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CATIONIC SURFMERS WITH BENZYL GROUPS: SYNTHESIS AND COPOLYMERIZATION WITH ACRYLAMIDE

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Abstract A series of cationic surfmers with benzyl groups (QARBCs) with different R groups on the benzene ring were synthesized and characterized by IR, ^{1}H-NMR, ^{13}C-NMR. The aggregation of QARBCs was studied by the steady-state fluorescence technique. It turned out that QARBCs had surface activity and their critical micelle concentration (CMC) values varied in the range of 10^{-2}–10^{-3} mol/L with slight increase with temperature. The copolymerization of acrylamide (M_1) and QARBCs (M_2) was studied below and above CMC, their reactivity ratios were determined by the Finemann-Ross method. It was found that below CMC, copolymerization took place in a homogeneous system and reactivity ratios of acrylamide and QARBCs were less than 1; while above CMC, reactivity ratios of QARBCs were greater than 1. The copolymerization mechanism of QARBC was observed to be similar to that of micellar polymerization. QARBCs tended to homopolymerization, which gave rise to micro-blocky sequences in the polymer backbone. The Q and e values of QARBCs were calculated according to the Alfrey-Price equation by using $r_{1\ (\mathrm{AM})}$ and $r_{2\ (\mathrm{QARBC})}$. Samples of poly(AM-*co*-QARBC) were prepared above and below CMC and their hydrophobic associations were studied by the steady-state fluorescence spectra and 2D NOESY spectra, and their critical associating concentrations (CAC) were estimated. The results showed that samples of poly(AM-*co*-QARBC) prepared above CMC had stronger hydrophobic association in aqueous solution than those prepared below CMC.

Keywords: Copolymerization; Finemann-Ross; Alfrey-Price; Reactivity ratio; 2D NOESY.

INTRODUCTION

In the past decade, many researchers have taken up interest in hydrophobically modified polyacrylamides (HMPAM) with a small amount of hydrophobic monomer incorporated into the polymer backbone for their increasing applications, such as in retention aids in papermaking[1], clarification of industrial wastewater[2], enhanced oil recovery[3, 4] and drug carriers[5]. In aqueous environments, HMPAMs have a strong tendency to associate together through intra- and intermolecular interactions, because the contact of hydrophobic units and water is unfavorable. At high concentrations, intermolecular hydrophobic association is predominant, which yields a transient network structure to offer excellent viscosity building capacity[6].

Nowadays, most of researchers always adapted the conventional micellar copolymerization technique to prepare HMPAM for the insolubility of hydrophobic monomers in water. But this technique has some shortcomings, such as the complicated post-treatment process and the negative effects on polymers caused by common surfactants[7]. Polymerizable surfactants as a kind of functional surfactants emerged as required, which not only have hydrophobic and hydrophilic groups but also contain polymerizable vinyl double bonds. They are called surface active monomers (abbreviated as surfmers)[8–10]. The conventional emulsion polymerization has been improved by using surfmers to substitute common surfactants to get HMPAM with better functionality[11].

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Cationic HMPAMs are more interesting than other HMPAMs due to their diverse commercial values[12–14]. For example, cationic HMPAM can remove organics with negative charge efficiently from waste-water, especially, dye wastewater, which is toxic and hard to remove from water[15]. It has also been reported that cationic HMPAM of quaternary salt-type possesses fine corrosion inhibition and sterilization functions[16]. Therefore, design and synthesis of new cationic surfmers is a research field of interest that is deserved to be explored. Up to now, reported cationic surfmers in the literature included mainly *N*-aminoalkyl-(meth)acrylate salts, *N*-aminoalkyl acrylamide salts and *N*-allylammounium salts and so on, among them, *N*,*N*-dimethylaminoethyl methacrylate (DMAEM) and its salts were reported widely. For example, DMAEM was widely used to prepare functional polymers[17], DMAEM salts with long alkyl chains were used as surfmers for copolymerization with acrylamide (AM) or for miniemulsion[18–20]. But few literatures reported a systematic study of DMAEM salts with benzyl group as surfmers. Benzyl ring as a hydrophobic group has its own advantages than long alkyl chains, such as its moderate hydrophobicity and solubility. Therefore, the purpose of this article is to introduce a new kind of cationic surfmers with benzyl groups (QARBC) and present the copolymerization of cationic surfmers with AM, and their copolymerization mechanism, hydrophobic association of copolymers, as well as in future the attempt to characterize the sequence distribution and tactility of monomer sequences in copolymers.

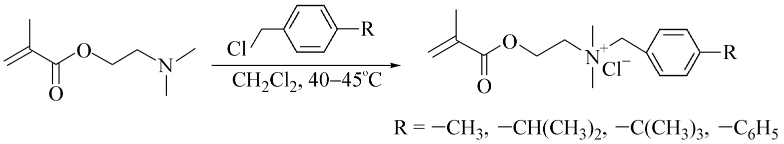
EXPERIMENTAL

Materials

N,*N*-dimethylaminoethyl methacrylate (DMAEM), *p*-methylbenzyl chloride, *p*-*iso*-propyl benzyl chloride, *p*-*tert*-butylbenzyl chloride, *p*-phenylbenzyl chloride, 2,2′-azo-bis(2-amidino propane) dihydrochloride (V-50), hydroquinone and analytical reagents were supplied by Aldrich Chemical Company. Acrylamide (AM, Shanghai Chemical Co. Ltd) was recrystallized twice from acetone and vacuum dried at room temperature. Pyrene (Aldrich Chemical Company) was recrystallized twice from ethanol before use. D_2O was supplied by Sigma Chemical Co. with a minimum deuterium content of 99.8%. Dichloromethane, ethanol, 1,4-dioxane and sodium chloride were analytical reagents from Beijing Chemical Reagent Factory and used without further purification.

Synthesis and Characterization of QARBCs

QARBCs were prepared according to Scheme 1. In a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, a cooler and a thermometer, 100 mL of dichloromethane, 50 mL of DMAEMA (about 46.6 g, 0.296 mol) and a small amount of hydroquinone were added. An expected amount of benzyl chloride (benzyl chloride/DMAEMA 1.1/1 mol) was added. After that, the system was heated to 40–45°C and kept for a period of time[21]. Finally, white powdery solids were obtained by cooling and filtering the reaction solution, and then washing with dry dichloromethane three times and drying under vacuum at room temperature. The overall yields of cationic surfmers were 80%–90%. Melting points were measured by an X-4A type instrument (Keyi, China). IR spectra were recorded with an Excalibur 3100 spectrometer (Varian, USA). ^{1}H-NMR and ^{13}C-NMR spectra of samples were obtained by using an Avance Π-400 instrument (Bruker Company, Germany).



Scheme 1 Synthesis of QARBCs

Aggregation of QARBCs in Aqueous Solutions

Aggregation of QARBCs in aqueous solutions was investigated by the steady-state fluorescence technique using pyrene as a probe, which could clarify the micelle formation behavior in aqueous solution[22–24]. Different concentrations of QARBCs in saturated pyrene water (approximately 5×10^{-7} mol L^{-1}) were prepared and allowed to equilibrate overnight with stirring. The fluorescence spectra of probe pyrene in various concentrations of QARBCs were performed on a Hitachi F-4500 at 25°C, 30°C, 35°C, 40°C and 45°C, with excitation wavelength 335 nm, slit widths both 5 nm and in a scanning range of 345–450 nm; the first (I_1) and third peaks (I_3) of the pyrene emission spectra were situated at 374 and 385 nm, respectively. The plots of I_3/I_1 values versus concentrations were depicted and critical micelle concentration (CMC) values of QARBCs were estimated from the abrupt change-points on the plots.

Copolymerization of AM (M_1) and QARBC (M_2)

Determination of reactivity ratios

In these experiments, overall monomer conversions were kept less than 10 wt% in order to satisfy the Finemann-Ross equation[25]. The procedure was as follows: varying quantities of the ingredients (QARBCs were kept above and below CMC, respectively) were dissolved in water in a glass tube. The glass tube in 0–5°C ice-water bath was degassed by dry nitrogen gas for 30 min and then 0.1 mol% of V-50 (based on the total monomers) was added before it was sealed. The sealed tube was placed in a constant-temperature bath thermostatically controlled at 45°C and shaken occasionally. After a definite period of time, hydroquinone was added to stop the polymerization. The copolymers were precipitated by pouring the aqueous solution into ethanol and purified by repeated precipitations from an aqueous system to ethanol. The purified copolymers were dried to constant weight under high vacuum with P_2O_5. The total conversion of monomers was determined by the weight method, and the composition of copolymers was determined by UV spectrophotometer[26]. The reactivity ratios of $r_{1\,(AM)}$ and $r_{2\,(QARBC)}$ were determined by the Finemann-Ross method. According to the Alfrey-Price equation, Q and e values of QARBCs were calculated from reactivity ratios of $r_{1\,(AM)}$ and $r_{2\,(QARBC)}$. $Q_1 = 0.61$ and $e_1 = 0.75$ for AM were selected[27].

Preparation of poly(AM-co-QARBC)

Samples of poly(AM-*co*-QARBC) were prepared with QARBCs above and below CMC, respectively. The molar ratios of QARBC to AM were 1:9 and the initiator V-50 was 0.1 mol% based on the total monomers; the mixture solution in 0–5°C ice-water bath was degassed by dry nitrogen gas for 30 min and polymerization was carried out in a water bath maintained at 45°C and shaken occasionally for 16 h. After cooling the reaction mixture, the copolymers were precipitated by pouring the aqueous solution into ethanol and purified by repeated precipitations from the aqueous system to ethanol. The purified copolymers were dissolved in deionized water for dialysis to remove low molecular weight species (the membrane cut-off was 10000). The copolymers were finally recovered by freeze-drying. Likewise, the composition of copolymers was determined by UV spectrophotometer. Intrinsic viscosities of copolymer samples solutions were measured with an Ubbelhode type viscometer at 30°C using 1 mol L^{-1} NaCl solution as solvent. Their weight-average molar masses, M_w, were calculated from their intrinsic viscosities according to the Mark-Houwink equation[28]:

$$[\eta] = 3.684 \times 10^{-2} M_w^{0.646} \tag{1}$$

Hydrophobic Association of Poly(AM-co-QARBC) in Aqueous Solutions

For these series of poly(AM-*co*-QARBC) samples, their hydrophobic associations in aqueous solutions were also proven by steady-state fluorescence and their CAC values (critical associating concentration) were determined by the abrupt change-points of I_3/I_1 values versus poly(AM-*co*-QARBC) concentrations[29]. Likewise, sample solutions of different concentrations were prepared by dissolving a known amount of copolymer in pyrene-saturated (approximately 5×10^{-7} mol L^{-1}) water. The emission spectra of pyrene in various polymer solutions were measured on air-equilibrated solutions at 25°C using a Hitachi F-4500 with excitation wavelength 335 nm, slit widths both 5 nm; the first (I_1) and third (I_3) peaks of the pyrene emission spectra were situated at 374 and 385 nm, respectively.

Additionally, the benzyl group in this series of poly(AM-*co*-QARBC) samples was found to be weakly fluorescent. Steady-state fluorescence spectra of poly(AM-*co*-QAPBC) samples in pure water were also studied. Likewise, the spectra were recorded on a Hitachi F-4500 with excitation wavelength 255 nm, slit widths both 5 nm.

The methods of two-dimensional NMR spectroscopy techniques, Nuclear Overhauser Enhancement Spectroscopy (NOESY) and Heteronuclear Overhauser Enhancement Spectroscopy (HOESY) provide a deeper insight into the relative arrangement of polymer chain in an associating assembly[30]. So, in this article, 2D NOESY experiments were performed with standard three-pulse sequence and mixing time 80 ms in order to analyze the interaction of hydrophobic groups among the associating assembly.

RESULTS AND DISCUSSION

Synthesis and Characterization of QARBCs

Four QARBCs were synthesized easily by quaternization. Different R groups (R = methyl, *iso*-propyl, *tert*-butyl, phenyl) had steric hindrance effect on this reaction, the yields decreased gradually in order (methyl, *iso*-propyl, *tert*-butyl, phenyl), but the overall yields were still 80%–90% because of easiness of quaterinzation. The characterization results were as follows.

QAMBC (R = methyl), yield 90%; Mp. 149–151°C; IR (KBr): 2958 cm^{-1} (C—H), 1718 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 1477 cm^{-1} (phenyl ring), 1296 cm^{-1} and 1166 cm^{-1} (C—O), 812 cm^{-1} (Ar—H). ^{1}H-NMR (D_2O, 400 MHz): δ 7.51 (d, 2H), 7.12 (d, 2H), 6.19 (s, 1H), 5.80 (s, 1H), 4.72 (s, 2H), 4.56 (s, 2H), 3.80 (t, 3H), 3.15 (s, 6H), 2.43 (s, 3H), 1.97 (s, 3H); ^{13}C-NMR (D_2O, 400 MHz, 1,4-dioxane as internal standard): δ 169.2, 142.6, 136.0, 133.8, 130.6, 128.6, 124.6, 69.9, 63.2, 59.2, 50.9, 21.2, 18.1.

QAIBC (R = *iso*-propyl), yield, 87%; Mp. 165–167°C; IR (KBr): 2958 cm^{-1} (C—H), 1718 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 1458 cm^{-1} (phenyl ring), 1294 cm^{-1} and 1165 cm^{-1}, (C—O), 873 cm^{-1} (Ar—H). ^{1}H-NMR (D_2O, 400 MHz): δ 7.52 (q, 4H), 6.19 (s, 1H), 5.80 (s, 1H), 4.72 (m, 3H), 4.60 (s, 2H), δ 3.79 (q, 2H), 3.15 (s, 6H), 1.96 (s, 3H), 1.27 (d, 6H); ^{13}C-NMR (D_2O, 400 MHz, 1,4-dioxane as internal standard): δ 169.3, 153.5, 136.0, 134.0, 128.5, 128.2, 125.0, 69.9, 63.3, 59.2, 50.9, 34.3, 23.9, 18.1.

QATBC (R = *tert*-butyl), yield, 84%; Mp. 175–180°C; IR (KBr): 2960 cm^{-1} (C—H), 1724 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 1458 cm^{-1} (phenyl ring), 1296 cm^{-1}and 1165 cm^{-1} (C—O), 875 cm^{-1} (Ar—H); ^{1}H-NMR (D_2O, 400 MHz): δ 7.66 (d, 2H), 7.53 (d, 2H), 6.19 (s, 1H), 5.80 (s, 1H), 4.71 (t, 2H), 4.60 (s, 2H), 3.80 (q, 2H), 3.15 (s, 6H), 1.36 (s, 9H); ^{13}C-NMR (D_2O, 400 MHz, 1,4-dioxane as internal standard): δ 169.3, 155.7, 136.0, 133.7, 128.6, 127.1, 124.8, 69.7,63.3, 59.2, 51.0, 35.1, 31.2, 18.1.

QAPBC (R = phenyl), yield, 80%; Mp. 156–160°C; IR (KBr): 2978 cm^{-1} (C—H), 1732 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 1485 cm^{-1} (phenyl ring); 1294 cm^{-1} and 1155 cm^{-1}, (C—O), 769 cm^{-1} (Ar—H). ^{1}H-NMR (D_2O, 400 MHz): δ 7.85 (d, 2H), 7.76 (d, 2H), 7.66 (d, 2H), 7.56 (t, 2H), 7.50 (t, 1H), 6.18 (s, 1H), 5.79 (s, 1H), 4.73 (t, 2H), 4.67 (s, 2H), 3.83 (q, 2H), 3.18 (s, 6H), 1.96 (s, 3H); ^{13}C-NMR (D_2O, 400 MHz, 1,4-dioxane as internal standard): δ 169.2, 143.7, 140.1, 136.0 134.4, 130.1, 129.2, 128.6, 128.4, 127.9, 126.7, 69.7, 63.4, 59.2, 51.0, 18.1.

Aggregation of QARBCs in Aqueous Solutions

According to the experiment results, the plots of I_3/I_1 values versus QARBCs concentrations were depicted and the CMC values of QARBCs were estimated from the abrupt change-points in the plots and listed in Table 1. The CMC values of the same QARBC were increased slightly with temperature, from 25°C to 45°C, which is one of the quaternary ammonium surfactant properties[31]. Those of QARBCs with different R groups decreased gradually as expected (*i.e.* methyl, *iso*-propyl, *tert*-butyl, phenyl in order). This was consistent with the general trend, for larger R groups favored micellization.

Table 1. CMC values of QARBCs in aqueous solutions at different temperatures

Cationic monomer	CMC (mmol L^{-1})				
	25°C	30°C	35°C	40°C	45°C
QAMBC (mw298.82)	10.51	10.86	11.05	11.65	12.18
QAIBC (mw325.87)	5.82	6.02	6.42	6.82	7.24
QATBC (mw339.90)	5.65	5.96	6.35	6.64	6.98
QAPBC (mw359.89)	1.61	1.79	1.88	2.03	2.18

Determination of Reactivity Ratios of $r_{1\,(AM)}$ and $r_{2\,(QARBC)}$

The experimental results of copolymerization were processed by Finmann-Ross method[25] and the reactivity ratios were calculated (as illustrated in Table 2). The results showed that the same QARBC had different reactivity ratios below and above CMC. This might be due to different mechanisms of polymerization. Below CMC, QARBCs and AM had approximate reactivity ratios, lesser than 1, the solution was a homogeneous system and copolymerization was liable to process randomly as usual, which meant QARBCs might distribute randomly in the polymer backbone. While above CMC, QARBCs aggregated into micelles in aqueous solution and once polymerization began in micelles, chain reaction was unavoidable in micelles, reactivity ratios of QARBCs were larger than 1, which meant QARBCs tended toward homopolymerization and might distribute in micro-blocky sequences in the polymer backbone.

Table 2. Reactivity ratios of AM and QARBCs

Cationic monomer		$r_{1\,(AM)}$	$r_{2\,(QARBC)}$	$r_1 \times r_2$	Q_2	e_2
QAMBC	below CMC	0.75	0.90	0.675	0.508	0.123
	above CMC	0.67	1.39	0.931	0.745	0.483
QAIBC	below CMC	0.77	0.87	0.670	0.493	0.117
	above CMC	0.68	1.35	0.918	0.721	0.457
QATBC	below CMC	0.78	0.86	0.671	0.487	0.118
	above CMC	0.69	1.34	0.925	0.717	0.470
QAPBC	below CMC	0.81	0.82	0.664	0.466	0.110
	above CMC	0.73	1.28	0.934	0.688	0.490

The reactivity ratios of different QARBCs showed a little difference at the same conditions. This may be attributed to the same double group (*i.e.* methacrylate) and different R groups. Different *R* groups have stronger and stronger steric hindrance, (*i.e.* methyl, *iso*-propyl, *tert*-butyl, phenyl in order), which made their copolymerization reactivity ratios decreased gradually at the same conditions.

According to Alfrey-Price equation, Q and e values for various QARBCs were calculated from reactivity ratios ($Q = 0.61$, $e = 0.75$ for AM), and the calculated results were shown in Table 2. Q and e values suggested that QARBCs were liable to copolymerize with AM because of their approximation. The changes of Q and e values of QARBCs reconfirmed the effect of different *R* groups on copolymerization.

Hydrophobic Association of Poly(AM-co-QARBC) in Aqueous Solutions

The characteristic parameters of poly(AM-*co*-QARBC) samples were listed in Table 3. As expected, the cac values of copolymer samples decreased gradually (methyl, *iso*-propyl, *tert*-butyl, phenyl in order). Additionally, it was apparent that samples prepared above CMC had lower CAC values than those below CMC. A lot of literatures had reported that HAPAMs with micro-blocky hydrophobic groups had stronger hydrophobic aggregation than those with random hydrophobic groups[32]. Therefore, these results were also consistent with the preceding copolymerization mechanism speculations that QARBCs might distribute in micro-blocky sequences in the polymer backbone above CMC.

Table 3. Characteristic of poly(AM-*co*-QARBC) samples

Copolymer samples		Cationic degree (τ, mol%)	Intrinsic viscosity $[\eta]$ (mL/g)	$M_w \times 10^{-4}$	CAC (g/L)
Above CMC	Cp-1a (AM/QAMBC)	10.51	96.4	19.53	1.9
	Cp-2a (AM/QAIBC)	10.23	102.8	21.57	1.4
	Cp-3a (AM/QATBC)	10.15	105.3	22.39	1.2
	Cp-4a (AM/QAPBC)	10.01	119.8	27.33	0.35
Below CMC	Cp-1b (AM/QAMBC)	9.45	87.2	16.98	2.6
	Cp-2b (AM/QAIBC)	8.98	88.5	17.38	2.3
	Cp-3b (AM/QATBC)	9.03	89.6	17.71	2.0
	Cp-4b (AM/QATBC)	8.93	90.5	17.99	0.97

The benzyl group in this series of cationic polymers was found to be weakly fluorescent, so in order to further study the structure effect of the two kinds of copolymers, the emission spectra of copolymer samples Cp-4a and Cp-4b in different concentrations were recorded with their λ_{max} as excitation wavelength. The results were shown in Fig. 1 and Fig. 2. The spectra of Cp-4b against concentrations (Fig. 1) were entirely different from those of Cp-4a (Fig. 2). In Fig. 1, the fluorescent spectra had no evident changes with increasing concentration except that the intensity decreased, but in Fig. 2, a new peak appeared in the longer wavelength and its intensity increasing with increasing concentration, which was assigned to an excimer emission of the benzyl groups in the hydrophobic cores in water[33, 34]. The results confirmed that micro-blocky copolymer Cp-4a could form more tightly hydrophobic microdomains, among which, benzyl groups could aggregate very closely to one another for the formation of benzyl excimers.

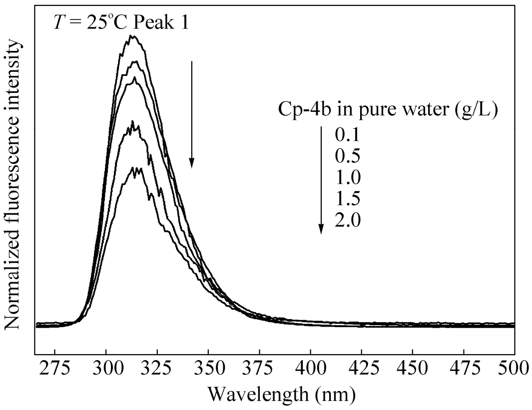


Fig. 1 Fluorescence spectra of different concentrations of Cp-4b in pure water

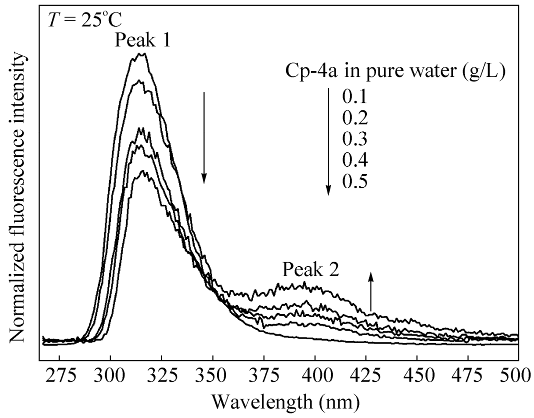


Fig. 2 Fluorescence spectra of different concentrations of Cp-4a in pure water

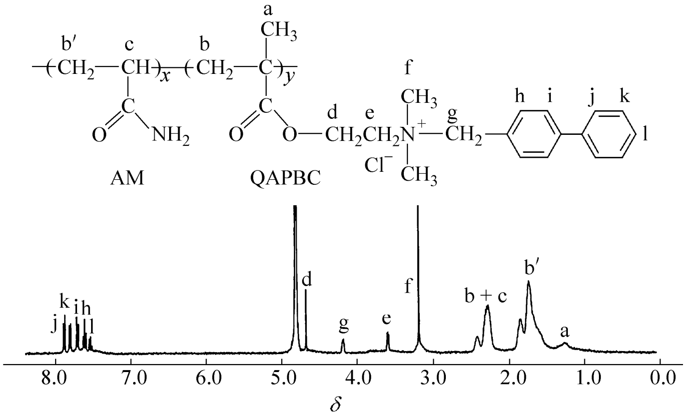


Fig. 3 ^{1}H-NMR Spectrum of Cp-4b in D_2O

2D NOESY spectra of Cp-4a and Cp-4b in D_2O above their CAC were measured and shown in Figs. 3, 4. It is well-known that protons with such spatial distances (< 0.5 nm) would show interactions on 2D NOESY spectra. In Fig. 4(A) (Cp-4b), there appeared only cross-peaks of the protons attached on adjacent carbon atoms of the benzyl group such as H_h-H_i, H_k-H_j, H_i-H_j, H_l-H_k, which meant intramolecular interactions of aromatic protons and no intermolecular interactions. However, in Fig. 4(B) (Cp-4a), there appeared more cross-peaks of the distant protons such as H_h-H_l H_h-H_j H_h-H_k, H_i-H_k, H_i-H_l, including what occurred in Fig. 4(A), which meant coexistence of intermolecular and intramolecular interactions of aromatic protons. This result showed that the benzyl groups were stacked very closely in the hydrophobic associating cores in Cp-4a aqueous solution so that the protons in the benzyl groups had mutual effects in space. This result indirectly proved the formation of benzyl excimers in the hydrophobic microdomains in Cp-4a aqueous solution.

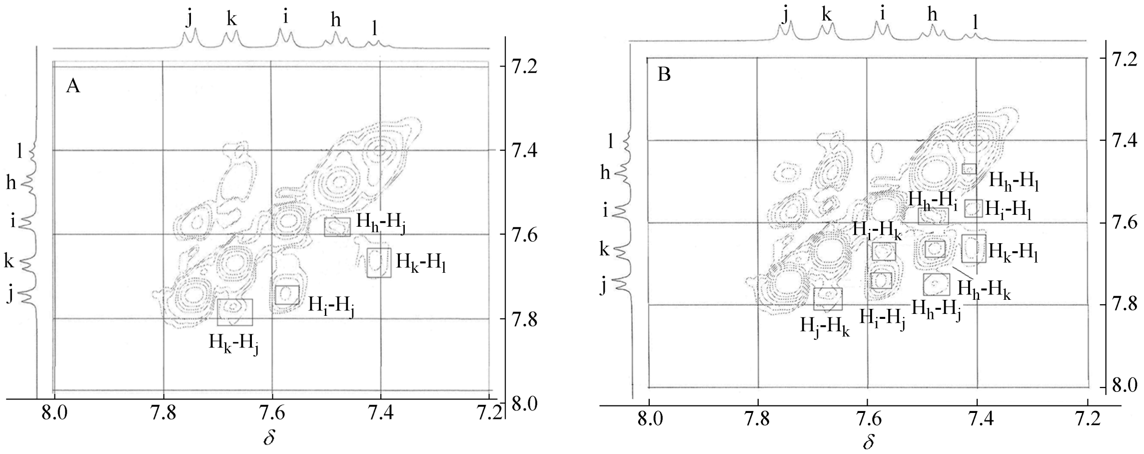


Fig. 4 Contour plots of 2D NOESY map of Cp-4b (A) and Cp-4a (B) above their CAC (an expansion of the aromatic region)

CONCLUSIONS

A series of QARBCs were synthesized and characterized. The experiments suggested that QARBCs were liable to form micelles in water and their CMC values varied in the range of 10^{-2}–10^{-3} mol L^{-1} and increased slightly with temperature. QARBCs showed different reactivity ratios above and below CMC when copolymerizing with AM due to different polymerization mechanisms. Above CMC, copolymerization was similar to micellar copolymerization, reactivity ratios of QARBCs were larger than 1, which meant QARBCs predominantly polymerized within micelles and distributed in micro-blocky sequences in the polymer backbone; below CMC, reactivity ratios of QARBCs were less than 1, which meant QARBCs copolymerized with AM in aqueous solution as usual and distributed randomly in the polymer backbone. These speculations had been proved by their hydrophobic association. Samples prepared above CMC showed obvious stronger hydrophobic associating (such as lower CAC values) than those prepared below CMC. In the hydrophobic cores, benzyl groups of micro-blocky copolymers were stacked closely to cause the formation of benzyl excimers, which were proved by their self-fluorescence emission spectra and 2D NOESY spectra in D_2O.

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