

Synthesis, Characterization and Properties of Amphiphilic Fluorine-Containing Copolymer

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A series of amphiphilic fluorine-containing copolymers PAMDF were synthesized from varying amounts of acrylamide (AM) and diallylamine derivatives (DF) with a fluorinated side chain *via* solution copolymerization. The diallylamine derivatives monomer was synthesized by reacting perfluorohexyl ethyl acrylate (PFHEA) with diallylamine to introduce fluorinated side-chains and rigid plane structure with strong fluorescence property into the copolymers. The amphiphilic fluorine-containing copolymers were characterized by ¹H NMR, ¹⁹F NMR, Elemental analyze and static light scattering measurements. The basic physico-chemical properties of the copolymers in an aqueous medium were investigated by means of surface tension, dynamic laser light scattering and resonance light scattering. The surface tension measurement indicated that the surface activity of the copolymers in aqueous solution increased with increasing the diallylamine derivatives content of amphiphilic copolymers. Dynamic laser light scattering measurement revealed the hydrophobic association behaviour of copolymers in aqueous solutions depended on the copolymer concentration, the content of hydrophobic diallylamine derivatives side chains and the addition of salt. The resonance light scattering results demonstrated the critical aggregation concentration of the copolymers was 0.01-0.05 mg mL⁻¹ in aqueous solutions.

Keywords: Water soluble polymer, Hydrophobic association, Fluorocarbon structure, Aggregation behaviour.

INTRODUCTION

Since fluorine is a remarkable element which has a mass of 19 but is only about 30 % larger than H, an R_F radical is massive and electronegative when compared with its hydrocarbon analogue¹. Moreover, fluorocarbon is more hydrophobic than the hydrocarbon analogue; one CF₂ group corresponds to about 1.7 CH₂ group² as far as the hydrophobic effect³ is concerned. Compared to the non-fluorinated analogues, fluorine can impart outstanding properties to macromolecule including low surface energy, low refractive index, high thermal and mechanical stability, enhanced chemical resistance, low dielectric constants, oil- and water-repellency and so on⁴⁻⁷. Hence, the fluorine-containing polymers can be applied in many fields of high technology such optics⁸, paints and coatings⁹, microlithography¹⁰ and microelectronics¹¹. Recently, much attention has been paid to amphiphilic copolymers with fluorocarbon-hydrocarbon hybrid architectures¹². When fluorinated olefins are copolymerized with hydrophilic monomers, the amphiphilic fluorine-containing copolymers are obtained and used as macromolecular surfactants, magnetic resonance imaging contrast agents, surface modifiers, or membranes¹³.

Diallylamine is a low cost commercial product that is applied as pharmaceutical intermediates and the intermediates

for agricultural chemicals, dye and pigment, organic synthesis and resin modifying agent. The difunctional allyl analogues have been found to be polymerized to high molecular weights through a five-membered cyclopolymerization, as discovered by Butler's pioneering work¹⁴. These cyclopolymers have found wide usage in industry because of their advantageous physical and chemical properties¹⁵. In one study¹⁶, a novel quaternary ammonium salt, which contains both perfluoroalkyl group and diallyl groups, was synthesized. The introduction of diallyl groups into the quaternary ammonium salt not only can enhance the antimicrobial activity, but also extend its application fields. It can also be used as a perfluoroalkyl-containing monomer in the polymer field, which is a convenient method incorporating perfluoroalkyl chain in the polymer.

The common feature of amphiphilic copolymers is the presence¹⁷ of a hydrophilic main chain and a few hydrophobic substituents, which may be randomly attached to the main chain or appended at one or both ends of the chain¹⁸. The combination of fluorinated monomer with hydrophilic monomer may lead to a new class of amphiphilic copolymers, which have unique advantage in drug delivery field because they can transmit both hydrophilic and fluorinated molecules at the same time to the target sites¹⁹. A sizable body of publications focused on molecular level studies of the amphiphilic fluorine-

containing polymers with emphasis on characterizing the hydrophobic microdomains and establishing the relationship between the hydrophobic microstructure and macroscopic properties²⁰.

This study aims at the synthesis and characterization of the amphiphilic fluorine-containing copolymer containing a novel diallylamine derivative (DF) with a fluorinated side chain [-CH₂-CH₂-COO-(CH₂)₂-(CF₂)₅CF₃] and acrylamide (AM). Surface tension, dynamic laser light scattering (DLS) and resonance light scattering (RLS) were employed to investigate the properties of the synthesized copolymers with various fluorocarbon groups in aqueous solution. The hydrophobic aggregation behaviour of the synthesized copolymers in aqueous solution is interpreted as a function of copolymer concentration, the content of hydrophobic diallylamine derivatives side chains and salt concentration. The effects of different surfactants on the rheological properties of the fluorine-containing copolymers will be investigated for potential applications in future research.

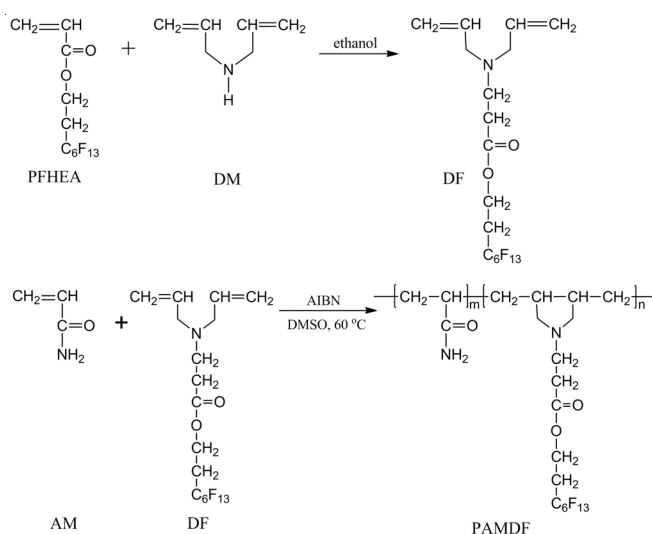
EXPERIMENTAL

Acrylamide (AM) was purchased from Tianjin Kemiou Chemical Reagent Co. (Tianjin, China, chemical purity) and was recrystallized from acetone and vacuum dried at room temperature. The initiator, analytical grade 2,2'-azobisisobutyronitrile (AIBN), was obtained from J&K Chemical, recrystallized from ethanol and dried in a vacuum desiccator and stored in a light resistant container at low temperature before use. Diallylamine (DA) was purchased from Zouping Mingxing Chemical Co. (Zouping, China, chemical purity). 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (PFHEA, CH₂=CH₂-COO-(CH₂)₂-(CF₂)₅-CF₃) was supplied by China Fluoro Technology Co., Ltd (Jinan, China, chemical purity) and was used without further purification. All the other chemical reagents were analytical grade and used as received. Deionized water was used in all the preparation and characterization processes.

Synthesis of fluorinated diallylamine monomer: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (8.644 g, 20 mmol) was dissolved in 30 mL of ethanol and stirred at 60 °C for 10 min. Diallylamine (1.943 g, 20 mmol) was added to the flask by stirring and the reaction was conducted at 60 °C for additional 8 h. When reaction was completed, solvent was removed by a rotary evaporator to give a final product 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorohexyl-3-(diallylamino) ethyl propionate (DF). The synthesis route of diallylamine derivatives monomer is illustrated in **Scheme-I**.

Preparation of amphiphilic fluorine-containing copolymer PAMDF: The amphiphilic fluorine-containing copolymers were synthesized *via* conventional free radical

copolymerization in DMSO. Diallylamine derivatives monomer (0.1320 g, 0.2494 mmol), acrylamide (3.5321 g, 0.0497 mol) and DMSO (40 mL) were added into a 100 mL round bottom flask equipped with a magnetic mechanical stirrer, drop funnel and N₂ inlet/outlet. The flask was deoxygenated and backfilled with nitrogen three times. Then the initiator AIBN (0.041 g, 0.2497 mmol) dissolved in DMSO (10 mL), which was deoxygenated with nitrogen, was poured into the flask. The polymerization was carried out at 65 °C for 10 h. When the reaction was completed, the copolymer products were precipitated in a mixture of acetone and diethyl ether (V_{acetone}:V_{diethyl ether} = 1:1) and the precipitate was purified by re-precipitation repeatedly in acetone. The final product was gathered and dried under vacuum at 40 °C for 24 h. The polymerization conditions of the synthesized samples are listed in Table-1. The synthesis route is illustrated in **Scheme-I**.



Scheme-I: Synthesis route of fluorinated diallylamine monomer diallylamine derivatives (DF) and amphiphilic fluorine-containing copolymer PAMDF

The ¹H NMR and ¹⁹F NMR spectra were recorded on a Bruker AVANCE400 NMR spectrometer. CDCl₃ or D₂O were used as the solvent and for field-frequency lock. The observed ¹H and ¹⁹F chemical shifts were reported in parts per million (ppm) relative to an internal standard.

Weight percentages of carbon, hydrogen, nitrogen and oxygen atoms were assessed by elemental analysis at an Elementar Vario E1 III analyzer (German).

Static light scattering measurements were performed in a DAWN HELEOS light scattering instrument (Wyatt Technology). The system light source was a linearly polarized gallium arsenide laser and the laser is positioned to polarize the incident beam vertically. The copolymer was examined in 0.1 mol mL⁻¹

TABLE-1
MONOMER FEED RATIOS, REACTION TIME, REACTION TEMPERATURE AND CONVERSION FOR THE PREPARATION OF PAMDF

Sample code	Acrylamide (mol)	Diallylamine derivatives (mmol)	AIBN (mmol)	Temperature (°C)	Yield (%)
PAMDF-1	0.0497	0.2494	0.2497	65	93.72
PAMDF-2	0.0495	0.5988	0.2497	65	81.45
PAMDF-3	0.0493	0.7482	0.2497	65	78.14

NaCl solution. A differential refractive index detector was used to measure the refractive indices (dn/dc) of different sample solutions at 25 °C.

The surface tension measurement was carried out by the pendant drop method using a Kruss K12 Processor Tensiometer equipped with a Wilhelmy plate at 25 °C. For the measurements, the concentrated stock copolymer solutions were obtained by dissolving an appropriated amount of copolymer powder into deionized water or NaCl solutions with a certain concentration. And the stock solutions were stirred using a gentle magnetic stirring for overnight or several days depending on the concentrations of copolymer sample. Then the solutions were allowed to stand for some time until bubbles disappeared absolutely. Final desired concentrations of copolymer solutions were prepared by diluting the stock solution with corresponding solvents. All the solutions were kept standing overnight for equilibrium prior to measurements.

Dynamic laser light scattering measurement was conducted on a multiangle laser photometer equipped with linearly polarized gallium arsenide laser (Wyatt Technology Co. DAWN HELEOS). It was employed to characterize the average hydrodynamic radius (R_h) of copolymers in aqueous solution at different concentration and added salt concentration. The copolymer solutions were filtrated through a 0.8 μm Millipore filter before the measurement.

Resonance light scattering measurements (RLS) were performed on a Hitachi F-7000 fluorescent spectrometer with synchronous scanning at $\lambda_{\text{ex}} = \lambda_{\text{em}}$ (*i.e.*, $\Delta\lambda = 0$ nm). The resonance light scattering spectra were recorded from 200 to 600 nm at 25 °C.

TGA measurements were estimated using a TGA apparatus (SDT Q600 V8.3 Build 101) with a nitrogen gas velocity of 100 mL min^{-1} . The TGA curves were recorded at a heating rate of 10 °C min^{-1} from room temperature up to a maximum of 600 °C. The sample size of copolymers varied between 2.5 and 3.8 mg.

RESULTS AND DISCUSSION

Synthesis and basic characterization of diallylamine derivatives monomer and amphiphilic fluorine-containing copolymers PAMDF: The fluorinated diallylamine monomer was successfully synthesized from the reaction of diallylamine with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate in ethanol. The process of synthesis has been introduced previously and the synthesis route of diallylamine derivatives monomer was illustrated in **Scheme-I**. The diallylamine derivatives monomer was characterized by ^1H NMR spectra and the peak assignments are presented in Fig. 1. The ^1H NMR spectrum clearly demonstrates that the

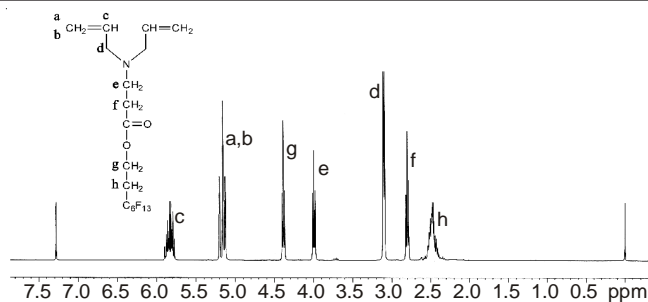


Fig. 1. ^1H NMR spectrum of fluorinated diallylamine monomer

diallylamine derivatives monomer is obtained and the result indicated that there was no polymerization reaction during diallylamine derivatives monomer preparation.

The amphiphilic fluorine-containing copolymers were easily obtained *via* conventional free radical copolymerization of diallylamine derivatives monomer and acrylamide using DMSO as solvent and AIBN as initiator. The ^1H NMR spectrum and assignment of the signals derived from the amphiphilic fluorine-containing copolymer are shown in Fig. 2. To better characterize the structure of the amphiphilic copolymer, ^{19}F NMR is used to determine the fluorocarbon moiety in the copolymer structure. The ^{19}F NMR spectrum of PAMDF sample depicted in Fig. 2 confirms the presence of six different kinds of fluorine resonances originating from the side chains of diallylamine derivatives monomer. The ^1H NMR and ^{19}F NMR results confirm that the amphiphilic fluorine-containing copolymers have been successfully synthesized. However, it does not give quantitative information of the monomer proportion in the obtained copolymers in the spectra. The composition of all the samples was determined by elemental analyze and the results are displayed in Table-2.

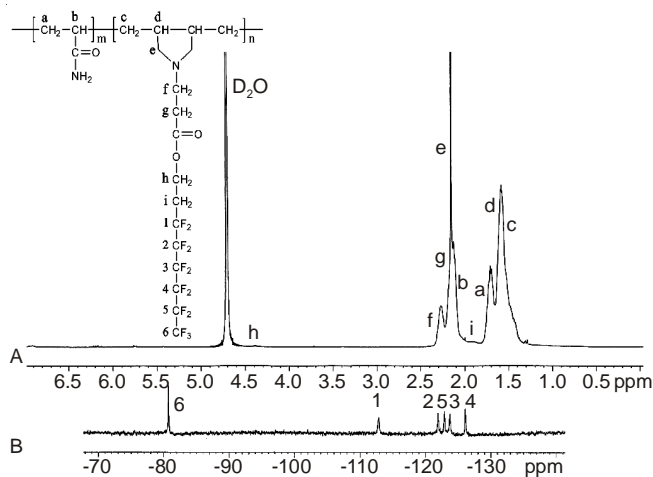


Fig. 2. ^1H NMR and ^{19}F NMR spectra of the copolymer PAMDF

TABLE-2
CHARACTERISTIC DATA FOR THE COPOLYMER PAMDF SAMPLES

Sample	Elemental analysis			Diallylamine derivatives in copolymer (mol %)	M_w (10^{-5} g mol^{-1})	dn/dc (mL g^{-1})
	C (wt. %)	H (wt. %)	N (wt. %)			
PAMDF-1	50.437	6.962	19.343	0.301	1.370	0.1498 ± 0.0062
PAMDF-2	50.055	6.848	18.805	0.753	1.523	0.1486 ± 0.0036
PAMDF-3	49.816	6.776	18.469	1.048	1.781	0.1478 ± 0.0070

The weight-average molecular weight M_w and the specific refractive index increment dn/dc were demonstrated in static light scattering measurement from the angular dependence of the excess absolute scattering intensity, known as the Rayleigh ratio $R(\theta)$, on the basis of

$$\frac{K^*C}{R(\theta)} = \frac{1}{M_w} \left(1 + \frac{1}{3} \langle r_g^2 \rangle q^2 \right) + 2A_2C \quad (1)$$

where $K^* = 4\pi(dn/dc)^2 n_0 / (N_A \lambda_0^4)$ and $q = (4\pi n_0 / \lambda_0) \sin(\pi/2)$, with n_0 , λ_0 and θ being the solvent refractive index, the wavelength of the incident light in vacuum and the scattering angle, respectively²¹. The molecular weight determination of the copolymer samples was conducted in 0.1 mol L⁻¹ NaCl aqueous solution. The values of M_w calculated on the basis of eqn. 1 using the projection $\theta = 0$ and $C = 0$ and dn/dc are listed in Table-2.

Thermal properties: The thermal properties of copolymer PAMDF was studied by TGA from 25 to 600 °C under nitrogen atmosphere. Fig. 3 indicates that the volatilization of small molecules occurs from 50 to 200 °C and the copolymer starts to decompose from 271 °C with 10 % of weight loss. The second decomposition temperature of copolymer was about 350 °C with 20 % of weight loss and the another decomposition occurred at about 375 °C. The thermogravimetric analysis of all samples shows a satisfactory thermal stability.

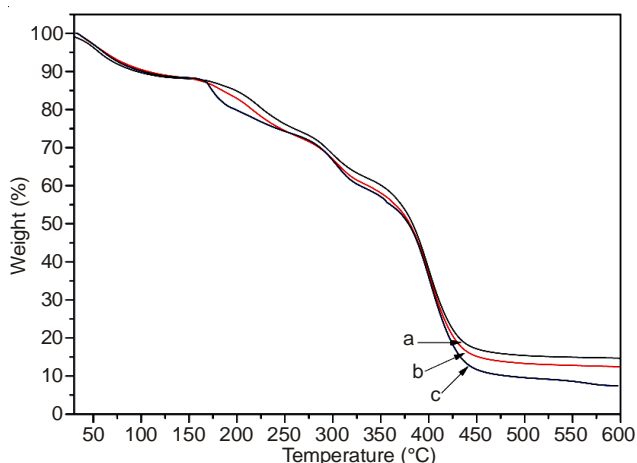


Fig. 3. TGA curves of PAMDF copolymers (a: PAMDF-1; b: PAMDF-2; c: PAMDF-3)

Surface tension measurements: Surface tension measurements of the amphiphilic fluorine-containing copolymers were carried out on aqueous copolymer solutions over a wide range of concentrations at 25 °C. The relationship between concentration and surface tension of PAMDF samples and the effects of different fluorocarbon side chains contents in the amphiphilic copolymer on the surface activity are shown in Fig. 4. The result indicates all the amphiphilic fluorine-containing copolymers were surface-active in aqueous solution. The surface tension decreases slowly below a threshold concentration of copolymer (above 0.5 mg mL⁻¹). When the copolymer concentration is increased up to 0.5 mg mL⁻¹, it is seen that the surface tension of copolymer solutions tended to decrease rapidly. There is no characteristic concentration as an inflection point above which the surface tension remains almost constant. Among the copolymer samples, PAMDF-3-

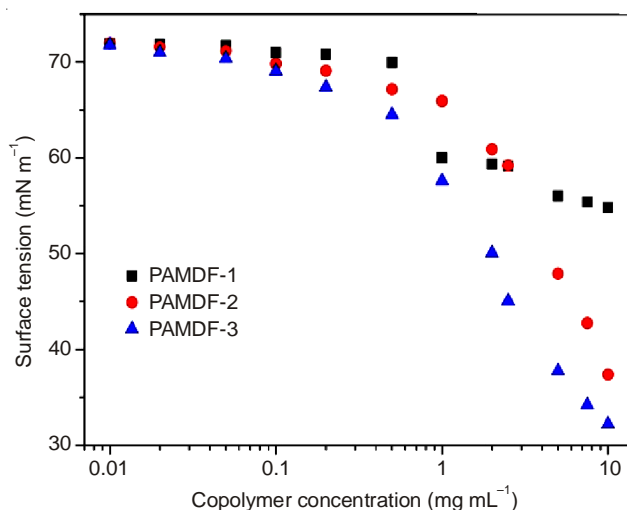


Fig. 4. Changes in the surface tension of PAMDF aqueous solutions as a function of copolymer concentration at 25 °C

was the most effective in reducing the surface tension of water, which may be taken as an indication that the surface activity of copolymer tended to increase with adding the amount of fluorinated diallylamine in copolymer structure.

Dynamic laser light scattering: The dynamic laser light scattering measurement was employed to investigate the aggregation behaviour of PAMDF in aqueous solution. The relationship between the distribution of hydrodynamic radius (R_h) and concentration of PAMDF-3 samples is displayed in Fig. 5. The concentrations of copolymer solution was arranged from 0.01 to 5 mg mL⁻¹. As shown in part A, the radius distribution shift to smaller R_h with the increase of copolymer concentration, when the concentration of PAMDF-3 is less than 1 mg mL⁻¹. And the radius distribution of copolymer shift to the larger value of R_h with the copolymer concentration increased above 1 mg mL⁻¹. The results indicate that the intramolecular hydrophobic association is primary for PAMDF-3 at lower copolymer concentration and the aggregates of macromolecular shrink with increasing copolymer concentration leading to the decrease of R_h values. When the content of copolymer in solution is increased up to 1 mg mL⁻¹, the aggregation behaviour of copolymer translate to intermolecular hydrophobic association. And the size of aggregates increase as copolymer concentrations increase, result in the increase of R_h values.

The effects of added sodium chloride on the aggregation behaviour of PAMDF in aqueous solution obtained by dynamic laser light scattering measurement are shown in Fig. 6. The concentration of copolymer is fixed to 0.2 mg mL⁻¹ and the intramolecular hydrophobic association exist primarily in copolymer solution at this condition. The concentration of added sodium chloride has a range value from 0 to 2 mol L⁻¹. When a small amount of sodium chloride (less than 0.5 mol L⁻¹) is added into copolymer solution, the value of R_h decrease with the increase of NaCl concentration. This is attributed to the enhancement of solution polarity with the addition of NaCl, leading to the volume shrinkage of intramolecular aggregates. The R_h value increase gradually with NaCl concentration increased up to about 0.5 mol L⁻¹, due to the transform from intramolecular hydrophobic association to intermolecular hydrophobic association of PAMDF in aqueous solution. When

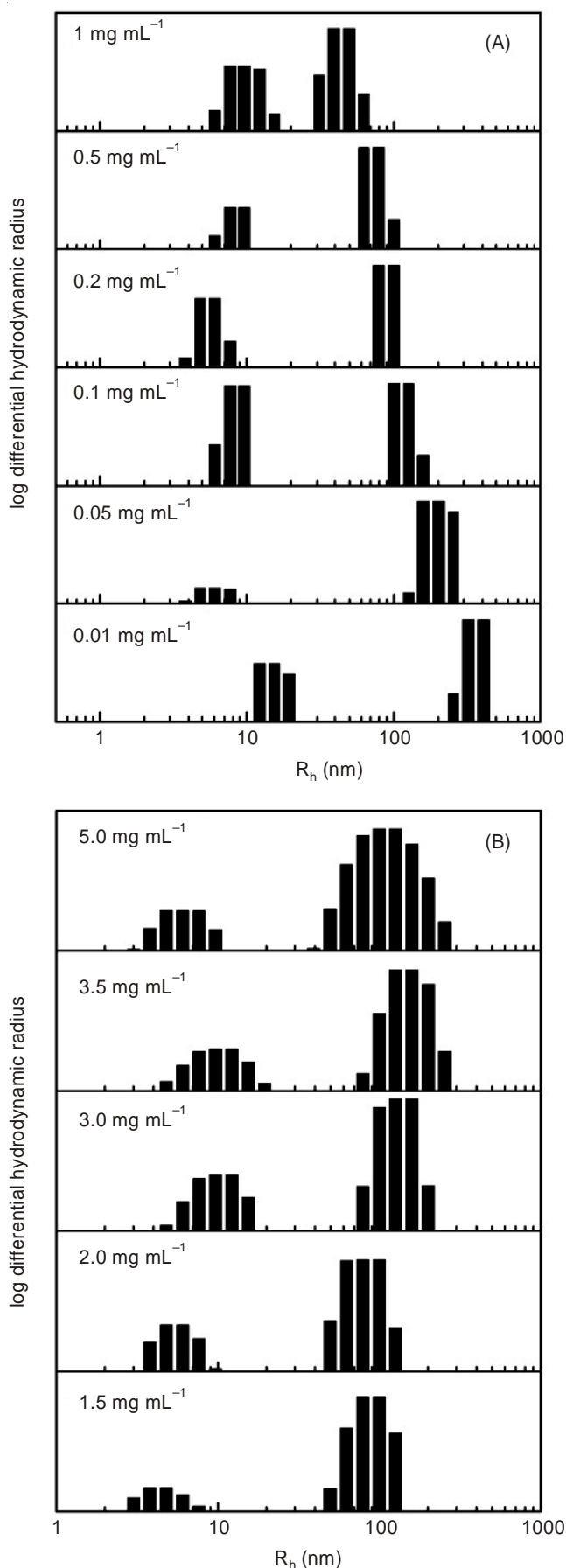


Fig. 5. Hydrodynamic radius distribution of PAMDF-3 in aqueous solution at different copolymer concentration at 25 °C. A: $C_{\text{PAMDF-3}} \leq 1 \text{ mg mL}^{-1}$; B: $C_{\text{PAMDF-3}} \geq 1.5 \text{ mg mL}^{-1}$

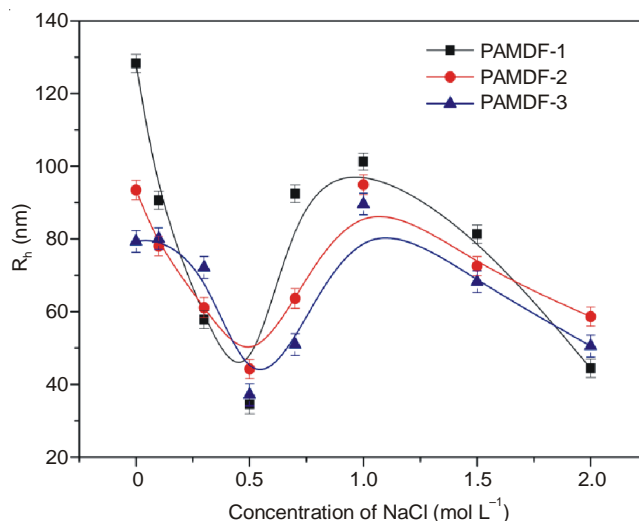


Fig. 6. Variation of the average hydrodynamic radius of copolymer as a function of sodium chloride concentration in water at 25 °C, and the copolymer concentration is 0.2 mg mL^{-1}

the concentration of NaCl is higher than about 1 mol L^{-1} , the R_h values of copolymer shift to lower with increasing the amount of added salt in solution. It is likely that the hydrophobic microdomains of intermolecular aggregation shrink further to avoid contacting with water.

Resonance light scattering: The resonance light scattering technique was employed to describe the aggregation behaviour of molecular chains of PAMDF samples in aqueous solutions. The resonance light scattering spectra were recorded from 200 to 600 nm with synchronous scanning at $\lambda_{\text{ex}} = \lambda_{\text{em}}$ (i.e., $\Delta\lambda = 0 \text{ nm}$). Fig. 7 reveals the resonance light scattering spectra of PAMDF solution of different compositions at 25 °C. It can be seen that PAMDF exhibits the maximum wavelength at 279 nm and the absorption approaches zero in the range over 550 nm. Moreover, the intensity at λ_{max} increases but the resonance light scattering peak scarcely changes with increasing the concentration of copolymer samples. Hence, the changes of the resonance light scattering peak at 279 nm were selected to investigate the aggregation process of copolymer.

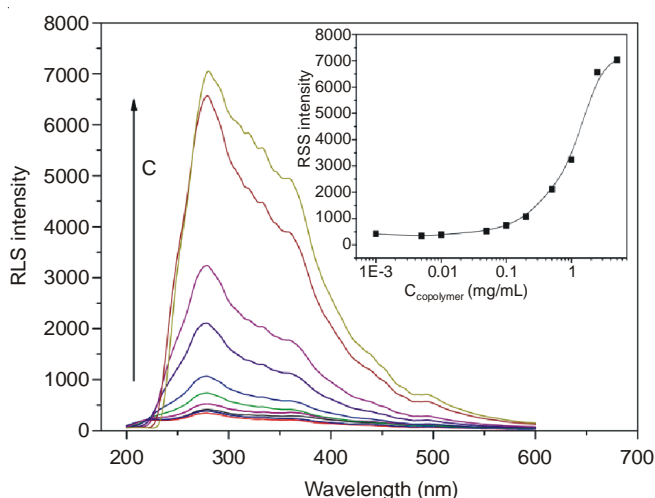


Fig. 7. RLS spectra of copolymer PAMDF-1 in aqueous solutions (inset showing the variation of resonance light scattering intensity at 279 nm)

The relationship between the resonance light scattering intensity and concentration of aqueous solutions of PAMDF is shown in Fig. 8. It can be seen from the figure that the resonance light scattering intensity of PAMDF aqueous solutions increases along with the increase of copolymer concentration, which is less than 0.5 mg mL^{-1} . The increase in resonance light scattering intensity results from the fact that the intramolecular hydrophobic association occurs, leading to the macromolecular chains curling with the increase of the concentration. And with increasing the concentration of PAMDF samples up to 0.5 mg mL^{-1} , the intensity of copolymer increases obviously. It manifests that hydrophobic interactions of copolymer hydrophobic moieties are mainly intermolecular hydrophobic association at high concentrations, which causes the volume of hydrophobic aggregations increasing. For PAMDF samples, the concentration corresponding to the onset of increase in resonance light scattering corresponds closely to the onset of association concentration determined by surface tension experiments.

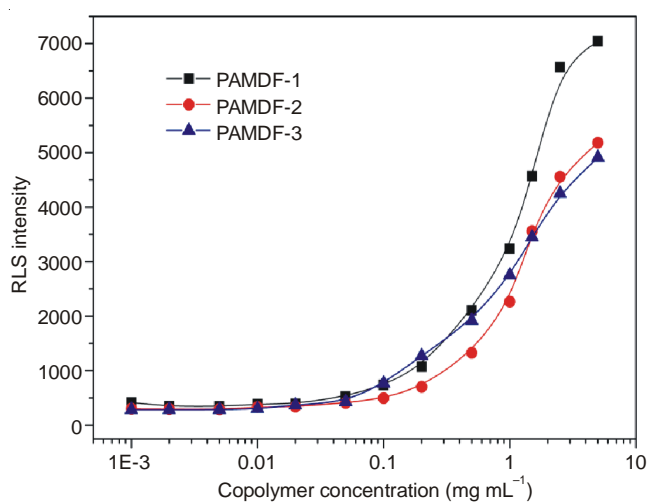


Fig. 8. RLS intensity of aqueous solutions of PAMDF as a function of copolymer concentration

Conclusion

In this work, we have successfully synthesized a novel diallylamine derivative (DF) with a fluorinated side chain and prepared a series of fluorine-containing amphiphilic copolymers PAMDF. The chemical structure of PAMDF was ascertained by ^1H NMR, ^{19}F NMR spectra and elemental analysis. The molecular weight was obtained by static light scattering measurements. The basic physico-chemical properties such as surface tension and aggregation behaviours were studied as a function of copolymer concentration. The results of surface tension measurement indicate that all copolymer samples are surface-active above a threshold copolymer concentration of 0.5 mg mL^{-1} and the ability to reduce the surface tension of

water improve with adding the amount of the fluorinated diallylamine in copolymer structure. The hydrodynamic radius distribution of copolymer was detected by dynamic laser light scattering measurement to investigate the aggregation behaviour of PAMDF in aqueous solution and the concentration of added sodium chloride has an obvious effect on the hydrophobic association of copolymer. The results of resonance light scattering demonstrate that the hydrophobic aggregation behaviour of the copolymers is dependent on the content of DF in copolymer structures. The critical aggregation concentration of copolymers decreases from 0.05 to 0.01 mg mL^{-1} with the ratio increasing of fluorocarbon groups and the resonance light scattering intensity increased with increasing the concentration of all samples. The curves of thermogravimetric analysis reveal the fluorine-containing copolymers show a satisfactory thermal stability.

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REFERENCES

1. N.O. Brace, *Fluor. Chem.*, **96**, 101 (1999).
2. J.C. Ravey and M. Stébé, *Colloids Surf. A*, **84**, 11 (1994).
3. K. Szczubialka, L. Moczek, A. Goliszek, M. Nowakowska, A. Kotzev and A. Laschewsky, *Fluor. Chem.*, **126**, 1409 (2005).
4. D. Valade, C. Boyer, B. Ameduri and B. Boutevin, *Macromolecules*, **39**, 8639 (2006).
5. J.C. Salamone, *Polymeric Materials Encyclopedia*, CRC Press: Boca Raton, FL, USA, vol. 4 (1996).
6. G. Hougham, *Fluoropolymers*, Kluwer Academic: New York, USA (1999).
7. S. Ebnesajjad, *Fluoroplastics*, Plastic Design Library: New York, USA (2002).
8. S.T. Iacono, S.M. Budy, J. Jin and D.W. Smith Jr., *J. Polym. Sci. A Polym. Chem.*, **45**, 5705 (2007).
9. R. Bongiovanni, G. Malucelli, A. Pollicino, C. Tonelli, G. Simeone and A. Priola, *Macromol. Chem. Phys.*, **199**, 1099 (1998).
10. D. Valade, F. Boschet and B. Ameduri, *Polym. Sci. Part A: Polym. Chem.*, **49**, 4668 (2011).
11. J. Sha and C.K. Ober, *Polym. Int.*, **58**, 302 (2009).
12. G. Liu, W. Fan, L.J. Li, P.K. Chu, K.W.K. Yeung, S. Wu and Z. Xu, *Fluor. Chem.*, **141**, 21 (2012).
13. S.D. Xiong, L. Li, S.L. Wu, Z.S. Xu and P.L.J. Chu, *Polym. Sci. Part A: Polym. Chem.*, **47**, 4895 (2009).
14. G.B. Butler and F.L. Ingley, *J. Am. Chem. Soc.*, **73**, 1512 (1951).
15. N.S. Tüzün and V.J. Aviyente, *Phys. Chem.*, **106**, 8184 (2002).
16. H. Shao, L. Jiang, W.-D. Meng and F.-L. Qing, *Fluor. Chem.*, **124**, 89 (2003).
17. J.L. He, P.H. Ni and C.C.J. Liu, *Polym. Sci. Part A: Polym. Chem.*, **46**, 3029 (2008).
18. M. Li, M. Jiang, Y.-X. Zhang and Q. Fang, *Macromolecules*, **30**, 470 (1997).
19. C.C. Liu, J.L. He, Q. Zhao, M. Zhang and P. Ni, *J. Polym. Sci. A Polym. Chem.*, **47**, 2702 (2009).
20. Y.C. Wang and M.A. Winnik, *Langmuir*, **6**, 1437 (1990).
21. Y.J. Che, Y.B. Tan, J. Cao, H.P. Xin and G.Y. Xu, *Polym. Bull.*, **66**, 17 (2011).