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Quenching in the excited singlet state of amphiphilic copolymers with pendant carbazolylalkyl groups in aqueous solution

Yoshihiro Itoh*, Tadao Yasue, Makoto Gouki and Akira Hachimori
Institute of High Polymer Research, Faculty of Textile Science and Technology, Shinshu University, Tokida 3-15-1, Ueda, Nagano 386, Japan
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Amphiphilic polyanions containing 2-(9-carbazolyl)ethyl methacrylate and 3-(9-carbazolyl)propyl methacrylamide (r-CzEMA(x) and r-CzPMAm(x), respectively) were prepared and their fluorescence properties were compared with those of various *N*-vinylcarbazole-containing copolymers (r-VCz(x)). The fluorescence spectra for those former polymers with a higher carbazolyl (Cz) content showed monomeric but diminished emission in aqueous solution, indicating that some excited-state quenching occurred in these polymers. The energy transfer to hydrophobically bound perylene and the fluorescence quenching by fumaric acid (FA), a water-soluble electron acceptor, were facilitated for r-CzPMAm(x) with a higher Cz content when compared to that observed for r-VCz(x). These facts suggest a large effect of the excited-state quenching on the photochemical reactions, as well as providing a contribution of energy migration to such reactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: amphiphilic polymer; carbazole; fluorescence quenching)

INTRODUCTION

Amphiphilic polymers which are highly loaded with hydrophobic chromophores such as polycyclic aromatic groups are known to take on micelle-like structures in aqueous solution, resulting in the modification of a variety of photophysical and photochemical properties[1]. One of the most important and profitable features of these polymers for 'photon-harvesting' or the utilization of excited energy is the rapid and efficient energy migration in the polymer microdomains[2]. However, hydrophobic aggregation of the chromophores concurrently enhances various energy-wasting photoprocesses, such as excimer formation and self-quenching. We have reported several approaches for inhibiting these deactivation processes by using chromophore alternation[3,4] and the introduction of bulky groups on the chromophores or polymer chains[4,5]. Contrary to our expectations, however, all of these polymers showed remarkable self-quenching in aqueous solution, probably because of the further accelerated energy migration to a very small number of quenching sites.

Recently, we reported on the photophysical behaviour of alternating and random copolymers of 2-(9-carbazolyl)ethyl methacrylate (CzEMA) and styrene[6,7]. Contraction of the polymer coils in poor solvents induced the hypochromic effect, but caused only a little quenching and excimer formation, even for the random copolymers. It can thus be supposed that the excited state of this class of amphiphilic copolymer is much less quenched in aqueous solution.

In this present study, we have prepared two kinds of water-soluble random copolymers (*Figure 1*), namely copolymers of CzEMA and sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) (r-CzEMA(x)), and 3-(9-carbazolyl)propyl methacrylamide (CzPMAm) and AMPS (r-CzPMAm(x)), where x represents the carbazolyl (Cz) content of the copolymer in mol%. One might expect that the latter copolymers would be further advantageous for retardation of the mutual interaction of the Cz groups, and thus the excited-state quenching in aqueous solution, because of the following:

1. A longer spacer chain, such as the propyl group, would decrease the possibility of the Cz groups encountering one another spatially[8].
2. The rigidity and/or hydrogen bonding of the amide bond in CzPMAm would decrease the local motion of the side groups, including the Cz chromophores[9–11]. In addition, the amide bond would cause hydrophilicity of the polymer.
3. CzPMAm would polymerize with AMPS in a highly random fashion, giving shorter successive sequences of Cz monomers than CzEMA[9].

We will, however, find that the excited states of both type of copolymers are quenched to the same extent. We will also compare the fluorescence behaviour of these copolymers with that of random copolymers of *N*-vinylcarbazole (VCz) and AMPS (r-VCz(x)), where an excimer could be easily formed (*Figure 1*).

EXPERIMENTAL

Materials

2-(9-Carbazolyl)ethyl methacrylate (CzEMA) was

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* To whom correspondence should be addressed

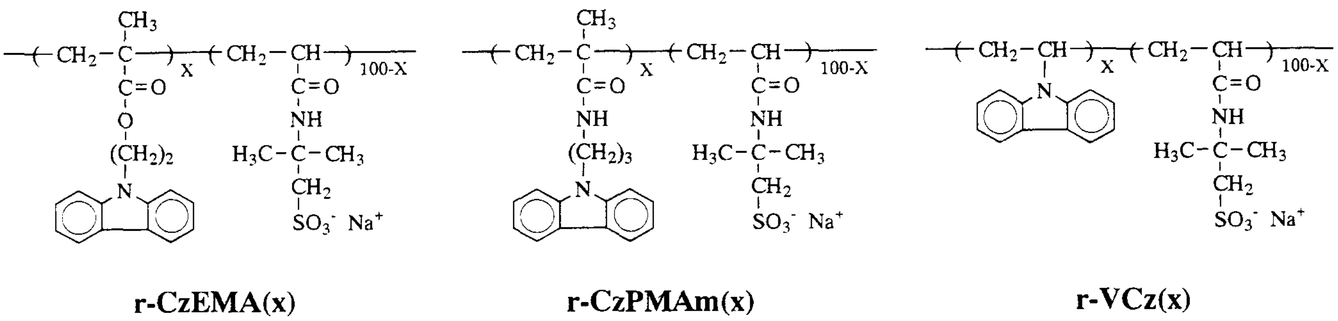

Figure 1 Chemical structures of r-CzEMA(x), r-CzPMAm(x), and r-VCz(x); x represents the Cz content in mol%

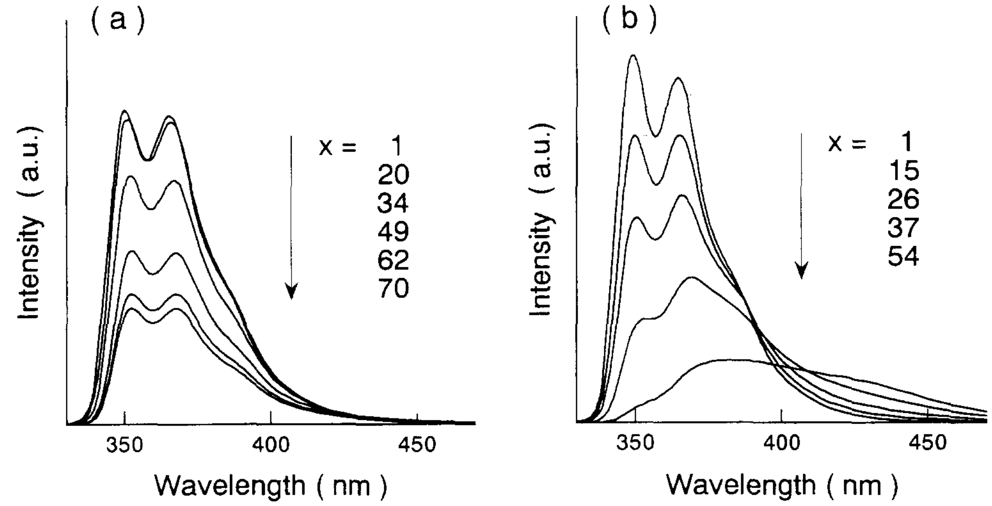

Figure 2 Fluorescence spectra of (a) r-CzEMA(x) and (b) r-VCz(x) in H_2O: $[Cz]_{residue} = 7 \times 10^{-6}$ M; excitation wavelength, 293 nm; Cz contents in mol% (x) are indicated on the figure

synthesized as reported previously[7]. 9-(3-Methacryloylaminopropyl)carbazole (CzPMAm) was prepared by the reaction of 9-(3-aminopropyl)carbazole[12] with methacryloyl chloride, and purified by column chromatography on silica gel with benzene as the eluent (m.p. 152.5–153.5°C). 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was obtained from Nitto Chemical Industry Co. and used as received. *N*-Vinylcarbazole (VCz) (Nakalai) and fumaric acid (FA) (Wako) were recrystallized from *n*-hexane and methanol (MeOH), respectively.

The copolymerization of the Cz monomers with AMPS was performed in degassed *N,N*-dimethylformamide (DMF) at 60°C by using 2,2′-azobisisobutyronitrile (AIBN), and then purified as reported in a previous paper[5]. The compositions of the copolymers were determined by absorption spectroscopy.

Steady-state fluorescence spectra and fluorescence lifetimes were measured as described previously[6].

RESULTS AND DISCUSSION

Copolymerization

It has been reported that the copolymerization of AMPS and methacrylamides gives completely random copolymers[9]. In this present case, the monomer reactivity ratios determined from a Fineman–Ross plot for the CzPMAm(M_1)–AMPS(M_2) system were $r_1 = 0.87$ and $r_2 = 0.94$, thus indicating a highly random distribution of the monomers in r-CzPMAm(x). On the other hand, the CzEMA(M_1)–AMPS(M_2) system showed a lower tendency for copolymerization ($r_1 = 3.11$ and $r_2 = 0.52$).

Fluorescence spectra

In agreement with our previous results for the copolymers of CzEMA and styrene in organic solution[6], both of the copolymers, r-CzEMA(x) and r-CzPMAm(x), only showed strong monomer fluorescence in DMF, and their fluorescence decay curves fitted a single exponential function (lifetime (τ) = 14 ns). These results confirm that separation of the Cz chromophores from the main chain is effective for the inhibition of intramolecular excimer formation.

Figure 2a compares the fluorescence spectra of r-CzEMA(x) with different Cz contents in aqueous solution. The copolymers exhibited essentially monomeric emission, while the fluorescence intensity decreased with the increase in Cz content. The same tendency was observed for the r-CzPMAm(x) system. We previously observed decreased emission for the CzEMA polymers in poor organic solvents, which was caused primarily by the apparent decrease in absorbance due to the mutual interactions of the ground-state chromophores, i.e. the hypochromic effect, rather than by the excited-state quenching[7]. In contrast, these present copolymers showed only a small hypochromic effect. We do not have a clear explanation for this. We also found that the fluorescence decay curve for r-CzEMA(49) showed multiexponential behaviour, with a short-lifetime component (*Table 1*). On the other hand, Cz chromophores bound to polyelectrolytes are known to exhibit intense fluorescence with a longer lifetime when placed in hydrophobic microenvironments[4,13]. Therefore, it can be safely said that the excited states of r-CzEMA(x) and r-CzPMAm(x) are quenched in aqueous solution, although the influence of the heterogeneous distribution of the Cz groups in the polymer domain on their fluorescence is not neglected. In the case of r-VCz(x), those copolymers with higher Cz contents exhibited a significant decrease in the fluorescence intensity accompanying more enhanced excimer emission (*Figure 2b*).

In *Figure 3*, the relative fluorescence intensity at 350 nm (I_{rel}) is plotted against the Cz contents of the copolymers. The intensities for r-CzEMA(x) and r-CzPMAm(x) decreased with the Cz content. The extent of the decrease, however, was far less than those found for r-VCz(x) and most other amphiphilic copolymers reported so far[3,4]. This fact confirms again that the present type of copolymers are greatly advantageous in the retardation of excited-state quenching, even in condensed chromophore systems[7,14]. It should be noted that the data for both r-CzEMA(x) and r-CzPMAm(x) lie almost on a curve, i.e. there is no influence of the polymer structure on their fluorescence behaviour. This is unexpected because r-CzPMAm(x) contains longer spacer chains and more rigid amide bonds between the polymer main chain and the Cz rings, and has shorter Cz monomer sequences than r-CzEMA(x), which would decrease the mutual interaction of the Cz groups and thus retard the quenching, as described in the Introduction. We speculate here that the propyl groups in r-CzPMAm(x), being more flexible and having longer spacer chains than the ethyl groups in r-CzEMA(x), may facilitate the Cz–Cz interactions, hydrophobically if they do, in order to compensate for the decreased interactions owing to the rigidity of the amide bonds and the highly random distribution of the Cz monomers. We will discuss this further below.

Table 1 Fluorescence decay parameters for r-CzEMA(x) and r-VCz(x) in aqueous solution[a]

Polymer	τ_i (ns)/α_i		
r-CzEMA(1)	12.5/1.00		
r-CzEMA(34)	13.1/0.87	21.8/0.13	
r-CzEMA(49)	14.3/0.53	19.5/0.21	6.8/0.26
r-VCz(1)	14.7/1.00		
r-VCz(26)	14.1/0.57	20.6/0.09	5.8/0.34
r-VCz(54)	9.9/0.24	26.2/0.13	1.1/0.63

[a] Fitting function, $I(t) = \Sigma a_i \exp(-t/\tau_i)$; excitation wavelength, 316 nm; emission wavelength, 345 nm

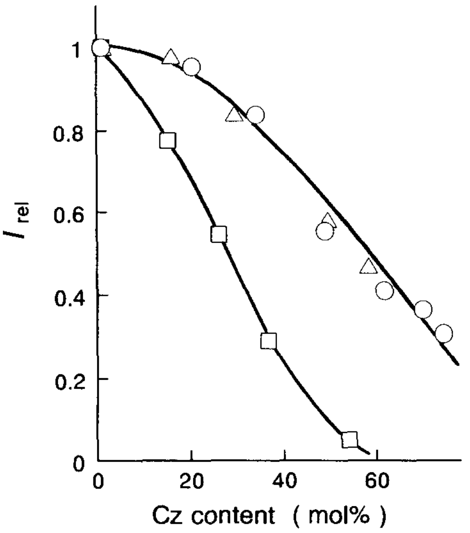

Figure 3 Dependence of relative fluorescence intensities (I_{rel}) at 350 nm on the Cz content for Cz polymers in aqueous solution: (○) r-CzEMA(x); (△) r-CzPMAm(x); (□) r-VCz(x). I_{rel} is normalized to the intensity of each polymer with $x = 1$ mol%

In many cases, fluorescence quenching in solution can be analysed conventionally by using the Stern–Volmer equation, as follows:

$$I_0/I = 1 + K_{sv}[Q] \qquad (1)$$

where I_0 and I are the fluorescence intensities in the absence and presence of a quencher, respectively, K_{sv} the quenching constant, and [Q] the quencher concentration. If the quenching occurs via nearest-neighbour chromophore interactions, just as in the case of intramolecular excimer formation in aromatic polymers[15,16], [Q] should be proportional to the Cz–Cz diad fraction of Cz in the copolymer (F_{11})[17]. *Figure 4* shows the almost linear relationship between I_0/I and F_{11} for both r-CzEMA(x) and r-CzPMAm(x). This clearly indicates that the quenching is due mainly to nearest-neighbour chromophore interactions in the successive Cz sequences, and that non-nearest-neighbour interactions, which should be induced in the copolymers with higher Cz contents in aqueous solution, have little effect on the quenching. However, why the quenching in these polymers occurs in aqueous solution remains obscure.

From the above results, it can be concluded that there is no difference in the fluorescence behaviour between r-CzEMA(x) and r-CzPMAm(x). As described above, this may be closely related to the flexibility of the alkyl chain spacers. Morishima *et al.* recently demonstrated that highly bulky and rigid hydrophobic groups, such as cyclododecyl, adamantyl and 1-naphthylmethyl groups, attached to the backbone through amide bonds cause extremely restricted mobility of the hydrophobes[9–11] and thus suppress the self-quenching[9]. These facts imply that this present type of amphiphilic polymers containing shorter spacer bonds is favourable for further suppression of the quenching. A study is now in progress along these lines.

Fluorescent probe study

In order to examine the hydrophobic nature of the copolymers, perylene was used as a fluorescent probe. *Table 2* shows the fraction of perylene solubilized in the hydrophobic polymer domains, which has been estimated from the peak intensity for perylene in the excitation spectrum. Until the Cz content reached 40 mol%, r-CzEMA(x) showed a more efficient uptake of perylene when compared with r-CzPMAm(x), which may reflect the hydrophobic nature of CzEMA itself. In contrast, the extent of the uptake was greater for r-CzPMAm(50) and r-VCz(54) than for r-CzEMA(49), indicating that the former polymers are more hydrophobic. These results

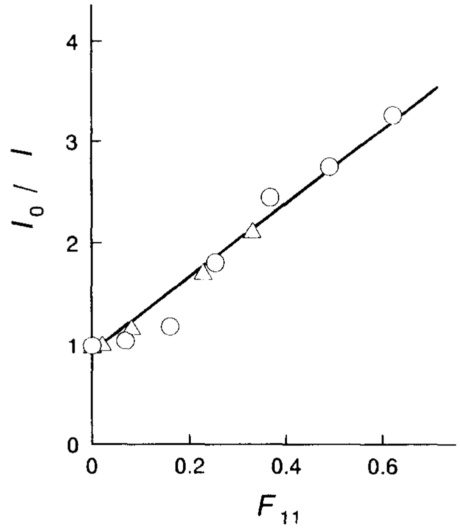

Figure 4 Relationship between the fluorescence intensity ratio (I_0/I) and the Cz–Cz diad fraction (F_{11}): (○) r-CzEMA(x); (△) r-CzPMAm(x). I_0 is the fluorescence intensity for each polymer with $x = 1$ mol%

Table 2 Fluorescence properties of perylene in the presence of Cz polymers in aqueous solution[a]

Polymer	Uptake[b] (%)	Transfer yield[c] (%)
r-CzPMAm(1)	0.02	~0
r-CzPMAm(29)	0.6	1
r-CzPMAm(50)	4.8 (3.9)[d]	15 (43)[d]
r-CzEMA(34)	1.8	4
r-CzEMA(49)	3.6 (3.6)[d]	19 (49)[d]
r-VCz(37)	0.8	4
r-VCz(54)	7.6 (5.5)[d]	36 (36)[d]

[a] $[\mathrm{Cz}]_{\mathrm{residue}} = 1.7 \times 10^{-4}$ M; [perylene] $= 1.7 \times 10^{-6}$ M

[b] The fraction of perylene adsorbed in the polymer domains; calculated from the calibrated peak intensity at 410 nm for perylene in the excitation spectrum monitored at 466 nm

[c] The efficiency of energy transfer from the Cz moiety to the adsorbed perylene; calculated from the calibrated peak intensity at 293 nm for the Cz moiety in the excitation spectrum monitored at 466 nm for perylene

[d] Figures in parentheses represent results obtained in 0.6 M aqueous NaCl

may support the above speculation that the Cz–Cz interaction, or association, is more feasible in r-CzPMAm(x) than in r-CzEMA(x).

Excitation of the Cz residues enhances the fluorescence of the solubilized perylene, which is indicative of energy transfer occurring from the excited Cz chromophores to the perylene traps. In *Table 2*, the energy transfer yield was calculated from the peak intensity for the Cz moiety in the excitation spectrum in a similar manner to that described above. The increased transfer yield reflected the higher solubility of perylene, but did not perfectly parallel the uptaken amount. This is because the transfer efficiency depends not only on the acceptor concentration but also on the donor–acceptor distance (i.e. the location of the solubilized perylene). Interestingly, the addition of NaCl remarkably increased the transfer yield for r-CzEMA(49) and r-CzPMAm(50), but caused no enhancement of the yield for r-VCz(54), while the solubility of perylene tended to decrease in these polymers. Considering the fact that the latter polymer is the most hydrophobic (*Table 2*), the higher values for the former polymers in aqueous NaCl strongly suggest that retardation of excited-state quenching contributes favourably to the efficient energy transfer.

Fluorescence quenching

The fluorescence quenching of these present copolymers by fumaric acid (FA)[18], a water-soluble electron acceptor, was investigated. In order to minimize the influence of electrostatic interactions between FA and the anionic segments in the copolymers, the quenching experiments were performed in an aqueous solution of pH 2.5, which was below the pKa_1 of FA (3.03)[19]. The data obeyed simple Stern–Volmer kinetics (equation (1)). The K_{SV} values estimated from the slope are given in *Table 3*. The data obtained in organic solvents are also listed. The quenching constants tended to increase with the Cz content of the copolymers in both organic and aqueous solutions, indicating some contribution of energy migration to the quenching. A remarkable feature is that the quenching for r-CzPMAm(50) was extremely efficient in aqueous solution. The second-order rate constant (k_q) calculated from K_{SV} and the fluorescence lifetime ($\tau \sim 14$ ns) was ca. $2 \times 10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which significantly exceeded the diffusion limit ($k_{\mathrm{diff}} \sim 7 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in H_2O)[20]. The addition of NaCl further increased the quenching efficiency (*Table 3*).

There are two possibilities to be considered here, namely (1) the associative binding of FA to r-CzPMAm(50), which is possibly of the hydrophobic type, increases the effective concentration of FA around the Cz chromophores, and (2) an extremely efficient energy migration in the polymer microdomains facilitates the quenching processes. It should be noted that r-VCz(54), the most hydrophobic polymer, did not have so large a quenching constant and that FA is known to be a hydrophilic quencher[18]. Furthermore, the linear Stern–Volmer plot for r-CzPMAm(50) implies much less contribution of the static quenching by the bound FA, although it does not satisfy the necessary and sufficient condition for the dynamic quenching mechanism. Therefore, these results may rule out the former possibility, i.e. enhancement due to the hydrophobic binding of FA to the polymer. Such enhanced quenching was also observed for poly(*N*-vinylcarbazole-*alt*-citraconic acid) (a-CzCa) with a less hydrophobic character[4]; the fluorescence of a-CzCa at pH 3 was quenched efficiently by an amphiphilic quencher, namely bis(2-hydroxyethyl)terephthalate. We have speculated that efficient energy migration in the polymer microdomains, which is further facilitated by some contraction of the polymer chain in an acidic solution, contributes to the increased quenching efficiency.

In order to examine the effect of the polymer coil density on the fluorescence quenching, a quenching experiment on the present copolymers was carried out in 1,4-dioxane, a poor organic solvent. The K_{SV} values were estimated to be 70 and 384 M^{-1} for r-VCz(54) and r-CzPMAm(50), respectively. These values were close to those obtained in aqueous solution (*Table 3*). These observations support the above speculation that there is little or no attractive interaction between FA and r-CzPMAm(50), even in aqueous solution, and efficient energy migration in the compact polymer domain facilitates the quenching.

Another notable feature is that the K_{SV} values for

Table 3 Stern–Volmer constants (K_{sv}) for the fluorescence quenching of the copolymers with FA in aqueous and organic solutions[a]

Polymer	K_{sv} (M^{-1}) H_2O[b]	K_{sv} (M^{-1}) DMF or MeOH
CzEtOH[c]	92	109[d]
r-CzPMAm(1)	30	42[e]
r-CzPMAm(29)	110	84[e]
r-CzPMAm(50)	300 (477)[f]	105[d]
r-VCz(1)	17	42[e]
r-VCz(37)	120	79[e]
r-VCz(54)	90 (90)[f]	77[d]

[a] $[Cz]_{residue} = 1.0 \times 10^{-5}$ M; excitation wavelength, 293 nm
[b] Measured at pH 2.5
[c] *N*-(2-hydroxyethyl)carbazole
[d] Measured in DMF
[e] Measured in MeOH
[f] Figures in parentheses represent results obtained in 0.6 M aqueous NaCl

r-VCz(54) were almost the same in all of the solutions, whether it had random or compact coils. Remarkable self-quenching and excimer formation might obstruct energy migration, thus resulting in little effect of the coil dimensions on the quenching efficiency.

CONCLUSIONS

Effective but imperfect retardation of the excited-state quenching was achieved in amphiphilic copolymers with pendant carbazolylalkyl groups in aqueous solution. The quenching is due mainly to interactions between the nearest-neighbour Cz groups in the polymer chain. The energy transfer to perylene solubilized in the polymer microdomains and fluorescence quenching by fumaric acid were much more effective for these copolymers than for the *N*-vinylcarbazole polymers. These results strongly suggest that efficient energy migration in the compact domains and a diminished quenching of the excited state are responsible for the facilitation of photochemical reactions in amphiphilic polymer systems.

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