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Self-emulsifying polymerization (SEP) of 3,6-dioxa-Δ^7-4-trifluoromethyl perfluorooctyl trifluoromethyl sulfonimide with tetrafluoroethylene

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Dedicated to Professor Herbert W. Roesky on the occasion of his 70th birthday.

Abstract

The copolymerization of an insoluble gaseous monomer with a soluble monomer that behaves as its own surfactant is described. This process is called self-emulsifying polymerization (SEP). A variety of sulfonamide monomers can be used in SEP, but current work has focused on copolymers of tetrafluoroethylene with 3,6-dioxa-Δ^7-4-trifluoromethyl perfluorooctyl trifluoromethyl sulfonimide **1**. ^{19}F NMR was used to determine the critical micelle concentration of the sodium salt of the monomer **1** for the SEP with tetrafluoroethylene.
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Keywords: Perfluorinated ionomers; Solid polymer electrolyte; Sulfonimide; Ion exchange polymer; Proton exchange membrane; Self-emulsifying polymerization; SEP

1. Introduction

Emulsion polymerizations, which were first used in the production of synthetic rubbers during World War II, have become the predominant process for the production of numerous polymers including poly(vinyl acetate) and poly(chloroprene). These systems employ an insoluble monomer(s), a dispersing medium, such as water, an emulsifier, and a soluble initiator [1]. When the concentration of the emulsifier (surfactant) exceeds the critical micelle concentration (cmc), the emulsifier molecules aggregate together to form small colloidal clusters known as micelles [2]. These micelles serve to solubilize the otherwise insoluble monomer(s). Polymerization of the monomer(s) occurs almost exclusively in these micelles. In our case, one of the monomers can behave as an emulsifier solubilizing the insoluble tetrafluoroethylene gas and stabilizing the latex formed; this type of polymerization will be referred to as a self-emulsifying polymerization (SEP).

We became interested in self-emulsifying polymerizations while researching polymers with a new functional group for use as polymer electrolyte membranes (PEMs) in fuel cells. The emphasis of this work was to produce a PEM which operates at higher temperatures (>120 °C) and that has better proton conducting properties than the current sulfonic acid polymers, such as Nafion or Dow XUS [3]. The original polymers, known as perfluorosulfonimide ionomers or PFSI, were produced by the copolymerization of a perfluorovinylethersulfonimide monomer, e.g. $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)SO_2CF_3$, with tetrafluoroethylene in an aqueous emulsion polymerization system using $C_7F_{15}CO_2NH_4$ as the emulsifying agent [4]. In the course of performing this work, it was noticed that the perfluorosulfonimide monomers had surfactant-like properties and questions arose about their emulsifying role in the polymerization process. It soon became apparent that these monomers were excellent anionic fluorinated surfactants and could sustain a copolymerization with tetrafluoroethylene without the need for additional surfactants.

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Herein, we report the class of polymerizations known as self-emulsifying polymerizations. We further report the critical micelle concentration (cmc) of the monomer CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2NNaSO_2CF_3$ and copolymerizations of this monomer with tetrafluoroethylene using SEP.

2. Experimental

2.1. General methods

Infrared spectra were obtained on a Perkin-Elmer 1600 and 2000 series FTIR spectrometer. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC 200 (^{1}H—200.33 MHz and ^{19}F—188.13 MHz). ^{19}F NMR spectra were measured using solutions of 1–2 mmol/l concentrations (unless otherwise stated) in an appropriate deuterated solvent. ^{1}H chemical shifts were referenced to CD_3CN, ^{19}F chemical shifts were referenced to $CFCl_3$. Unless indicated otherwise, samples were a minimum of 99.5% pure by ^{19}F NMR. Compounds without hydrogen were checked by ^{1}H NMR for hydrogen-containing impurities and were found to be free of impurities by the procedure given. Thermogravimetric analysis and differential scanning calorimetry were recorded under nitrogen on a Perkin-Elmer TGA7 and DSC7, respectively, with heating rates of 10 °C/min. Sample size for the TGA was normally 10–20 mg and for the DSC 5–15 mg.

2.2. Reagents

The starting materials were obtained from commercial sources and used as received unless otherwise stated. The monomer CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2NNaSO_2CF_3$ was prepared as previously described [4]. The $C_7F_{15}CO_2NH_4$ surfactant was donated by Dow Chemical Company.

2.3. NMR study of CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2NNaSO_2CF_3$ and $C_7F_{15}CO_2NH_4$

The solutions used in the NMR study were made by placing 2.2209 g $C_7F_{15}CO_2NH_4$ or 3.0634 g of sulfonimide monomer into a 25 ml volumetric flask. The flask was then filled with DI water to the mark indicated. Then, 25 ml of this solution and 10 ml of DI water were mixed to give the next concentration and so on. The procedure was repeated until 10 dilutions were made. ^{19}F NMR was run using sealed d_6-acetone capillary inserts with F_{11} as the reference.

2.4. Copolymerization of CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2NNaSO_2CF_3$ with tetrafluoroethylene

Care must be taken in the polymerization. Tetrafluoroethylene forms a shock sensitive explosive with oxygen. The amounts of each chemical used in the polymerization are listed in Table 3. The continuous copolymerization of the perfluorosulfonimide monomer with TFE was initiated by $(NH_4)_2S_2O_8/NaHSO_3$ with Na_2HPO_4/NaH_2PO_4 as pH buffer. For the classical emulsion polymerization, $C_7F_{15}COONH_4$ was added as the emulsifier. In the case of the self-emulsifying polymerization, no additional surfactants were added. A 450 ml or 1 l autoclave was precleaned with nitric acid, rinsed, and thoroughly dried. Approximately 800 ml of distilled water was degassed overnight using nitrogen and constant stirring. To prepare the solution for the autoclave, the surfactant (if any), $Na_2HPO_4{\cdot}7H_2O$, and NaH_2PO_4 were dissolved into the appropriate amount of degassed DI water. Once the salts were dissolved, the sulfonimide monomer **1** was added to the solution and the solution was cooled to 8 °C while constantly sparging with nitrogen. The addition solution was prepared by dissolving $Na_2HPO_4{\cdot}7H_2O$, NaH_2PO_4, and sulfonimide monomer **1** in the appropriate amount of degassed DI water. The initiators were added to the autoclave solution approximately 5 min before adding to the fully evacuated autoclave which had been purged with nitrogen three times. The addition solution was added to a metering pump reservoir and was degassed with helium for at least 20 min. The autoclave solution was sucked into the fully evacuated autoclave followed by the appropriate amount of DI degassed water for a total volume of 260 ml (for the 450 ml autoclave) or 600 ml (for the 1 l autoclave). When the reactor was at 10 °C, the TFE was added to a pressure of 150 psi and the continuous addition pump was then started. The TFE was added throughout the run to maintain a TFE pressure between 145 and 150 psi. When the desired amount of TFE was added as determined based on pressure drops and calculated using the Van der Waals equation, the remaining TFE was then vented and the solution was filtered through Whatman filter paper to remove any PTFE. The filtrate was then acidified with 70% HCl to precipitate the polymer. The polymer was then rinsed until the rinse water was neutral and dried at 120 °C under full vacuum for at least 12 h. Yields and characterization of the polymer are shown in Table 3.

2.5. Titration and characterization of copolymers

Titrations of the copolymers were performed in order to determine the The ion exchange capacity (IEC) and EW of the polymer. The copolymer (0.3618 g), 0.30 g of sodium chloride, and three drops of phenolphthalein were added to 50 ml of DI water in a 125 ml Erlenmeyer flask. A blank was also prepared which consisted of 0.30 g of sodium chloride and three drops of phenolphthalein in 50 ml of DI water. Both solutions were placed into an oil bath at 80 °C for 30 min with constant stirring. After 30 min, the solutions were titrated with 0.0960 M NaOH. It is important to note that the solutions remained in the oil bath during the titration process. The end point was determined to be the point at which the pink color remained for 1 h.

3. Results and discussion

Typical emulsion polymerizations employ a water-soluble initiator with an insoluble monomer. The insoluble monomer is made soluble in the medium using an emulsifying agent. These emulsifying agents or surfactant molecules vary in chemical composition; however, each of these molecules has a lyophobic and a lyophilic portion. In a highly polar solvent, such as water, the lyophobic group is typically a hydrocarbon, fluorocarbon, or a siloxane [2]. The lyophilic region is typically a highly polar or ionic group. Since we are interested in perfluorocarbon polymers, the emulsifier is typically a perfluorinated anionic species. These emulsifiers are often expensive, non-biodegradable, and are difficult to separate from the polymer and unreacted monomer [5]. In the course of performing work on perfluorosulfonimide polymers, questions arose about the surfactant role of the perfluorosulfonimide monomers in the polymerization process. These monomers (Fig. 1) have similar structures to anionic fluorinated surfactants, such as perfluorinated carboxalates ($R_fCOO^-M^+$), sulfonates ($R_fSO_3^-M^+$), sulfates ($R_fOSO_3^-M^+$), and phosphates ($R_fOP(O)O_2^{2-}M_2^+$) [2]. Both the typical fluorinated surfactants and the perfluorosulfonimide monomers are composed of a fluorocarbon tail with an ionic head; this led us to believe that these monomers could have good surfactant properties. Therefore, work was initiated to determine the critical micelle concentration of these monomers and carry out their polymerization without additional surfactant. In this paper, we will look at only one of these monomers herein labeled monomer **1** [4].

In order to determine if the perfluorosulfonimide monomer **1** could be used as its own surfactant, the critical micelle concentration of the perfluorosulfonimide monomer needed to be determined. Common techniques to measure the cmc include electrical conductivity, surface tension, light scattering, refractive index, and NMR spectroscopy [2]. Considerable work has been performed using ^{19}F NMR spectroscopy for investigating the micellar structures of fluorinated surfactants [6–12]. Micelle formation of surfactants has been obtained from proton and carbon chemical shift, spin relaxation time of water, and solute proton resonance [2]. ^{19}F NMR spectroscopy can also yield structural information on surfactants, their micelles, values of free energy of micellization, and corresponding enthalpy and entropy changes [6]. Muller et al. have shown that the solvent environment plays an important role on the chemical shifts of fluorine atoms in the micelle of partially fluorinated and fluorinated surfactants and that these chemical shifts can be used to determine the cmc [6–9,12]. The fluorocarbon surfactants show a strong concentration dependence during the micelle formation on the ^{19}F chemical shift. As a result, the fluorine nucleus is more susceptible to environmental changes than the proton nucleus which makes ^{19}F NMR spectroscopy so appealing [8].

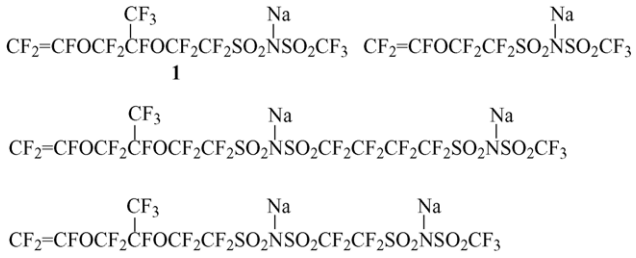


Fig. 1. Examples of perfluorosulfonimide monomers.

The ^{19}F NMR experiment to determine the critical micelle concentration was performed on both a standard and on the sulfonimide monomer **1**. As a comparison, the $C_7F_{15}CO_2NH_4$ surfactant which was originally used in the emulsion polymerization of **1** with tetrafluoroethylene [4] was used as the standard. In the ^{19}F NMR micelle experiment, the greatest accuracy for the cmc can be obtained from the fluorine which gives the greatest chemical shift change from dilute to concentrated solution [9]. In the case of the standard $C_7F_{15}CO_2NH_4$, the terminal CF_3 gives the greatest chemical shift change; for the sulfonimide monomer **1**, the greatest chemical shift change was shown by the *cis*-vinyl fluorine. The chemical shifts of the terminal CF_3 in $C_7F_{15}CO_2NH_4$ and the *cis*-vinyl fluorine in monomer **1** are listed in Tables 1 and 2, respectively.

The process of micelle formation has been explained by several theories which view the micelle as either a separate phase or a separate chemical species. For our analysis, we use the mass action model which regards the micelle as its own chemical species. In this model, the monomeric surfactant molecules, S_m, are in dynamic equilibrium with the micelles, mS, as shown in the equilibrium equation:

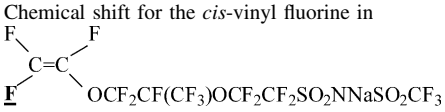
$$m\mathrm{S} \rightleftarrows \mathrm{S_m}, \quad K = \frac{[\mathrm{S_m}]}{[\mathrm{S}]^m} \tag{1}$$

where S is the surfactant ion and m the aggregation number [2,5]. This equation assumes that the aggregation number is the same for all micelles in a given solution; however, micelles are not definite stoichiometric entities but a combination of various size aggregates. Examples in the literature have shown that the mass action model can be used as a good approximation for determining the critical micelle concentration (cmc) in a given solution using ^{19}F NMR [7]. In classical terms, the critical micelle concentration is

Table 1
Chemical shift for the trifluoromethyl group in $C_7F_{15}CO_2NH_4$

Concentration (mmol/l)	PPM shift (Hz), terminal CF_3
100.62	−82.670
71.87	−82.384
51.34	−81.950
36.67	−81.313
26.19	−80.736
18.71	−80.715
4.87	−80.705

Table 2
Chemical shift for the *cis*-vinyl fluorine in



Concentration (mmol/l)	PPM shift (Hz), *cis*-vinyl fluorine
102.60	−113.906
73.28	−113.692
52.34	−113.356
37.39	−112.856
26.71	−112.156
19.08	−111.304
13.63	−110.818
9.73	−110.776
6.95	−110.766
4.97	−110.757

defined as the point at which half of the surfactant molecules in the solution are present in the monomeric form or when $[S] = m[S_m]$ [2,7]. A further assumption assumes that the equilibrium defined in (1) occurs at a rapid rate which causes a complete coalescence of the signals from the monomeric, $\delta(S)$, and from the micellar species, $\delta(S_m)$ [2,7]. Therefore, we can define the equation:

$$\delta = \delta(S_m) + \left(\frac{cmc}{S_o}\right)[\delta(S) - \delta(S_m)] \quad (2)$$

which states that the cmc can be determined by plotting δ, the chemical shift, against $1/[S_o]$, the surfactant concentration. By plotting the chemical shifts of the terminal CF_3 (Table 1) and the *cis*-vinyl fluorine (Table 2) against $1/[S_o]$, two straight line segments are produced as shown in Figs. 1 and 2, respectively. The intersection of these two line segments gives the critical micelle concentration. These plots resemble analogous plots for other surfactants whose cmc were determined using ^{19}F NMR [6–8,12]. The cmc for the $C_7F_{15}CO_2NH_4$ was determined to be 28.6 mmol/l (cmc = $1/S_o$ = 1/0.035) and the cmc of monomer **1** was determined to be 16.7 mmol/l (cmc = $1/S_o$ = 1/0.06). These values seem reasonable based on cmc values for other fluorinated anionic surfactants of roughly the same chemical length. Likewise, comparison of the cmc value obtained for the $C_7F_{15}CO_2NH_4$ versus the literature value for the cmc of $C_7F_{15}CO_2NH_4$ using surface tension measurements (33 mmol/l) are fairly close [2]. By extrapolation of the two lines in Figs. 2 and 3, the value of $\delta(S_m)$ can be determined when $1/[S_o] = 0$. Likewise, the value of $\delta(S_{aq})$ is determined when $S_o <$ cmc.

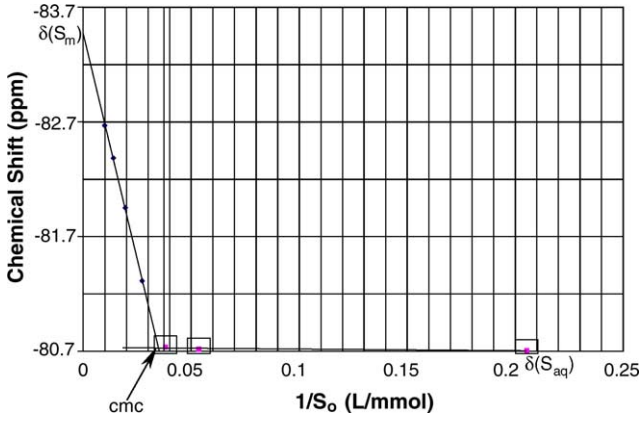


Fig. 2. Chemical shift of trifluoromethyl group of $C_7F_{15}CO_2NH_4$ as a function of the reciprocal of the surfactant concentration.

It is common to refer to the micelle formed by the surfactants by the degree of organic-like character of the inner micellar region, Z, which can be calculated from the following equation:

$$Z = \frac{\delta(S_m) - \delta(S_{aq})}{\delta(S_{fc}) - \delta(S_{aq})} \quad (3)$$

where $\delta(S_{fc})$ is the chemical shift of the surfactant in a fluorocarbon medium [9,12]. Therefore, it is implied that when no water is present in the inner micellar region, the environment should be fluorocarbon-like and we can define $Z = 1$ and $\delta(S_m) = \delta(S_{fc})$. If the inner micellar region was completely aqueous-like, than we can define $Z = 0$. The Z value for the CF_3 in $C_7F_{15}CO_2Na$ is 0.84, in $C_3F_7CO_2H$ is 0.82, and in $CF_3(CH_2)_nCO_2Na$ (n = 9, 11, and 12) is 0.53 [2]. So, the chemical shift for the micellized terminal CF_3 groups in $CF_3(CH_2)_nCO_2Na$ (n = 9, 11, and 12) are close to 0.5; this would indicate that the CF_3 groups find their surroundings to be about 50% aqueous-like and about 50% fluorocarbon-like [9]. This would indicate there is some water in the inner micellar region and that the surfactant is not as effective as might be expected in eliminating fluorocarbon–water contact [6]. In the case of the sulfonimide monomer, the Z value is 0.89 ($\delta_{fc} = -115.001$, $\delta_{aq} = -110.757$, and $\delta_m = -114.52$) and for $C_7F_{15}CO_2NH_4$ the Z value is 0.76 ($\delta_{fc} = -84.364$, $\delta_{aq} = -80.705$, and $\delta_m = -83.466$). All $\delta(S_{fc})$ values were measured in Freon 113 solvent. The Z values of the common surfactants and the sulfonimide monomer are less than 1 which indicate that the polar hydrophilic groups do not

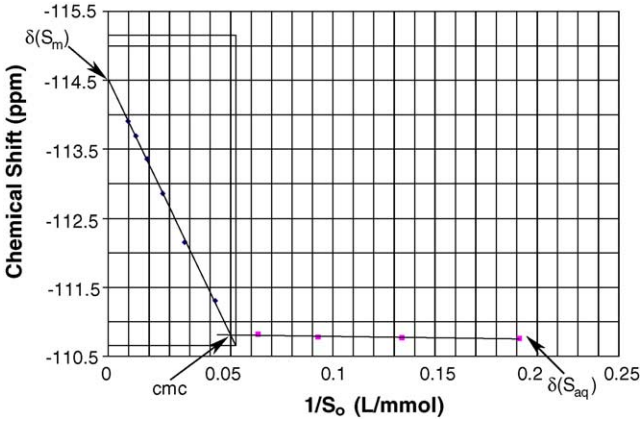
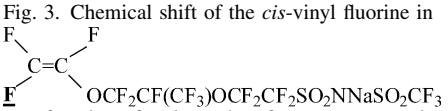


Fig. 3. Chemical shift of the *cis*-vinyl fluorine in



as a function of reciprocal surfactant concentration.

completely cover the micelle surface and leave some of the hydrophobic surface exposed [6]. This suggests that even the vinyl fluorine atoms are exposed to water to some extent; however, because the *Z* value of the sulfonimide monomer is very close to 1, the monomer has a tighter micelle and is more effective at eliminating fluorocarbon–water contact than the micelles formed from the $C_7F_{15}CO_2NH_4$ surfactant.

3.1. Copolymerization

Tetrafluoroethylene (TFE) and the perfluorosulfonimide monomer **1** readily undergo a free radical polymerization in both a classical aqueous emulsion system and a self-emulsifying polymerization system. The copolymerization of the perfluorosulfonimide monomer **1** with tetrafluoroethylene does not behave as a typical emulsion polymerization. Typical emulsion polymerizations use a hydrophobic monomer with some of the monomer solubilized in the interior of the micelle using a surfactant [13]. The majority of the monomer will be dispersed throughout and stabilized by the emulsifying agent. In the case of the perfluorosulfonimide monomer **1**, the monomer is the salt of a long perfluorocarbon chain and can behave as its own emulsifying agent with both a hydrophobic region and a hydrophilic region. Therefore, the monomer will readily dissolve in the aqueous medium which is opposite to that of a typical emulsion polymerizations. The sulfonimide monomer can then form micelles with the reactive vinyl ether linkages in the inner micellar region and the ionic sulfonimide head on the surface of the micelle. The sulfonimide monomer micelles can then solubilize some of the TFE molecules into the interior of the micelle, and thus, can sustain the polymerization without the need for additional emulsifying agents. For a comparison, a standard emulsion polymerization using $C_7F_{15}CO_2NH_4$ as the emulsifying agent and a SEP polymerization using only the monomer as its own emulsifying agent were run.

Table 3
Comparison of a SEP polymerization vs. a classical emulsion polymerization

Conditions	SEP	Classical
Reactor	450 ml	1 l
Monomer in the autoclave (g)	4.169	6.422
$C_7F_{15}CO_2NH_4$ (g)	0	4.69
$Na_2HPO_4{\cdot}7H_2O$ (g)	2.97	6.66
NaH_2PO_4 (g)	1.45	3.36
$(NH_4)_2S_2O_8$ (g)	0.3126	0.6998
$NaHSO_3$ (g)	0.2838	0.6395
H_2O (ml)	260	600
Pressure of TFE (psi)	145–150	143–151
Stirring speed (rpm)	660	150
Temperature (°C)	9–10	9–11
Reaction time (h)	7.5	9.3
Total TFE drop (psi)	46.42	57.95
Average TFE drop rate (psi/h)	6.2	6.21
TFE consumed (g)	3.4	6.01
Added monomer (g)	2.156	4.565
$Na_2HPO_4{\cdot}7H_2O$ in addition (g)	0.32	0.76
NaH_2PO_4 in addition (g)	0.18	0.39
Addition volume (ml)	18	41.4
PTFE recovered after reaction (g)	0	1.18
Polymer weight (g)	7.31	12.93
IEC (mg H/g)	0.94	0.93
EW	1061	1075
TFE in polymer (g)	3.35	6.01
Monomer in polymer (g)	3.96	6.91

The semi-continuous copolymerizations of the perfluorosulfonimide monomer **1** with TFE was initiated by

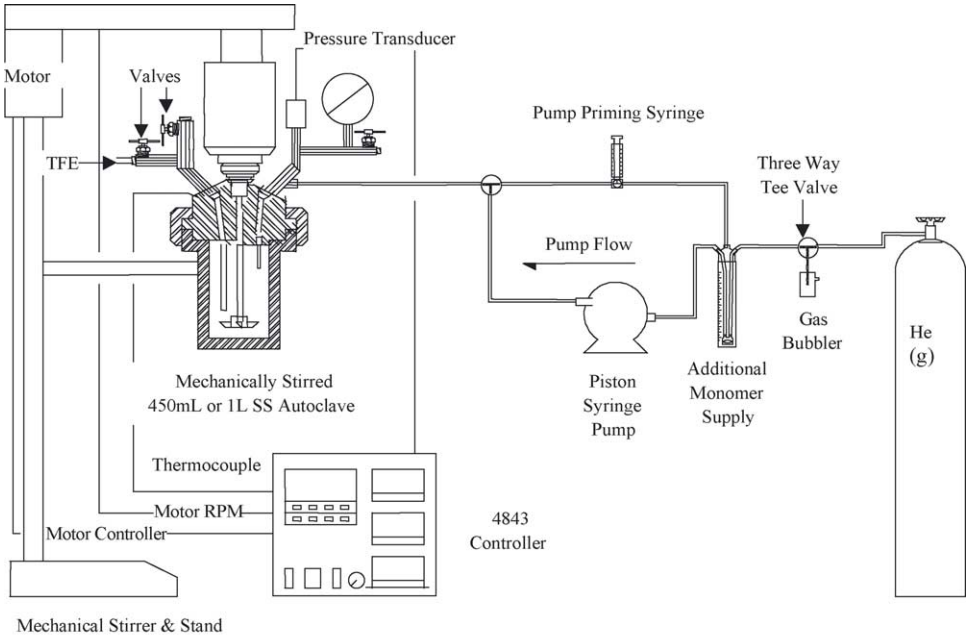


Fig. 4. Continuous addition polymerization system.

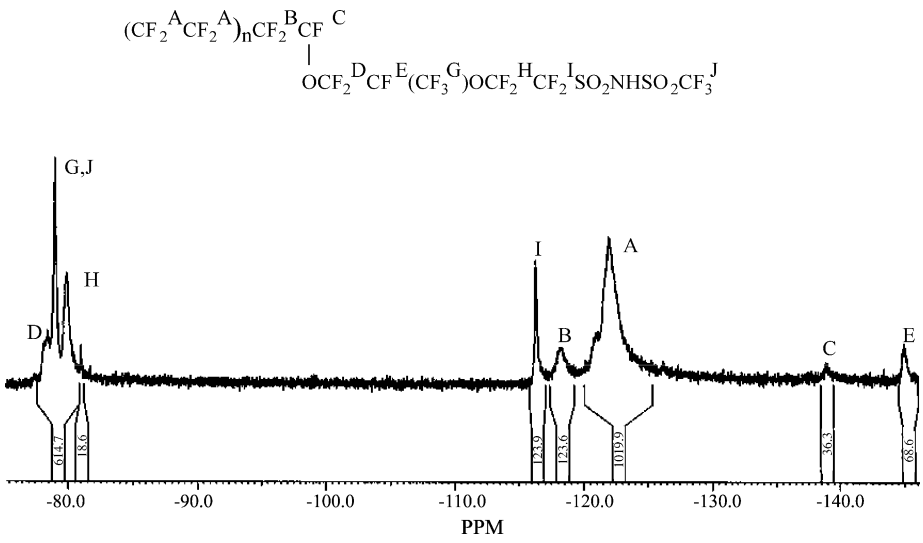


Fig. 5. ^{19}F NMR of copolymer of TFE and **1** prepared by SEP.

$(NH_4)_2S_2O_8/NaHSO_3$/catalytic iron and Na_2HPO_4/NaH_2PO_4 as the pH buffer. The polymerization of the perfluorosulfonimide monomer **1** with TFE employed a semi-batch reactor system as shown in Fig. 4. The continuous semi-batch reactor system uses a metering pump for the continuous addition of perfluorosulfonimide monomer **1** to the autoclave. TFE was added batchwise to the reactor to maintain a pressure between 145 and 150 psi. The TFE consumed in the reaction is monitored based on pressure drop and then the consumed moles of TFE can be calculated using the Van der Waals equation. The polymerization was stopped when the desired amount of TFE was consumed. Unlike typical emulsion polymerizations, the latex at the end of the polymerization is extremely

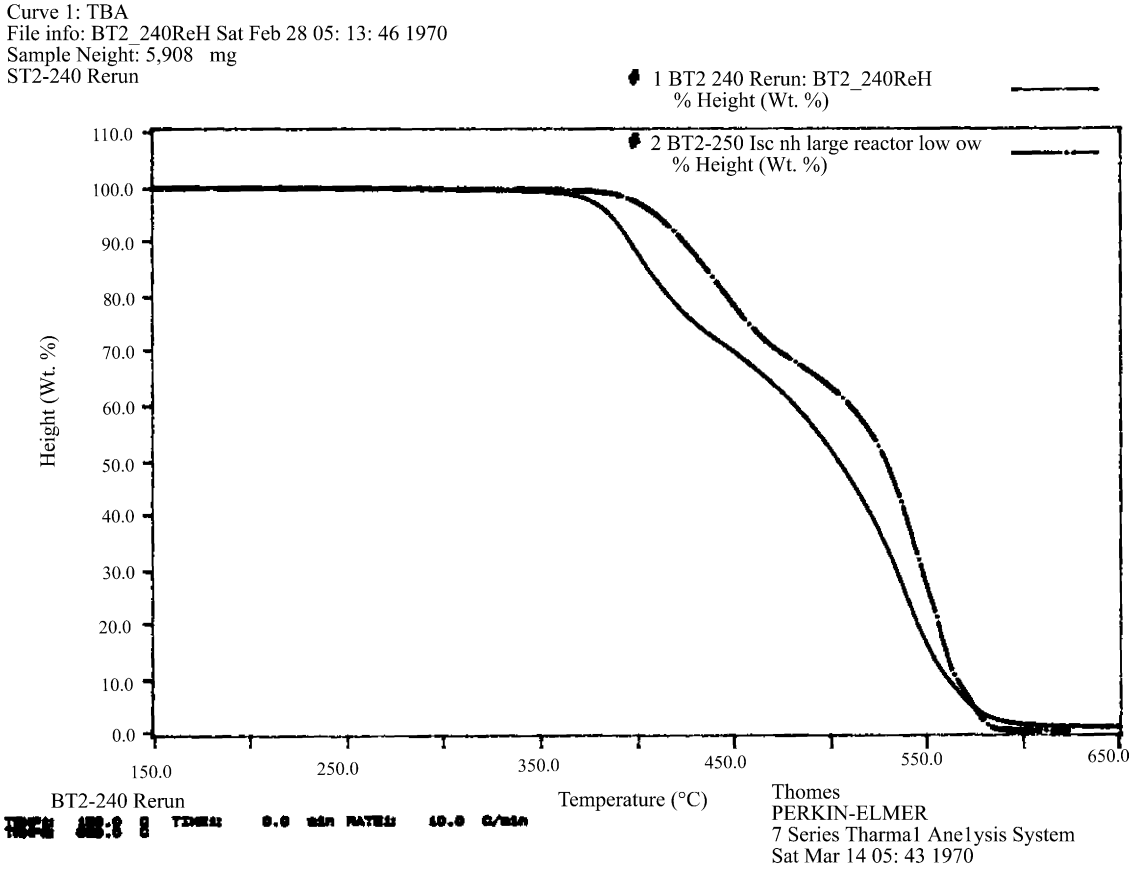


Fig. 6. Thermal gravimetric analysis of a classical emulsion polymerization (upper) and a SEP.

viscous. The polymer can be coagulated from the thick latex emulsion using 70% HCl and produces a white, fibery polymer when dried. A comparison of a typical emulsion polymerization and a self-emulsified polymerization is shown in Table 3.

3.2. Characterization

The ion exchange capacity of both the classical emulsion polymerization (0.93 mg H/g) and the SEP (0.94 mg H/g) were determined by titration with standardized sodium hydroxide and show that these two copolymers are similar.

Fig. 5 shows the ^{19}F NMR of the solubilized SEP polymer. This spectrum is essentially identical with the spectrum of a classical emulsion polymer of similar equivalent weight (see Ref. [4]). One can easily assign the respective fluorine resonances and integration provides an independent determination of equivalent weight of the copolymer. Comparison of fluorine labeled **A** with **I** gives EW = 1000, compared to the 1061 by titration. Other area comparisons give a similar result. The lower value by NMR is believed to be due to the fact that not all the bulk polymer is solubilized when heated in the water/alcohol mixture [4]. TGA of the unsolubilized polymer (typically 2–8%) shows a much higher TFE content and thus a much higher EW. Thus, the effective fractionation of the bulk polymer leads to an effective lower EW for the solubilized polymer.

Both the classical emulsion polymerization and the SEP polymers have excellent thermal stability with an onset for thermal decomposition around 404 °C (classical) and 378 °C (SEP) in the acid form. Fig. 6 shows thermograms of the bulk copolymer material for two equivalent weight polymers in the acid form using both SEP and classical emulsion polymerization. The first step in the weight loss corresponds to the loss of the perfluorosulfonimide side chain. Fig. 7 shows a typical DSC spectrum of the copolymer in acid form prepared by the classical emulsion system and SEP. A broad endotherm at 155–200 °C is indicative of coordinated water. The second endotherm at 320–350 °C occurs at nearly the same temperature as the melting temperature of virgin poly(tetrafluoroethylene)[14]; therefore, this peak is assigned to the melting (T_m) of PTFE crystallites in the copolymer. The heat of fusion (ΔH_f) can be calculated for the second endotherm and is related to the extent of crystallinity in the polymer [15]. In the second heating cycle, there is no broad endotherm at 155–200 °C associated with the coordinated water. If the sample is opened to the atmosphere for some time or if water is added to the sample, the endotherm returns. It is also interesting to note that after initial heating, the second endotherm related

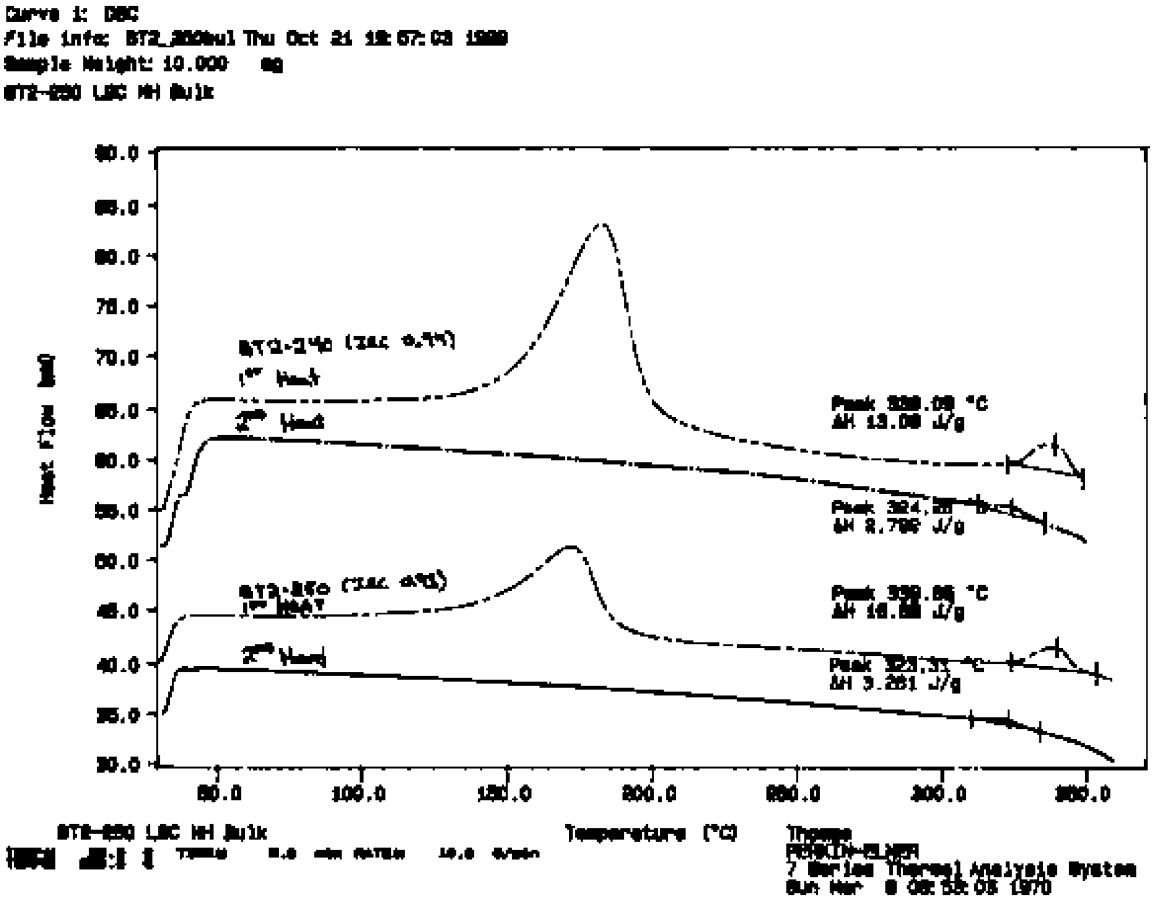


Fig. 7. Differential scanning calorimetry of a classical emulsion polymerization and a SEP (upper).

to the PTFE crystallite melting has also decreased. This is not unusual to see for polymers which have no thermal history. During the initial polymerization, the crystallites formed vary in size and perfection and thus, the transition is not sharp [13]. As is common in Teflon-like polymers, after thermal processing the heat of fusion for the PTFE crystallite region is lower and is due mainly to the reorientation of the polymer to its more thermodynamic equilibrium state. Likewise, in charged ionomers, the polymer chain reorients through the thermal heating to form ionic clusters which break up the crystallinity of the polymer and reduces the endothermic transition [16].

4. Conclusions

Sodium 3,6-dioxa-Δ^7-4-trifluoromethyl perfluorooctyl trifluoromethyl sulfonimide monomer is an excellent surfactant with a cmc of 16.7 mmol/l as determined by ^{19}F NMR analysis. The sulfonimide monomer readily copolymerizes with tetrafluoroethylene using an aqueous redox initiation system in either a classical emulsion type polymerization or a self-emulsifying polymerization. Both systems yield polymers which are similar in ion exchange capacities, thermal stability, and crystallinity; however, the self-emulsifying system allows for easy recovery of the unreacted monomer which is difficult using a classic emulsion system. Likewise, fluorinated surfactants are often expensive, and thus, self-emulsifying polymerizations offer a more cost-effective approach to polymerizing these ionic monomers.

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