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Preparation and properties of semifluorinated block copolymers of 2-(dimethylamino)ethyl methacrylate and fluorooctyl methacrylates

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Abstract

Semifluorinated block copolymers of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) and poly(fluorooctyl methacrylates) (PFOMA) were prepared using group transfer polymerisation via sequential monomer addition. Wide ranges of copolymers were obtained with good control over both molecular weight and composition by adjusting the monomers/initiator ratio. The micellar characteristics of the copolymers in water and chloroform were investigated by quasi-elastic light scattering and transmission electron microscopy. The size and morphologies of micelles were greatly influenced by copolymer composition, pH, and temperature. In addition, the solubility of copolymers and the formation of water-in-carbon dioxide (W/C) microemulsions were described in terms of the cloud points. The block copolymers exhibited the excellent ability of stabilizing W/C microemulsions.

Keywords: Block copolymer; Micelle; Semifluorinated copolymer

1. Introduction

Semifluorinated block and graft copolymers are of growing interest as membrane for water treatment [1] and emulsifier in liquid and supercritical carbon dioxide [2]. Especially, emulsions consisting of the environmentally benign solvents carbon dioxide and water, which are nontoxic, nonflammable and inexpensive, may be substituted for toxic organic solvents in chemical processing. Applications include dry cleaning [3], photoresist drying [4], nanoparticle synthesis [5], enzymatic catalysis [6], and organometallic catalysis [7]. So far, several attempts have been applied to prepare semifluorinated block copolymers by means of cationic [8–10], anionic [11,12], living radical [13], and group transfer polymerisation (GTP) [14]. Solution properties of block copolymers are greatly influenced by the length and the ratio of block segments, so precise controlling of the chemical structure and the molecular weight is very important to manipulate the properties. Recently, we reported on the synthesis of poly(ethylene oxide) (PEO)-*b*-PFOMA copolymers by ATRP using a PEO macroinitiator [15]. The polymerisation yielded well-defined block copolymers with controlled molecular weight. It was demonstrated that the block copolymers formed micelles where PEO is the shell and PFOMA is the core in water and chloroform and the micelle formation depended on the block ratio in the copolymers. The copolymer surfactant lowered the interfacial tension of the water–CO_2 interface due to both hydrophilicity of PEO block and highly CO_2-philic nature of PFOMA block allowing the formation of stable W/C emulsions.

The present article describes the synthesis of PDMAEMA-*b*-PFOMA copolymers via GTP. GTP has been extensively utilized for the preparation of various types of block copolymers with controlled molecular weight and narrow molecular weight distribution. A series of block copolymers are prepared by varying the ratio of monomers to an initiator, and the micellar characteristics of the copolymers are investigated by quasi-elastic light scattering (QELS) and transmission electron microscopy (TEM). In addition, the solubility of copolymers in dense carbon

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dioxide and the formation of water-in-CO_2 microemulsions stabilized by the copolymer are studied.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was distilled from sodium naphthalide under reduced pressure prior to use. DMAEMA (Aldrich) was purified by passing through a basic alumina column, to remove the inhibitor, stored over CaH_2 at below 0 °C, and distilled prior to use. The GTP catalyst, tetrabutyl ammonium bibenzoate (TBABB) was synthesized according to the procedure in Ref. [16]. The initiator, methyl trimethysilyl dimethyl ketene acetal (MTSDA) (Aldrich) was distilled under high vacuum and stored under argon atmosphere. 1H,1H-perfluorooctyl methacrylate (DHFOMA) (SynQuest), and 1H,1H,2H,2H-perfluorooctyl methacrylate (THFOMA) (SynQuest) were passed through a neutral alumina column, stored over CaH_2 and then vacuum distilled before use. 1,1,2-trichlorotrifluoroethane (F-113) (Aldrich), hexane, chloroform were used as received.

2.2. General procedure of GTP for PDMAEMA-b-PFOMA

GTP was carried out under argon atmosphere in a previously flamed glass reactor. In a typical polymerisation for PDMAEMA-*b*-PDHFOMA, 15 ml of THF and 5 mg (0.01 mmol) of TBABB were transferred into a reactor by means of a cannula. Then 0.087 g (0.5 mmol) of MTSDA was added to the mixture via syringe. After 5 min of stirring, 3 g (19 mmol) of freshly distilled DMAEMA was added slowly via syringe and the polymerisation proceeded for 30 min under argon. An aliquot of the reaction mixture was withdrawn for GPC analysis. For the block copolymerisation, 1.5 g (3.2 mmol) of freshly distilled DHFOMA was added to the living PDMAEMA solution. The mixture was stirred for additional hour and quenched with degassed methanol (2 ml). THF and methanol were removed by evaporation and a possible unreacted FOMA and DMAEMA homopolymer were extracted with hexane and water, respectively. The product was collected, dried, and weighed to give 4.25 g of polymer. The molecular weights of PDMAEMA and PFOMA block of the copolymer were determined to be 5700 and 3400 by ^1H NMR analysis, respectively. Control over the copolymer molar mass was achieved by varying monomers/initiator ratio.

2.3. Synthesis of PDMAEMA-ran-PDHFOMA

Statistical copolymer of PDMAEMA-*ran*-PDHFOMA was synthesized by charging 0.5 g of DMAEMA, 0.75 g of DHFOMA and 0.018 g AIBN into a 25 ml flask equipped with a stir bar. The flask was then closed and purged with argon. The flask was heated to 65 °C and the reaction run for 24 h. After the reaction, the reaction mixture was dissolved in mixed solvent of F-113 and chloroform and precipitated into hexane. The product was collected and weighed. The random copolymer was composed of 37 mol% DHFOMA and 63 mol% DMAEMA as determined by ^1H NMR.

2.4. Characterization

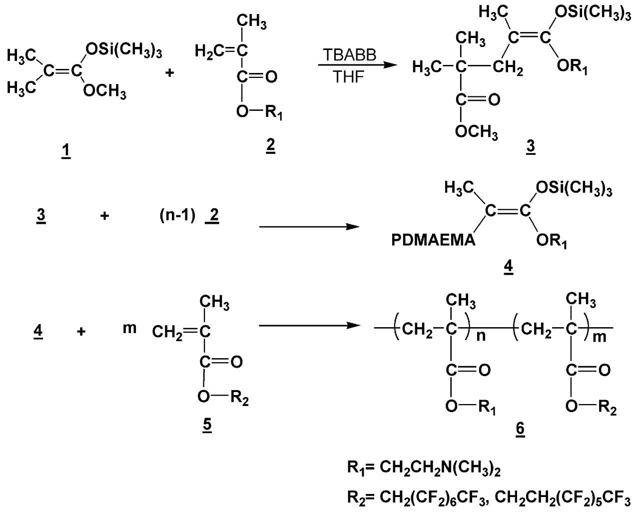
Size exclusion chromatography (SEC) was carried out with a HP1100 apparatus equipped with a set of four columns ($10^5-10^4-10^3-10^2$ Å: polymer standards service) with THF as the eluent. Polystyrene samples were used as standards to construct the calibration curve. ^1H NMR spectra were recorded using a JNM-ECP 400 (JEOL). ^1H NMR spectra of the PDMAEMA-*b*-PFOMA copolymers were obtained in a mixed solvent of F-113 and $CDCl_3$. QELS experiment were performed to measure the apparent hydrodynamic diameter of the PDMAEMA-*b*-PFOMA copolymer micelles. The sample solution (1 g/l) was purified by passing it through a 0.45 μm filter. The scattered light of a polarized diode laser (659 nm) was measured at 90° and collected on a Brookhaven BI 9000 AT autocorrelator. The hydrodynamic diameter (d_h) was calculated from the measured diffusion constant using the Stokes equation, $D = kT/3\pi\eta d_h$, where k, T, and η are the Boltzmann's constant, the absolute temperature and the solvent viscosity, respectively. The polydispersity of the micelle is given by μ_2/Γ^2, where μ_2 is the second cumulant of the decay function and Γ is the decay rate of the scattering correlation function.

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. The cloud-point was determined by simple visual inspection, using a 28 ml stainless steel variable-volume view cell equipped with a sapphire window that permitted visual observation of microemulsion formation and phase behavior [17]. A piston inside the view cell was used to vary the volume of sample of constant weight fraction and the pressure independently of temperature. The cloud point pressure was defined as the point at which the solution becomes so opaque that it was no longer possible to see the stir bar in CO_2.

3. Results and discussion

3.1. Polymerisation

The synthesis of PDMAEMA-*b*-PFOMA copolymers is illustrated in Scheme 1. Block copolymers of PDMAEMA and PFOMA of various block lengths could be prepared by varying the ratio of monomer to initiator in the polymerisation. DMAEMA was polymerized first in all cases because



Scheme 1.

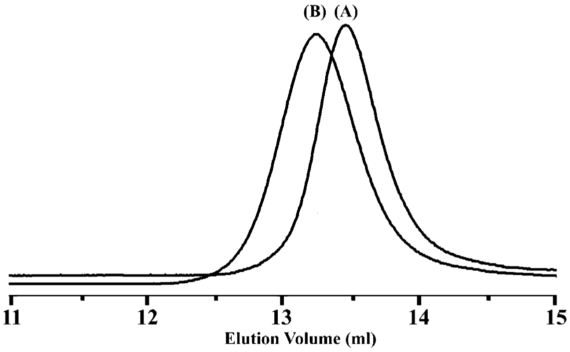


Fig. 1. GPC trace of (A) starting PDMAEMA$_{5.8\ \mathrm{K}}$ ($M_w/M_n = 1.12$) and (B) PDMAEMA$_{5.8\ \mathrm{K}}$-*b*-PTHFOMA$_{6.3\ \mathrm{K}}$ ($M_w/M_n = 1.16$).

of the bad solubility of homo PFOMA in THF. A sample was picked out from the reactor before the addition of FOMA in order to analyse the molecular weight and the conversion. The PDMAEMA had a low polydispersity of 1.12 with unimodal shape in GPC trace, and no monomer could be detected in the ^{1}H NMR spectrum. Thus the complete reaction of DMAEMA was confirmed before the addition of second monomer. The GTP of second monomer proceeded successfully, but a small amount of unreacted FOMA (less than 10%) remained even after prolonged reaction time. The incomplete reaction of FOMA may be attribute to the micellization of block copolymer in the reaction solvent upon increasing of PFOMA content. A reactive center tends to be at the core of polymer coil as PFOMA content increases, and therefore the possibility of propagation is inhibited.

The block copolymer was subject to extractions with hexane and water in order to remove unreacted FOMA and PDMAEMA homopolymer, respectively. A trace of homo PDMAEMA in the extracted water solution was detected.

The GPC analysis has been attempted to characterize the molecular weight and molecular weight distribution of the block copolymer. Fig. 1 illustrates the GPC curves of the polymers. The peak of starting PDMAEMA shifts toward the higher molecular weight copolymer with slight increase of polydispersity. These results indicate that the polymerization of FOMA is initiated efficiently by the living PDMAEMA.

Above ca. 50 mol% of FOMA content, the block copolymers did not dissolve in THF solution, thus the molecular weight and composition of the copolymer was determined by ^{1}H NMR spectroscopy. The block length and composition was calculated from the peak integrals among the methoxy protons (at 3.6 ppm) in the terminal initiator moiety, the 1,1-dihydro protons (at 4.5 ppm) in the fluoroalkyl groups, and the methylene protons (at 4.2 ppm) next to the ester moieties in DMAEMA groups. Table 1 summarizes the theoretical and observed number-average molecular weights (M_n) and compositions. Good yields (above 95%) were obtained in all copolymerisations, with excellent control being achieved over both molecular weight and block copolymer composition. Furthermore, generally good agreement was observed between the theoretical molecular weights and the values from ^{1}H NMR analysis.

3.2. Micellar characteristic

Micellar characteristics of block copolymers were studied by QELS in water and chloroform. PDMAEMA is hydrophilic as well as lypophilic and PFOMA is lipophobic,

Table 1
GTP of DMAEMA and FOMA via sequential monomer addition

Block copolymer	Theor Mn (g mol^{-1})	Obsd Mn^a (g mol^{-1})	Theor molar composition (mol%)	Obsd molar composition^a (mol%)
PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$	10,000	10,400	92:8	92:8
PDMAEMA$_{5.7\ \mathrm{K}}$-*b*-PDHFOMA$_{3.4\ \mathrm{K}}$	9000	9100	86:14	83:17
PDMAEMA$_{5.8\ \mathrm{K}}$-*b*-PTHFOMA$_{6.3\ \mathrm{K}}$	11,000	12,100	79:21	72:28
PDMAEMA$_{4.3\ \mathrm{K}}$-*b*-PTHFOMA$_{5.4\ \mathrm{K}}$	9000	9700	69:31	69:31
PDMAEMA$_{2.5\ \mathrm{K}}$-*b*-PTHFOMA$_{7\ \mathrm{K}}$	9000	9500	44:56	50:50
PDMAEMA$_{2\ \mathrm{K}}$-*b*-PTHFOMA$_{10.7\ \mathrm{K}}$	12,000	12,700	35:65	34:66
PDMAEMA$_{1\ \mathrm{K}}$-*b*-PTHFOMA$_{7.7\ \mathrm{K}}$	8000	8800	28:72	26:74
PDMAEMA$_{1.4\ \mathrm{K}}$-*b*-PTHFOMA$_{12.4\ \mathrm{K}}$	13,000	13,800	19:81	24:76
PDMAEMA-*ran*-PDHFOMA	–	–	66:34	63:37

[a] Calculated from ^{1}H NMR spectrum.

Table 3
Characteristics of PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$ micelles in water at different pH and temperatures

Temperature (°C)	PH	Diameter (nm)[a]	Polydispersity (μ_2/Γ^2)
30	3.72	57	0.063
	8	45	0.164
	11	44.8112	0.841
40	8	40.6648[b]	0.138
50	8	34.8043	0.453
60	8	24.8107	0.761

0.1 wt% polymer solution

[a] Effective diameter at 30 °C.

[b] Minor population.

indicating amphiphilicity of PDMAEMA and amphiphobicity of PFOMA. Thus the copolymer may be expected to form micelles both in aqueous and nonaqueous media. Characteristics of PDMAEMA-*b*-PFOMA micelles are given in Table 2. As expected, PDMAEMA-*b*-PFOMA copolymers were soluble in water and chloroform to form micelles consisting of a core of PFOMA and a shell of PDMAEMA within a range of block compositions. However, when the FOMA content is greater than approximately 31 and 66 mol%, the block copolymers become insoluble in water and chloroform, respectively, which is similar behavior for PEO-*b*-PFOMA [15].

The effects of pH and temperature on the size of the micelles formed by PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$ copolymer have been investigated. The results are shown in Table 3. At pH = 3.14, below pK_a of PDMAEMA (pK_a ~ 8), aggregates of d_h of ca. 57 nm were formed at 30 °C with narrow size distribution. The polydispersity increased as pH increased at constant temperature and at least two populations of aggregates coexisted at pH = 11. Larger aggregates coexisted with small micelles, most likely as a result of the increased association number due to the deprotonation of PDMAEMA. Uncharged PDMAEMA is known for a cloud point at ca. 40 °C [18], hence the micelles consisting of an uncharged PDMAEMA corona may flocculate due to the collapse of the PDMAEMA steric barrier above 40 °C. As may be expected, the micelle size increased dramatically above 40 °C at pH = 8. At and above 50 °C, solution became turbid and very large aggregates of ca. 8 μm were detected along with small micelles.

The morphology of PDMAEMA-*b*-PFOMA copolymer has been examined by TEM for three different block compositions. Fig. 2 depicts the TEM images of the micelles of PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$, PDMAEMA$_{5.7\ \mathrm{K}}$-*b*-PDHFOMA$_{3.4\ \mathrm{K}}$, and PDMAEMA$_{4.3\ \mathrm{K}}$-*b*-PTHFOMA$_{5.4\ \mathrm{K}}$. The dark core regions correspond to the PFOMA in accordance with the higher electron density of the fluorinated block. It is shown in Fig. 2 that the micellar images of PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$ and PDMAEMA$_{5.7\ \mathrm{K}}$-b-PDHFOMA$_{3.4\ \mathrm{K}}$ are uniformly spherical and the average diameter of cores slightly increases with the internal PFOMA block size. In contrast, the larger spheres in deformed crateriform film are observed for the block copolymer of higher PFOMA content, PDMAEMA$_{4.3\ \mathrm{K}}$-*b*-PTHFOMA$_{5.4\ \mathrm{K}}$. It may be suggested that the system becomes unstable at high ratio of core to shell block length and a deformation takes place [14,19]. In our previous work [15], the morphologies were observed to be spherical and rod in chloroform solution of PEO$_{5\ \mathrm{K}}$-*b*-PDHFOMA$_{4.5\ \mathrm{K}}$ and PEO$_{5\ \mathrm{K}}$-*b*-PDHFOMA$_{12.5\ \mathrm{K}}$, respectively. However, rodlike aggregates were not seen for these three PDMAEMA-*b*-PFOMA copolymers of different block ratios.

3.3. Solubility of PDMAEMA-b-PFOMA in CO$_2$

The solubility of PDMAEMA-*b*-PFOMA in dense CO$_2$ was studied in temperature range 30–70 °C and at pressure up to 6000 psi. The results in Fig. 3 indicate that most surfactants are soluble in CO$_2$ in these conditions. It is well-known that fluorinated methacrylate component is very CO$_2$-philic, so the solubility of block copolymers in CO$_2$ increases with the mole fraction of PFOMA. Furthermore, it is found that the block copolymer dissolved at lower pressure and temperature conditions than corresponding random copolymer with the similar mole fraction, which is possibly due to the formation of micelles with a PDMAEMA block in the core and PFOMA forming corona of the micelle in CO$_2$ [20].

3.4. Microemulsion phase behavior

It is reported that stable water-in-carbon dioxide microemulsions are formed with cationic or anionic

Table 2
Characteristics of PDMAEMA-*b*-PFOMA micelles

Block copolymer	Solvent[a]	Diameter (nm)[b]	Polidispersity (μ_2/Γ^2)
PDMAEMA$_{2.5\ \mathrm{K}}$-*b*-PTHFOMA$_{7\ \mathrm{K}}$	Chloroform	105	0.091
PDMAEMA$_{4.3\ \mathrm{K}}$-*b*-PTHFOMA$_{5.4\ \mathrm{K}}$	Chloroform	64	0.066
PDMAEMA$_{5.7\ \mathrm{K}}$-*b*-PDHFOMA$_{3.4\ \mathrm{K}}$	Chloroform	45	0.007
	Water	271	0.071
PDMAEMA$_{8.3\ \mathrm{K}}$-*b*-PTHFOMA$_{2.1\ \mathrm{K}}$	Water	45	0.164

[a] 0.1 wt% polymer solution.

[b] Effective diameter at 30 °C.

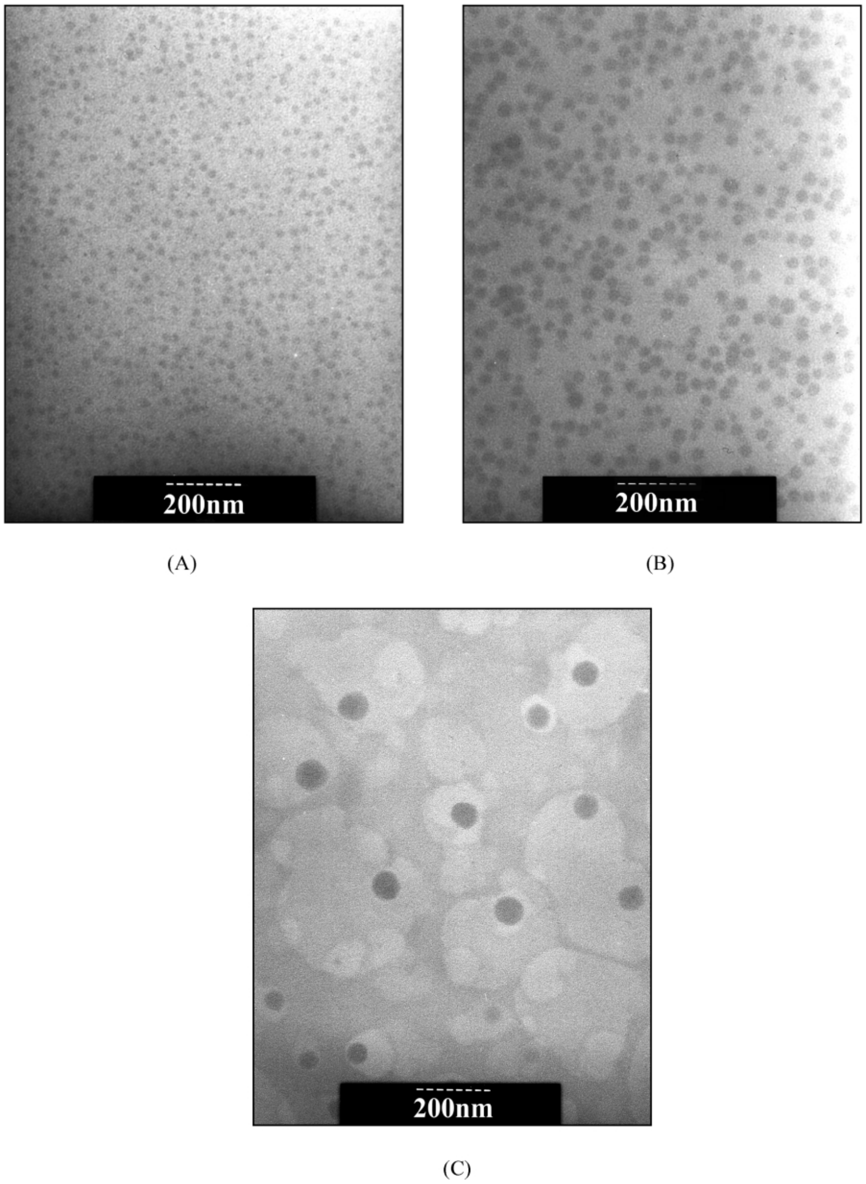


Fig. 2. TEM picture of PDMAEMA-*b*-PFOMA aggregates made in chloroform: (A) $\text{PDMAEMA}_{8.3\text{ K}}$-*b*-$\text{PTHFOMA}_{2.1\text{ K}}$ (B) $\text{PDMAEMA}_{5.7\text{ K}}$-*b*-$\text{PDHFOMA}_{3.4\text{ K}}$ (C) $\text{PDMAEMA}_{4.3\text{ K}}$-*b*-$\text{PTHFOMA}_{5.4\text{ K}}$.

perfluoropolyether surfactants [21,22]. The hydrophilic head groups form a core and CO_2-philic tails interact with carbon dioxide, where the water partitions into the hydrophilic core forming microscopic water pools. Above 31 mol% of PFOMA composition, the bock copolymer is very soluble in CO_2 and has a low solubility in water, thus it is expected to make W/C microemulsions where natural curvature is about water. Moreover PDMAEMA-*b*-PFOMA copolymers may be expected to act in much the same way as cationic perfluoropolyether surfactant because DMAEMA segments are probably protonated in W/C microemulsions whose pH was measured to be about 3 [22]. Cloud point studies confirmed that optically transparent and thermodynamically stable microemusion solutions were formed with the copolymer surfactants. Pressure-temperature phase behavior of W/C microemulsions at $w_0 = 15$ and 30 stabilized by the $\text{PDMAEMA}_{2.5\text{ K}}$-*b*-$\text{PTHFOMA}_{7\text{ K}}$ is represented in Fig. 4. The one-phase microemulsion region is above the curve in the plot. The copolymer stabilized the W/C emulsion with relatively low cloud point. It is also noted that cloud point increases slightly as w_0 increases. The W/C microemulsions may prove to useful for making particles of colloidal dimensions as excellent nanoreactors. In this respect, we have demonstrated the hydrolysis of titanium tetraisopropoxide within W/C microemulsions, that was briefly described earlier [23].

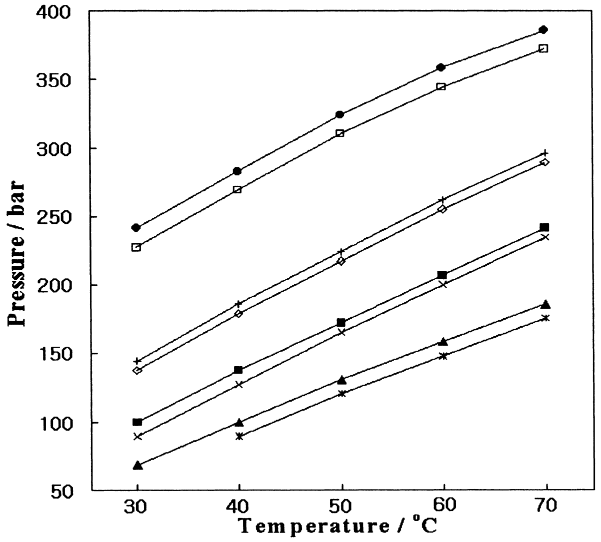


Fig. 3. Cloud point profiles of copolymers in CO_2 at a concentration of 0.25 wt%. (●: $\text{PDMAEMA}_{8.3\ \text{K}}$-*b*-$\text{PTHFOMA}_{2.1\ \text{K}}$, □: $\text{PDMAEMA}_{5.7\ \text{K}}$-*b*-$\text{PDHFOMA}_{3.4\ \text{K}}$, +: PDMAEMA-*ran*-PDHFOMA, ◇: $\text{PDMAEMA}_{4.3\ \text{K}}$-*b*-$\text{PTHFOMA}_{5.4\ \text{K}}$, ■: $\text{PDMAEMA}_{2.5\ \text{K}}$-*b*-$\text{PTHFOMA}_{7\ \text{K}}$, ×: $\text{PDMAEMA}_{2\ \text{K}}$-*b*-$\text{PTHFOMA}_{10.7\ \text{K}}$, ▲: $\text{PDMAEMA}_{1\ \text{K}}$-*b*-$\text{PTHFOMA}_{7.7\ \text{K}}$, *: $\text{PDMAEMA}_{1.4\ \text{K}}$-*b*-$\text{PTHFOMA}_{12.4\ \text{K}}$).

4. Conclusions

Block copolymers containing PDMAEMA block and semifluorinated PFOMA block were synthesized by sequential addition of monomers using GTP. Precise control over molecular weight and copolymer composition was achieved by changing the monomers/initiator ratio. It has been demonstrated that the block copolymers formed stable micelles where PDMAEMA is the shell and PFOMA is the core in both water and chloroform. QELS studies indicated the micellar sizes in water varied depending on the solution pH and temperature. In chloroform, the micellar morphology was observed to be spherical, and their size increased with the ratio of PFOMA to PDMAEMA block length. The solubility of copolymers in CO_2 increased as the mole fraction of PFOMA increased. The formation of water-in-carbon dioxide microemulsions was tested using $\text{PDMAEMA}_{2.5\ \text{K}}$-*b*-$\text{PTHFOMA}_{7\ \text{K}}$ as a stabilizer. The block copolymer exhibited the excellent ability of stabilizing W/C microemulsions at relatively low pressure and temperature.

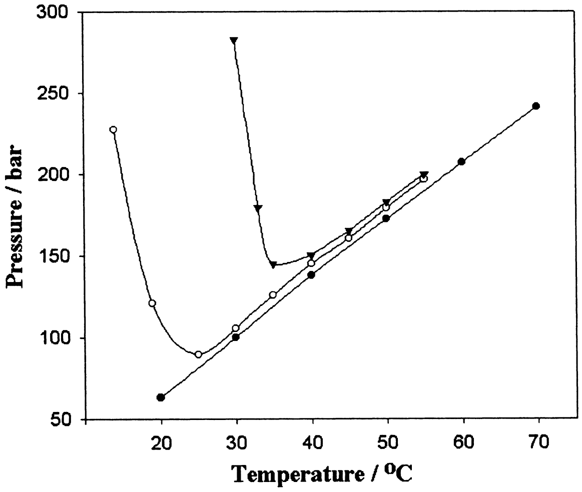


Fig. 4. Phase behavior of the water/$\text{PDMAEMA}_{2.5\ \text{K}}$-*b*-$\text{PTHFOMA}_{7\ \text{K}}$/$CO_2$ system as a function of w_0 at surfactant concentration of 0.25 wt% in CO_2 (●: no water, ○: $w_0 = 15$, ▼: $w_0 = 30$).

Acknowledgements

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