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Fluorescence properties of carbazolyl-containing amphiphilic copolymers

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Abstract

Amphiphilic random copolymers of 2-(9-carbazolyl)-1-methylethyl methacrylate, 2-(9-carbazolyl)ethyl methacrylate or 2-(9-carbazolyl)ethyl acrylate with methacrylic acid were synthesized and their fluorescence properties in aqueous solution were examined. The fluorescence spectra of the copolymers showed monomeric emission. The fluorescence intensity decreased with increase of the content of carbazolyl groups in the copolymers, indicating that some excited-state quenching occurs in these systems. The fluorescence intensity of the copolymers also changed with the change of pH of the solutions. The character of these changes was dependent on the content of carbazole chromophores in the copolymer. Solubilization of 8-anilino-1-naphthalenesulfonic acid ammonium salt and perylene by the copolymers synthesized has been studied. The energy transfer to hydrophobically-bound perylene was facilitated for carbazolylalkylmethacrylate copolymers when compared to that observed for carbazolylalkylacrylate copolymers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amphiphilic polymer; Carbazole; Fluorescence quenching

1. Introduction

Amphiphilic polyelectrolytes which are covalently functionalized with hydrophobic chromophores such as polycyclic aromatic groups have a variety of interesting features worthy of study. They “solubilize” hydrophobic chromophores in water because of their covalent bonding to the polymer backbone. This provides an unusual opportunity to study photophysics of such otherwise water-insoluble chromophores in aqueous solution. A number of investigations have focused on the photophysics of such polyelectrolyte-bound chromophores and have demonstrated that the photophysical behavior is strongly dependent on the nature of the microphase structure created by the polymer chains in aqueous solution [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 domains [2]. However, hydrophobic aggregation of the chromophores concurrently enhances various energy-wasting photoprocesses, such as excimer formation and self-quenching. Inhibitation of excimer formation and other quenching processes is crucial not only for the design of “photon-harvesting” polymers but also for increasing understanding of the complicated physical behavior of polymer systems. A lot of effort has been directed to avoid excimer formation in various types of polymers, e.g. introduction of bulky groups on chromophores, fixing of chromophores to the rigid polymer chain, separation of chromophores from the main chain, and alternation of chromophores [2]. Ito et al. demonstrated that poly(2-(9-carbazolyl)ethyl methacrylate) does not form an excimer even in the neat film [3]. There are only a few papers concerning photophysical studies of carbazolyl chromophores containing amphiphilic electrolytes in aqueous solution [4,5].

In the present study, we have synthesized water-soluble random copolymers of methacrylic acid and carbazole-containing monomers and studied their fluorescence properties in aqueous solution. The following monomers were copolymerized with methacrylic acid: 2-(9-carbazolyl)-1-methylethyl methacrylate, 2-(9-carbazolyl)ethyl methacrylate and 2-(9-carbazolyl)ethyl acrylate. In addition, hydrophobic character and solubilization ability of the prepared amphiphilic polyelectrolytes were examined by using fluorescence probes.

2. Experimental

2.1. Materials

Methacrylic acid (MA) was prepolymerized (UV radiation) and fractionally vacuum distilled prior to use.

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2,2′-Azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from methanol. An ethereal solution of diazomethane was prepared according to the literature [6]. The solvents, hexane, methanol, ethanol, acetone, diethyl ether, dichloromethane, tetrahydrofuran, dimethylformamide, chloroform were purified by standard procedures [7]. Benzene used for polymerizations was dried over sodium and distilled. *N*-ethylcarbazole (Aldrich) was recrystallized repeatedly from methanol. Perylene (99%, Aldrich) was purified by three recrystallizations from ethanol. 8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANS) (Aldrich) was recrystallized three times from distilled water.

2.2. Synthesis

2-(9-Carbazolyl)ethyl methacrylate (CEMA) (mp, 82–83°C) and 2-(9-carbazolyl)-1-methylethyl methacrylate (CMEMA) (mp, 69–70°C) were obtained by esterification of methacryloyl chloride (Aldrich) with 9-(2-hydroxyethyl)carbazole and 9-(2-hydroxypropyl)carbazole, respectively as described in [8]. 2-(9-Carbazolyl)ethylacrylate (CEA) (mp, 75–76°C) was prepared by the same method using acrylolyl chloride (Aldrich) instead of methacryloyl chloride (Aldrich). The crude products were purified by column chromatography with dichlorometane as eluent. 9-(2-Hydroxyethyl)carbazole and 9-(2-hydroxypropyl)carbazole were prepared from carbazole and ethylene carbonate and propylene carbonate, respectively, by refluxing in dimethylformamide with the small amounts of K_2CO_3 [9]. These monomers were recrystallized from carbon tetrachloride.

2.3. Copolymerization

Copolymerizations of carbazolylalkyl(meth)acrylates (CAMA) and MA were performed as follows. A 20 ml benzene solution containing carbazolylalkyl(meth)acrylate and MA in a known ratio (10 mmol in total) and 0.5 mol% (on the basis of total monomers) of AIBN was repeatedly evacuated and purged with nitrogen. Polymerizations were carried out under the nitrogen blanket at 60°C. The monomer conversion was kept under 10%. The copolymers with high molar fraction of carbazolylalkyl(meth)acrylates were isolated and purified by precipitation from THF into hexane. The copolymers with high molar fraction of MA were isolated and purified by precipitation from methanol into diethyl ether. The copolymerizations were carried out with various mole fractions of carbazolylalkyl(meth)acrylates in monomer feed. Since solubilities of carbazolylalkyl(meth)acrylates and MA homopolymers is very different and the solubility of the copolymers is different from that of the homopolymers the three-fold reprecipitation yielded pure copolymers.

Esterification of thus, obtained copolymers was carried out as follows. To a suspension of the copolymer (0.1 g) in 100 ml of benzene 100 ml of an ethereal solution of diazomethane was added. The reaction mixture was stirred at room temperature for 24 h to result in a clear solution. In order to secure the completion of the reaction another 50 ml of the ethereal diazomethane was added, and the stirring was continued for additional 24 h. The mixture was then concentrated by evaporation of the solvents to about one-tenth its original volume. The copolymer was precipitated by an excess of ether and purified by the three-fold reprecipitation from benzene into ether. Finally the benzene solution was lyophilized. Complete esterification was confirmed by FTIR spectroscopy using a Bio-Rad Digilab FTS-40 spectrophotometer.

2.4. Characterization

In order to determinate the copolymer composition ^{1}H NMR spectra of the copolymers (converted into their methyl esters forms) were recorded in DMSO at room temperature by using Bruker AC 250 spectrometer. The copolymer composition was calculated from the integrals of the total aromatic and aliphatic proton regions.

For an estimation of molecular weight GPC measurements were carried out for a $CHCl_3$ solutions of the methyl ester derivatives of the copolymers (GPC traces of the acidic groups containing copolymers are broad and skewed to a higher elution volumes, implying some interactions with the column material) using a Waters system including a Waters 440 UV detector (254 nm). GPC measurements of the poly(carbazolylalkyl(meth)acrylates) were carried out using THF as eluent. Monodisperse polystyrene samples were used as standards to calculate molecular weights of the homopolymers and copolymers in the corresponding methyl ester form. The molecular weight of the poly(methacrylic acid) (PMA) was estimated from the intristic viscosity in 0.1N LiCl methanol solution at 26°C and calculated by the Mark–Houwink equation [10].

2.5. Fluorescence spectra

Steady state fluorescence spectra were recorded on a Perkin-Elmer LS-5 luminescence spectrometer at the room temperature. Copolymer solutions were prepared by using doubly distilled water. The polymers were 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 (with the content of carbazole higher than 30 mol%), aqueous solutions were prepared by adding a DMF stock solution to water at pH 10 with vigorous stirring. The final solution contained less than 1 vol.% of DMF. Solubilization of perylene and ANS in aqueous polymer solutions was achieved by slowly injecting microlitre quantities of probe dissolved in acetone into milliliter quantities of polymer solution. The final aqueous polymer solution contained less than 0.1 vol.% acetone. The mixture was shaken for 20 min, allowed to equilibrate in the dark for 4 h and filtered by using fine filter paper.

3. Results and discussion

The copolymerization of carbazolylalkyl(meth)acrylates (CMEMA, CEMA and CEA) with methacrylic acid (MA) at 60°C in the presence of AIBN was studied in a wide composition range. The results of these copolymerizations are shown in the Table 1. The monomer reactivity ratios determined according to the Kelen–Tüdös procedure [11] for the CMEMA(M_1)–MA(M_2) system were $r_1 = 0.88$ and $r_2 = 0.93$, CEMA(M_1)–MA(M_2) system $r_1 = 0.72$ and $r_2 = 0.98$, CEA(M_1)–MA(M_2) system $r_1 = 0.29$ and $r_2 = 1.7$, thus, indicating a highly random distribution of the monomers in r-CMEMAMA(*x*), r-CEMAMA(*x*) and r-CEAMA(*x*), where *x* represents the carbazolyl content of the copolymer in mol%.

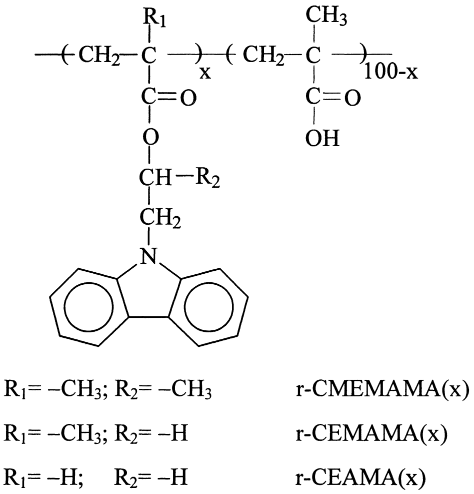

Fig. 1. Chemical structures of r-CMEMAMA(*x*), r-CEMAMA(*x*) and r-CEAMA(*x*).

Fluorescence properties of the synthesized copolymers (Fig. 1) in aqueous solution were studied. Fig. 2 compares the fluorescence of r-CMEMAMA(*x*) with different carbazolyl contents in aqueous solution in basic (a) and acidic media (b). The copolymers exhibited essentially monomeric emission, while the fluorescence intensity decreased with the increase in carbazolyl content. This observation can be apparently explained by some excited-state quenching which is more obvious in acid media, in which the conformation of macromolecules is more favorable for the interaction of the chromophores. For both r-CEMAMA(*x*) and r-CEAMA(*x*) also only monomer fluorescence was observed in all pH range. These results confirm the rule

Table 1
Copolymerization of carbazolylalkyl(meth)acrylate (CAMA) with MA and copolymer characteristics

Polymer	Fraction of CAMA (mol%)		Polymer (time/min)	Conversion (wt.%)	$M_n \times 10^{-4}$ (g/mol)	M_w/M_n	F_{11}[a]
	Monomer feed	Polymer					
PMA	0	0	20	7.34	5.8	–	–
r-CMEMAMA(1)	1.5	1.01	20	7.34	5.1	–	0.00021
r-CMEMAMA(9)	10	9.41	60	10.6	4.68	3.58	0.00934
r-CMEMAMA(18)	20	18.31	110	9.65	2.45	3.12	0.03704
r-CMEMAMA(37)	40	36.71	195	8.14	3.98	2.56	0.14734
r-CMEMAMA(56)	60	55.95	270	3.54	2.83	2.33	0.33502
r-CMEMAMA(71)	80	70.77	350	4.2	1.92	2.17	0.6119
r-CMEMAMA(81)	90	81.52	390	6.91	1.84	4.05	0.7902
r-CEMAMA(1)	1.5	1.13	20	6.85	4.84	–	0.00016
r-CEMAMA(9)	10	9.25	50	6.89	4.25	3.14	0.00734
r-CEMAMA(15)	20	15.02	70	4.62	4.3	1.86	0.02951
r-CEMAMA(28)	30	28.34	110	5.44	3.68	2.86	0.06715
r-CEMAMA(35)	40	34.71	145	5.08	3.47	2.19	0.12152
r-CEMAMA(46)	50	45.95	180	6.66	2.68	2.48	0.19459
r-CEMAMA(54)	60	53.79	220	5.24	2.85	3.46	0.28928
r-CEMAMA(59)	70	58.86	245	6.13	2.65	2.16	0.40976
r-CEMAMA(65)	80	65.13	280	4.2	2.52	3.25	0.56195
r-CEMAMA(80)	90	79.77	320	7.41	1.46	3.14	0.75446
r-CEAMA(1)	1.5	0.81	20	7.26	5.62	–	0.00013
r-CEAMA(2)	10	2.24	60	8.16	3.2	3.14	0.00186
r-CEAMA(12)	20	12.02	85	7.24	3.54	3.54	0.00818
r-CEAMA(18)	30	17.8	100	6.31	2.19	2.96	0.0204
r-CEAMA(22)	40	22.15	120	5.64	2.54	3.42	0.04076
r-CEAMA(34)	50	34.23	145	5.21	2.67	2.48	0.0727
r-CEAMA(44)	60	43.74	180	6.36	2.83	2.91	0.12191
r-CEAMA(62)	80	62.5	225	4.52	1.96	2.48	0.32362
r-CEAMA(72)	90	71.6	260	7.4	1.23	1.86	0.75226

[a] Fraction of carbazolyl–carbazolyl diad.

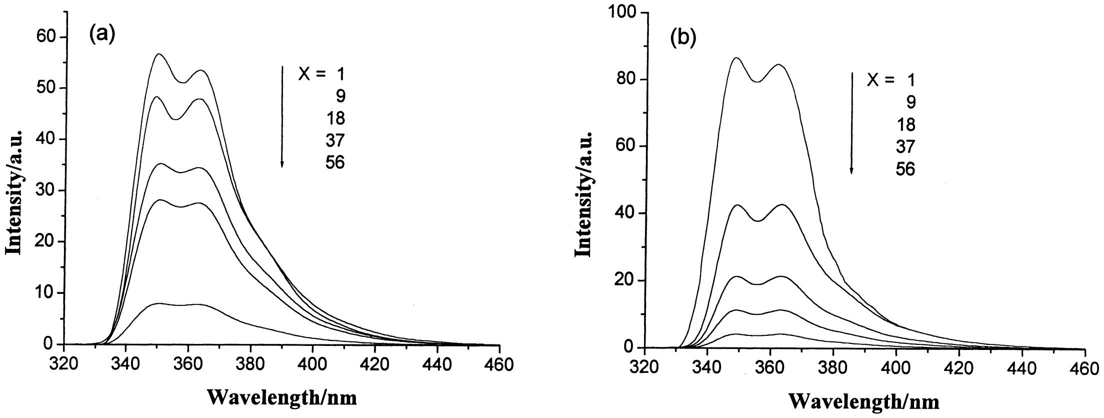

Fig. 2. Fluorescence spectra of r-CMEMAMA(x) in H_2O: (a) pH = 10; (b) pH = 2. $(\mathrm{CMEMA})_{\mathrm{residue}} = 1 \times 10^{-5}$ M; $\lambda_{\mathrm{ex}} = 293$ nm.

of Ledwith [12] that separation of the carbazolyl chromophores from the main chain by alkyl spacers is effective for the inhibition of intramolecular excimer formation in the carbazolyl-containing polymers and copolymers.

Fig. 3 shows the dependence of relative fluorescence intensity of r-CEMAMA on pH of the solution. The copolymer containing very low content of carbazolyl-containing units r-CEMAMA(1) exhibited an intensive 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 [4]. At lower pH, when polyacid is coiled tightly and the chromophores are protected from the action of external quenchers by hydrophobic domains of PMA, solutions show intensive fluorescence. Neutral and basic solutions (pH > 6), in which polyacid coils are expanded and the fluorescent labels are approachable by the external quenchers, show fluorescence of lower intensity. r-CEMAMA with higher CEMA contents exhibits totally different behavior. Fluorescence intensity of the aqueous solutions of these samples at low values of pH is lower than that at high values of pH. The dramatic increase of the fluorescence intensity is observed at pH ca. 4. With the increase of content of CEMA units 35 mol% fluorescence intensity becomes less dependent on pH while r-CEMAMA(65) no longer exhibits pH dependence. These observations are explicable in terms of enhanced self-quenching of the exited state, which results from hydrophobic association of chromophore groups. It was established that singlet state energy migration of excited chromophores along the polymer chain occurs in homopolymers and copolymers of carbazolylalkylmethacrylates [13]. The similar dependencies of fluorescence intensity on the pH was observed for the CEAMA samples containing different amounts of CEA units (Fig. 4). In Fig. 5, the relative fluorescence intensity is plotted against carbazolyl contents of the copolymers. The intensities for r-CMEMAMA, r-CEMAMA and r-CEAMA decreases with the carbazolylalkyl(meth)acrylate content in the copolymer. The character of these dependencies is similar for all the copolymers studied. In alkaline media a rectlinear decrease of relative fluorescence intensity with the increase of the content of carbazolylalkyl(meth)acrylate units in the copolymers is observed. In acid media the dependence is exponential. In acid media a significant decrease in the fluorescence intensity for all copolymers was observed.

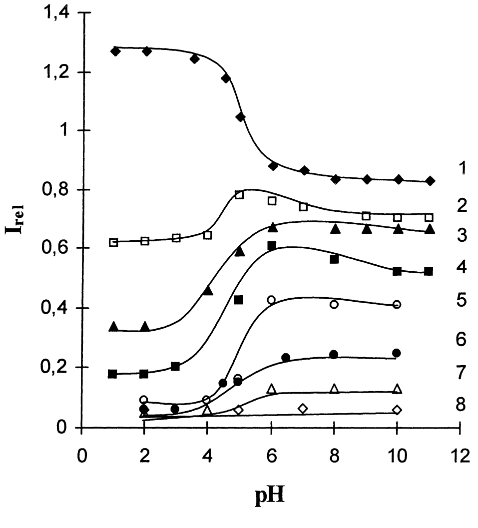

Fig. 3. pH dependence of the relative fluorescence intensities (I_{rel}) for r-CEMAMA at 350 nm in aqueous solution with various content of carbazolyl groups in mol%: (1) 1; (2) 9; (3) 15; (4) 28; (5) 35; (6) 46; (7) 54; (8) 65. I_{rel} is normalized to the intensity of N-ethylcarbazole in DMF. $(\mathrm{CEMA})_{\mathrm{residue}} = 1 \times 10^{-5}$ M; $\lambda_{\mathrm{ex}} = 293$ nm.

Hydrophobic association of chromophores may facilitate the carbazolyl–carbazolyl interactions and efficient energy migration in the compact polymer domain facilitates the exited-state quenching. In many cases, fluorescence

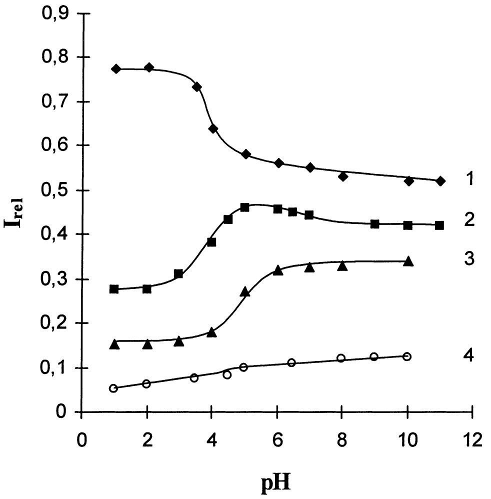

Fig. 4. pH dependence of the relative fluorescence intensities (I_{rel}) for r-CEAMA at 350 nm aqueous solution with various content of carbazolyl groups in mol%: (1) 1; (2) 12; (3) 22; (4) 44. I_{rel} is normalized to the intensity of *N*-ethylcarbazole in DMF. $(CEA)_{residue} = 1 \times 10^{-5}$ M; $\lambda_{ex} = 293$ nm.

quenching in solution can be analyzed conventionally by using Stern–Volmer equation, as follows:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \tag{1}$$

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-neighbor chromophore interactions $[Q]$ should be proportional to the carbazolyl–carbazolyl diad fraction in the copolymer (F_{11}) [14]. Fig. 6 shows the almost linear relationship between I_0/I and F_{11} for r-CMEMAMA(x), r-CEMAMA(x) and r-CEAMA(x) in alkaline aqueous solution. This clearly indicates that the quenching is due mainly to nearest-neighbor chromophore interactions in successive carbazolylalkyl(meth)acrylate (CAMA) sequences, and that nonnearest-neighbor interactions, which should be induced in the copolymers with higher carbazolyl contents in aqueous solution, have little effect on the quenching. In acidic media no linear relationship between I_0/I and F_{11} for all r-CAMAMA copolymers was observed. This shows that quenching in this media does not proceed exclusively due to nearest-neighbor carbazolyl interactions. Compact polymer domain formation of these carboxylic acid copolymers and hydrophobic association of chromophores in acidic media may facilitate not only nearest-neighbor but also induce nonnearest-neighbor carbazolyl–carbazolyl interactions. On the other hand, the influence of the heterogeneous distribution of the carbazolyl groups in the copolymer domain on their fluorescence properties should be not neglected.

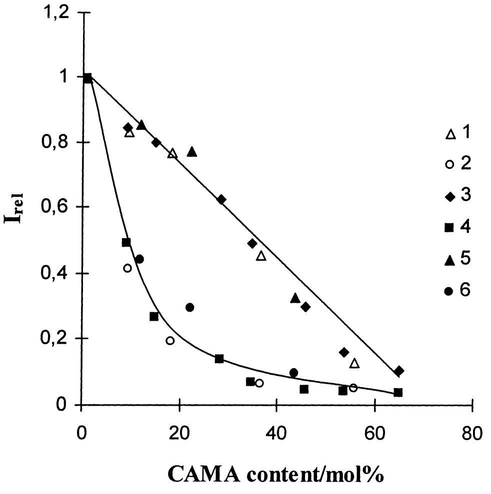

Fig. 5. Dependence of relative fluorescence intensities (I_{rel}) at 350 nm on the carbazolylalkyl(meth)acrylate (CAMA) content for the copolymers in aqueous solution: (1) r-CMEMAMA(x), pH = 10; (2) r-CMEMAMA(x), pH = 2; (3) r-CEMAMA(x), pH = 10; (4) r-CEMAMA(x), pH = 2; (5) r-CEAMA(x), pH = 10; (6) r-CEAMA(x), pH = 2. I_{rel} is normalized to the intensity of each polymer with $x = 1$ mol%. $(CAMA)_{residue} = 1 \times 10^{-5}$ M; $\lambda_{ex} = 293$ nm.

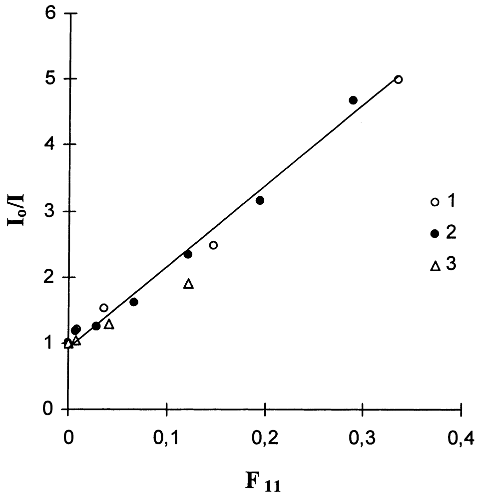

Fig. 6. Relationship between the fluorescence intensity ratio (I_0/I) and the carbazolyl–carbazolyl diad fraction (F_{11}): (1) r-CMEMAMA(x); (2) r-CEMAMA(x); (3) r-CEAMA(x). I_0 is the fluorescence intensity for each polymer with $x = 1$ mol%, pH = 10.

In order to examine the hydrophobic nature of the synthesized copolymers, solubilization of fluorescencent probes, 8-anilino-1-naphthalenesulfonic acid ammonium salt (ANS) and perylene by the copolymers has been studied. These probes are well-known to show very high emission intensity when solubilized in the hydrophobic polymer cores. Table 2 summarizes the fluorescence parameters in the presence of the copolymers at pH 2. In alkaline media only a little enhancement of the ANS fluorescence intensity by all the copolymers was observed. In acid media all the copolymers studied enhance the fluorescence of ANS and shift the emission maximum towards shorter wavelength. r-CMEMAMA(x) has appeared to be the most effective

Table 2
Fluorescence parameters of ANS and perylene in the presence of r-CAMAMA in aqueous solution at pH 2

Polymer[a]	ANS[b]		Perylene[c]
	λ_{max}[d] (nm)	I_{rel}[e]	I_{rel}[e]
–	512	1	1
PMA	508	2.6	1.9
r-CMEMAMA(1)	479	7.5	4
r-CMEMAMA(9)	471	24	16
r-CMEMAMA(18)	468	31	33
r-CEMAMA(1)	493	6.3	2
r-CEMAMA(9)	482	10.4	9
r-CEMAMA(15)	475	25	24.7
r-CEMAMA(28)	470	29	26
r-CEAMA(1)	494	4.1	2
r-CEAMA(12)	486	12	12
r-CEAMA(22)	479	28	20

[a] Polymer $= 10^{-2}$ wt.%.

[b] ANS $= 1 \times 10^{-5}$ M; $\lambda_{ex} = 365$ nm.

[c] Perylene $= 5 \times 10^{-6}$ M; $\lambda_{ex} = 410$ nm; $\lambda_{em} = 472$ nm.

[d] Wavelength at emission maximum.

[e] Relative fluorescence intensity at emission maximum.

solubilizer while in case of r-CEAMA(x) the shortest blue shift and the lowest increase of the fluorescence intensity was observed. This observation can apparently be explained by the lower hydrophobicity of r-CEAMA(x) than that of r-CMEMAMA(x) or r-CEMAMA(x). Similar results were observed perylene as a probe. Fluorescence behavior of perylene confirms that with the increase of carbazole content in the solubilizing copolymer the fraction of probe adsorbed in the hydrophobic polymer domains increased. Table 3 shows the fraction of perylene solubilized in the hydrophobic polymer domains, which has been estimated from the calibrated peak intensity for perylene in the emission spectrum. r-Carbazolylalkylmethacrylate-MA(x) again showed more efficient uptake of perylene compared with r-CEAMA(x). The extent of the perylene uptake was greater for r-CMEMAMA(x) than for r-CEMAMA(x) indicating that the former copolymer is more hydrophobic. Excitation of the carbazolyl residues enhances the fluorescence intensity of the solubilized perylene, which is indicative of energy transfer occurring from the exited carbazolyl chromophores to the perylene traps. The energy transfer yield was calculated from peak intensity of the carbazolyl moiety in the excitation monitored at 472 nm for perylene. 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) in the system. The transfer yield was higher for r-CMEMAMA and r-CEMAMA when compared to that observed for r-CEAMA. These results may support the above speculation that these carbazolylalkylmethacrylate copolymers are more hydrophobic than carbazolylalkylacrylate copolymers.

Table 3
Fluorescence properties of perylene in the presence of r-CAMAMA in aqueous solution[a] at pH 2

r-CAMAMA(x)	Uptake[b] (%)	Transfer yield[c] (%)
r-CMEMAMA(1)	0.2	2.32
r-CMEMAMA(9)	0.8	19
r-CMEMAMA(18)	4.8	49
r-CEMAMA(1)	0.08	1.86
r-CEMAMA(9)	0.6	12.5
r-CEMAMA(15)	3.6	19
r-CEMAMA(28)	7.6	54
r-CEAMA(1)	0.02	0
r-CEAMA(12)	0.4	4
r-CEAMA(22)	1.8	36

[a] $(\mathrm{CAMA})_{residue} = 1 \times 10^{-5}$ M; perylene $= 5 \times 10^{-6}$ M.

[b] The fraction of perylene adsorbed in the polymer domains; calculated from the calibrated peak intensity at 472 nm for perylene in the emission spectrum, $\lambda_{ex} = 410$ nm.

[c] The efficiency of energy transfer from the carbazolyl moiety to the adsorbed perylene; calculated from the calibrated peak intensity at 293 nm for the carbazolyl moiety in the excitation spectrum monitored at 472 nm for perylene.

4. Conclusions

The dilute aqueous solutions of the random copolymers of carbazolylalkyl(meth)acrylates and methacrylic acid show monomeric fluorescence the intensity of which is dependent on the content of carbazolyl groups in the copolymers. The decrease of the fluorescence intensity with the increase of the content of the carbazole chromophores show that excited-state quenching resulting from hydrophobic association of carbazolyl groups occurs in these systems. The fluorescence intensity of the solutions of the copolymers is also dependent on pH. The character of this dependence changes with the change of the content of carbazolyl groups in the copolymers. At higher contents of the chromophores low pH facilitates carbazolyl–carbazolyl interaction and excited-state quenching. Solubilization of 8-anilino-1-naphthalenesulfonic acid and perylene by the copolymers indicates the increase of the fraction of probe absorbed in the hydrophobic polymer domains with the increase of carbazole content in the solubilizing copolymers. The energy transfer to hydrophobically-bound perylene is facilitated for carbazolylalkylmethacrylate copolymers as compared with the corresponding carbazolylalkylacrylate copolymers.

References

[1] Y. Morishima, Prog. Polym. Sci. 15 (1990) 949.
[2] S.E. Webber, Chem. Rev. 90 (1990) 1469.
[3] S. Ito, et al., Chem. Phys. Lett. 117 (1985) 171.
[4] Y. Itoh, et al., Macromolecules 27 (1994) 1434.
[5] Y. Itoh, T. Yasue, M. Gouki, A. Hachimori, Polymer 37 (1996) 5433.

[6] Th.J. De Boer, H.J. Backer, in: N. Rabjohn (Ed.), Organic Synthesis, Coll. Vol. IV, Wiley, New York, 1963, p. 251.
[7] L.M. Harwood, C.J. Moody, Expermental Organic Chemistry, Blackwell Science, Oxford, 1996, p. 742.
[8] P. Strohriegl, Mol. Cryst. Liq. Cryst. 183 (1990) 261.
[9] J. Degutis, A. Undzenas, A. Urbonavicius, USSR Patent 466,227 (1975).
[10] E.A. Bekturov, Z.Kh. Bakauova, Synthetic Water-Soluble Polymers in Solution, Hüthig and Wepf, Basel, 1986, p. 27.
[11] T. Kelen, F. Tüdös, J. Macromol. Sci. Chem. A9 (1) (1975) 1.
[12] A. Ledwith, N.J. Rawley, S.M. Walker, Polymer 22 (1981) 435.
[13] F.-S. Du, et al., J. Polym. Sci. Part A: Polym. Chem. 38 (2000) 679.
[14] K. Tada, T. Fueno, J. Furukawa, J. Polym. Sci. A1 (4) (1966) 2981.