



Synthesis, characterization and properties of a novel fluorinated methacrylate polymer

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ABSTRACT

A fluorinated monomer of 2-(2,2,2-trifluoroethoxy)ethyl methacrylate (FEMA) was prepared by a “one pot” process and then a novel fluorinated methacrylate polymer, poly[2-(2,2,2-trifluoroethoxy)ethyl methacrylate] (PFEMA), was successfully synthesized via miniemulsion polymerization using cetyltrimethyl ammonium bromide (CTAB) as emulsifier, hexadecane (HD) as co-stabilizer and 2,2'-azobisisobutyronitrile (AIBN) as initiator. The chemical structure of PFEMA was characterized by FT-IR, ¹H NMR and ¹⁹F NMR. GPC results show that the number average molecular weight (M_n) of PFEMA was as high as 8.5×10^5 g/mol and the polydispersity index (PDI) was only 1.3. SEM and DLS characterizations showed that the morphology of PFEMA latex was uniform spheres with the diameter of about 110–125 nm. It was also found that PFEMA has high thermo-stability ($T_d > 200$ °C), low glass transition temperature ($T_g = 13.0$ °C), and nice hydrophobicity ($\theta_{\text{water}} = 99.9^\circ$). Comparison studies on PFEMA and poly(2,2,2-trifluoroethyl methacrylate) show that an introduced functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) has a significant effect on lowering T_g and improving hydrolysis resistance without impairing surface properties.

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1. Introduction

It is well known that fluorinated polymethacrylates or polyacrylates, rich in trifluoromethyl functional groups, exhibit superior performance of chemical inertness, low dielectric constant, excellent weatherability, low refractive index, and special surface properties [1–4]. Poly(2,2,2-trifluoroethyl methacrylate) (PFMA) was an important class of such materials, which has excellent water-repellent capacity [5], good gas permeability for oxygen [6], lower water-absorption, and stain resistance [7]. It has been extensively used in high-performance coatings [8–11], photoelectric communication and microelectronics [12–14], contact lenses [15,16], and so on. PFMA is easily produced by free radical polymerization using bulk, solution, and emulsion polymerization methods [2,17–19]. However, as an environment-protecting waterborne coating, the glass transition temperature (T_g) of PFMA polymer was 82 °C [20], which was so high that the film-forming property was poor. One of traditional methods is

based on the copolymerization of soft monomers with 2,2,2-trifluoroethyl methacrylate (FMA) to improve the film-forming property, nevertheless this approach would reduce the fluorine content of these fluorinated polymethacrylates and affect surface properties of these polymer films. In order to lower T_g without impairing the properties of fluorinated polymethacrylates, another approach is to extend the side chain [21]. Recently, our group has an idea to introduce a functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) into the fluorinated side chain in order to reduce T_g and enhance the film-forming property.

Classical emulsion polymerization is an undesirable method for making fluorinated dispersion because this technique relies on monomer transport from the droplets to the growing particles and yet the solubility of fluorinated monomers in water is very low [22–24]. Miniemulsion polymerization is an alternative approach that produces stable fluorinated methacrylate polymer latexes. In miniemulsion polymerization, both the particle nucleation and subsequent propagation reaction occur primarily in submicrometer monomer droplets of 50–500 nm [25–26]. In this system, each miniemulsion droplet can be perceived as a separated nanoreactor that does not interact with the others and is also independent of the amount of the initiator as well as the particle size. In addition, polymerization in miniemulsion does not rely on monomer transport through the water phase, and the predominant initiation

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mechanism is droplet nucleation. All these unique features enable miniemulsion polymerization to be a good method for preparing fluorinated methacrylate polymers [2,5,27].

In 1989, FEMA was reported in a Japanese patent [28], where FEMA was synthesized using a common esterification reaction and the yield was low. In this paper, we used a “one pot” process to synthesize this fluorinated methacrylate monomer and its yield was as high as 89%. Almost 22 years have already been passed since 1989, unfortunately, there is no information reported on the synthesis, chemical structure and properties of PFEMA. For this reason, we carefully studied on the synthesis of PFEMA via miniemulsion polymerization using CTAB as emulsifier, HD as co-stabilizer and AIBN as initiator. Meanwhile, we have also discussed the effect of the functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) introduced to the fluorinated side chain on the properties of PFEMA compared with those of PFMA, such as glass transition temperature, thermo-stability, oil and water resistance as well as hydrolysis resistance.

2. Results and discussion

2.1. Chemical structure analysis

Spectroscopic techniques were employed to characterize the structures of the obtained monomer and polymer. All the products give satisfactory analysis data corresponding to their expected structures. The FT-IR spectra of monomer FEMA (trace a), polymer PFEMA (trace b) and PFMA (trace c) are shown in Fig. 1. Here we emphasized the analysis of PFEMA. The characteristic stretching peaks of C–H and C=O group were obviously shown at $2850\text{--}3000\text{ cm}^{-1}$ and 1732 cm^{-1} , respectively, resulting from PFEMA containing $-\text{CH}_2-$, $-\text{CH}_3$ and C=O groups. The peaks at 1450 and 1385 cm^{-1} were the two characteristic bands of C–H in $-\text{CH}_3$ of PFEMA. In addition, the bands at 1278 and 666 cm^{-1} were attributed to the stretching and bending vibration of C–F in $-\text{CF}_3$, respectively. In comparison with the FT-IR spectrum of FEMA (trace a), unambiguous disappearance of the characteristic peak of C=C at 1639 cm^{-1} was observed, this indicated the completion of the polymerization. In comparison with the FT-IR spectrum of PFMA (trace c), the FT-IR absorption peak at $2850\text{--}3000\text{ cm}^{-1}$ in the spectrum of PFEMA (trace b) is larger because of the stretching vibration of $-\text{CH}_2-$ in the functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) of PFEMA.

The ^1H NMR spectra of FEMA, PFEMA and PFMA and the peak assignments are presented in Fig. 2. Fig. 2(a) is ^1H NMR spectrum of FEMA. ^1H NMR (400.13 MHz, CDCl_3) of FEMA: δ (ppm) 1.8 ($-\text{CH}_3$, 3.00H), 3.7–3.9 ($-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2\text{CF}_3$, 4.00H), 4.2–4.3 ($-\text{OCH}_2\text{CH}_2-$, 2.01H), 5.0 and 6.1 ($\text{CH}_2=\text{C}(\text{CH}_3)-$, 2.00H). Fig. 2(b) is ^1H NMR spectrum of PFEMA. ^1H NMR (400.13 MHz, CDCl_3) of PFEMA: δ (ppm) 0.8–1.3 ($-\text{CH}_3$, 3.63H), 1.7–2.1 ($-\text{CH}_2-$, 2.12H),

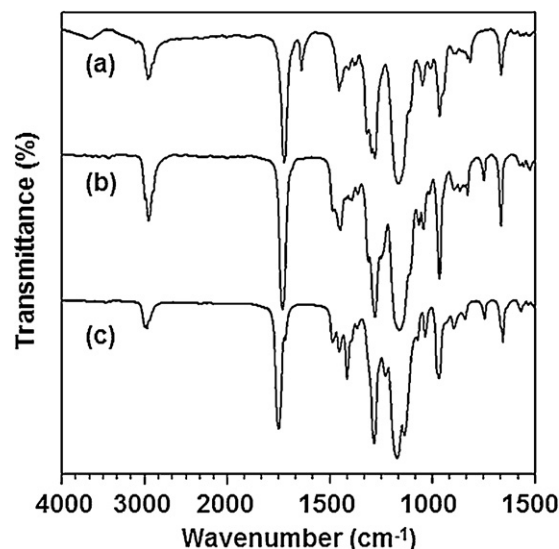


Fig. 1. FT-IR spectra of FEMA (a), PFEMA (b) and PFMA (c).

4.0–4.2 ($-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2\text{CF}_3$, 4.45H), 4.2–4.3 ($-\text{CH}_2-\text{CH}_2-$, 2.22H). Fig. 2(c) is ^1H NMR spectrum of PFMA. ^1H NMR (400.13 MHz, CDCl_3) of PFMA: δ (ppm) 0.8–1.3 ($-\text{CH}_3$, 3.05H), 1.8–2.1 ($-\text{CH}_2-$, 2.00H), 4.2–4.3 ($-\text{CH}_2-\text{CF}_3$, 2.01H). No signals for the protons associated with double bond of FEMA could be detected in Fig. 2(b) compared with Fig. 2(a), also indicating that the monomers were polymerized. The ^{19}F NMR spectra of PFEMA (Fig. 3(a)) and PFMA (Fig. 3(b)) both exhibited a signal centered at -74.28 and -73.30 ppm, respectively, corresponding to $-\text{CF}_3$ group. These FT-IR, ^1H NMR and ^{19}F NMR results confirmed that the fluorinated methacrylate monomer and its polymer have been successfully prepared.

2.2. Molecular weight of PFEMA

The weight average molecular weight (M_w), number average molecular weight (M_n) and the polydispersity index (PDI) of PFEMA were obtained from gel permeation chromatography (GPC). The results show that M_w and M_n are as high as 1.1×10^6 and 8.5×10^5 g/mol respectively and the PDI is narrow (PDI = 1.3). The reasons may be attributed to the special characteristic of miniemulsion polymerization. In miniemulsion polymerization, almost all monomer droplets are initiated to propagate at the same time, and every droplet is just like an individually independent nanoreactor in which the possibility of biradical termination is

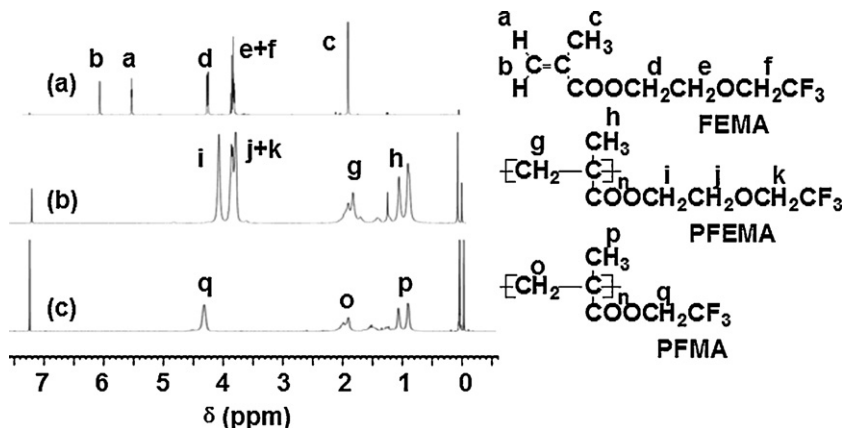


Fig. 2. ^1H NMR spectra of FEMA (a), PFEMA (b) and PFMA (c).

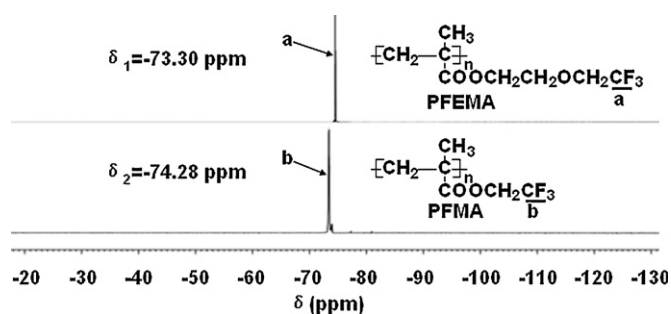


Fig. 3. ^{19}F NMR spectra of PFEMA (a) and PFMA (b).

much higher than that in conventional emulsion systems [27,29–32]. Therefore the relatively high molecular weights and narrow molecular weight distribution are obtained in this miniemulsion polymerization. Similar results are also observed in the synthesis of fluorinated acrylate ternary copolymer latex by miniemulsion polymerization [33].

2.3. Size and morphology of PFEMA latex particles

Fig. 4 shows the average particle size of PFEMA miniemulsion and the results indicated that the average particle size is 112.9 nm and the polydispersity obtained from dynamic light scattering (DLS) analysis is 0.039. The low polydispersity value implied the narrow monomial particle size distribution of the resulting latex. The SEM micrograph of the PFEMA miniemulsion, shown in Fig. 5, indicated that the particles were uniform spheres with the diameter of about 110–125 nm, which was consistent with the result measured by DLS analysis.

2.4. Stability of miniemulsion

After the polymerization reaction was finished, there was no gel in miniemulsion, indicating the emulsifying system composed of CTAB/HD was beneficial to the stability of PFEMA miniemulsion polymerization. The stability of PFEMA miniemulsion was also investigated under the following conditions: room temperature for 3 months; then 80 or -5°C for 24 h; and putting it into a centrifugal separator (3000 rpm) for 60 min. No miniemulsion breaking could be observed in the whole test processes, implying that the proposed miniemulsion has an excellent stability.

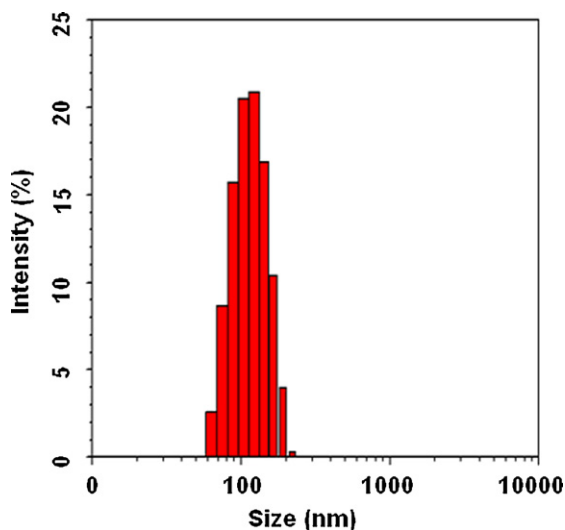


Fig. 4. Partial size distribution of PFEMA miniemulsion.

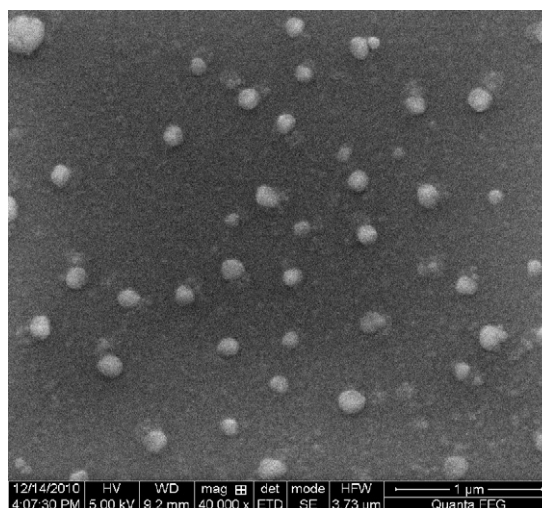


Fig. 5. SEM image of PFEMA latex.

2.5. Thermal properties

Fig. 6 illuminates the DSC curves of PFEMA (trace a) and PFMA (trace b). As shown in Fig. 6, only one glass transition appeared on each traces. The results of DSC showed glass transition temperatures (T_g) of PFEMA and PFMA were 13.0 and 81.2°C , respectively. The T_g of PFEMA, compared with that of PFMA, decreased by 68.2°C owing to the introduced functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) to the fluorinated side chain. The thermal stabilities of PFEMA and PFMA were also investigated by TGA and the results are shown in Fig. 7. It could be seen that the initial decomposition temperatures (T_d) of PFEMA and PFMA were about 200 and 254°C , respectively. The difference may be derived from the introduction of the functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) to the fluorinated side chain in PFEMA. It is well known that the bond energy of ether bond is lower than that of carbon-carbon bond, so the introduction of the functional group will have a small effect on the thermal stability of PFEMA polymer.

2.6. Contact angle of polymer films

The contact angles of water (θ_{water}) and ethylene glycol (θ_{oil}) of PFEMA and PFMA films before and after acid–base treatment were examined. Obtained results are summarized in Table 1.

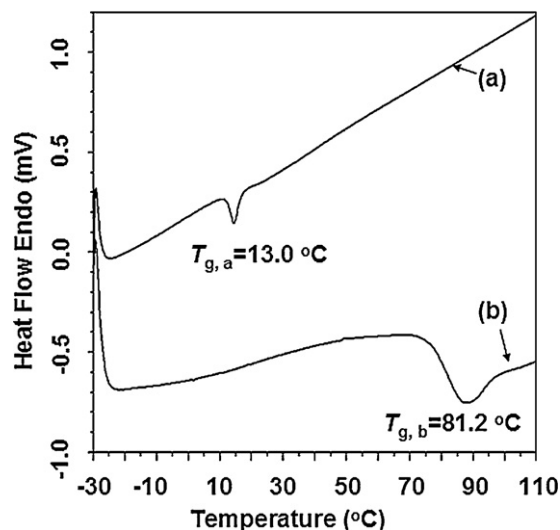


Fig. 6. DSC thermographs of PFEMA (a) and PFMA (b).

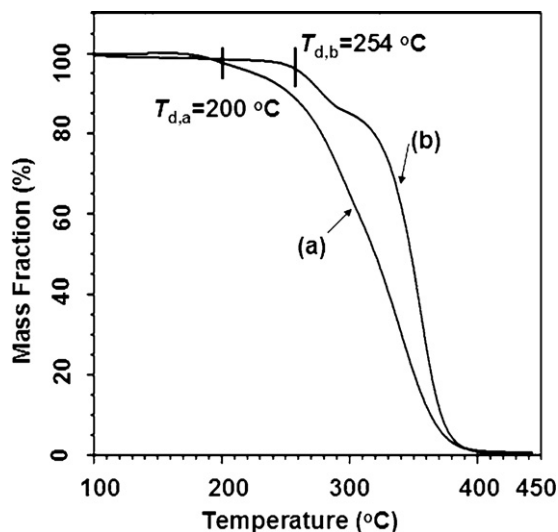


Fig. 7. TGA thermographs of PFEMA (a) and PFMA (b).

When these two polymer films were not treated by acid–base solution, the θ_{water} of PFEMA film was 99.9°, which is a little higher than that of PFMA film (95.6°); whereas the θ_{oil} of PFEMA film (80.3°) was lower than that of PFMA film (85.7°). Because of the fluorinated side chain of PFEMA longer than that of PFMA, the fluorinated groups may be easier to spread to the solid surface of PFEMA film, thus improving its hydrophobicity; moreover the functional groups ($-\text{CH}_2\text{CH}_2\text{O}-$) in the fluorinated side chains may have a good affinity to ethylene glycol, so the θ_{oil} of PFEMA film was lower than that of PFMA film.

From Table 1, it can be observed that the contact angles of water and ethylene glycol of PFEMA films both have significant changes after acid–base treatment. The θ_{water} of PFMA film had a little decrease after acid treatment; yet it decreased greatly after base treatment. These two facts indicated that PFEMA film had an excellent acid-resistant ability and an unfortunate base-resistant ability.

Compared with PFMA films, PFEMA films showed smaller changes on the θ_{water} and θ_{oil} after they were treated by acid solution. The difference can be explained considering that the introduction of functional group ($-\text{CH}_2\text{CH}_2\text{O}-$) will suppress the hydrolysis of ester bond. Trifluoroethyl is a strong electron withdrawing group, while the $-\text{CH}_2\text{CH}_2\text{O}-$ group introduced to the side chain of fluorinated polymethacrylates can be able to reduce the electron-attracting ability of trifluoroethyl group, so the introduction of this functional group could improve the hydrolysis resistance of fluorinated methacrylates.

Table 1
Contact angles of PFEMA and PFMA films before and after acid–base treatment.

Sample	PFEMA film		PFMA film	
	θ_{water} (°)	θ_{oil} (°)	θ_{water} (°)	θ_{oil} (°)
1 ^a	99.9	80.3	95.6	85.7
2 ^b	94.3	72.4	82.3	67.2
3 ^c	77.5	59.3	72.9	57.5

^a No treated PFEMA and PFMA films.

^b After immersed into 10% H_2SO_4 under room temperature for 24 h, films are rinsed with enough deionized water to neutrality and dried under atmosphere at 25 °C for 24 h.

^c After immersed into 8% NaOH under room temperature for 24 h, films are rinsed with enough deionized water to neutrality and dried under atmosphere at 25 °C for 24 h.

3. Conclusions

In summary, 2-(2,2,2-trifluoroethoxy)ethyl methacrylate was synthesized using a “one pot” process and its stable polymer (PFEMA) latex was also successfully prepared by miniemulsion polymerization using CTAB as emulsifier, HD as co-stabilizer and AIBN as initiator. The miniemulsion particles are uniform spheres with the diameter of about 110–125 nm and the molecular weight polydispersity index was narrow. These two aspects reflect the special characteristic of miniemulsion polymerization. In comparison with PFMA, PFEMA has lower glass transition temperature, more excellent hydrophobicity and better acid–base resistant ability. The results of these facts demonstrated that the functional groups ($-\text{CH}_2\text{CH}_2\text{O}-$) introduced to the fluorinated side chain would have a significant effect on the properties of PFEMA.

4. Experimental

4.1. Materials

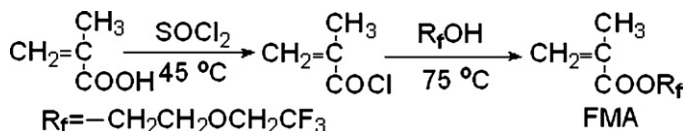
Both methacrylic acid and thionyl chloride were purchased from Kemiou Chemical Co. (Tianjin, China). Thiodiphenylamine was obtained from Shanghai Chemical Reagents Co. (Shanghai, China) used as polymerization inhibitor. Both ethylene oxide (Shanghai Chemical Reagents Co., Shanghai, China) and 2,2,2-trifluoroethanol (Weihai Newera Chemical Co. Ltd., Weihai, China) were used to synthesize 2-(2,2,2-trifluoroethoxy)ethyl ethanol using potassium hydroxide as catalytic agent. Cetyltrimethyl ammonium bromide (CTAB) (Shanghai Chemical Reagents Co., Shanghai, China) served as the emulsifier was used as received. Hexadecane (HD) was purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China) and did not require purification prior to use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol, dried under vacuum at 20 °C for 24 h, and stored at 0 °C before use. Deionized water was used in all the polymerization and treatment processes.

4.2. Synthesis of FEMA

FEMA was synthesized by a “one pot” process (Scheme 1). First, 297.43 g thionyl chloride and 1.00 g thiodiphenylamine were added to a 250 ml glass reactor flask equipped with a mechanical stirrer, a dropping funnel, a thermometer and a reflux condenser. Second, the glass reactor was initially heated to 45 °C and then a mixture of 236.75 g methacrylic acid and 0.3 g N,N-dimethylformamide was introduced into the glass reactor by dripping slowly through a constant pressure funnel for 2.5 h. Afterwards, the glass reactor was heated up to 60 °C and the reaction was allowed to proceed for 5 h. Third, 239 g 2-(2,2,2-trifluoroethoxy)ethyl alcohol was added slowly for 2.5 h. Then, the reactor was heated up to 75 °C and kept for 4 h. Sulfur dioxide and hydrogen chloride, produced in the experimental process, were absorbed by 20% sodium hydroxide solution. After the steps such as neutralization reaction, separation, drying, and vacuum distillation, FEMA was obtained as colorless oil with a yield of 88.6%, collected at 100 °C (12.0 mmHg).

4.3. Miniemulsion polymerization of PFEMA and PFMA

The miniemulsions were prepared according to the following procedures. The monomer was first mixed with HD and AIBN. The



Scheme 1. Schematic representation of FEMA monomer prepared by a “one pot” process.

mixture was then added to the aqueous phase (water and CTAB) under stirring. After 20 min, the resultant emulsion was then homogenized by ultrasonication for 150 s at 50% amplitude and 0 °C to prevent polymerization. The miniemulsion polymerization was charged into a 100 ml glass reactor flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and then purged with nitrogen for 30 min. The latex was synthesized at 75 °C for 6 h. A typical miniemulsion polymerization comprised 40 ml of water, 0.2 g of CTAB, 10 g of FEMA, 0.5 g of HD, and 0.05 g of AIBN. In that case, the solid content was close to 20% and the final conversion of FEMA monomer, as high as 93.2%, was determined gravimetrically.

4.4. Measurements

FT-IR spectra were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer (Perkin-Elmer Co., USA). ¹H NMR and ¹⁹F NMR spectra were measured on Avance III 400 MHz NMR spectrometer (Bruker, Faellanden, Switzerland) in CDCl₃ solvent with tetramethylsilane as the internal standard at room temperature. Molecular weights and polydispersity were determined using gel permeation chromatography (GPC) (Waters 1500) with tetrahydrofuran as eluent at a flow rate of 1.0 ml/min. Monodisperse polystyrene standards were used for molecular weight calibration. The particle size of PFEMA latex was obtained from dynamic light scattering (DLS) measurements using Nano ZS (Malvern Co., England) at 25 °C. The morphology of the latex particles was characterized by scanning electron microscopy (SEM) (S-2500, HitachiSeikiLtd, Japan). Differential scanning calorimetry (DSC) measurements were conducted on a Mettler DSC822e (Mettler-Toledo Co., Switzerland). The scanning temperature ranges from –40 to 120 °C for each sample with a heating or cooling rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed on a Pryris Diamond TG/DTA (Perkin-Elmer Co., USA) with a heating rate of 10 °C/min and scanning range of 30 – 500 °C in a nitrogen atmosphere. Contact angles of water and ethylene glycol on the films were measured by the sessile drop method using an OCA40 drop shape analyzer (Dataphysics Co., Germany) at 25 °C. The volume of the liquid drops used was 3.0 μl.

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