

Synthesis, Characterization and Solution Properties of Hydrophobically Modified Polyelectrolyte Poly(AA-co-TMSPMA)

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Abstract The hydrophobically modified polyelectrolyte was synthesized using precipitation polymerization of acrylic acid and 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TMSPMA) in various molar ratios in supercritical carbon dioxide. FT-IR, ^1H NMR, capillary viscometry, rotational viscometer, transmission electron microscopy and fluorescence spectroscopy were used to characterize this copolymer. The viscosity of the copolymers showed a strong dependence on pH with a maximum at $\text{pH} = 5.5$. Associating morphologies of the copolymer were observed by TEM. Associating morphologies of poly(AA-co-TMSPMA) solution changed from a global structure to a shell-core structure with increasing hydrophobic levels. A solution of sample PAT4 with a shell-core structure had the largest viscosity value. In addition, the critical micelle concentration of copolymer solution, cmc, was determined from the relative viscosity. The critical micelle concentration was further confirmed by fluorescence spectroscopy using 1-pyrenemethylamine hydrochloride, PyMeA-HCl, as a cationic fluorescent probe. The cmc was determined from the intensity ratios, the first to the third emission peaks I_1/I_3 , and the excimer to monomer I_E/I_M ratio of the pyrene probe as a function of concentration.

Keywords Hydrophobically modified polyelectrolyte · Supercritical carbon dioxide · pH-sensitive · Associating morphologies · Critical micelle concentration

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1 Introduction

Hydrophobically modified polyelectrolytes are of great experimental and theoretical interest, as they find many applications in various fields, such as enhanced oil recovery, paints formulations, coatings, printing, paper, ceramics, pharmaceuticals, cosmetics and personal-care goods, etc. One of the most important properties of amphiphilic polyelectrolytes is their ability to solubilize hydrophobic substances that are otherwise only sparingly soluble in water. The other is their ability to produce highly viscous aqueous solutions above a threshold polymer concentration. This viscosity enhancement, in comparison to the unmodified precursor, is due to the strong tendency of the hydrophobic parts of associating polymers to form intermolecular aggregates in aqueous solutions. The remarkable rheological properties of amphiphilic polyelectrolytes lead to their use as associative thickeners, rheology modifiers, polymer-based surfactants, emulsifiers, solubilizers, coagulants and colloids. Moreover, aqueous systems containing amphiphilic polymers are excellent candidates for environmentally benign substitutes for organic-solvent systems being currently used in various commercial processes [1–7].

Polymerization of acrylic acid is commonly conducted in water. Because hydrophobes are insoluble in water, the copolymerization of acrylic acid and hydrophobes in water is very difficult. At the same time, utilizing organic solvents might cause another problem of pollution of the product, which would be a more serious problem when the polymer is used in personal-care products, food, and even medical products. Supercritical carbon dioxide as an alternative to conventional organic solvents for polymerization has attracted increasing attention in recent years. Using supercritical carbon dioxide as the reaction medium has the attractive advantage that the product is virtually free from contamination and is easily obtained as dry powder just by releasing the carbon dioxide at the end of the reaction. At the same time, no contaminant is released into our environment. In addition, the supercritical-fluid extraction process can be used in-situ to remove the unreacted monomer [8–12].

Hydrophobically modified pH-responsive polymers have a sensitive balance between charged repulsion and hydrophobic interactions. Introducing hydrophobic effects cause aggregation of the polymer chains from the aqueous environment [13]. Polymeric micelles are characterized by a core-shell structure, which are considerably more stable than surfactant micelles and can solubilize substantial amounts of hydrophobic compounds in their inner core. These systems possess a variety of interesting applications for encapsulation, controlled delivery, etc. At the critical micelle concentration, cmc, a significant quantity of solvent can be found inside the micellar core and micelles are described as loose aggregates that exhibit larger sizes than micelles formed at higher concentrations [14]. In this work a hydrophobically modified polyelectrolyte was synthesized in supercritical carbon dioxide. The viscosities of the polyelectrolyte as a function of pH, the associating morphologies and the critical micelle concentration were investigated.

2 Experimental Sections

2.1 Materials

The silicone-containing co-monomer 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (TMSPMA) was obtained from Aldrich and was used as received. Acrylic acid (AA) was purchased from Tianjing Chemical Reagents Co. (Tianjing, China) and purified by distillation under reduced pressure. The cationic fluorescence probe, 1-pyrenemethylamine

hydrochloride (PyMeA·HCl), was obtained from Aldrich and used as received. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. The CO₂ with a purity of 99.9% was used as received.

2.2 Polymerization in Supercritical Carbon Dioxide

A series of copolymers of acrylic acid with different amounts of co-monomer, 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate, were synthesized by free-radical polymerization initiated by AIBN in supercritical carbon dioxide in a 20 mL high-pressure reactor with a magnetic stirring bar. The high-pressure reactor was charged with acrylic acid (2.0 g), AIBN (0.02 g), and different amounts of co-monomers, then purged with CO₂ at 0.5 MPa and 0.1 L·min⁻¹ for ca. 1 min to remove O₂. The reactor was sealed and enough liquid carbon dioxide was added through a syringe. The temperature was gradually increased to 60 °C and carbon dioxide was added to 16 MPa. All reactions proceeded for 4 h. The reactor was cooled and vented slowly. The product was obtained in the form of a white powder.

The products were extracted by supercritical carbon dioxide in-situ at 45 °C and 15 MPa to remove the unreacted monomers until the mass of the products did not change. The yield of these polymerizations is calculated according to the mass of final products and the added monomer.

2.3 Solution Preparation

The homopolymer PAA dissolves easily in water and gives a clear solution, but the hydrophobically modified polyelectrolyte PAT does not dissolve easily. The pH was adjusted by addition of 2 mol·L⁻¹ NaOH aqueous solutions. Solutions were kept at room temperature to give optically clear solutions.

2.4 Measurements

- (a) FT-IR measurements: FT-IR spectra of dry polymers were recorded on a RFX-65A FT-IR spectrometer (Analect, USA) using a KBr pellet method.
- (b) ¹H NMR spectra: the copolymer was characterized by ¹H NMR as solutions in DMSO-d₆ using the Bruker DRX-400 MHz spectrometer. The appropriate chemical shifts, 12.25 ppm for the -COOH and 0.08 ppm for the Si-CH₃ groups, were used to determine the molar ratio of AA / TMSPMA.
- (c) Transmission electron microscopic observation: the size and associating morphologies of polymer particles in aqueous solutions were determined by a JEM-100CXII transmission electron microscope (Hitachi, Japan). Samples for the TEM experiments were prepared from a drop of dilute solution of micelles on a copper grid that was evaporated under air to form a thin film. These samples were not stained.
- (d) Viscometric measurements in dilute solution: The intrinsic viscosities and relative viscosities of the polymer were measured in 2 mol·dm⁻³ aqueous NaOH solutions and distilled water at 30 °C using a capillary viscometer (Ubbelohde type) at polymer concentrations in the range 0.005–3.0 g·L⁻¹. The molecular weights were calculated using the equation [15]: $\eta = 3.38 \times 10^{-3} M^{0.43}$. The apparent viscosity was measured with a rotational viscometer, NDJ-1A (Shanghai), to study the viscosity dependence on pH, and a 2 mol·dm⁻³ aqueous NaOH solutions were used to adjust the pH of the solutions.
- (e) Fluorometric measurements: Steady-state fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrometer. All solutions were kept for more than 24 h to

ensure that the binding equilibrium was attained and then were stirred prior to measurement. All measurements were performed on air-equilibrated solutions at 25 °C. The excitation wavelength was 340 nm. The I_1/I_3 is the emission intensity ratio for the first peak (375 nm) to the third peak (386 nm) of pyrene. I_E/I_M is defined as the emission intensity ratio of the excimer (480–490 nm) to monomer (395 nm) of the pyrene residue. All polymer solutions had the same probe concentration $[\text{PyMeA} \cdot \text{HCl}] = 2.5 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$.

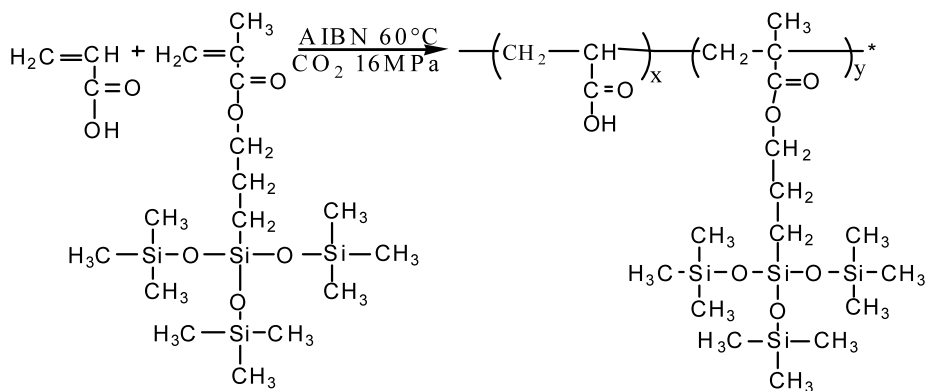
3 Results and Discussion

3.1 Characterization of Polymers

The copolymerization method employed ‘precipitation polymerization in supercritical carbon dioxide’. In the present case, hydrophobic TMSPMA and acrylic acid was solubilized within in the continuous supercritical carbon dioxide medium. The propagating species migrated randomly through the supercritical carbon dioxide medium to form long-hydrophilic and short-hydrophobic sequences. A series of Poly(AA-co-TMSPMA) copolymers were prepared by changing the hydrophobic level. Scheme 1 depicts the chemical formulae of the random copolymers used in the present study. The homopolymer of acrylic acid and copolymer Poly(AA-co-TMSPMA) obtained at 60 °C and 16 MPa are fluffy, white, free-flowing powders. There is no remarkable difference between the homopolymer PAA and the copolymers with different TMSPMA contents.

The composition and characterization of the polymers are summarized in Table 1. It shows that the content of TMSPMA in the copolymers is higher than in the feed, which indicates that TMSPMA is more active than acrylic acid in such a copolymerization. It also shows that high siloxane-containing monomer feed ratios lead to a high siloxane content in the copolymer. Viscosity-averaged molecular weights of the copolymer also increase with the hydrophobic level in the feed. The viscosity-averaged molecular weight of sample PAT4 was reached at 9.8×10^{-5} . The yield of these polymerizations was always greater than 92%.

The chemical structure of the copolymers was characterized by FT-IR and ^1H NMR. The IR spectrum of sample PAT4 is shown in Fig. 1 and illustrates the existence of the stretching



Scheme 1 A schematic depiction of chemical formulae of the random copolymers used in the present study

Table 1 Reaction conditions and properties of copolymers produced in supercritical carbon dioxide^a

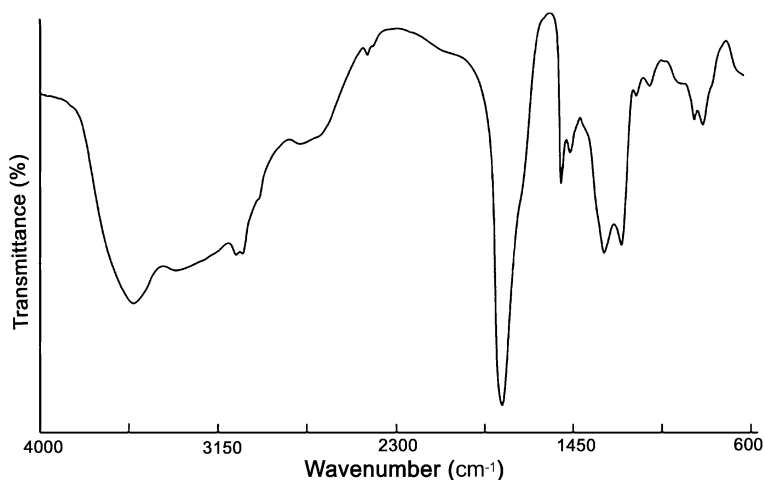
Sample	$[M]^b$ g·L ⁻¹	Polymer appearance	TMSPMA		TMSPMA		$M\eta^d \times 10^{-5}$	Yield %
			in feed		in copolymer ^c			
			mol%	wt. %	mol%	wt. %		
PAA	105	Fine powder	0	0	0	0	5.6	93.0
PAT1	106	Fine powder	0.16	0.95	0.17	0.99	5.9	93.1
PAT2	107	Fine powder	0.28	1.74	0.31	1.79	6.1	92.8
PAT3	108	Fine powder	0.56	3.21	0.62	3.53	7.3	92.6
PAT4	119	Fine powder	0.68	3.86	0.71	4.03	9.8	93.5

^aCopolymerizations were carried out at a temperature of 60 °C and an initial pressure of 16 MPa, concentration of initiator $[I]$ 6.1 mmol·L⁻¹, and reaction time 4 h

^bConcentration of feed monomers

^cDetermined by ¹H NMR

^dViscosity-average molecular weight $\eta = 3.38 \times 10^{-3} M^{0.43}$

**Fig. 1** FT-IR spectrum of sample PAT4

vibrations of the C=O bond and Si–O–Si bond with the bands at ca. 1712 and 1053 cm⁻¹. The stretching vibration of the Si–C bonds was found at 844 cm⁻¹. Symmetric deformation vibration and asymmetric deformation vibrations of the Si–CH₃ bond were found at 1251 and 1415 cm⁻¹, respectively. The stretching vibration bands of O–H of the COOH group were also found at ca. 3435 cm⁻¹. The disappearance of the stretching vibration of the C=C bond at 1645–1620 cm⁻¹ indicates that the copolymer solution does not contain any monomers.

The molecular ratio in the copolymer was estimated with the ¹H NMR technique. The ¹H NMR spectrum of sample PAT4 is shown in Fig. 2. The peak at 0.08 ppm corresponds to methyl protons (Si–CH₃) relative to the peak at 12.25 ppm, which corresponds to the protons (COOH), was used for the molecular ratio determination.

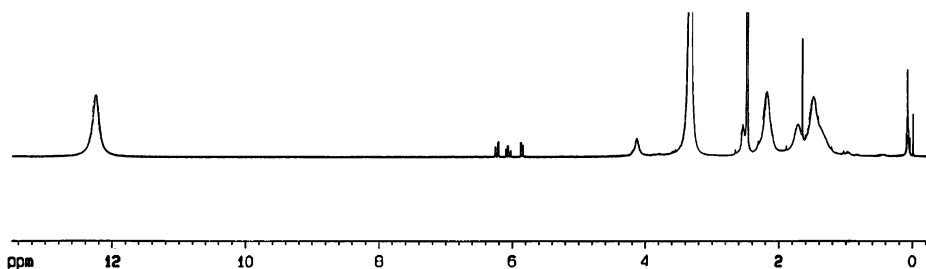
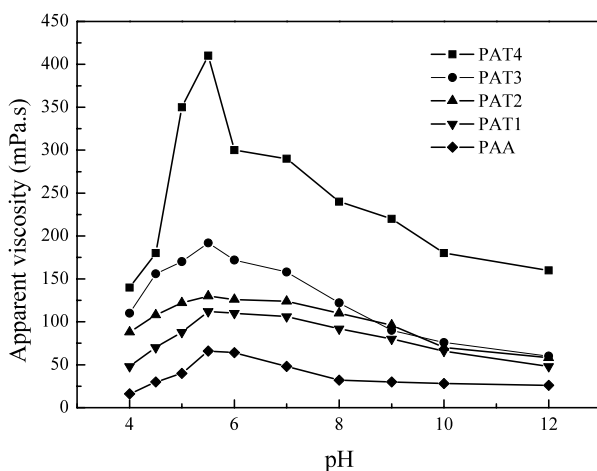


Fig. 2 ^1H NMR spectrum of sample PAT4

Fig. 3 Effect of pH on the apparent viscosity of the poly(acrylic acid) and polyelectrolyte copolymers solutions ($t = 30\text{ }^\circ\text{C}$, $C = 2.9\text{ g}\cdot\text{L}^{-1}$, shear rate = 30 s^{-1})



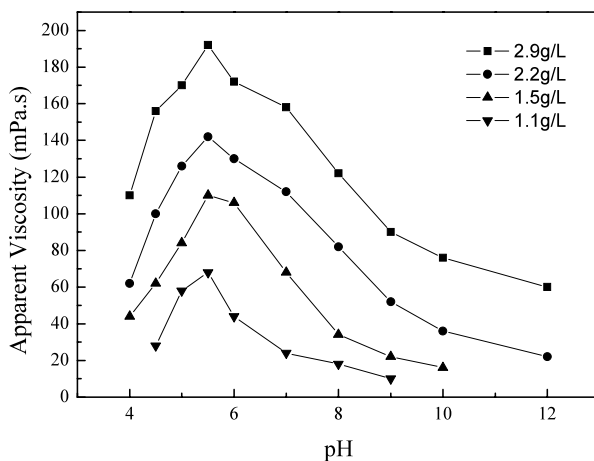
3.2 Effect of pH on Apparent Viscosities

The dissolution of copolymers in water becomes more difficult with the increasing of hydrophobic levels, qualitatively indicating the association characteristic of the copolymers. A high foaming ability of the copolymers was observed during the preparation of the sample solutions and the measurement of their viscosities. This behavior also reflects the amphiphilic nature of the copolymers [16].

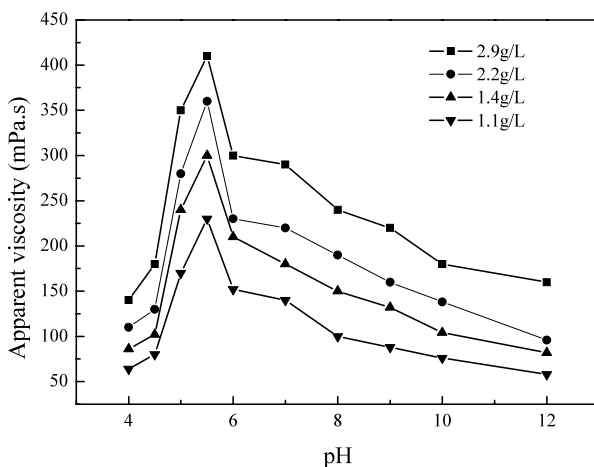
The effect of pH on the viscosity for different samples is shown in Fig. 3. The viscosity of the copolymer solutions increases gradually with increasing pH with a maximum at $\text{pH} = 5.5$ and then decreases with increasing pH. There are two reasons for this pH effect: 1. Neutralization of the carboxyl groups leads to intramolecular electrostatic repulsion and then extension of the polymer chains. In the copolymers, the chain extension exposes the hydrophobic groups embedded in polymer chains, then intermolecular hydrophobic association occurs, so the viscosity increases sharply. 2. Neutralization also leads to intermolecular electrostatic repulsion, which destroys the intermolecular association and then reduces the viscosity. Effect 1 dominates when the pH is below 5.5, whereas effect 2 dominates at pHs above 5.5.

Figure 3 also indicates that the solution viscosity increases with increasing content of the hydrophobic group in the copolymer. The viscosity of the copolymer PAT4 is much higher than those of other polyelectrolyte copolymers at the same concentration and pH. The effect

Fig. 4 Effect of pH on the apparent viscosity of samples with different concentrations with different concentrations ($t = 30\text{ }^{\circ}\text{C}$, shear rate = 30 s^{-1}): (a) PAT3; (b) PAT4



(a)



(b)

of pH on viscosity at different copolymer concentrations is shown in Fig. 4. The viscosity of the copolymer PAT4 with increasing pH becomes larger than the viscosity PAT3 at the same concentrations. The reason is that sample PAT4 has a stronger hydrophobic association than others because PAT4 has a higher TMSPMA content. That the presence of the copolymer PAT4 produces a different structure in water is another reason (see Sect. 3.3).

3.3 Associating Morphologies of the Polyelectrolyte

The Poly(AA-co-TMSPMA) hydrophobic polyelectrolyte can self-associate when placed in water that is a selective solvent for the hydrophilic polymer. Associating morphologies of polyelectrolytes are formed at equilibrium between micelles and monomers above critical micelles concentration. Formation of associating morphologies occurs as a result of two forces. One is an attractive force that leads to the association of molecules, whereas the other

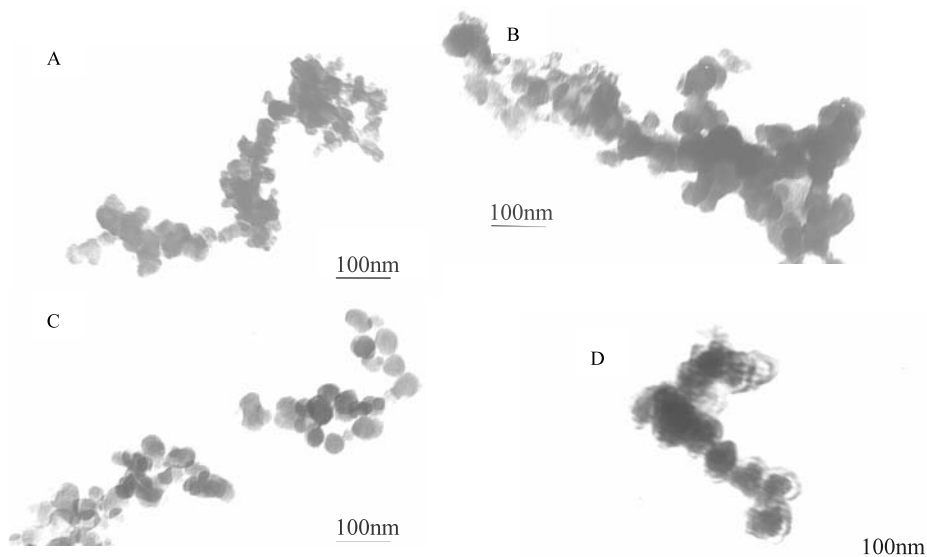


Fig. 5 TEM images of hydrophobic polyelectrolyte micelles ($C = 1.0 \text{ g}\cdot\text{L}^{-1}$): (a) PAT1; (b) PAT2; (c) PAT3; (d) PAT4

one, a repulsive force, prevents unlimited growth of the micelles to a distinct macroscopic phase.

The associating morphologies can be readily observed using TEM. The associating morphologies formed by Poly(AA-co-TMSPMA) in water are shown in Fig. 5. The associating morphologies of samples PAT1, PAT2 and PAT3 are characterized by aggregates with a spherical structure. However, the associating morphologies of sample PAT4 are characterized by a core-shell structure. In this case, the core consists of the hydrophobic TMSPMA polymer whereas the corona (shell) contains the hydrophilic polymer PAA. Figure 3 shows that the sample PAT4 exhibits a different viscosity behavior than the other samples. The reason is that the sample PAT4 in aqueous solution can form associating morphologies with core-shell structures whereas samples PAT1, PAT2 and PAT3 are characterized by aggregates with spherical structures.

3.4 Critical Micelle Concentration

The critical micelle concentration (cmc) can be determined by several methods [17]. Theoretically, any physical property (e.g., interfacial tension, conductivity, osmotic pressure) that shows sudden changes at or near the cmc could be used. Usually, the variation in plots of such properties as a function of concentration is used as an indicator of the onset of intermolecular association. The relative viscosities of the poly(acrylic acid) and copolymer solutions versus concentration are shown in Fig. 6. The relative viscosity of the copolymer solution is much higher than that of poly(acrylic acid) at the same concentration, and it increases dramatically with an increase in the TMSPMA content of the copolymer. The relative viscosity of poly(acrylic acid) and the copolymers increase with increasing concentration, and those of the polyelectrolyte copolymers all sharply increased at $0.6 \text{ g}\cdot\text{L}^{-1}$. The critical micelle concentration of the sample PAT1, PAT2, PAT3 and PAT4 is ca. $0.6 \text{ g}\cdot\text{L}^{-1}$.

Fig. 6 Relative viscosity of the poly(acrylic acid) and polyelectrolyte copolymers solutions versus concentration

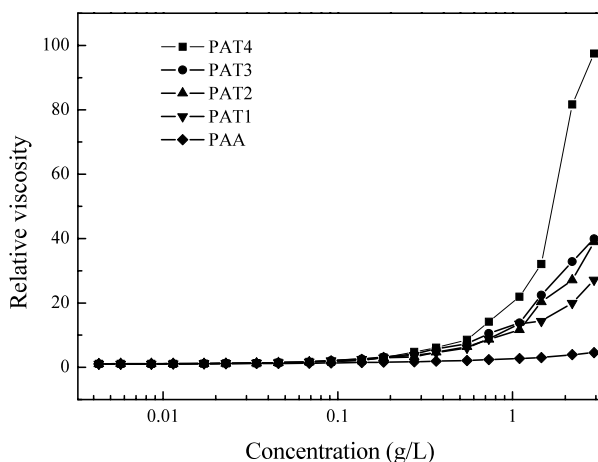
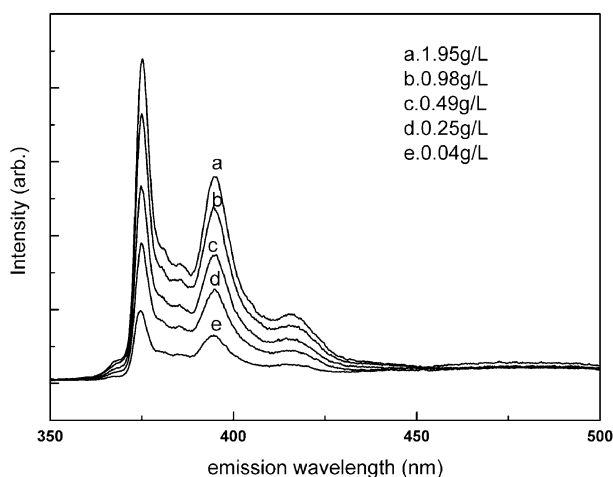


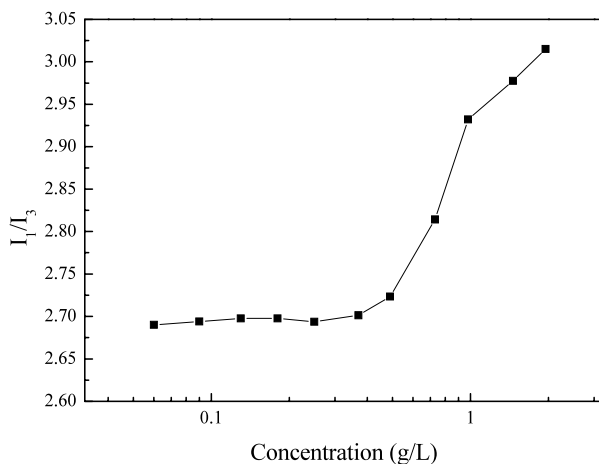
Fig. 7 Fluorescence emission spectra of PyMeA·HCl in solutions of copolymer PAT4 at different concentrations



Fluorescence spectra of PyMeA·HCl in copolymer PAT4 solutions at different concentrations are shown in Fig. 7. At low polymer concentrations, the probe shows the spectral characteristic of a weak monomer band with a peak at 395 nm without fine structure and a weak broad band around 490 nm associated with excimer emission. As the concentration of the polymer is increased, the monomer emission strengthens considerably, accompanied by the appearance of a fine structure. Meanwhile, the excimer emission gradually disappears. The two noteworthy features of these spectra are that the intensity increases with increasing polymer concentration and that there are small changes in the intensity ratio of the first and third vibrational bands, I_1/I_3 .

A preferred method to determine the cmc involves the use of fluorescent probes [18]. Fluorescence techniques are powerful in determining the cmc value for polyelectrolytes. We use a cationic pyrene probe, 1-pyrenemethylamine hydrochloride (PyMeA·HCl). In water, PyMeA·HCl dissociates into the cation probe PyMeAH⁺ and Cl⁻. PyMeAH⁺ can bind on the anionic polyelectrolyte PAT4 by electrostatic attraction. The intensity ratio I_1/I_3 of the first to the third emission peak of the labeled pyrene is known to be sensitive to the

Fig. 8 Determination of the cmc of copolymer PAT4 from the intensity ratio I_1/I_3 obtained from the fluorescence emission spectra



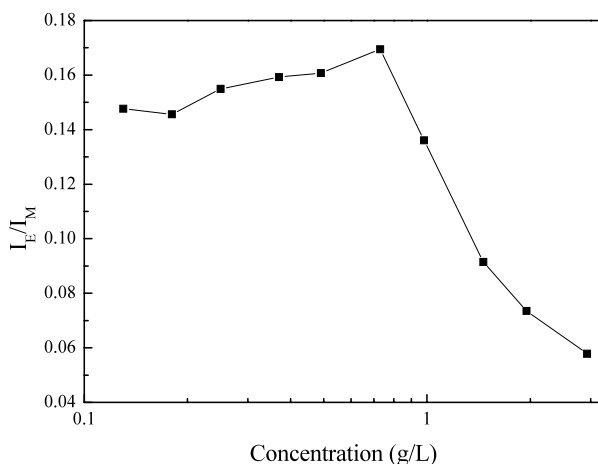
microenvironmental polarity, which becomes lower in less-polar media. The I_1/I_3 ratio of the pyrene-labeled sample PAT4 in aqueous solution is plotted in Fig. 8. The I_1/I_3 value is constant at 2.70 at $C < 0.4 \text{ g}\cdot\text{L}^{-1}$, then increases with increasing concentration and achieves a high value of 3.0.

Pyrene is a condensed aromatic hydrocarbon that is highly hydrophobic and sensitive to the polarity of the surrounding environment. Below the cmc, pyrene is solubilized in water, a medium of high polarity. When micelles are formed, pyrene partitions preferentially toward the hydrophobic domain afforded by the micellar core and thus, experiences a non-polar environment. Consequently, the apparent cmc can be obtained from the plot of the fluorescence of pyrene, the I_1/I_3 ratio from emission spectra against concentration: a major change in the slope indicates the onset of micellization [19].

Our research reflected that the I_1/I_3 value increased with increasing concentration in the labeled-pyrene system. The I_1/I_3 value is constant at 2.70 at very low concentration. The reason is that intramolecular association is dominant. At the cmc there exist both intra- and intermolecular associations so that the I_1/I_3 value starts to increase. At higher concentrations, the I_1/I_3 value continues to increase. The reason is that intermolecular associations become dominant, which prevent the pyrene labels from being incorporated into the micelle. Morishima et al. concluded that the difference between the polymer bound pyrene and free pyrene is that the pyrene labels in PyPAMPS are prevented from penetrating into the hydrophobic core of the micelle by constraints exerted by the polymer chain [20]. The intensity ratio I_1/I_3 of the first to the third emission peak of labeled pyrene is known to be sensitive to the microenvironmental polarity so the critical micelle concentration can be determined by the sudden changes for I_1/I_3 . The critical micelle concentration of the sample PAT4 determined from the intensity ratio I_1/I_3 is $0.6 \text{ g}\cdot\text{L}^{-1}$.

The excimer to monomer intensity ratio I_E/I_M of the pyrene probe as a function of concentration is plotted in Fig. 9. With increasing PAT4 concentration the I_E/I_M value first increases, reaches a maximum, and then decreases. This is due to the binding of PyMeAH⁺ on the polyelectrolyte PAT4, which results in an increase in the local concentration of the probe chromophore along the polymer chain and promotes excimer formation. It induces a typical pyrene excimer emission as the broad, structureless band centered around 490 nm and causes a reduction in the monomer intensity. The resulting emission intensity ratio, I_E/I_M , of the excimer to monomer of pyrene increases. At a high PAT4 concentration the

Fig. 9 Determination of the cmc of copolymer PAT4 from the intensity ratio I_E/I_M obtained from the fluorescence emission spectra



probe cation can be redistributed along the polymer chain owing to the increased number of available binding sites. Pyrene excimer emission is reduced and then the I_E/I_M value gradually decreases. The intensity ratio I_E/I_M of labeled pyrene is known to be sensitive to the spatial distance between the pyrenes. As suggested by Chandar et al. [21], the concentration corresponding to the I_E/I_M maximum in Fig. 9 can be considered as the cmc, where the associating aggregation begins to take place. The critical micelle concentration of the sample PAT4 determined from the intensity ratio I_E/I_M is $0.7 \text{ g}\cdot\text{L}^{-1}$.

4 Conclusions

A series of hydrophobically modified polyelectrolytes were prepared. The products were obtained in the form of white powders. The yield of these polymerizations was always >92%. The results of TEM, ^1H NMR spectra, and fluorescent emission spectra, etc, showed that the resulting copolymers are amphiphilic in nature and self-assemble to form micelles in aqueous solution. This trend is strengthened with increasing hydrophobic comonomer, tris(trimethylsiloxy)methacryloxypropylsilane (TMSPMA), in the feed. The viscosity of the copolymers showed a strong dependence on pH with a maximum at $\text{pH} = 5.5$. Solutions of poly(AA-co-TMSPMA) form micellar structures from a global to a shell-core structure with increasing hydrophobic levels. Sample PAT4 with a shell-core structure in solution has the largest viscosity value. The critical micelle concentration of the copolymer PAT4 determined by relative viscosity was $0.6 \text{ g}\cdot\text{L}^{-1}$. The cmc of the copolymer PAT4 determined by the intensity ratios of the first to the third emission peaks, I_1/I_3 , and of the excimer to monomer, I_E/I_M , of the pyrene probe as function of concentration are 0.6 and $0.7 \text{ g}\cdot\text{L}^{-1}$, respectively.

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