Synthesis and Characterization of Surfactant PEG Macromonomers with Fluorocarbon End-capped Groups and its Copolymers

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Fluorocarbon (R_F) or hydrocarbon (R_H) end-capped PEG macromonomers were prepared by coupling method. Several factors that affect the synthesis were studied and optimum condition was obtained. The critical micelle concentrations (CMC) of these macromonomers were determined by fluorescence method. A new type of fluorocarbon-containing hydrophobically modified alkali swellable/soluble copolymers were obtained by copolymerization of R_F or R_H alkyl end-capped PEG macromonomers with acrylic acid in organic solvent. The preliminary researches on viscosity property of these copolymer solutions were conducted under different conditions, such as various macromonomer content in the copolymer, polymer concentration, shear rate, pH value and temperature. All the results proved that there existed a very strong hydrophobic association among hydrophobes in these copolymer solutions.

Keywords   Macromonomers, PEG, fluorocarbon-containing, hydrophobically associating, coupling method, viscosity, fluorescence

Introduction

The macromonomer ('macromer') techniques have been made it possible to prepare a variety of graft copolymers with well-defined structure in the past two decades, as reviewed by Yamashita and Ito et al.[1-4] Poly(ethylene glycol) (PEG) macromonomers were a subject of many recent publications, which can be rather easily designed either by living anionic polymerization of ethylene oxide using a special functionalized initiator or terminator, or by appropriate transformation reaction of their terminal groups in both the α- and ω-end groups on PEG molecules.

PEG is one of the simplest macromolecules, yet exhibits the most complicated solution properties. It is amphiphilic and soluble in many solvents including benzene (non-polar) and water (polar), which is a unique property that can not be expected for other conventional polymers. PEG is also used in a variety of practical applications. Its macromonomers are often used in biomaterials, such as controlled release of drugs, bioabsorbance surgical sutures and wound covering materials and also used to prepare graft amphiphilic copolymer with capability to form stable aggregate structure in solution. Indeed, hydrophilic-hydrophobic balance can be modulated to a wide extent by changing R and n of the PEG macromonomers ($R\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CO\text{-}CH(CH_3) = CH_2$).[5] Through copolymerization of PEG macromonomer with other monomers, amphiphilic comb- or star-like

graft polymers with very high molecular weight could be prepared.[2]

Since hydrophilic monomers and hydrophobic comonomers are mutually incompatible, special copolymerization techniques (e.g. alcohol or surfactant homogenization, microemulsion or micellar polymerization) are required in the process of polymerization of hydrophobically associating polymers, which are often characterized by low molecular weights of product and/or large usage of external surfactants. High surfactant/monomers ratios of 20—100 wt% are common in order to dissolve the hydrophobic monomers in the aqueous phase.[6] To avoid the need for external surfactants and also to improve the solubility of the final copolymers, the amphiphilic PEG marcromonomers with built-in surfactant character are used.[7]

Schultz et al. reported that long hydrocarbon end-capped PEG ($n = 20$—40) acrylate macromonomers were used as macromonomer surfactants to synthesize hydrophobically associating polymers without addition of external surfactants.[7] So far, there are several methods[2] to synthesize PEG macromonomer: (a) end-capping of a living polymer (termination method), (b) initiation of living polymerization (initiation method), (c) transformation of any functional end-group, (d) polyaddition.

In our previous work, a series of fluorocarbon-containing hydrophobically associating polymers (FHAP) were synthesized and the strong aggregation in FHAP solutions was found.[8-10] In this paper, we would like to report the synthesis of fluorocarbon end-capped PEG macromonomers by coupling method using various fluorocarbon hydrophobes and ready-made PEG or PEG macromonomers with – OH as precursors, and preliminary results of synthesis and characterization of poly-(acrylic acid-co-R_F-PEG-macromonomers). The synthetic route was designed and shown in Scheme 1.

Scheme 1 Synthesis of fluorocarbon end-capped PEG macromonomers
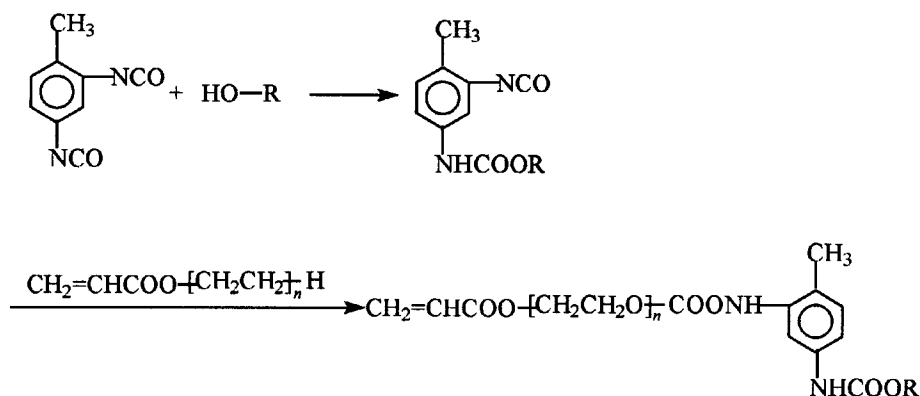
Experimental

Materials

Acrylic acid, 2,4- and 2,6-toluene diisocyanate (TDI), n-tetradecanol, 1,1,7-trihydroperfluoroheptanol (THFE) and 1,1,9-trihydroperfluorononanol (purchased from pilot plant of SIOC), pentadecafluorooctanoic acid (Shanghai 3F company), dibutyltin laurate (A.R.) were used as received. α-Monoacrylate-ω-monohydroxy poly(ethylene glycol) (PEG 1000 monoacrylate) and poly(ethylene glycol) monomethylether monomethacrylate were purchased from Monomer-Polymer & dajac. Labs, Inc. and Polysciences, Inc., respectively. Azo-

bisisobutyronitrile (AIBN) was recrystallized from methanol. Ammonium persulfate (APS) was recrystallized from water and dried under vacuum. 1,4-Dioxane was vacuum distilled before using.

Synthesis (take macromonomer-2 as an example)

Mono(1,1,7-trihydroperfluoroheptanol) substituted 2,4- and 2,6-toluene-diisocyanate

Into a 250 mL of three-necked round-bottom flask were added 33.05 g (189.7 mmol) of 2,4- and 2,6-toluene-diisocyanate (freshly distilled) (TDI) and 100 mL of dry THF (freshly distilled over sodium wire). The

resulting solution was purged with nitrogen, 10 g of 1,1,7-trihydroperfluoroheptanol ($H(CF_2)_6CH_2OH$) (THFH) (30.1 mmol) in 50 mL of dry THF was slowly dropped into the flask. The mixture was stirred over night at 60℃. The system was sealed by oil and protected by anhydrous $CaCl_2$ during the whole time. After 24 h, the system was evacuated by oil pump and oil bath temperature was raised to 130—140℃ so as to revome most of the excess TDI. The remaining TDI was successively removed by extraction with dry *n*-hexane (freshly distilled over CaH_2). The oily residue was refluxed with 80 mL of hexane, then the flask was cooled with dry ice for 2 h. The supernate was quickly decanted from the waxy residue. The above treatment was repeated four times to ensure complete removal of excess TDI from the mono(1,1,7-trihydroperfluoroheptanol) substituted 2,4- and 2,6-toluene-diisocyanate (TDI-*m*THFH) product. This intermediate was dried under vacuum for several hours, finally 2 g yellow solid was obtained. ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.3—7.7, 6.6—7.2 (m, 4H, benzene), 6.9—6.0 (t, 1H, CF$_2$H), 4.4—4.8 (t, 2H, OCH$_2$CF$_2$), 3.7 (s, 1H, NH), 2.1 (s, 3H, CH$_3$). ^{19}F NMR (CDCl$_3$, 300 MHz) δ: 43 (s, 2F), 45—46 (s, 2F), 46—47 (s, 4F), 52—53 (s, 2F), 59—61 (d, 2F). IR (film) υ: 3200—3500 ($ν_{N-H}$), 2300 ($ν_{NCO}$), 1720—1740 ($ν_{-C=O}$), 1650 ($ν_{O=C-NH}$, amide I band), 1600, 1550, 1450 ($ν_{C=C}$), 1200—1250 ($ν_{C-F}$), 1555 ($δ_{NH}$ amide II band) cm^{-1}.

α-Monoacrylate-ω-mono(1,1,7-trihydrododecafluoroheptanol) substituted 2,4- and 2,6-toluene-diisocyanate) end-capped poly(ethylene glycol) macromonomer (macromonomer-2)

PEG (MW = 1,000) monoacrylate (40 g, 37.91 mmol) was dissolved in 75 mL of benzene in a flask, a little amounts of copper powder as inhibitor was added. The PEG monoacrylate was dried under vacuum by azeotropic distillation. TDI-*m*THFH (20.15 g, 39.8 mmol), 100 mL of anhydrous diglyme (freshly distilled over sodium wire) and 1—3 drops of dibutyltin laurate as catalyst were added into the flask. The mixture was stirred for 15 h at 60℃ with nitrogen purging during the reaction. After copper powder was filtrated off, the filtrate was poured into *n*-hexane, precipitated and dried under vacuum at ambient temperature, 50.5 g of brown waxy solid product was obtained as macromonomer-2,

yielding 85%. ^{1}H NMR(CDCl$_3$, 300 MHz) δ: 6.9—7.2, 7.6—7.8 (m, 4H, aromatic ring), 6.3—6.4, 6.0—6.1, 5.7—5.8 (m, 3H, CH$_2$=CHC=O), 6.0—6.1, 5.7—5.8 (m, 1H, CF$_2$H), 4.7—4.8 (t, 2H, CH$_2$CF$_2$), 4.2 (t, 2H, CH$_2$OC=O), 3.5—3.9 (m, CH$_2$O(CH$_2$CH$_2$O)$_{n-2}$CH$_2$), 2.1 (s, 3H, CH$_3$), 8.0—8.1, 9.2 (CONH). ^{19}F NMR(CDCl$_3$, 300 MHz) δ: 43 (s, 2F), 45—49 (m, 6F), 52—53 (s, 2F), 60—61 (m, 2F).

Copolymerization of acrylic acid and R$_F$-PEG *macromonomers*

Acrylic acid (2 g) and a certain amount of fluorocarbon-containing PEG macromonomer-2 were put into a round-bottom flask. 1,4-Dioxane was added to dissolve the monomers. The concentration of all monomers was kept at about 20 wt%. Solution of AIBN (dissolved in 1,4-dioxane) or AMPS (dissolved in water) was injected into the flask. The weight ratio of initiator, APS or AIBN, to monomer was 1/1000. The solution was purged with pure nitrogen in an ice/water bath for 30 min and then moved into 50 ± 0.5℃ oil bath with vigorous stirring. The reaction was left to proceed for 15 h, then a gel-like solution was formed. More 1,4-dioxane was added to dilute the solution and then it was poured into diethyl ether to precipitate the polymer. The products were vacuum dried at 50℃ for at least 20 h. The dried solid product was poly(AA-co-macromonomer-2) in its acid form. It was dissolved in deionized water with pH value adjusted to be around 11 with 1 mol/L of NaOH, and then the polymer solution was poured slowly into large excess of anhydrous diethyl ether to precipitate the product. The final dried product in its sodium salt form or neutralized form was denoted as poly(NaAA-co-macromonomer-2).

Characterization and measurement

IR spectra were recorded on a PE-983G by methods of a KBr pellet or KBr film. ^{1}H NMR spectra and ^{19}F NMR spectra were made on a Bruker 300AM instrument (300 MHz) respectively with TMS and trifluoroacetic acid (TFA) as external standard. The critical micelle concentrations (CMC) of macromonomers were determined by fluorescence method and recorded on a static FZ-I fluorescent spectrometer with a slit of 7.5 nm for

excitation and 2.5 nm for emission. The excitation wavelength was 333 nm for Pyrene. The fluorine contents (wt%) of copolymers were determined by anionic chromatography and recorded on a Dionex2010I instrument.

The viscosity property of the polymer solution was measured using a Wells Brookfield viscometer equipped with two different sizes of spindles (18 # and 34 #). All detections of the viscosity properties were carried out at the constant temperature of $25 \pm 0.5\,^{\circ}\text{C}$. The polymer solutions were prepared in deionized water. 10 wt% NaOH solution was used to neutralize the polymer solutions to the desired pH values. If the pH value exceeded the desired value, a small amount of 1 mol/L hydrochloric acid was added to compensate. Commonly, the pH value of polymer solutions was adjusted to be about 9, except that the research was on the effect of pH on the viscosity of polymer solutions.
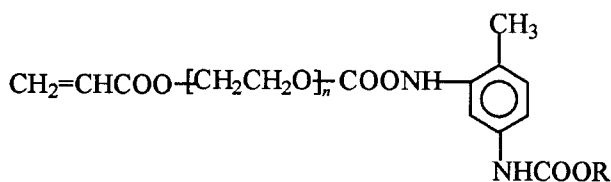
Results and discussion

Synthesis of fluorocarbon-containing PEG macromonomers

The fluorocarbon end-capped PEG macromonomers were synthesized and confirmed successfully by the results of IR, ^1H NMR and ^{19}F NMR. The structures of six PEG macromonomers are shown in Chart 1.

To the two steps of the reaction, the first step is more demanding than the second due to the difficulty to remove the excessive reactants and purify the product. There are many factors that could affect the yield and purity of R-TDI, such as solvent, temperature, reaction time, molar ratio of two reactants and addition pattern of reactants. For the second step, reaction temperature and amount of catalyst are two key factors. From our results listed in Table 1, it can be seen that catalyst can improve conversion of reaction, but also can enhance side reaction and effect the purity of product too. The appropriate amount of catalyst is very delicate and correlates with reaction time, temperature, and concentration of reactants in the system. Temperature should be controlled as low as possible since side reaction became enhanced at high temperature. Appropriate choice of the ratio of TDI-*m*THFH to αA-ωH-PEG would also give good results.

Chart 1 Chemical structures of PEG macromonomers

$$\text{CH}_2\text{=CHCOO} \{\text{CH}_2\text{CH}_2\text{O}\}_n \text{COONH} - \left\langle\begin{array}{c}\text{CH}_3\\ \\ \text{NHCOOR}\end{array}\right\rangle$$

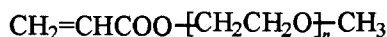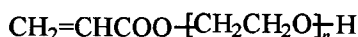Macromonomer-1: $\text{R} = -\text{CH}_2 \{\text{CF}_2\}_6 \text{CF}_3$

Macromonomer-2: $\text{R} = -\text{CH}_2 \{\text{CF}_2\text{CF}_2\}_3 \text{H}$

Macromonomer-3: $\text{R} = -\text{CH}_2 \{\text{CF}_2\text{CF}_2\}_4 \text{H}$

Macromonomer-4: $\text{R} = \{\text{CH}_2\}_3 \text{CH}_3$

$$\text{CH}_2\text{=CHCOO} \{\text{CH}_2\text{CH}_2\text{O}\}_n \text{CH}_3$$

Me end-capped PEG macromonomer

$$\text{CH}_2\text{=CHCOO} \{\text{CH}_2\text{CH}_2\text{O}\}_n \text{H}$$

HO end-capped PEG macromonomer

Table 1 Results of reaction[a] in different temperature and amount of catalyst

Temp. ($^{\circ}\text{C}$)	Catalyst[b] (g)	Yield[c] (%)	State[d]
60	-	79	Liquid
80	-	85	Liquid
100	-	50	Liquid
60	0.0443	105	Solid
60	0.0176	88.5	Liquid
40	0.0499	72	Solid

[a] The second step to produce macromonomer-2.

[b] Dibutyltin laurate in our work.

[c] Mono(1,1,7-trihydroperfluoroheptanol) substituted 2,4- and 2,6-toluene-diisocyanate obtained in the first step.

[d] The solid state of pure mono(1,1,7-trihydroperfluoroheptanol) substituted 2,4- and 2,6-toluene-diisocyanate in atmosphere condition is yellow liquid, so from its state we can estimate its purity and extent of side-reaction indirectly.

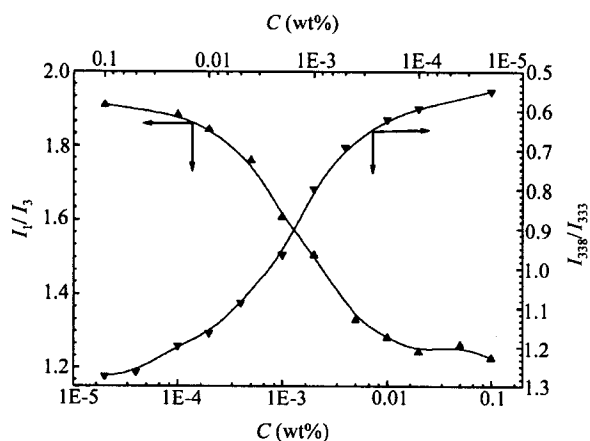*Critical micelle concentration (CMC) of surfactant macromonomers*

It is well known that the changes in intensity ratios I_1/I_3,[11,12] i.e. the ratio of the first to the third bands of the pyrene emission spectra, and I_{338}/I_{333},[13,14] i.e. the ratio obtained from (0, 0) bands of pyrene excitation spectra, can be used to determine the critical micelle concentration (CMC) for surfactant molecules because

pyrene is preferentially dissolved in the hydrophobic microdomains of micelles. Therefore, an abrupt change of I_1/I_3 and I_{338}/I_{333} ratios with the surfactant concentration indicates the formation of the hydrophobic aggregates in solutions. Macromonomers obtained in our work can be characterized as surfactants because of the coexistence of the long hydrophilic PEG units in the molecular chains and hydrophobic fluorocarbon or hydrocarbon units in the ends. The intensity ratios I_1/I_3 and I_{338}/I_{333} as functions of the logarithm of surfactant macromonmer-4 concentration are shown in Fig. 1. At low concentration, both ratios keep constant values and show no hydrophobic aggregates existing in the solutions. As the concentration increases above a certain concentration, the gradual decrease of I_1/I_3 and increase of I_{338}/I_{333} indictes that the hydrophobic aggregates begin to form and pyrene starts to transfer from water into the micelles. With the further increase of the macromonomer concentration, the microenviroment of pyrene becomes increasingly hydrophobic, indicated by the continuous decrease of I_1/I_3 and increase of I_{338}/I_{333}. Over a concentration range, the ratios of both I_1/I_3 and I_{338}/I_{333} remain constant, which implies that the property of the hydrophobic domain formed by aggregate was no more improved despite of the increasing macromer concentration. This means that there have been enough hydrophobic microdomains to accommodate pyrene and the solution concentration has exceeded the CMC. The CMC values of these macromonomers are listed in Table 2. Among the four macromonomers, the CMC of macromonomer-4 is the lowest. This is understandable as macromonomer-4 has much longer hydrophobe than the others. The CMC values of other three macromonomers are surprisingly in the same magnitude, which indicates that their hydrophobic association strength is comparable despite of the difference in hydrophobic lengths and end units.

Fig. 1 Intensity ratio I_1/I_3 and I_{338}/I_{333} of pyrene as functions of macromonomer-4 concentration.

Copolymers of acrylic acid (AA) with macromonomer-2

Copolymerization of fluorocarbon end-capped macromonomers with acrylic acid produced a new type of associating thickeners (AT's) which can be classified as R_F hydrophobically modified alkali soluble copolymers, their composition and molecular structure are similar to those of R_H hydrophobically modified alkali swellable/soluble emulsion (HASE).[16,17] HASEs are commonly synthesized by emulsion copolymerization of carboxyl-containing vinyl monomers with a small amount of comonomer containing a long hydrophobe. Often there is a third comonomer in molecular, called as chain-extending monomer,[15] to adjust the concentration of carboxyl groups in the copolymers. Jenkins *et al*. used methacrylic acid as the monomer, ethyl acrylate as the chain-extending monomer and acrylate with a long poly(ethylene-oxide) segment end-capped by a long hydrocarbon hydrophobe as the hydrophobic comonomer and synthesized high-performance AT's,[15] then did a thoroughly research on their characterization and rheological property of their solutions.[15,18] The most important character of the copolymer is nearly insoluble in water at low pH value while becomes soluble and shows a very high thickening efficiency at high pH value. It can be explained by a dual thickening mechanism compared with the classical mechanism of the conventional aqueous thickeners.[19] At low pH value, the high hydrophobicity of the copolymer makes it insoluble in water. As the carboxyl groups were neutralized, the electrostatic repulsion between the neutralized carboxylic groups makes molecular expand and copolymer dissolve in water. The in-

Table 2 Critical micelle concentration (CMC) values of PEG macromonomers

Sample	End-capped group	CMC* (wt%)
HO-PEG macromonomer	HO –	2×10^{-1}
Me-PEG macromonomer	Me –	3.5×10^{-1}
Macromonomer-1	$CF_3(CF_2)_6CH_2$ –	3×10^{-3}
Macromonomer-2	$H(CF_2CF_2)_3CH_2$ –	1.6×10^{-3}
Macromonomer-3	$H(CF_2CF_2)_4CH_2$ –	2.6×10^{-3}
Macromonomer-4	$CH_3(CH_2)_{13}$ –	3×10^{-4}

* Determined by fluorescence method.

creased hydrodynamic volume caused by the thorough molecular expansion and the intermolecular association of hydrophobes will enhance the viscosity of its solution dramatically. Based on our privious study of fluorocarbon-containing hydrophobically modified polymers[8] and polyelectrolytes,[12] acrylic acid and R_F-macromonomer were used to synthesize the R_F modified polyelectrolytes and no chain-extending monomer was added so that the factors can be simplified for the investigation of R_F hydrophobic association. Besides that, when the amount of macromonomer in copolymers is low enough, there may exist hydrogen bonding or 'complexation' between ether and carboxyl groups[20,21] which may enhance the viscosity of copolymer solutions under certain circumstances.

Copolymerization

The results of copolymerization of macromonomer-**2** with AA in different molar ratio were listed in Table 3. It can be seen that the macromonomer conversions are

Table 3   Copolymerization of macromonomer-**2** with AA in different conditions

Sample[a]	Yield[b] (%)	F content[c] (wt%)	F conversion[d] (%)
PAA	90	0	0
Co-M2A-0.5	73	0.038	3.37
Co-M2A-1.0	41	0.099	4.69
Co-M2A-1.5	51	0.127	4.28
Co-M2A-2.0	61	0.266	7.13
Co-M2A-1.5-1 #	95	0.39	16.45
Co-M2A-2.0-1 #	94	0.46	15.45
Co-M2A-1.5-2 #	82	0.54	22.79
Co-M2A-2.0-2 #	76	0.57	19.14
Co-M2A-1.5-3 #	31	1.30	54.84
Co-M2A-2.0-3 #	52	1.55	52.06
Co-M2A-1.5-4 #	69	0.69	29.10
Co-M2A-2.0-4 #	68	0.38	12.76

[a] PAA is the homopolymer of acrylic acid. Co-M2A-0.5 means the feed of macromonomer-**2** in copolymerization with AA is 0.5 molar percent. Others can be analogized. 1 # were copolymerized in 1,4-dioxane/water (1/1 volume ratio) at 50℃, 2 # in 1,4-dioxane at 80℃, 3 # in 1,4-dioxane/cyclohexane (1/1 volume ratio) at 50℃, 4 # in 1,4-dioxane/ethyl acetate (1/1 volume ratio) at 50℃, and the others in 1,4-dioxane at 60℃.
[b] Total conversions of copolymers, determined by weight method according to the acid form of polymers.
[c] Copolymer samples are in their sodium forms and determined by anionic chromatography.
[d] Conversions of macromonomer, calculated by experiment values and theory values of F (wt%) in polymers in their sodium forms.

very low, which are comparable to the results reported by Piculell.[22,23] It can be owning to the low reactivity of R_F-PEG macromonomer, which is a common problem in the application of macromonomer method in some cases. The low reactivity of macromonomer correlates with its high molecular weight and the enhanced diffusion controlled effects in system.[1,2,24]

Improvement of the macromonomer conversion can be achieved by appropriate choice of copolymerization conditions which were also listed in Table 3. It was obvious that the higher conversion of macromonomer in dioxane/cyclohexane compared with others may be due to the solvent effect on the macromonomers' reactivity.[24] Details will be discussed in our following paper.

Effect of macromonomer content in copolymers on solution property of the copolymer

Fig. 2 shows the effect of hydrophobic modifying degree on the solution viscosity varying with the polymer concentration. The solution viscosity of homopolymer is
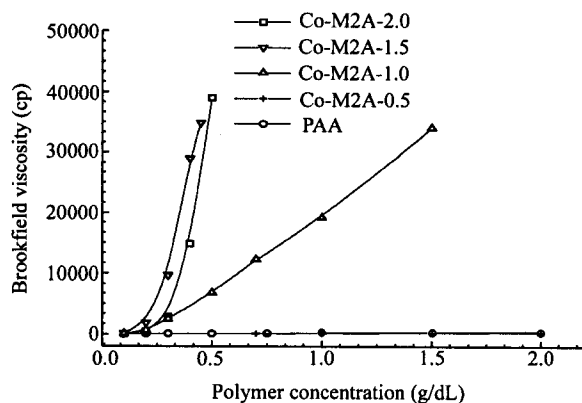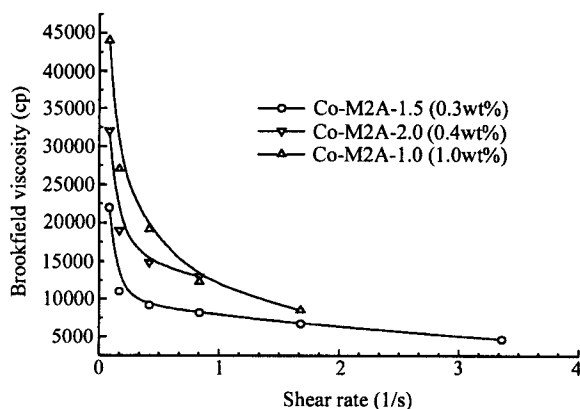

Fig. 2   Dependence of Brookfield viscosity of polymer solution on polymer concentration at 25℃ (shear rate = 0.42 s^{-1}).

nearly unchangeable as a function of polymer concentration in the region from 0.1 to 2.0 wt%. To copolymers of low macromonomer content, such as Co-M2A-0.5, the viscosity change is similar to the homopolymer. To copolymers of higher macromonomer content, however, the solution viscosity increases sharply when the solution concentration exceeds the critical aggregation concentration (cac) of about 0.1—0.2 wt% for Co-M2A-1.5, which is much lower than that for poly(AA-co-FX-14) (~1.0 wt%).[25] This phenomenon shows very strong

hydrophobic association and the effect of PEG spacer on the association at the same R_F comonomer mol% in the copolymer.

Effect of shear rate on Brookfield viscosity of copolymer solution

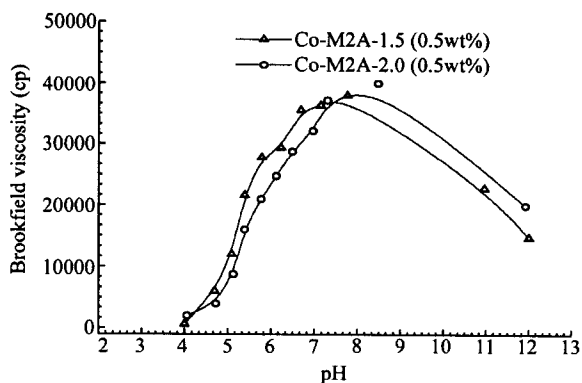Brookfield viscosity of copolymers as a function of shear rate in the range of 0.084—8.4 (1/s) at 25 ℃ is showed in Fig. 3. The viscosity decreases sharply in a very narrow region of shear rate, then almost keeps constant for all three copolymers. It is typical pseudoplastic behavior (shear-thining). Upon the removal of shear, the viscosity recovered simultaneously. The sharp decrease in viscosity with shear rate and restorement upon the removal of shear are consistent with the existence of reversible network structure caused by strong intermolecular hydrophobic association of fluorocarbon units.

Fig. 3 Dependence of Brookfield viscosity of polymer solution on shear rate at 25 ℃.

Effect of pH *value on the viscosity of copolymers*

The copolymers obtained in our work could be classified as a new type of associative polyelectrolyte. Viscosity property of associative polyelectrolyte polymers is dependent highly on the pH of polymer solution due to its carboxylic groups on the backbone. The neutralization extent is related to the strength of electrostatic repulsion between side groups and affects the extent of expansion of macromolecule backbone and also the association of hydrophobic group. Fig. 4 shows the curve of Brookfield viscosity of Co-M2A-1.5 and 2.0 versus pH value, the maximum occurs at pH range of 7—8.

Fig. 4 Brookfield viscosity of polymer solution as a function of pH value at 25 ℃ (shear rate = 0.42 s^{-1}).

Effect of temperature on the Brookfield viscosity of copolymer solution

In Fig. 5, the influence of temperature on the solution viscosity of Co-M2A-2.0 is plotted. It was found that the solution viscosity decreases with increasing the temperature. It can be explained that the reversible networks formed *via* the inter- or intramolecular hydrophobically associations of fluorocarbon groups become unstable while increasing temperature. As the temperature goes down, the reversible networks regain their strength again, resulting in the restorement of solution viscosity.
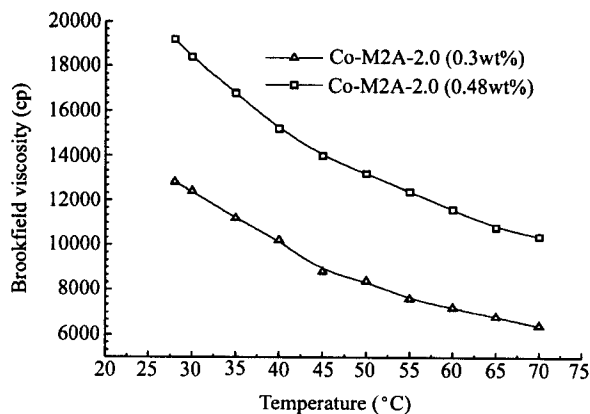
Fig. 5 Brookfield viscosity of polymer solution as a function of temperature (shear rate = 0.42 s^{-1}).

Conclusions

Fluorocarbon- or hydrocarbon-containing PEG macromonomers were synthesized by coupling method and the synthetic conditions were systematically studied.

Appropriate control of reaction time, amount of catalyst, molar ratio of reactants and other factors can bring about satisfactory results. The cmc values of macromonomers showed they were at same level despite of different lengths of fluorocarbon groups and end units (CF_3 or CF_2H). Copolymers of macromonomers with acrylic acid were synthesized by solution copolymerization. The conversion of macromonomers was low compared with that of AA due to their low reactivity in the system. Changing copolymerization medium can improve their conversion, details will be discussed in our next paper. The experimental results of the effect of macromonomer content in copolymers, shear rate, pH value and temperature on Brookfield viscosity of copolymer solution, show that these copolymers may be used as thickener due to the strong hydrophobic association between fluorocarbon groups existing in the copolymers.

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