdeuteriated alkyl spacers (n = 10 methylene units) shown in Chart I. The conformational model which allowed a successful interpretation of experimental data can be briefly referred to as the "alternate model" and includes the ensemble of highly elongated conformers which is obtained by fixing in the trans rotational isomeric state (RIS) every second bond (starting from the O–CH$_2$ attached to the rigid (phenylene) unit), while intermediate bonds can take on all conformations among the three available RIS of a polymethylene chain (see Figure 1). Orientational order parameters were independently obtained from ^{2}H NMR and ^{1}H NMR spectra recorded at different temperatures, showing a very encouraging self-consistency. Some criticisms have been expressed, however, after the publication of this work, which stimulated, in our opinion, the need of a more detailed analysis of the model adopted for the interpretation of observed NMR data.

The criticisms, involving some geometrical features of the model, are substantially two: (i) the rather arbitrary choice of the O–phenylene–O direction as representing the average chain axis and (ii) the smallness of the phenylene–O–CH$_2$ valence angle χ (see Figure 1) which was set at 112° (i.e., the same value used for the methylene groups), while many crystallographic model compounds indicate, as more likely, a value in the range 117–120°. These two remarks are only apparently different, while both of them involve, as a consequence, a revision of the orientation of both the rigid units and the flexible spacers with respect to the average chain axis.

Chart I



The differences involved are, in this case, on the order of few degrees and are therefore expected to produce only small changes in the calculated spectra, but this is not true. As an example we report in Figure 2 the ^{2}H NMR spectrum calculated by setting the valence angle at the oxygen atom at 112° (a), as already done in paper 1, and 120° (b) (an order parameter of 1 is assumed for both calculations). The effect is quite large on the quadrupolar splitting of the α-CD$_2$ groups, so that we see no longer a single splitting, as experimentally observed, but two.

The critical role played by geometry in our model is a consequence of the assumption that conformational jumps occur on the same time scale as the uniaxial reorientations of the single chain around the nematic director. This assumption was not explicitely stated in paper 1 but it became implicitly active as soon as we decided that the same order parameter must describe both the orientations of C–D bonds and those of the average chain axis.

The observed profile shows one single quadrupolar splitting for all five (in principle) motionally distinguishable CD$_2$ groups. Under the previous asssumptions we were able to reproduce these data only be defining the average chain axis along a direction which is parallel to the CD$_2$–CD$_2$ bonds which, according to the alternate model, can undergo transitions among the three available RIS's. The valence angle at the oxygen was set at 112° so that the rigid units lay parallel to the average chain axis.

The results from NMR relaxation data[2] and Monte Carlo simulations referred to a real time scale through comparison of the effect of a large number of steps with the overall diffusion rate[3] show that conformational changes occur with correlation times much smaller than those affecting chain reorientations. At the high temperature considered (≅480 K) the correlation time for conformational isomerizations can be estimated[2] on the order of 10^{-10} s while chain reorientations occur with a

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[†] This work was partially carried out while the author was at the Max-Planck-Institut fur Polymerforschung, Mainz, FRG, as visiting scientist.