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Journal of Fluorine Chemistry 129 (2008) 125–130

JOURNAL OF FLUORINE CHEMISTRY

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Synthesis and surface characterization of an amphiphilic fluorinated copolymer via emulsifier-free emulsion polymerization of RAFT

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Received 4 September 2007; received in revised form 17 September 2007; accepted 29 September 2007
Available online 7 October 2007

Abstract

The hydrophobic monomer dodecafluoroheptyl methacrylate has been copolymerized with hydrophilic monomer methacrylic acid in aqueous solution without any additional emulsifier used via a two-step polymerization process of RAFT. The FTIR and GPC results indicated that amphiphilic copolymers with a narrow molecular weight distribution and well-defined blocks have been synthesized successfully. And the copolymers are likely to form steady micelles in the emulsion. Indicated by TEM, it is clear that micelles with a diameter of 70–120 nm have been formed. Despite a content of 22 wt% of hydrophilic carboxyl, films formed by casting the emulsion onto the baseplate can be hydrophobic after heating treatment.

Keywords: Amphiphilic copolymer; Fluorinated; RAFT; Emulsifier-free

1. Introduction

Fluorinated polymers are attractive functional materials due to their excellent chemical and thermal stability, low surface energy and low refractive index; however, most of these fluorinated polymers, exhibit extremely low solubility in a variety of solvents. Luckily, impart fluorinated chains into polymers such as acrylated, methacrylated and acrylamide polymers can made the polymer dissolvable in fluorinated solvents and even in polar solvents such as acetone and chloroform while maintain most of the properties of the fluorinated polymer [1,2].

Further more, when the fluorinated monomers copolymerized with hydrophilic groups, amphiphilic copolymers will be formed [3–5]. As it is known that among various types of hydrophobic chains, fluorinated carbon chain is the most hydrophobic and its tendency to separate from water or hydrophilic groups is the strongest [6]. Since the amphiphilic copolymer has a hydrophobic moiety and a polar hydrophilic moiety, they are more likely to self-assembled to form aggregates such as micelles, lamellar liposomes, and liquid crystals in solution [7]. And these aggregates may have potential importance in a lot of fields drug carriers, coatings, cosmetics, food, enhanced oil recovery, etc. [8,9]. As a result, the amphiphilic copolymer deserves of intense research, stemming from both the academic and application point of view.

However, to enhance the self-organization behavior hydrophilic and hydrophobic groups are supposed to be well defined into hydrophilic blocks and hydrophobic blocks in the structure [6]. And the controlled radical polymerizations might be among the best methods for producing copolymers with well-defined structures [10]. Of the controlled radical polymerization methods, the RAFT requires few demanding conditions, the only difference from a free radical polymerization system is the addition of a chain transfer agent (CTA), while other polymerization conditions, such as the temperature and the operating pressure are not changed [11]. Besides, RAFT is tolerant of a number of functional groups in the monomer including carboxylic acids, carboxylic acid salts, hydroxyl groups, amides and tertiary amines. Most monomers polymerizable by free radical methods can be polymerized by RAFT [10,12,13]. And the RAFT can be applied to produce amphiphilic copolymers in aqueous solution [14–18].

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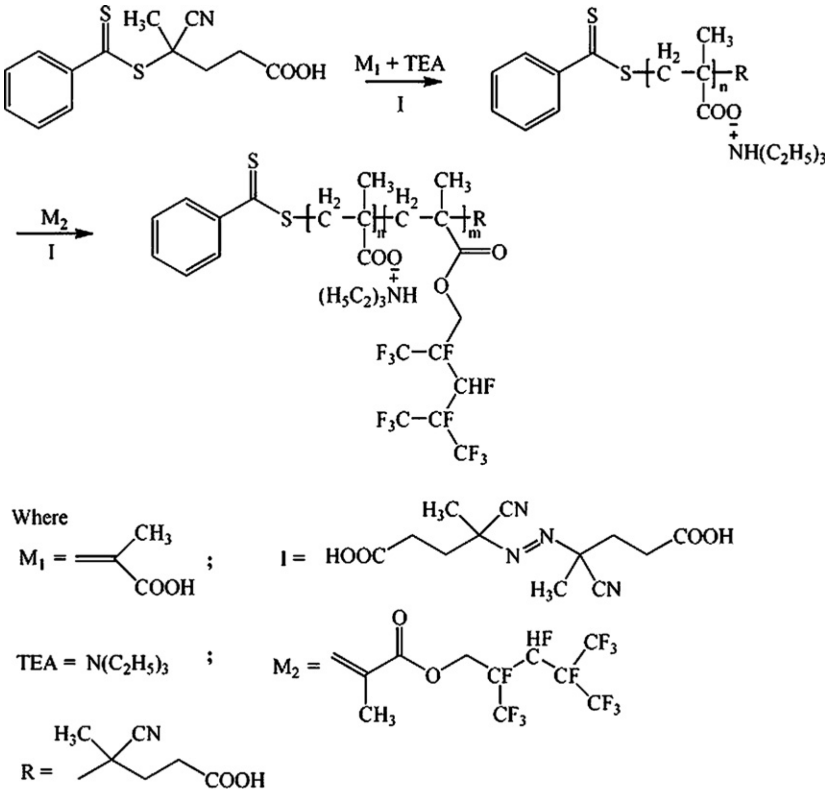
doi:10.1016/j.jfluchem.2007.09.008



Scheme 1. Preparation of well-defined fluorinated copolymer via a two stepped RAFT process.

In this article, we highlight the application of RAFT [19] to copolymerize a hydrophilic monomer (M_1, methacrylic acid) with the hydrophobic dodecafluoroheptyl methacrylate [M_2, $CH_2{=}C(CH_3)COOCH_2CF(CF_3)CHFCF(CF_3)_2$] directly in emulsifier-free emulsions.

2. Results and discussion

2.1. The polymerization of the copolymer

In this article, the RAFT has been applied to copolymerize two kinds of monomers via a two-step polymerization process in emulsifier-free emulsion, as presented in Scheme 1. In the first step, the hydrophilic methacrylic acid (M_1) was polymerized to produce a macro-chain transfer agent (macro-CTA), which would also act as emulsifier later; in the second step, the hydrophobic monomer dodecafluoroheptyl methacrylate (M_2) was polymerized successfully in the aqueous medium, while the macro-CTA acted as both the chain transfer agent and the emulsifier.

2.2. Characterization of the copolymer

The two-step polymerization has been confirmed by GPC. As can be seen from Fig. 1, macro-CTA (trace a) with a narrow molecular weight distribution (MWD) of 1.12, has been synthesized, and after reacting with M_2, a significant shift toward higher Mn could be observed in the GPC chromatograms (trace b) and the MWD is quite narrow about 1.22.

Fig. 2 shows the FTIR spectra of macro-CTA (a) and the fluorinated block copolymer (b), which confirms the successful copolymerization of the very hydrophobic monomer dodecafluoroheptyl methacrylate (M_2), with the key bands at 1251 and 692 cm^{-1} [20], which are caused by the typical stretching vibration and wagging vibrations of C–F.

Both (a) and (b) exhibit the characteristic peaks at 3450 cm^{-1} the stretching vibration of O–H of the carboxyl; peak at 2937 cm^{-1} the stretching vibration of C–H; peak at 1740 cm^{-1} the stretching vibration of C=O.

2.3. Self-assembly

Amphiphilic diblock copolymers in selective solvents generally yield colloidal aggregates or micelles [21]. As

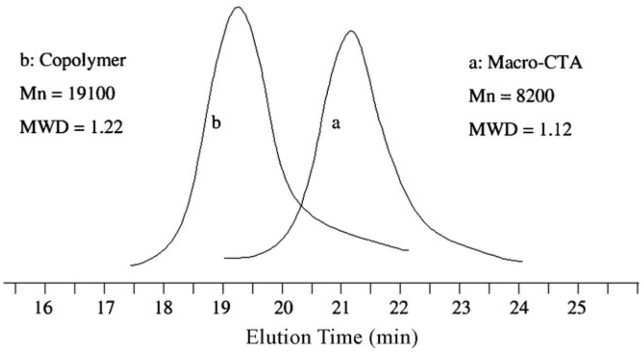


Fig. 1. GPC traces of the macro-CTA and the amphiphilic block copolymer. Trace (a) is of the macro-CTA and trace (b) is of the purified amphiphilic block copolymer.

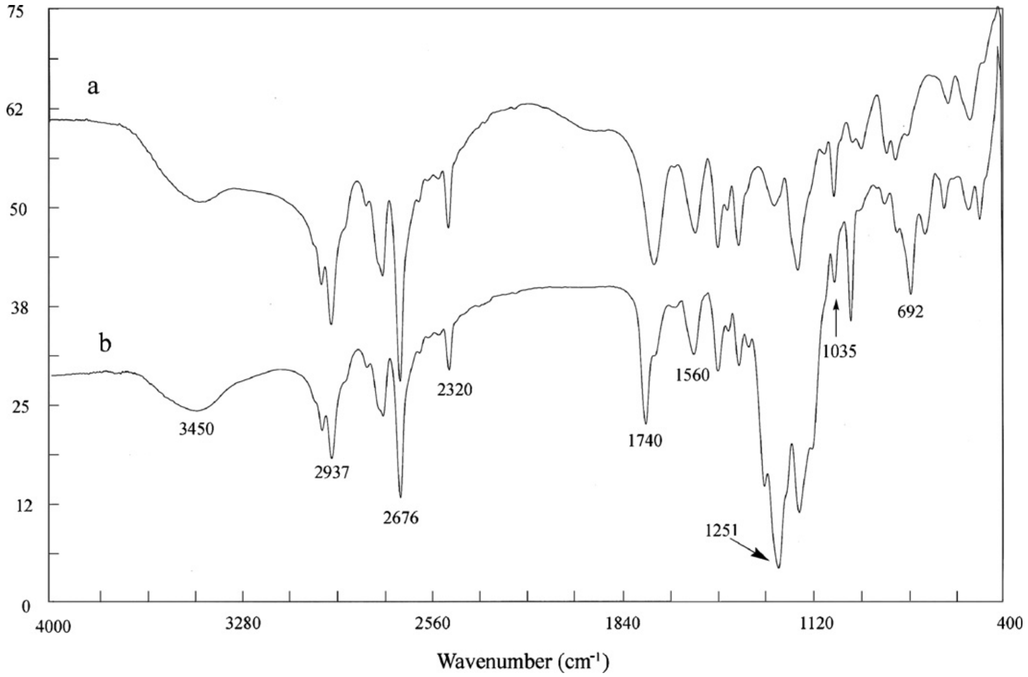


Fig. 2. FTIR spectrum of the macro-CTA and the amphiphilic block copolymer. Trace (a) is of the macro-CTA and trace (b) is of the amphiphilic block copolymer.

shown by the FTIR and GPC results, an amphiphilic diblock copolymer has been produced.

To investigate the aggregation behavior of the block polymer in water, TEM measurement of 1.0 wt% aqueous solutions were carried out. As shown in Fig. 3, micelles with a diameter of 70–120 nm have been formed.

All these aggregates consist of a core or layer of very hydrophobic fluorinated blocks and are all surrounded by a shell of poly(methacrylate acid) blocks which have been neutralized by triethylamine. As the emulsifier poly(methacrylate acid) blocks have been incorporated into the polymer structure, the aggregates turn out to be quite stable.

2.4. Surface property of the copolymer films

Fluorinated polymers are well known as low-surface tension materials, and the most natural approach to measure the surface tension may be by measuring the contact angle of a liquid drop on the film surface.

When the liquid drop is applied to the surface, the outmost surface layers will interact with the liquid. A hydrophobic surface with low free energy gives a high contact angle with liquid, whereas a high energy surface allows the drop to spread, which will cause a low contact angle [22].

To study the surface property of the solid copolymer, the dynamic advancing and receding contact angles of water and oleophilc hexadecane on the film, which was prepared by spin coat dilute emulsions on new-cleaned glass plates were tested. And the samples films were prepared as the following process, first cast dilute emulsions on new-cleaned glass plates, and dried in vacuum for 2 days under 70 °C, and that is the film before treatment; second, place the film in a 120 °C vacuum oven for 2 h. The time is recorded from the moment the liquid is dropped on the film surface till the data is taken, and is applied to study whether the acid group will move towards the surface when with water on top again.

As shown in Table 1, both advancing and receding contact angles of water and oleophilc hexadecane on the films

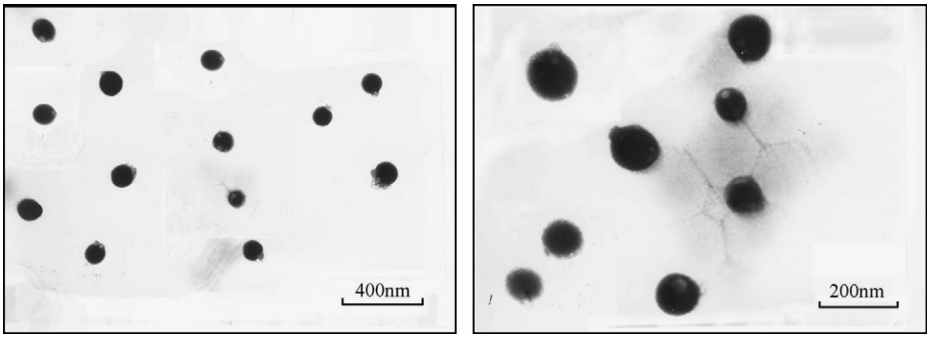


Fig. 3. TEM of the aggregates formed by the fluorinated amphiphilic copolymer. Concentration of the emulsion was 1 wt%.

Table 1
Contact angles of water and hexadecane on the copolymer films

Time/min	Sample	Contact angle (water)		Contact angle (hexadecane)	
		Advancing	Receding	Advancing	Receding
1	Before heating	86 ± 3	56 ± 3	36 ± 3	14 ± 3
	After heating	99 ± 3	60 ± 3	50 ± 3	41 ± 3
10	Before heating	84 ± 3	56 ± 3	36 ± 3	14 ± 3
	After heating	97 ± 3	58 ± 3	49 ± 3	40 ± 3
20	Before heating	83 ± 3	55 ± 3	34 ± 3	13 ± 3
	After heating	96 ± 3	57 ± 3	47 ± 3	39 ± 3

The samples ‘‘before heating’’ and ‘‘after heating’’ represent the films before and after the heating treatment separately. And the time is recorded from the moment the liquid is dropped on the film surface till the data is taken, and is applied to study whether the acid group will move towards the surface when with water on top again.

increased sharply after the heat treatment. That is to say the film becomes more repellent to both the water and the oil after heating.

It might because that the solvent is polar, and polar segments are supposed to be dissolved in it more easily [23]. When the solvent evaporated, polar poly(methacrylic acid) blocks will be brought to the surface of the film, as shown in Fig. 4. As a result, surface of the film is filled with hydrophilic carboxyl groups before heating treatment as presented by Fig. 5 (a), and energy of the film is quite high.

However, under high temperature, flexibility of the polymer chains will increase. As it is know that fluorinated groups have relatively low surface energy, and they have strong tendency to spread to the surface [24,25]. As a result, after 2 h heating treatment, the fluorinated segments moved to the interface, and formed a hydrophobic surface [26], as shown in Fig. 5.

As can be seen from Table 1, contact angles changed after a longer appearance to the liquid drop, it might because acid groups migrate toward the surface again, in the presence of solvents like water [27]. However, the change is not much, possibly it is because in room temperature (25–30 °C), flexibility of the polymer chain is poor and the movement of acid groups is limited. As a result, when is in presence of water, the acid group can hardly move towards the surface again.

3. Experimental

3.1. Material

As shown in Scheme 2, the main materials used in the polymerization are 4-cyanopentanoic acid dithiobenzoate (CTA, which is synthesized via a reported method [19]), methacrylic acid (M_1, Shanghai Jingrex Chemical Industry Co.

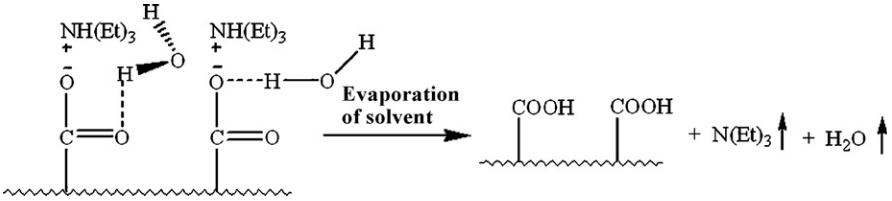


Fig. 4. Schematic illustration of the reasons for the formation of relatively hydrophilic films.

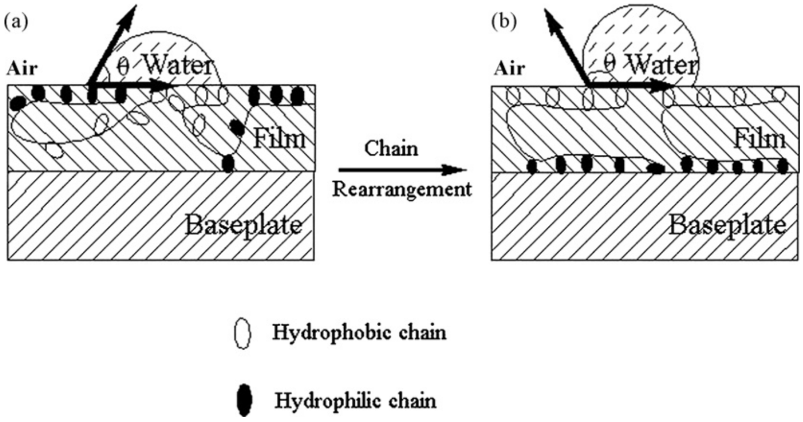
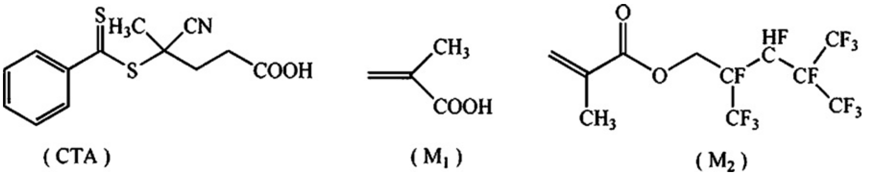


Fig. 5. Schematic illustration of the rearrangement of the amphiphilic copolymer before and after the heating treatment and the influence on the contact angle. Picture (a) is the schematic illustration of the distribution of hydrophobic and hydrophilic segments in the film before heating treatment; and picture (b) is the schematic illustration of these segments after heating treatment and the influence on the contact angle.



Scheme 2. Monomers used in the polymerization process.

Ltd.) and (M_2, Xeogia Fluorine-Silicon Chemical Co. Ltd.). Other chemicals used were purchased from Aldrich Chemical Companies.

3.2. Preparation of the fluorinated copolymer via a two-step polymerization process

The polymerizations were performed in 100 ml three-necked flask equipped with a mechanical stirrer, a thermometer, and an inlet system of nitrogen. CTA (0.28 g, 1 mmol), 4,4′-azobis(4-cyanopentanoic acid) (I) (0.17 g, 0.6 mmol), M_1 (8.6 g, 0.1 mol) and triethylamine (10 g, 0.1 mol) were dissolved in 25 g deionized water; and the solution was deoxygenated via purging with N_2 gas for 30 min before reaction. The polymerization was carried out at 75 °C for 12 h. The polymer was deposited by adding 18 ml HCl solution (6 mol/l) and then separated by filtration. After being dried in vacuum for 2 days, a dithiobenzoyl-end-capped poly(methacrylate acid) can be obtained, which will be used as a macro-chain transfer agent (macro-CTA) in the following polymerization. And the yield of the macro-CTA is about 93.2 wt%.

Dissolve the macro-CTA (4.1 g, 0.5 mmol), M_2 (6 g, 0.15 mol), 4,4′-azobis(4-cyanopentanoic acid) (I) (0.08 g, 0.3 mmol), and triethylamine (5 g, 0.05 mol) in 20 g deionized water by intense stir. Then deoxygenate the solution via purging with N_2 gas for 30 min, carry out the polymerization at 75 °C. After 12 h, a stable emulsion of the final polymer a dithiobenzoyl-end-capped poly(methacrylate acid) with well-defined fluorinated segments can be achieved. And the yield of the block copolymer containing RF-units is about 81.6 wt%.

And the copolymer was purified following the next steps. First, dry the sample by rotary-evaporation; second, stir the remained solids in 2-butanone, which is a selective solvent of dodecafluoroheptyl methacrylate and its homopolymer and then filtrate; third, wash the remained solid with 2-butanone for three times and dry it in vacuum. The yield of the purified copolymer is about 69.6 wt%, and the sample will be used for the GPC and FTIR tests.

3.3. Analyses and characterizations

The molecular weight distributions of the polymer samples were measured at 35 °C by gel permeation chromatography (GPC) on a waters 2410 instrument with THF as the solvent (1.0 ml/min), and with calibration by polystyrene standards.

The IR spectra were recorded on a WQF 410 Spectrophotometer made in Beijing China, using the KBr pellet technique.

Latex used for TEM test is prepared from diluted emulsion (the solid content was about 1 wt%), and is stained by phosphotungstic acid (PTA) solution (pH 2.4). Transmission electron micrograph (TEM) images are obtained by JEM-2000EX at 200 kV.

Films used in the contact angle measurement, were prepared by casting a dilute emulsion (10 wt% solid content) on new-cleaned glass plates, and were dried in vacuum for 2 days under 70 °C before test. Static contact angles were measured with a contact goniometer (Erma Contact Anglemeter, Model G-I, 13-100-0, Japan) by the sessile drop method with a micro-syringe at 30 °C. More than 10 contact angle values were averaged to get a reliable value for each sample.

4. Conclusion

The hydrophobic monomer dodecafluoroheptyl methacrylate has been copolymerized successfully to produce amphiphilic block copolymers with poly(methacrylic acid) at one side and poly(fluorinated methacrylate) at the other side via the reversible addition-fragmentation chain transfer radical polymerization (RAFT) in emulsifier-free aqueous emulsions. As a product of the controlled radical polymerization, molecular weight distribution of the copolymer is narrow as well.

And the copolymers are found to have self-aggregation behavior in the emulsion. Studied by TEM, steady micelles with a diameter of 70–120 nm can be observed. Surface energy of the film was also studied by measuring the contact angle. And it was found that films formed from the emulsion onto the baseplate can be hydrophobic after heating treatment.

Acknowledgement

Authors gratefully acknowledge the financial support from the Guangdong Natural Science Foundation of China (No: 07006841).

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