Amphiphilic Alternating Carbazole Copolymers: Photophysical Properties of Poly[*N*-vinylcarbazole-*alt*-citraconic acid] in Aqueous Solution

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ABSTRACT: Amphiphilic polyelectrolytes containing carbazolyl chromophores (a-CzCa) were prepared by hydrolysis of alternating copolymers of *N*-vinylcarbazole (VCz) and citraconic anhydride and their fluorescence properties were compared with those for alternating copolymers of VCz and maleic acid (a-CzMa) and random copolymers of VCz and methacrylic acid (r-CzMA(x)) in aqueous solution. The fluorescence spectrum of a-CzCa, derived from the anhydride copolymer with the equimolar monomer feed ratio, showed a predominant monomer emission in both organic and aqueous solutions, while the fluorescence intensity changed drastically upon dissociation of carboxyl groups in aqueous solution and had a minimum value at acidic pH which was rather smaller than that for the corresponding random copolymer. The solution behavior showed that a-CzCa had a less hydrophobic character and thus retained a loose form even at low pH. Therefore, the remarkable self-quenching occurring in a-CzCa may be caused primarily by efficient energy migration to very few quenching sites. Quenching experiments gave additional evidence for hydrophilicity of a-CzCa. The fluorescence of a-CzCa at pH 3 was found to be quenched less efficiently by an amphiphilic quencher, bis(2-hydroxyethyl) terephthalate (BHET), compared with the corresponding random copolymer.

Introduction

It is well-known that photophysical and photochemical behavior of amphiphilic polyelectrolytes containing pendant aromatic chromophores is strongly dependent on the microphase structure created by the polymer chains in aqueous solution.[1–3] An interesting class of amphiphilic polyelectrolytes consists of alternating copolymers. Morishima et al.[4] and Webber et al.[5,6] reported that alternating copolymers of vinylnaphthyl monomers with maleic acid and methacrylic acid exhibited prominent excimer emission in aqueous solution. We previously found a remarkably diminished emission in aqueous solution of an alternating copolymer of 9-vinylphenanthrene and methacrylic acid (a-MPh).[7] Such enhanced excimer formation and self-quenching can be attributed to efficient energy migration to a small fraction of preformed excimer-forming and self-quenching sites in the clusters of hydrophobic chromophores. Hydrophobic aggregation of aromatic groups is, of course, minimized in organic solution, which allows the copolymers to recover their normal monomer emission.

In the preceding paper, we compared the fluorescence properties of a series of alternating copolymers of *N*-vinylcarbazole (VCz) and electron-accepting monomers in organic solutions, and demonstrated that the higher degree of chromophore alternation and the introduction of bulky groups on comonomers play an important role in the inhibition of excimeric interactions in the copolymers.[8] Another advantage of these polymers is that the carbazole (Cz) chromophore with a large Föster radius for self-transfer would enable a long-range energy migration and transfer. Thus we except that these types of copolymers have a great potential for photon harvesting in more condensed chromophore systems such as in films and in aqueous media.

The present paper deals with water-soluble carbazole copolymers obtained by hydrolysis of the anhydride residues in the parent alternating copolymers.[8] We find that the fluorescence spectra for poly(VCz-*alt*-citraconic acid) (a-CzCa) are changed sharply as a function of pH compared with those for the corresponding maleic acid copolymers (a-CzMa) and random copolymers of VCz and methacrylic acid (r-CzMA(x); x represents the Cz content in the copolymer in mol %).

Experimental Section

Materials. The purification of *N*-vinylcarbazole (VCz), citraconic anhydride (CAn), and maleic anhydride (MAn) was described previously.[8] Methacrylic acid (MA) (Wako Pure Chemical) was distilled under reduced pressure before use. *N*-(2-Hydroxyethyl)carbazole (CzEtOH) was prepared according to the literature.[9] *N*-Ethylcarbazole (EtCz) (Nakalai Tesque) was recrystallized repeatedly from methanol. Bis(2-hydroxyethyl) terephthalate (BHET) (Kanto Chemical) was recrystallized twice from chloroform. Magnesium 8-anilino-1-naphthalenesulfonate (ANS) (Tokyo Kasei) was used as received.

Alternating Copolymers. Copolymers of VCz with CAn and MAn were prepared by the radical polymerization with an initiator, 2,2′-azobis(isobutyronitrile) (AIBN), in degassed benzene at 60 °C.[8]

Hydrolysis of the anhydride copolymers was performed as follows. A mixture of 0.4 g of the copolymer in 50 mL of tetrahydrofuran (THF) and 5 mL of 0.4 M sodium hydroxide was stirred at room temperature for 24 h. The precipitate was dissolved in 50 mL of 0.4 M sodium hydroxide and then allowed to stand for another 24 h. The resulting clear solution was

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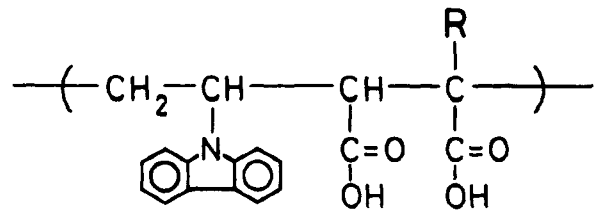
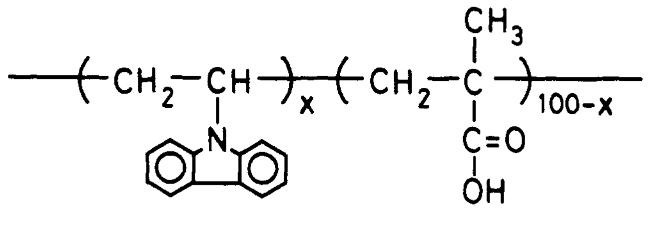


R = -H a-CzMa

-CH$_3$ a-CzCa



r-CzMA(x)

dialyzed against pure water for 1 week and finally lyophilized. Complete hydrolysis was confirmed by IR spectroscopy.

Esterification of the hydrolyzed copolymers with diazomethane was carried out according to the literature.[4]

Random Copolymers. VCz and MA were copolymerized in the presence of 0.5 mol % (on the basis of total monomers) of AIBN in *N,N*-dimethylformamide (DMF) at 60 °C. The copolymers were purified by repeated precipitations. Esterification of these polymers was also performed.

Polymer Characterization. Composition of the copolymers was determined primarily by using absorption spectra.

Molecular weights of the polymers in the methyl ester form were estimated by using a Toyo Soda HLC-802A. Monodisperse polystyrene samples were used as standards.

The composition and characteristics of the copolymers are listed in Table 1. The copolymer compositions of a-CzCa and a-CzMa used for the spectroscopic measurements were nearly equimolar, indicating a highly alternating tendency.[4]

Measurements. Steady-state fluorescence spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer at room temperature. All organic solutions were deaerated by bubbling with nitrogen for 15 min. The spectra in aqueous solutions were measured without deaeration. In the latter case, the polymer was first dissolved in water at pH 10 and then the pH was adjusted downward by addition of HCl. As with the samples insoluble in pure water (e.g., r-CzMA(36), r-CzMA(52), and CzEtOH), aqueous solutions were prepared by adding a DMF stock solution to water at pH 10 with vigorous stirring. The final solutions contained less than 2 vol % of DMF.

Fluorescence lifetime measurements were made on a homemade time-correlated single-photon-counting system equipped with a ca. 2 ns pulsed lamp using an excitation wavelength of 316 nm. Details of instrumentation will be described elsewhere.[10]

Results and Discussion

Table 1. Characterization of the Copolymers of VCz with Citraconic Acid, Maleic Acid, and Methacrylic Acid

	f_{Cz}[a]		
polymer	feed	polym[b]	M_n[c]
a-CzCa-1	0.40	0.46	3.0 × 10^4
a-CzCa-2	0.50	0.51	2.0 × 10^4
a-CzCa-3	0.64	0.51	2.8 × 10^4
a-CzCa-4	0.80	0.51	2.9 × 10^4
a-CzMa-1	0.39	0.36	4.4 × 10^4
a-CzMa-2	0.50	0.45	6.0 × 10^4
r-CzMA(1)	0.02	0.01	1.3 × 10^5
r-CzMA(12)	0.35	0.12	
r-CzMA(25)	0.60	0.25	2.1 × 10^6
r-CzMA(36)	0.70	0.36	
r-CzMA(44)	0.80	0.44	
r-CzMA(52)	0.90	0.52	3.1 × 10^5

[a] VCz mole fraction. [b] From absorption using poly(VCz) as a standard. [c] Polystyrene equivalent number-average molecular weights determined by GPC for the methyl ester derivatives.

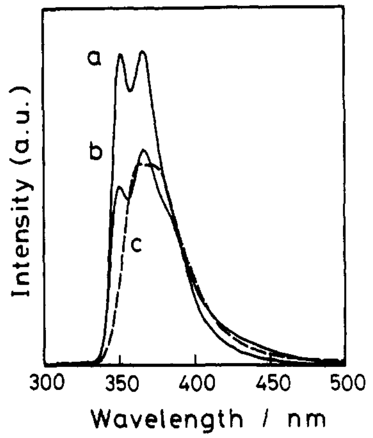


Figure 1. Steady-state fluorescence spectra of a-CzCa and a-CzMa in H$_2$O at pH 10: (a) a-CzCa-2 with f_{cz} = 0.5 in the feed; (b) a-CzCa-4 with f_{cz} = 0.8; (c) a-CzMa-2 with f_{cz} = 0.5. $[Cz]_{residue}$ = 1.0 × 10^{-5} M. Excitation wavelength was 293 nm.

Fluorescence Spectroscopy. Figure 1 compares the fluorescence spectra of a-CzCa and a-CzMa in aqueous solution at pH 10. The spectral features of a-CzCa were found to be practically identical with those of the corresponding anhydride copolymers in THF except for a ca. 5 nm red-shift of the emission maximum for the former polymer;[8] i.e., the copolymer obtained at 0.5 of the VCz mole fraction (f_{cz}) in the monomer feed (a-CzCa-2) showed a sharply structured emission, whereas the other copolymers at either a higher or lower f_{cz} in the feed exhibited a slightly broadened emission in the longer wavelength region along with a decrease in the intensity. These observations indicate that there are some excimer-forming sites in a-CzCa, the amount of which depends on the monomer feed ratios. In contrast with a-CzCa, any a-CzMa produced by different monomer feed ratios exhibited only a broad excimeric emission. Such a marked difference is obviously due to steric hindrance of the methyl group on the citraconic acid residue.[8]

In the case of a-CzCa, the extent of excimer formation can be compared conveniently by evaluating the ratios of the peak intensity at 365 nm to 350 nm (I_{365}/I_{350}) because the former peak includes the contribution of second excimer emission (Figure 2).[8] The relative fluorescence intensity at 350 nm (I_{rel}) is also plotted. The highest fluorescence intensity and the lowest intensity ratio for a-CzCa-2 (f_{cz} = 0.5 in the feed) clearly indicate that only a very few (but not negligible) excimer sites are formed in this polymer. Such favorable features for photon harvesting in aqueous solution are in a marked contrast with the common observation for amphiphilic copolymers containing aromatic chromophores that hydrophobic aggregation of chromophores causes preferential excimer formation and/or self-quenching.[1-7] Indeed, a significant decrease in the fluorescence intensity accompanying more enhanced excimer emission was observed for the random copolymers (r-CzMA(x)) with higher f_{cz} in aqueous solution

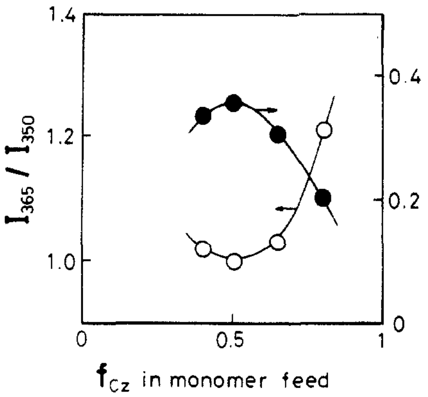


Figure 2. Dependence of the peak intensity ratio (I_{365}/I_{350}) (○) and the relative fluorescence intensity at 350 nm (I_{rel}) (●) on f_{cz} in the feed for a-CzCa in H_2O at pH 10. $[Cz]_{residue} = 1.0 \times 10^{-5}$ M. Excitation wavelength was 293 nm. I_{rel} is normalized to the intensity of EtCz in DMF.

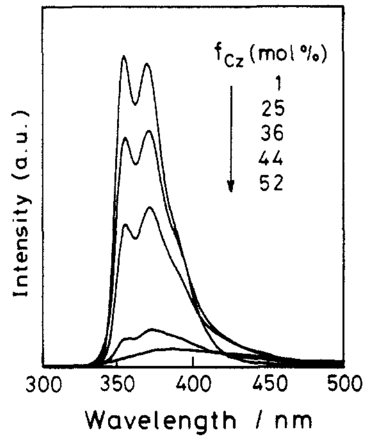


Figure 3. Steady-state fluorescence spectra of r-CzMA(x) with different f_{cz} in aqueous solution at pH 10. f_{cz} values in mol % are indicated in the figure. $[Cz]_{residue} = 1.0 \times 10^{-5}$ M. Excitation wavelength was 293 nm.

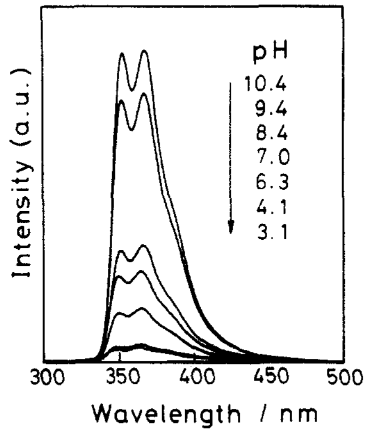


Figure 4. Steady-state fluorescence spectra of a-CzCa-2 with f_{cz} = 0.5 in the feed in aqueous solution at various pH values. $[Cz]_{residue} = 1.0 \times 10^{-5}$ M. Excitation wavelength was 293 nm.

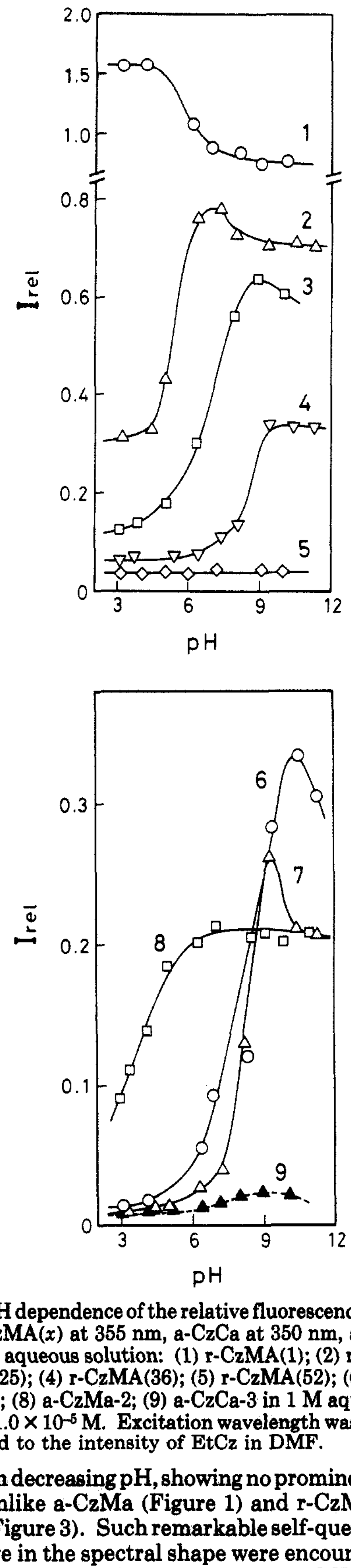


Figure 5. pH dependence of the relative fluorescence intensities (I_{rel}) for r-CzMA(x) at 355 nm, a-CzCa at 350 nm, and a-CzMa at 365 nm in aqueous solution: (1) r-CzMA(1); (2) r-CzMA(12); (3) r-CzMA(25); (4) r-CzMA(36); (5) r-CzMA(52); (6) a-CzCa-2; (7) a-CzCa-3; (8) a-CzMa-2; (9) a-CzCa-3 in 1 M aqueous NaCl. $[Cz]_{residue} = 1.0 \times 10^{-5}$ M. Excitation wavelength was 293 nm. I_{rel} is normalized to the intensity of EtCz in DMF.

(Figure 3). Consequently, a-CzCa seems to have a rather hydrophilic character and to have a loose or extended form in aqueous solution at pH 10, leading to suppression of chromophore aggregation. We will discuss this again in the following section.

Figure 4 compares the fluorescence spectra of a-CzCa-2 observed at various pH values. An unexpectedly large pH dependence was observed. The intensity decreased sharply between pH 9.4 and 8.4 probably because of the conformational change and it further decreased in acidic solution. The spectrum, however, was broadened only slightly with decreasing pH, showing no prominent excimer emission unlike a-CzMa (Figure 1) and r-CzMA(x) with higher f_{cz} (Figure 3). Such remarkable self-quenching and little change in the spectral shape were encountered with an alternating phenanthrene copolymer (a-MPh) in aqueous solution.[7] We have supposed that excited energy is efficiently captured by a few self-quenching sites, not emitting, via energy migration facilitated by the mutual chromophore aggregation in aqueous solution.

In Figure 5, the relative fluorescence intensity of monomer emission (I_{rel}) is plotted as a function of pH. The random copolymer, r-CzMA(1), exhibited an intense fluorescence in acidic solution and the intensity decreased with deprotonation of the carboxyl groups. These behaviors are typical for many poly(carboxylic acid)-bound aromatic chromophores and are interpreted as the result of exposing the chromophore to a more polar microenvironment at higher pH.[11] For r-CzMA(x) with higher f_{cz}, on the other hand, there was a decrease in I_{rel} at lower pH and r-CzMA(52) no longer exhibited pH dependence. These observations are explicable in terms of enhanced self-quenching of the excited state, which results from hydrophobic association of chromophore groups.[1-7]

As described above, a-CzCa exhibited a sharp change in I_{rel} at a pH between 8 and 10 and a decrease with increasing pH in more basic solution. Furthermore, the pH values at the maximum point of I_{rel} for a-CzCa differed from one another. Such pH dependence can be attributed to the conformational transition of a-CzCa from analogy with the viscosity behavior known for maleic acid copolymers (see below).[12] It is also noteworthy that a-CzCa has the lowest I_{rel} value at acidic pH among the copolymers used here irrespective of the higher value at basic pH. From the solution behavior a-CzCa is presumed to have a less hydrophobic character and thus not to have the most compact form in acidic solution (see below). Therefore, the remarkable self-quenching occurring in a-CzCa may be caused by efficient energy migration to a very few self-quenching sites rather than by the "simple" increase in the number of the sites due to chromophore aggregation. Such diminished fluorescence intensity due to some contraction of the polymer coil was also observed by adding an excess of NaCl to the a-CzCa solution at high pH (Figure 5). It is interesting to note again that a-CzMa exhibits only an excimeric emission at any pH (Figure 1) and that the fluorescence quantum yield for a-CzMa at acidic pH is not as low as that for a-CzCa (Figure 5). These indicate that hindered groups on comonomers largely modify the chromophore–chromophore interaction in aqueous solution, leading to extremely different photophysical events.[8]

We previously found that the addition of a nonsolvent, *n*-hexane, to the THF solution of poly(VCz-*alt*-diethylfumarate) (a-CzEF), a similar type of alternating copolymer, resulted in the increase of excimer emission intensity synchronized with the decrease of monomer emission intensity.[8] We have speculated that there are few quenching sites other than excimer-forming sites in a-CzEF and that more efficient energy migration facilitated by the polymer coil shrinkage occurs solely to these excimer sites in a very small amount. The situation is quite contrary to the behavior of a-CzCa in acidic solution. We have no concrete interpretation for this difference, except a few possibilities such as formation of an unstable excimer with a very low fluorescence quantum yield and efficient energy transfer to nonemitting impurities[13] in aqueous solution.[14]

Fluorescence decay curves of the random and alternating copolymers for the monomer emission were measured by using the single-photon-counting method. All of the decay curves except for r-CzMA(1) in DMF had to be fitted to a multiple-exponential function described by

$$I(t) = \sum a_i \exp(-t/\tau_i) \qquad (1)$$

where a_i is the preexponential factor ($\sum a_i = 1$) and τ_i the lifetime. These parameters obtained in DMF and water are given in Tables 2 and 3, respectively. The number-average lifetimes $\langle\tau\rangle$ calculated by eq 2 are also listed.

$$\langle\tau\rangle = \sum a_i \tau_i \qquad (2)$$

The observations in DMF that the monomer emission decays nonexponentially and that a longer-lifetime component appears are indicative of excimer formation in all the copolymers used here.[8] It was also found that in any case the average lifetime responded well to the fluorescence intensity; e.g., the remarkable self-quenching for a-CzCa in acidic solution leads to a significant shortening of the lifetime. The apparent absence of a longer-lifetime component (>15 ns) in the decay for a-CzCa in aqueous solution might be due to the lack of formation of an emissive excimer.

Table 2. Fluorescence Decay Parameters for VCz Copolymers in DMF[a]

polymer	τ_i/a_i,[b] ns			$\langle\tau\rangle$,[c] ns
a-CzCa-2	2.7/0.45	9.1/0.46	19.1/0.09	7.2
a-CzCa-3	1.8/0.59	7.3/0.35	18.5/0.06	4.8
r-CzMA(1)	15.7/1.00			15.7
r-CzMA(36)	2.9/0.13	10.3/0.76	18.8/0.11	10.2
r-CzMA(52)	2.2/0.47	10.0/0.48	31.0/0.05	7.5

[a] Emission wavelength, 345 nm. [b] See eq 1 in the text. [c] Number-average lifetime (see eq 2 in the text).

Table 3. Fluorescence Decay Parameters for VCz Copolymers in Aqueous Solutions[a]

polymer	pH	τ_i/a_i, ns			$\langle\tau\rangle$, ns
a-CzCa-2	11.2	0.3/0.85	7.3/0.12	14.5/0.04	1.6
	10.3	0.6/0.56	7.1/0.31	13.9/0.12	4.3
	7.0	0.6/0.56	6.9/0.31	14.6/0.13	4.3
	3.0	0.09/0.999	2.3/0.001	13.6/–0.0	0.09
r-CzMA(1)	10.4	10.5/0.88	17.3/0.12		11.3
	2.8	13.4/0.48	18.7/0.52		16.1
r-CzMA(52)	10.3	0.9/0.73	9.2/0.22	26.0/0.05	4.1
	2.8	0.7/0.86	8.7/0.12	26.2/0.02	2.2

[a] Symbols are the same as in Table 2; emission wavelength, 345 nm.

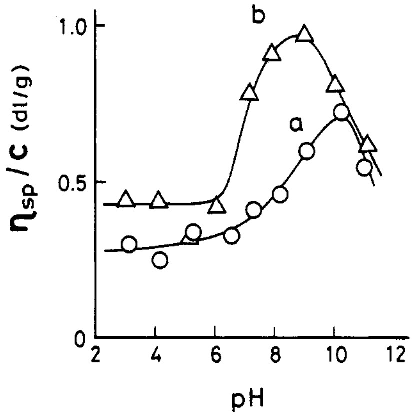


Figure 6. pH dependence of the reduced viscosities (η_{sp}/C) of a-CzCa-2 with f_{cz} = 0.5 in the feed (a) and a-CzCa-3 with f_{cz} = 0.65 (b) in aqueous solution at 30 °C. [polymer] = 0.1 g/dL.

Solution Properties. Maleic acid polymers are known to show unique conformational transitions upon ionization of the carboxyl groups, which has been established by potentiometric, viscometric, and other studies.[12,15] For example, the titration curve exhibits a two-step dissociation and the viscosity shows a maximum value at about 50% dissociation. We compare here the viscosity behavior for the present copolymers with the above fluorescence data. In Figure 6, the reduced viscosities (η_{sp}/C) for a-CzCa with different f_{cz} in the monomer feed were plotted as a function of pH. The viscosities for a-CzCa showed an increase at neutral pH and a decrease with increasing pH in basic solution, which were consistent qualitatively with those for maleic acid polymers.[12,15] Although these pH dependences were not as sharp as those for the fluorescence intensities (Figure 5), both the η_{sp}/C and I_{rel} values had

Table 4. Fluorescence Parameters of ANS and Perylene in the Presence of VCz Copolymers at pH 3[a]

polymer	ANS[b] $\lambda_{\max}$,[d] nm	ANS[b] I_r[e]	perylene[c] I_r[e]
	516	1	1
r-CzMA(1)	475	7.5	
r-CzMA(17)	473	15.0	33
a-CzCa-2	478	3.1	24

[a] [polymer] = 0.05 g/dL. [b] [ANS] = 5 × 10^{-5} M; excitation wavelength, 365 nm. [c] [perylene] = 1.7 × 10^{-6} M; excitation wavelength, 410 nm; emission wavelength, 445 nm. [d] Wavelength at emission maximum. [e] Relative fluorescence intensity at emission maximum.

Table 5. Stern–Volmer Constants (K_{SV}) for the Monomer Fluorescence Quenching with BHET[a]

polymer	DMF	pH 10	pH 3
CzEtOH	90	120	100
r-CzMA(1)	20	58	250
r-CzMA(36)	51	340	9500[b]
r-CzMA(52)	67	2300[b]	4000[b]
a-CzCa-2	87	290	1100[b]
a-CzCa-2 (in 1 M NaCl)		860	2600[b]

[a] $[\mathrm{Cz}]_{\mathrm{residue}}$ = (1.5–2.0) × 10^{-5} M; excitation wavelength, 325 nm. [b] *Calculated from the initial slope of the Stern–Volmer plot.*

a maximum at the same pH. The parameters were also dependent on f_{cz} in the feed. Similar trends have been reported for poly(2-vinylnaphthalene-*alt*-maleic acid) by Morishima et al.[4] They pointed out significant effects of the monomer sequence distribution in the copolymer on the polymer chain expansion and contraction and thus on the intramolecular excimer formation. In the present case, however, the chain contraction of a-CzCa did not lead to enhanced excimer emission but exclusively to self-quenching as described above.

An interesting observation is that a-CzCa still has a moderate η_{sp}/C value in acidic solution which is larger than those for r-CzMA(x)[16] and other alternating maleic acid copolymers.[4,12] This is unexpected because citraconic acid polymers seem to be more hydrophobic than maleic acid polymers and thus to have a more compact form at low pH. We speculate that the steric hindrance of the methyl substituents on citraconic acid residues inhibits the mutual interaction between the Cz residues in a-CzCa and thus weakens the hydrophobic cohesive forces. We will discuss this later in some detail.

To examine the hydrophobic nature of the present copolymers, fluorescence probes, 8-anilino-1-naphthalenesulfonate (ANS) and perylene, were used. These probes are well-known to show very high emission intensity when solubilized in the hydrophobic polymer cores. Table 4 summarizes the fluorescence parameters in the presence of polymers at pH 3. At basic pH there was little enhancement of the ANS fluorescence for any polymer, whereas at pH 3 r-CzMA(17) strongly enhanced the fluorescence along with a large blue-shift of the emission maximum. By contrast, a-CzCa exhibited a less enhanced ANS emission with the maximum of a longer wavelength. Its hydrophobicity is presumed to be even less than that of r-CzMA(1). In the latter polymer, the undissociated acid sequences, hydrophobic in nature,[17] make some contribution to the uptake of ANS. Similar tendency was observed in the fluorescence intensity of perylene (r-CzMA(x) > a-CzCa). We also found that excitation of the Cz residues sensitized the fluorescence of the solubilized perylene, reflecting the fraction of perylene in the polymer domains. Details will be described elsewhere.[18] All these results support the idea that a-CzCa retains some loose structure at acidic pH.

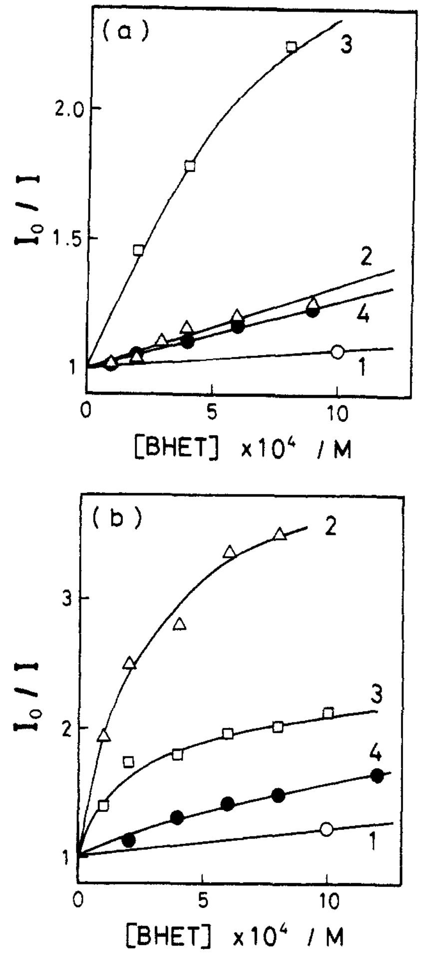


Figure 7. Stern–Volmer plots for monomer fluorescence quenching by BHET in aqueous solution at pH 10 (a) and at pH 3 (b): (1) r-CzMA(1); (2) r-CzMA(36); (3) r-CzMA(52); (4) a-CzCa-2. $[\mathrm{Cz}]_{\mathrm{residue}}$ = 1.0 × 10^{-5} M.

This peculiar behavior for a-CzCa may be explicable in terms of the steric hindrance of the substituents in the copolymer. Inspection of the molecular model reveals that the bulkiness of both Cz and methyl groups, connected directly to the polymer backbone, contributes not only to interruption of the direct contact between the Cz chromophores but also to restriction of the chain motion to a great extent. On the other hand, the substituents in poly(styrene-*alt*-citraconic acid) can rotate more freely because the steric hindrance of the styryl residues is much less than that of the Cz ones. In fact, we found that this polymer had a rather compact form and thus had an even more hydrophobic nature than a-CzCa at acidic pH.[18] Therefore, steric hindrance of the substituents in the vicinity of the polymer backbone is a factor governing the chain construction and hydrophobic association of amphiphilic copolymers. Conformational energy analysis for this type of polymers is required to fully understand these interesting solution and fluorescence behaviors, which remains for our future study.

Fluorescence Quenching. The fluorescence quenching of the alternating and random copolymers with bis(2-hydroxyethyl) terephthalate (BHET),[19] an amphiphilic quencher, was investigated. The data were analyzed conventionally by the Stern–Volmer equation

$$I_0/I = 1 + K_{sv}\,[\mathrm{Q}] = 1 + k_q\,\tau[\mathrm{Q}] \qquad (3)$$

The obtained parameters, however, were limited to the Stern–Volmer constants (K_{sv}) for fear that the nonexponential decays of the polymer fluorescence should lead to the erroneous lifetimes (τ) and second-order quenching rate constants (k_q). The K_{sv} values are shown in Table 5. There was only a little difference in the quenching efficiency for the monomer model (CzEtOH) in DMF and aqueous solutions, while the K_{sv} values for the copolymers in aqueous solution were always larger than those in DMF. These clearly indicate that the hydrophobic interaction between the copolymers and BHET facilitates the quenching in aqueous solutions. At pH 10, the fluorescence of r-CzMA(x) was quenched far more effectively with increasing f_{cz} in the copolymer compared with those in DMF and the Stern–Volmer plot for r-CzMA(52) showed a downward curvature (Figure 7). The apparent K_{sv} value for this polymer was calculated from the initial slope to be 2300 M^{-1} as listed in Table 5. These peculiar phenomena have been encountered with various types of amphiphilic copolymers, which are due to the hydrophobic binding of BHET with the hydrophobic microdomains in the copolymers. A possible interpretation of the downward curvature by a combination of the static and dynamic mechanisms has also been reported previously.[19,20] In contrast, the quenching of a-CzCa was ineffective compared with that of r-CzMA(52), reflecting the less hydrophobic nature of a-CzCa.

The undissociated acid sequences in the copolymers may play a role in facilitating hydrophobic binding of BHET around the Cz chromophores as described above. This is a reason that the quenching constants are much larger at pH 3 than at pH 10 (Table 5). In fact, the Stern–Volmer plots for the copolymers other than r-CzMA(1) deviated downward from the straight line, implying the strong binding of BHET to the polymers (Figure 7). It is important to note that the K_{sv} value of a-CzCa at pH 3 is still lower than those of the corresponding random copolymers. This is not in conflict with the result of the probe experiments. However, taking into accout that the excited state lifetime of a-CzCa is extremely short ($\langle\tau\rangle \sim 0.09$ ns), the quenching rate constant (k_q) is estimated to be very high ($>10^{12}$ M^{-1} s^{-1}), which is at least 2 orders of magnitude higher than that for a purely diffusional process (cf. $k_q = \sim 8 \times 10^9$ M^{-1} s^{-1} for CzEtOH at pH 3). We assume considerable contribution of efficient energy migration to the enhanced quenching of a-CzCa. As expected, the addition of NaCl to the a-CzCa solution strengthened the hydrophobic association, leading to the higher K_{sv} value at any pH.

Conclusion

The remarkable effect of the steric hindrance of comonomers in amphiphilic alternating copolymers on the solution behavior and photophysics was observed in aqueous solution by a comparison of a-CzCa and a-CzMa. It became apparent that the methyl groups in a-CzCa prevented the chain contraction and excimeric interaction. However, a-CzCa still had a very few self-quenching sites and some contraction of the polymer chain facilitated energy migration to these sites, resulting in a markedly decreased emission. On the other hand, a-CzMa and r-CzMA(x) with high f_{cz} showed a prominent excimer emission because the possibly direct interaction of the Cz groups enhanced the hydrophobic association and thus excimer emission. These differences were also reflected in the efficiency of quenching with an amphiphilic quencher. In addition, our preliminary experiments suggest that efficient photochemical reactions are performed with a-CzCa as a sensitizer in aqueous media.[18] The detailed study is now in progress.

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References and Notes

(1) (a) Morishima, Y. *Prog. Polym. Sci.* **1990**, *15*, 949. (b) Morishima, Y. *Adv. Polym. Sci.* **1992**, *104*, 51.

(2) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 3903, and references therein.

(3) (a) McCormick, C. L.; Hoyle, C. E.; Clark, M. D. *Macromolecules* **1990**, *23*, 3124. (b) McCormick, C. L.; Hoyle, C. E.; Clark, M. D. *Macromolecules* **1991**, *24*, 2397.

(4) (a) Morishima, Y.; Kobayashi, T.; Nozakura, S.; Webber, S. E. *Macromolecules* **1987**, *20*, 807. (b) Morishima, Y.; Lim, H. S.; Nozakura, S.; Sturtevant, J. L. *Macromolecules* **1989**, *22*, 1148.

(5) Bai, F.; Chang, C. H.; Webber, S. E. *ACS Symp. Ser.* **1987**, *No. 358*, 384.

(6) Sturtevant, J. L.; Webber, S. E. *Macromolecules* **1989**, *22*, 3564.

(7) Itoh, Y.; Webber, S. E.; Rodgers, M. A. *J. Macromolecules* **1989**, *22*, 2766.

(8) Itoh, Y.; Nakada, M.; Satoh, H.; Hachimori, A.; Webber, S. E. *Macromolecules* **1993**, *26*, 1941.

(9) Ito, S.; Ohmori, S.; Yamamoto, M. *Macromolecules* **1992**, *25*, 185.

(10) Satozono, H.; Suzuki, S.; Tokou, N.; Takehara, H.; Uno, Y. To be submitted for publication in *Nippon Kagaku* Kaishi.

(11) For example, Chu, D. Y.; Thomas, J. K. *Macromolecules* **1984**, *17*, 2142.

(12) (a) Sakurada, I.; Sakaguchi, Y.; Uehara, H. *Kobunshi Kagaku* **1970**, *27*, 82. (b) Ohno, N.; Nitta, K.; Sugai, S. *Kobunshi Kagaku* **1971**, *28*, 671.

(13) Tazuke, S.; Okamura, S. *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Gayload, N. G. Eds.; Wiley: New York, 1971; Vol. 14, p 281.

(14) Preliminary experiments on the solvent effect of the a-CzCa fluorescence favored the former possibility: Itoh, Y.; Yasue, T.; Hachimori, A. Unpublished result.

(15) (a) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842. (b) Kawaguchi, S.; Kitano, T.; Ito, K.; Minakata, A. *Macromolecules* **1991**, *24*, 6335, and references therein.

(16) Although no accurate viscosity data for r-CzMA(x) with $f_{cz} >$ 0.10 and a-CzMa were available owing to the restricted solubility in aqueous solution, their η_{sp}/C values at low pH were estimated to be extremely low (cf. $\eta_{sp}/C = 0.17$ dL/g for 0.05 g/dL of r-CzMA(1) at pH 3).

(17) Delben, F.; Crescenzi, V.; Quadrifoglio, F. *Eur. Polym. J.* **1972**, *8*, 933.

(18) Itoh, Y.; Yasue, T.; Hachimori, A. Manuscript in preparation.

(19) (a) Itoh, Y.; Morishima, Y.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 467. (b) Morishima, Y.; Itoh, Y.; Nozakura, S. *Chem. Phys. Lett.* **1982**, *91*, 258. (c) Morishima, Y.; Kobayashi, T.; Nozakura, S. *J. Phys. Chem.* **1985**, *89*, 4081.

(20) Owing to the poor solubility of the copolymers in aqueous solution, we could not study the dependence of polymer concentration on the quenching efficiency which would yield interesting kinetic parameters, association constant and average aggregation number of the chromophores.[19]