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Polymer Communication

Synthesis and properties of semifluorinated block copolymers containing poly(ethylene oxide) and poly(fluorooctyl methacrylates) via atom transfer radical polymerisation

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Abstract

Amphiphilic block copolymers of poly(ethylene oxide) (PEO) and poly(fluorooctyl methacrylates) were synthesised by atom transfer radical polymerisation of semifluorinated methacrylates such as $1H,1H$-perfluorooctyl methacrylate, and $1H,1H,2H,2H$-perfluorooctyl methacrylate using PEO macroinitiators. The use of mono- and difunctional initiator led to AB and ABA block copolymers with controlled molecular weights. The linear time dependence of $\ln([M]_0/[M])$ is consistent with a controlled polymerisation i.e. first-order in monomer concentration. Various block copolymers could be prepared by varying the ratio of monomer to macro-initiator. The copolymers self-assembled in chloroform to form micelles, which was evidenced by dynamic light scattering and transmission electron microscopy. Different morphologies of spheres and rods were observed by changing the copolymer composition. In addition, these surfactants lower the interfacial tension between water and supercritical carbon dioxide to stabilise water-in-carbon dioxide emulsions. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Semifluorinated block and graft copolymers are of growing interest because of their unique properties, such as very low surface energy and oil/water repellence [1]. They may be utilised in many applications for example, as surfactants for polyurethane foams [2] and as emulsifiers in liquid and supercritical carbon dioxide [3]. Although water-in-carbon dioxide (W/C) emulsions have been formed with perfluoroether surfactant and silicone based surfactants [4], they have not been reported with fluoromethacrylate polymers. These emulsions are of interest in environmentally benign solvent formulations for separations, polymerisations [5] and in material synthesis.

Several attempts have been reported to prepare semifluorinated copolymers by means of cationic [6], anionic [7], living radical [8], and group transfer polymerisation [9], but few studies have addressed the synthesis of block copolymers composed of a hydrophilic block and a semifluorinated block [10,11]. The limited number of studies may be attributed to the limited solubility of fluorinated polymers in common organic solvents and the limited mechanisms by which the fluorocarbon monomer can be polymerised.

Controlled free radical polymerisation techniques provide the best route for the preparation of these amphiphilic block copolymers due to the relative ease of synthesis and their compatibility with a wide range of solvents [12,13]. Specifically, atom transfer radical polymerisation (ATRP) is an attractive method for the synthesis of well-defined copolymers with controlled molecular weight, polydispersities, terminal functionalities, and chain architecture composition [13,14].

Recently, the synthesis of block copolymers containing poly(ethylene oxide) (PEO) and PS were reported by ATRP

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using a PEO macro-initiator obtained by functionalising the HO–PEO–OH with 2-bromo- or 2-chloropropionyl ester end group [15,16]. The polymerisation proceeded in a living manner to yield well-defined block copolymers, which are difficult to synthesise by the sequential anionic method. Thus, esterification of a hydroxyl group of a preformed macromolecule with halogenated acyl halide proved to be an excellent method for producing macroinitiators suitable for ATRP [16,17].

The present article describes this macro-initiator approach in the synthesis of novel PEO-*b*-PFOMA (PFOMA, poly(fluorooctyl methacrylates)) copolymers via copper (I)-mediated living radical polymerisation. Wide ranges of block copolymers consisting of PEO and either 1*H*,1*H*-perfluorooctyl methacrylate (DHFOMA) or 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (THFOMA) are prepared by varying the ratio of monomer to macro-initiator, and the micellar characteristics of the amphiphilic copolymers are investigated by dynamic light scattering (DLS) and transmission electron microscopy (TEM). In addition, morphology of a W/C emulsion is reported and described in terms of the interfacial activity.

2. Experimental

2.1. Materials

2-Chloropropionyl chloride (CPC) (Aldrich) was distilled under vacuum. Triethylamine (TEA) (Aldrich) was refluxed with *p*-toluenesulfonyl chloride and distilled. It was distilled again over CaH_2. 4-Dimethylamino pyridine (DMAP) (Aldrich) was recrystallised from toluene. MMA (Aldrich), DHFOMA (SynQuest), and THFOMA (SynQuest) were passed through a neutral alumina column to remove the inhibitor, stored over CaH_2 and then vacuum distilled before use. Methoxy polyethylene glycol 2000 (MPEO–OH, Sigma) and polyethylene glycol 2000 (HO–PEO–OH, Sigma) were dried by azeotropic distillation with toluene. Trace of residual toluene was removed under vacuum. The higher molecular weight MPEO–OH 5000 (Sigma) was dried by vacuum for 2 days before use. Methylene dichloride (CH_2Cl_2), trifluorotoluene (TFT), and benzene were stored over CaH_2 and then distilled before use. Copper(I) Chloride (99.999 + %, Aldrich), 2,2′-bipyridine (bipy) (Aldrich), 1,1,2-trichlorotrifluoroethane (F-113) (Aldrich), ether, ethanol, and chloroform were used as received.

The preparation of PEG macroinitiators (Cl–PEG–Cl and MPEG–Cl) was carried out by procedures similar to that published in the literature [15,16]. They were prepared quantitatively and determined by ^{1}H NMR and FT-IR. The peak of hydroxyl protons at 4.56 ppm disappeared and new signals at 4.24 (one methylene proton) and 1.78 ppm (three methyl protons) due to the chloro-substituted propionic ester group appeared. In the FT-IR spectra, the characteristic

hydroxyl band at 3300 cm^{-1} disappeared completely after the reaction.

2.2. General procedure for ATRP of FOMA using the PEG macro-initiator

PFOMA-*b*-PEG-*b*-PFOMA and PEG-*b*-PFOMA were synthesised in the mixed solvent of TFT and benzene by using Cl–PEG–Cl and MPEG–Cl as macroinitiators, respectively. In a typical polymerisation of PEG-*b*-PDHFOMA, 3 g (0.60 mmol) of MPEG–Cl (M_n = 5000 g/mol), 0.06 g (0.60 mmol) of CuCl and 0.28 g (1.8 mmol) of bipy were changed to a 50 ml round-bottom flask equipped with a stirring bar. The flask was sealed with a rubber septa and the contents of the flask were placed under vacuum for 2 h, and the flask was then back-filled with nitrogen (3 ×). Seven millilitre of the mixture of benzene and TFT (50:50 by weight) and 4.2 g (9.0 mmol) of DHFOMA were degassed and added to the flask via a syringe. A pre-degassed reflux condenser with gas inlet/outlet was attached to the flask quickly and the system was purged with nitrogen. The reaction proceeded at 120 °C for 5 h under nitrogen atmosphere. After cooling the reaction mixture to room temperature, the product was precipitated into ether, collected, and dried. The polymer was then diluted in chloroform/F-113 mixed solvent, filtered, and passed through a short column filled with activated Al_2O_3 to remove the catalyst. The crude product was extracted with fluorinated solvent (FC-5080) at room temperature for possible removal of PFOMA. The residue was extracted three times with distilled water in order to remove any unreacted PEG macroinitiator. The purified product was dried in vacuum at room temperature and weighed.

Samples were removed periodically for conversion and molecular weight analysis. The conversion of double bonds and the relative block length was determined by ^{1}H NMR obtained from unprecipitated samples.

2.3. Characterisation

Size exclusion chromatography (SEC) was carried out with a HP1100 apparatus equipped with a set of three columns (10^4–10^3–10^2 Å: polymer standards service) with THF as the eluent. Polystyrene samples were used as standards to construct the calibration curve. ^{1}H NMR spectra were recorded using a JNM-ECP 400 (JEOL). ^{1}H NMR spectra of the PEO–PFOMA block copolymers were obtained in a mixed solvent of F-113 and CDCl$_3$. For the calculation of monomer conversion during ATRP, samples of the solution were withdrawn at regular time intervals, diluted with mixed solvent of F-113 and CDCl$_3$ and analysed by ^{1}H NMR. The conversion from the ^{1}H NMR data was calculated using the integrated area for the olefinic $(CH_3)C=CH_2$ proton (5.7–6.3 ppm) for FOMA as compared to the methyl $(CH_3)C–CH_2–$ protons (0.9–1.5 ppm) for PFOMA. The block length of PFOMA was determined
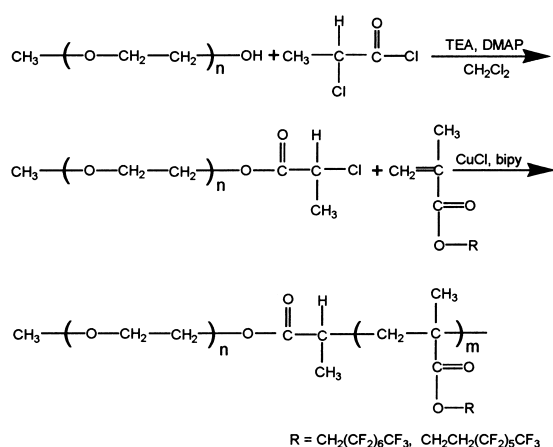
Scheme 1.

by taking the ratio of 1,1-dihydro protons (at 4.5 ppm) in the fluoroalkyl group to the methylene protons (3.7 ppm) in the PEO group. IR spectra were recorded on a Nicolet Avatar 360 FT-IR. The TEM image was obtained using a Hitachi H-7500 instrument operated at 80 kV. A drop of polymer solution (1.5 g/l) was applied onto a copper grid coated with carbon, which was in contact with a soaking tissue to remove the solution immediately. The sample was used without any staining procedure. Dynamic laser light scattering (DLS) measurements on the block copolymer micelles were carried out using a Brookhaven laser light scattering instrument (Brookhaven instruments Corporation), with diode laser (24 mV) at a wavelength of 659 nm at 20 °C. The sample solution (1 g/l) was purified by passing it through a 0.45 μm filter. The scattered light of a vertically polarised laser was measured at an angle of 90° and was collected on a Brookhaven BI 9000 AT autocorrelator. The hydrodynamic diameter was calculated from the measured diffusion constant using the Stokes equation. The polydispersity of the micelle is given by
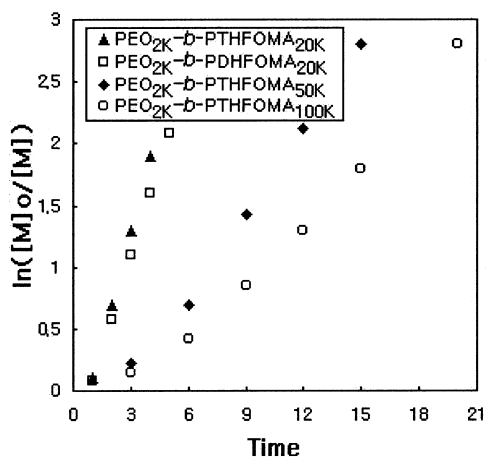

Fig. 1. First-order kinetic plots for the polymerisation of DHFOMA and THFOMA in mixed solvent of benzene and TFT at 120 °C initiated by PEO (2 K) macroinitiator with Cu(I)Cl/bipy catalyst. [I]/[CuCl]/[bipy] = 1/1/3: (▲) [M]/[I] = 44, (□) [M]/[I] = 46, (◆) [M]/[I] = 116, (○) [M]/[I] = 232.

μ_2/Γ^2, where μ_2 is the second cummulant of the decay function and Γ is the average characteristic line width.

2.4. Interfacial tension measurement

The interfacial tension of the ternary system (polymer/-supercritical carbon dioxide/water) was measured using a high pressure pendant drop apparatus [18]. Using the apparatus, drops of water were formed at the end of a surface modified silica capillary (Western Analytical Products) with a 183 μm o.d. and a 99 μm i.d.

2.5. Emulsion formation

The procedure and apparatus as described by Psathas et al. [18] was used to prepare the 50:50 (by mass) water and supercritical carbon dioxide emulsions. The emulsions were formed with isothermal high shear through a 127 μm capillary, and the contents were also stirred inside the cell with a magnetic stir bar.

3. Results and discussion

3.1. Polymerisation

Both MPEO–OH and HO–PEO–OH were converted into mono- and difunctional α-chloroester PEO macro-initiators suitable for ATRP via a simple condensation reaction with CPC, respectively. Diblock and triblock copolymers could be prepared using the corresponding macroinitiators. The synthesis of diblock copolymers is outlined in Scheme 1.

While characterisation of PEO macroinitiator prior to copolymerisation is straightforward, the analysis of the block copolymer proved to be very difficult because of the very low solubility in conventional solvents; the copolymer being soluble only in a mixed solvent of F-113 and organic solvents such as chloroform, benzene, and THF. The GPC analysis has been attempted without success to characterise the molecular weight and molecular weight distribution of the copolymer due to aggregation at very low concentration in THF.

Control experiments had been carried out with MMA using a PEO macroinitiator ($M_n = 2000$) to help establish the reaction conditions required for the ATRP of FOMAs. In the case of solution polymerisation in benzene at 110 °C, a 90% conversion was obtained after 15 h. The molecular weight of PMMA block determined by ^{1}H NMR was 11,000 and the initiation efficiency was calculated at 95% based on the amount of non-extractable macroinitiator with water. The molecular weight distribution of block copolymer was determined by GPC analysis to be 1.30.

The polymerisations of DHFOMA and THFOMA were carried out 120 °C in a mixed solvent of benzene and TFT. The polymerisations were followed by ^{1}H NMR to monitor

Table 1
ATRP of DHFOMA and THFOMA from PEO macroinitiators

Block copolymer	[M]/[I]	Time (h)	Monomer conv.[a] (%)	I_{eff}[b] (%)	Weight% of PEO
PEO$_{5 K}$-b-PDHFOMA$_{1.8 K}$	3	2	90	–	73.5
PEO$_{5 K}$-b-PDHFOMA$_{4.5 K}$	9	3	91	91	52.6
PEO$_{5 K}$-b-PDHFOMA$_{7.5 K}$	15	5	93	94	40.0
PEO$_{5 K}$-b-PDHFOMA$_{12.5 K}$	24	4	85	91	28.6
PEO$_{5 K}$-b-PDHFOMA$_{45 K}$	80	18	95	93	10.0
PDHFOMA$_{20 K}$-b-PEO$_{2 K}$-b-PDHFOMA$_{20 K}$	102	5	85	–	4.8

[I]/[CuCl]/[bipy] = 1/1/3; 120 °C; solvent/mixed solvent of benzene and TFT (50:50 by weight).
[a] calculated from ^{1}H NMR spectrum.
[b] initiation efficiency; calculated based on the amount of non-extractable macroinitiator with water.

conversions over time. Fig. 1 shows the first-order kinetic plot for the reactions of DHFOMA and THFOMA. The plots are close to linear, indicating that the concentration in active centres remains constant throughout the polymerisation. It is worth pointing out that an induction period was observed. Although unusual induction period was found sometimes in ATRP of MMA [19–21], in this case it can be attributed to the slow initiation of chloropropyonyl-terminal macroinitiator when compared to the chain propagation. The initiation step requires the cleavage of the C–Cl bond, which is more stable in the case of acrylate compared to methacrylate in relation to the reactivity of the secondary radical derived from acrylate, which is higher than that of the tertiary methacrylate radical [22]. In spite of short induction period, the initiation of methacrylates by macro-initiator seems to be quantitative, since the macroinitiator trace was not observed by GPC analysis (before product purification) in the case of MMA polymerisation. The polymerisation of THFOMA proceeded similar to DHFOMA with almost the same kinetic plot. The reactions in Fig. 1 were stopped below 95% conversion giving M_n = 20,000, 50,000 and 100,000 g mol^{-1}, respectively, for the PFOMA blocks with a PEO of 2000 g mol^{-1} in each case. The longer reaction time was needed in order to get same conversion as the ratio of [M]/[I] increases.

As listed in Table 1, various block copolymers have been synthesised using different molecular weight mono- or difunctional PEO macroinitiator. There was generally excellent agreement between the target degree of polym-

erisation and those calculated by ^{1}H NMR. The product was extracted with water and PF 5080 for removal of possible unreacted PEO macroinitiator and PFOMA, respectively. The amount of extractable was negligible, and the high initiation efficiencies calculated on this basis are given in Table 1. Therefore, the size of blocks could be controlled by varying the ratio of monomer to macroinitiator.

3.2. Micellar characteristic

It has been known for many years that when diblock copolymers are dissolved in a solvent which is selective for one of the blocks, colloidal size aggregates or micelles can form as a result of the association of the insoluble blocks. Some characteristics of PEO-b-PFOMA micelles in several solvents are given in Table 2. PEO$_{5 K}$-b-PFOMA$_{1.8 K}$ could be dispersed into water to form micelles consisting of a core of PFOMA and a shell of PEO. But it was observed that, if the FOMA content is greater than approximately 50 wt%, the block copolymers become insoluble in water. When the copolymers were dissolved in chloroform, which is a precipitant for PFOMA but a good solvent for PEO, even higher PFOMA block copolymers (up to 90 wt%) formed micelles. The copolymers were insoluble in pure F-113, which is a good solvent for PFOMA, but a precipitant for PEO. However, a few drops of chloroform made the solution clear with bluish tinge, and reverse micelles were detected by DLS. The solvent composition, where both PEO and PFOMA blocks are soluble depends on the block ratio

Table 2
Characteristics of PEO-b-PDHFOMA micelles

| Block copolymer	Solvent[a]	Diameter[b] (nm)	Polydispersity μ_2/Γ^2	Aqueous solubility
PEO$_{5 K}$-b-PDHFOMA$_{1.8 K}$	Water	130	0.21	Yes
PEO$_{5 K}$-b-PDHFOMA$_{4.5 K}$	Chloroform	50	0.16	No
PEO$_{5 K}$-b-PDHFOMA$_{45 K}$	Chloroform	na[c]	–	No
PEO$_{5 K}$-b-PDHFOMA$_{12.5 K}$	Chloroform/F-113[d]	0	–	No
PEO$_{5 K}$-b-PDHFOMA$_{12.5 K}$	F-113[f]	150	0.18	

[a] 0.1 wt% polymer solution.
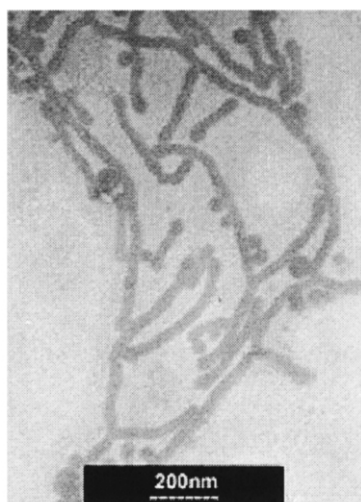[b] Effective diameter at 20 °C.
[c] Insoluble.
[d] Chloroform/F-113 = 0.1–0.3 by weight.
[f] A few drops of chloroform are added.
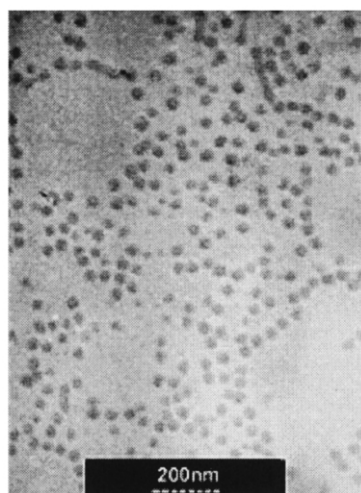
(A)

(B)

Fig. 2. TEM picture of PEO-*b*-PDHFOMA aggregates made in chloroform. (A) PEO$_{5 K}$-*b*-PDHFOMA$_{4.5 K}$; (B) PEO$_{5 K}$-*b*-PDHFOMA$_{12.5 K}$.
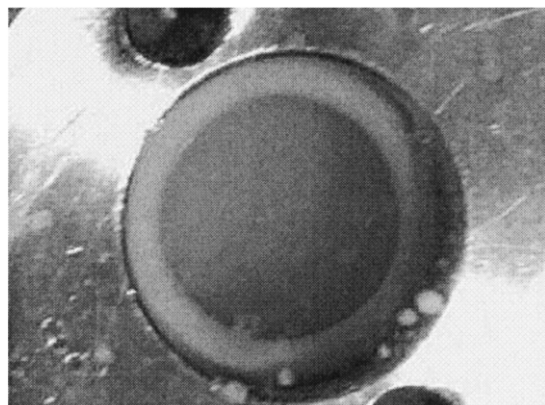

Fig. 3. Digital photograph of emulsion immediately after stopping recirculation and stirring.

in the copolymer to some extent. For most of the block copolymers, no micelles were formed in the mixed solvent of 0.1–0.3 weight fraction of chloroform. This was also verified by ^{1}H NMR which showed well-resolved signals for two blocks in the solvent composition range.

Fig. 2 depicts the TEM images of the micelles of PEO$_{5 K}$-*b*-PDHFOMA$_{4.5 K}$ and PEO$_{5 K}$-*b*-PDHFOMA$_{12.5 K}$. The dark core regions correspond to the PDHFOMA in accordance with the higher electron density of the fluorinated block. It is shown in Fig. 2(A) that the micellar images of PEO$_{5 K}$-*b*-PDHFOMA$_{4.5 K}$ are predominantly spherical. The average diameter of cores was calculated as ca. 24 nm. For the higher PFOMA block copolymer of PEO$_{5 K}$-*b*-PDHFOMA$_{12.5 K}$, primarily rod-like aggregates are formed (Fig. 2(B)). The micrograph suggests a narrow size distribution of the cylindrical micelle diameter, but a widely variable length. Several small spheres were also observed. The rods and spheres have a similar diameter of ca. 34 nm. TEM diameters appear too large considering the lengths of PDHFOMA block (ca. 2.2 and ca. 5.9 nm for 4.5 and 12.5 K, respectively) calculated based on a *trans–gauche* type configuration [23]. In contrast, Krupers et al. reported that PMMA$_{8.9 K}$-*b*-PTHFOMA$_{5.1 K}$ contaminated with PMMA macroinitiator formed spherical micelles in toluene, whose diameter was observed to be ca. 35 nm by TEM analysis [9]. This discrepancy is not well explained but might be associated with a large size of rigid dihydro perfluorooctyl side chain. This is currently under investigation.

Eisenberg et al. found various morphologies in crew-cut aggregates, where the soluble block was shorter than the insoluble block [24–26]. The morphological transition of spherical to non-spherical aggregates such as rod, lamellae, and vesicles occurred in aqueous solutions of the PS-*b*-PEO block copolymer as the hydrophilic PEO block length decreased [25]. In most cases, aggregates of several different morphologies were seen in the same micrograph. They explained that the transition is due to changes in the degree of stretching of the PS blocks in the core region as the block copolymer composition changes [25,26]. The same trend has been observed in chloroform solutions of PEO-*b*-PFOMA. At a constant PEO block, it has been found that the morphology changed from spherical to rod-like micelles with increasing PFOMA block length. The increase in volume of the internal PFOMA block with an increase in molecular weight makes the interface less curved favouring rods. The coexistence of the various morphologies is probably attributed to the heterogeneity of chemical composition of block copolymers.

3.3. Emulsion formation with PEO$_{5 K}$-*b*-PDHFOMA$_{7.5 K}$

Fig. 3 represents a digital photograph of a fine white water/supercritical carbon dioxide emulsion formed with PEO$_{5 K}$-*b*-PDHFOMA$_{7.5 K}$. The photograph was taken immediately after stopping the recirculation and the

Table 3
Interfacial tension at the water–CO_2 interface for $PEO_{5\ K}$-b-$PDHFOMA_{7.5\ K}$

T (°C)	P (MPa)	CO_2 density (g/ml)	γ (mN/m) DI H_2O
25	32	0.9755	4.40
			4.48[a]
			4.91[b]
			5.11[c]
25	28	0.9583	6.52
25	24	0.9385	8.59
25	20	0.9151	10.92
35	32	0.9396	7.08
35	30	0.9299	10.04
35	28	0.9195	11.10
45	32	0.9026	9.92
45	30	0.8913	10.74

[a] 0.05 M NaCl.
[b] 0.10 M NaCl.
[c] 0.15 M NaCl.

magnetic stir bar. The emulsion settled 20% in 30 min producing a clear excess phase on the top. This clearing of the top phase indicated that the emulsion consisted of dispersed water droplets settling in a CO_2 continuous phase, designated as water-in-CO_2 (W/C).

3.4. Interfacial activity

The results from an interfacial tension study for $PEO_{5\ K}$-b-$PDHFOMA_{7.5\ K}$ are summarised in Table 3. These results illustrate the dependence of the interfacial tension on the temperature, pressure, salinity, and CO_2 density. The surfactant concentration was 0.05 wt%.

The binary water-CO_2 interfacial tension is approximately 20 mN/m in the range investigated. The addition of surfactant lowered the interfacial tension enough for the formation of emulsion. Of particular importance are the effects of the CO_2 density and salinity on the interfacial tension. At all three temperatures examined, a decrease in the CO_2 density (and thus the solvent strength) resulted in an increase in the interfacial tension. This increase in the interfacial tension results from an increase in the binary water–CO_2 interfacial tension and a decrease in the solvation of the surfactant tails (PFOMA block).

Increasing the salinity of the system was also shown to increase the interfacial tension. For a W/C emulsion system, the addition of salt drives the system away from the balanced state by reducing the solubility of the surfactant in the aqueous phase [27]. The balanced state is the point, where the surfactant prefers the two phases the same. An increase in the interfacial tension is expected to accompany this movement away from the balanced state, and has been observed in typical water/oil emulsions [28,29]. Therefore, the effect of salt on the interfacial tension is consistent with the W/C morphology observed in the emulsion.

4. Conclusions

Amphiphilic block copolymers consisting of a hydrophilic PEO block and semifluorinated PFOMA block were synthesised using PEO macroinitiators containing chain ends with ATRP function. It has been demonstrated that PEO macroinitiators polymerise DHFOMA and THFOMA effectively with controlled molecular weights. The block copolymers formed stable micelles, where PEO is the shell, and PFOMA is the core in both water and chloroform. In chloroform, the micellar morphology changed from normal sphere to rod by increasing the ratio of PFOMA to PEO block length. The surfactant $PEO_{5\ K}$-b-$PDHFOMA_{7.5\ K}$ lowers the interfacial tension of the water–CO_2 interface allowing the formation of W/C emulsions.

Acknowledgements

References

[1] Kissa E. Fluorinated surfactants. New York: Marcel Dekker, Inc; 1994.

[2] Krupers MJ, Bartelink CF, Grunhauer HJM, Möller M. Polymer 1998; 39(10):2049–53.

[3] Kendall JL, Canelas DA, Young JL, DeSimone JM. Chem Rev 1999; 99(2):543–63.

[4] Psathas PA, da Rocha SRP, Lee Jr. CT, Johnston KP, Lim KT, Webber SE. Ind Engng Chem Res 2000;39:2655–64.

[5] Butler RD, Cait M, Cooper AI. Adv Mater 2001;13:1459–63.

[6] Percec V, Lee M. J Macromol Sci, Pure Appl Chem 1992;A29(9): 723–40.

[7] Iyengar DR, Perutz SM, Dai CA, Ober CK, Kramer EJ. Macromolecules 1996;29:1229–34.

[8] Betts DE, Johnson T, LeRoux D, DeSimone JM. Controlled radical polymerisation. ACS Symposium Series, 685.; 1998. p. 418–32.

[9] Krupers MJ, Sheiko SS, Möller M. Polym Bull 1998;40:211–7.

[10] Miyamoto M, Aoi K, Saegusa T. Macromolecules 1989;22:3540–3.

[11] Matsumoto K, Mazaki H, Nishimura R, Matsuoka H, Yamaoka H. Macromolecules 2000;33:8295–300.

[12] Guan Z, DeSimone JM. Macromolecules 1994;27:5527–32.

[13] Patten TE, Matyjaszewski K. Adv Mater 1998;10(12):901–15.

[14] Ueda J, Matsuyama M, Kamigaito M, Sawamoto M. Macromolecules 1998;31(3):557–62.

[15] Jankova K, Chen X, Kops J, Batsberg W. Macromolecules 1998;31: 538–41.

[16] Jankova K, Truelsen JH, Chen X, Kops J, Batsberg W. Polym Bull 1999;42:153–8.

[17] Kim H, Bes L, Haddleton DM, Khoshdel E. J Polym Sci, Part A: Polym Chem 2001;39:1833–42.

[18] Psathas PA, Sander EA, Lee MY, Lim KT, Johnston KP. J. Dispersion Sci Tech 2002;23(1–3):65–80.

[19] Haddleton DM, Jasieczek CB, Hannon MJ, Shooter AJ. Macromolecules 1997;30:2190–3.

[20] Moineau G, Minet M, Dubois Ph, Teyssié Ph, Senninger T, Jérôme R. Macromolecules 1999;32:27–35.

[21] Miller PJ, Matyjaszewski K. Macromolecules 1999;32:8760–7.

[22] Moineau G, Minet M, Teyssié Ph, Senninger T, Jérôme R. Macromolecules 1999;32:27–35.

[23] Imae T, Tabuchi H, Funayama K, Sato A, Nakamura T, Amaya N. Colloids Surf A, Physicochem Engng Aspects 2000;167:73–81.

[24] Zhang L, Eisenberg A. J Am Chem Soc 1996;118:3168–81.

[25] Yu K, Eisenberg A. Macromolecules 1996;29:6359–61.

[26] Yu Y, Zhang L, Eisenberg A. Macromolecules 1998;31:1144–54.

[27] Lee Jr. CT, Psathas PA, Johnston KP. Langmuir 1999;15:6781–91.

[28] Sottmann T, Strey R. J Chem Phys 1997;106:8606–15.

[29] Kahlweit M, Strey R, Schomacker R, Haase D. Langmuir 1989;5:305–15.