

“Abnormal” Micellization in Compressed CO₂: Solubility of Fluorinated Homopolymer and Block Copolymer

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ABSTRACT

Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) homopolymer, PFDA, and semifluorinated polystyrene-*b*-PFDA block copolymer, PS-*b*-PFDA, were synthesized and tailored by nitroxide-mediated radical polymerization. The solubility of the polymers was investigated in carbon dioxide (CO₂) using cloud point and light scattering techniques. The solvent quality of CO₂ for PFDA homopolymer was shown to increase with CO₂ density and this information coupled with the size of the block copolymer species indicated the formation of PS-*b*-PFDA micelles. “Abnormal” micellization was induced by residual PS homopolymer which remained soluble in PS-*b*-PFDA micelles at low density and induced the formation of a second population of larger aggregates when the solvent quality was improved.

INTRODUCTION

Carbon dioxide (CO₂) is a promising alternative to traditional solvents due to a combination of its easily accessible critical conditions ($T_c = 31.1^\circ\text{C}$, $P_c = 73.8$ bar) and its desirable qualities (i.e. environmentally benign, readily recyclable, and nonflammable). In this context, a variety of CO₂ applications are currently under development including materials synthesis, particle generation and stabilization, foaming, coating, extraction, and submicron lithography [1-3]. Whereas most traditional compounds including polymers and polar species are not CO₂-soluble [4,5], fluoropolymers [6-8] and polysiloxanes [8-11] are at least two classes of polymers readily soluble in CO₂ even at high molecular weight. A handful of reports have investigated the solvent quality variation or the molecular weight, composition, conformation and phase transitions of amphiphilic polymers in CO₂ using tools such as NMR [12] and scattering techniques [11,13-21]. In order to pursue the characterization of molecularly engineered polymeric surfactants compatible with compressed CO₂, we report on the solution properties of poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (PFDA) homopolymer and its associated polystyrene block copolymer (PS-*b*-PFDA) (Figure 1a & b).

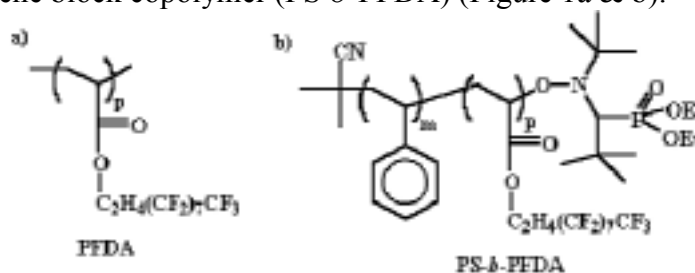


Figure 1 : a) PFDA; b) PS-*b*-PFDA block copolymer.

The CO₂ solubility of PFDA and PS-*b*-PFDA was investigated through both cloud point and light scattering techniques. At 25°C and as a function of density, the CO₂-PFDA chains

interactions were studied, and “abnormal” micellization of PS-*b*-PFDA was evidenced in liquid CO₂.

I – EXPERIMENTAL SECTION

Materials

PFDA homopolymer ($M_{n,P-NMR} = 98.5$ kDalton, determined by ³¹P-NMR chain-end analysis in 1,1-dichloro 1-fluoro ethane F141b) and PS-*b*-PFDA block copolymer ($M_{n,SEC} = 52.3$ kDalton, $M_w/M_n = 1.16$, determined by size exclusion chromatography analysis, and $M_{n,H-NMR} = 49.4$ kDalton (PFDA block) / 3.8 kDalton (PS block) determined by ¹H-NMR analysis in α,α,α -trifluorotoluene) were synthesized by nitroxide-mediated radical polymerization as detailed elsewhere [22,23]. CO₂ (SFC grade, purity 99.99996%, Air Product) and solvents were used as received unless specified.

Characterization

Cloud Point Investigation: The phase behavior of the fluorinated polymers in CO₂ was examined at a constant amount of polymer defined in weight/weight percent (w/w %) by visual observation of the reversible one-phase/two-phases transition in a pressure controlled variable volume view cell.

Light Scattering Investigations: These studies were performed in dilute regime with an homemade light scattering cell, using an argon ion laser source (Coherent) in conjunction with a computer controlled motor-driven variable angle detection system (Brookhaven Instruments). Because of the small size of the PFDA chains the experiments were performed around $\theta = 90^\circ$, the polymer concentration dependence of the excess Rayleigh ratio, $R(C)$, is [24]:

$$\frac{KC}{R(C)} = \frac{1}{M_w} (1 + 2M_w A_2 C + \dots) \quad (1)$$

where A_2 is the second virial coefficient, related to the relative strength of the polymer-polymer versus polymer-solvent interactions, M_w is the weight average molecular weight, and K is an optical constant defined as:

$$K = 4\pi^2 n_s^2 (dn/dC)^2 / \lambda^4 N_A \quad (2)$$

where dn/dC is the refractive index increment of the polymer measured in CO₂, and N_A is Avogadro’s number. For small concentrations of PS-*b*-PFDA, the interaction contribution can be neglected and the dn/dC of the block copolymer is given by the combination of the weight fraction, w , and the refractive index increment of each block [25]:

$$dn/dC = w_{PFDA} (dn/dC)_{PFDA} + w_{PS} (dn/dC)_{PS} \quad (3)$$

The PS block dn/dC values were approximated by linear interpolation, $dn/dC \approx (n_s - n_{PS}) / \rho_{PS}$, with n_{PS} and ρ_{PS} the refractive index and the density of the PS block, respectively [26].

In Dynamic Light Scattering experiments, the wave vectors, q was calculated as $4\pi n_s \sin(\theta/2)/\lambda$, where θ is the scattering angle, n_s is the carbon dioxide refractive index measured at the appropriate density, and $\lambda = 514$ nm is the laser wavelength. The experimental time autocorrelation function of the scattered intensity was expressed in terms of the field autocorrelation function of the polymer concentration fluctuations, $g^{(1)}(q,t)$ [24]:

$$g^{(1)}(q,t) = \langle \delta C^*(q,0) \delta C(q,t) \rangle / \langle \delta C(q,0)^2 \rangle = \sum \alpha_i \exp(-t / \tau_{ci}) \quad (4)$$

where $\delta C(q,t)$ and $\delta C(q,0)$ represent the fluctuations of the polymer concentration at time t and zero, respectively. In the case of a solution having a multimodal particle size distribution, $g^{(1)}(q,t)$ can be decomposed into a sum of exponentials with α_i , the relative proportion of each

particle's population, and τ_{ci} , its associated characteristic time. The mutual diffusion coefficient $D_c = 1/\tau_c q^2$ varies linearly with the polymer concentration, $D_c = D_o(1+k_d C + \dots)$, with k_d the diffusional second virial coefficient. The translational diffusion coefficient of the polymer, D_o , is related to the hydrodynamic radius, R_h , through the Stokes-Einstein relation, $D_o = kT / 6 \pi \eta_s R_h$, where k is the Boltzmann constant, T is the absolute temperature, and η_s is the solvent viscosity which is a function of both temperature and solvent density [27].

II - RESULTS AND DISCUSSION

Cloud point curves are commonly used to obtain a picture of the CO₂ soluble species, and are typically represented as a plot of pressure versus temperature [4,7]. Figure 2 shows the cloud point curves of both PFDA and PS-*b*-PFDA, demonstrating their general CO₂ solubility. The decreasing CO₂ density required to solubilize the polymeric species as temperature increases was present for both series. At 25 °C, the density required to solubilize PS-*b*-PFDA is higher than the density needed to solubilize the PFDA chains, which was expected since PS is essentially insoluble in CO₂ [4]. These results coupled with observations of similar amphiphilic systems in CO₂ [14,28] suggest that PS-*b*-PFDA presented herein forms micelles with a PS-core and a PFDA-shell.

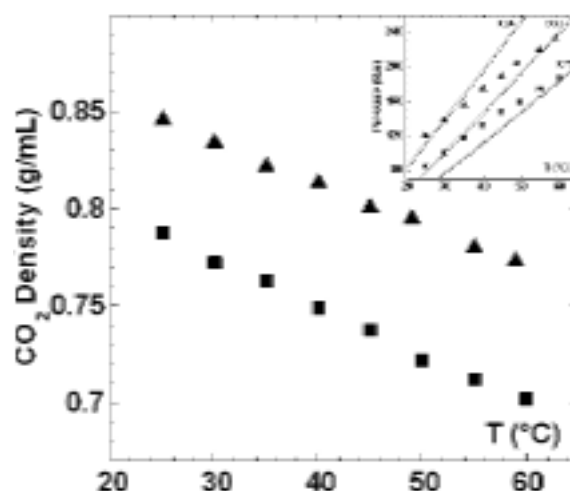


Figure 2 : Cloud point densities as a function of temperature for PFDA homopolymer (■) and PS-*b*-PFDA block copolymer (▲), performed at 3.9 %w/w in neat CO₂. (Inset: Cloud point pressures).

The PFDA weight average molecular weight, M_w , was calculated with $R(C)$ extrapolated at zero concentration and with the experimental variation of the refractive index increment shown in Figure 3A. $M_{w,SLS} = 147 \pm 15$ kDalton stands for the average value and the deviation from this average M_w over the investigated CO₂ densities. The isotherm plot in Figure 3B of $M_w A_2$ against increasing density indicates better solvent quality is reached for PFDA at higher CO₂ densities. The Theta point is associated with the limit above which the polymer is favourably dissolved in CO₂ regardless of its molecular weight. For PFDA at 25°C, the theta density, corresponding to $M_w A_2 = 0$ mL/g, is around 0.89 g/mL (160 Bar) consistent with the fact that linear fluorinated polymers are CO₂-soluble even at high molecular weight. Below this theta point and above the cloud point density (≈ 0.79 g/mL), the polymer is kept in solution because of entropic contributions on the small sized PFDA chains [24]. The quantitative improvement of the solvent quality revealed by the positive second virial coefficient above the Theta conditions can not however be extrapolated to higher CO₂

densities as recently highlighted with PDMS-CO₂ solutions [10,11], where an increase in CO₂ density was shown to first improve and then reduce the CO₂ solvent quality.

The field autocorrelation functions, $g^{(1)}(t)$, obtained by dynamic light scattering in PFDA-CO₂ solutions were all characterized by a single exponential behaviour (Figure 4A), with a characteristic time, τ_c , inversely proportional to q^2 . Because of their small hydrodynamic radius, $R_{h,PFDA} = 4.8 \pm 0.5$ nm, the PFDA chains did not show a variation larger than 10%, and no swelling was experimentally observed when the solvent quality was tuned.

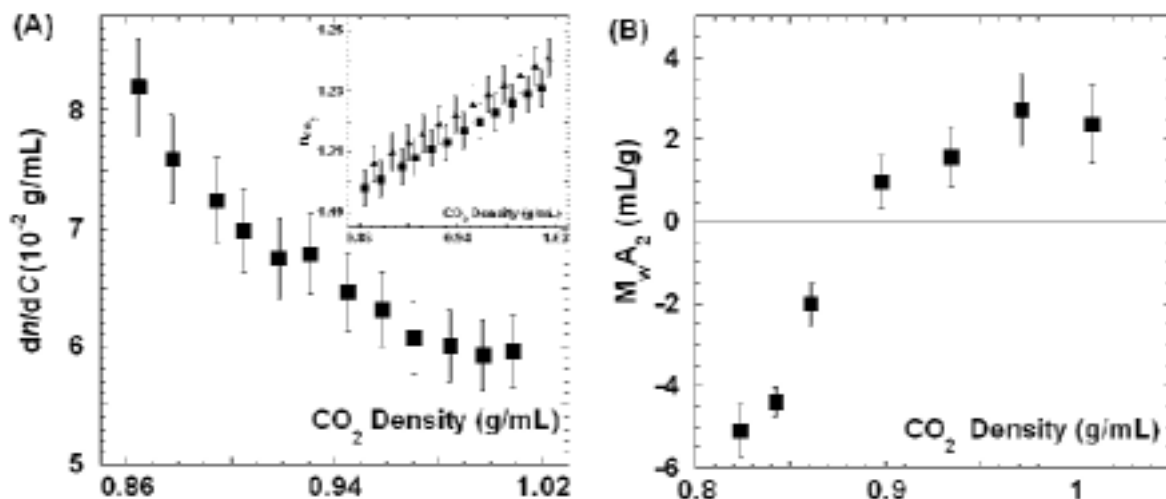


Figure 3 : PFDA solution at 25°C. As a function of CO₂ density (A) dn/dC with error bars of 5% (Inset : CO₂ refractive index determined experimentally (■) and calculated [29] (▲), both plotted with error bars of 0.5% for illustration purposes), (B) weight average molecular weight times second virial coefficient.

With the PS-*b*-PFDA diblock at low CO₂ density (0.87 g/mL), the exponential autocorrelation function was characterized as expected by a single characteristic time, τ_c , inversely proportional to q^2 (Figure 4B). The deduced hydrodynamic radius of the diblock, $R_{h,PS-b-PFDA} = 17 \pm 1$ nm, is much larger than the size of the PFDA component confirming the formation of PS-*b*-PFDA micelles. The aggregation number, p , was assessed with the ratio of the average mass of the micelle, $M_{micelles}$, to the mass of a copolymer chain $M_{unimers}$ [17,30] and by neglecting the effects both of the second virial coefficient between the micelles and of the end-group reported for other short polymers [25,31]. At 25°C and for the lowest densities investigated in this study, p was found to be around 250 unimers per micelle. Because of the approximations, this approach only gives an upper value whose order of magnitude is in reasonable agreement with micelle CO₂ solutions of PTAN-*b*-poly(vinyl acetate) ($p \approx 125 \pm 5$, $R_h \approx 15.3 \pm 1$ nm) and PFOA-*g*-poly(ethylene oxide) ($p \approx 120$, $R_g \approx 17.4$ nm) [17,32].

Above the theta point of PFDA, the autocorrelation functions of PS-*b*-PFDA started to deviate from the single exponential behaviour (Figure 4B) indicating that a second population of larger aggregates was formed. The polydispersity of both the micelles and the aggregates were neglected and the autocorrelation functions measured for various carbon dioxide pressures were fitted with a double exponential. Even though the number of fitting parameters, the time window available for these measurements and consequently the limited amplitude of the decay of the autocorrelation functions limited the accuracy associated with determining the order of magnitude of the aggregates size, it was found to be at least 30 times larger than the initial micelles size.

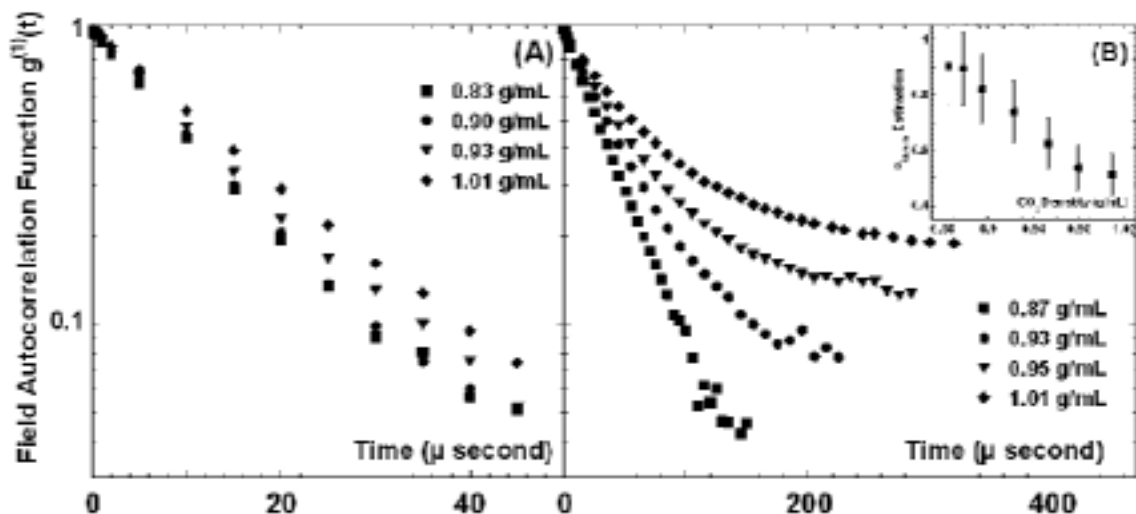


Figure 4 : Variation of the normalized field autocorrelation functions, $g^{(1)}(t)$, with time and CO_2 density solution at 25°C with 51° as a detection angle (A) PFDA concentration 0.031g/mL, (B) PS-*b*-PFDA concentration 0.0018g/mL (Inset: Estimation of the micelles population variation with CO_2 density).

The decay of the micelle population α_i with the increase of the CO_2 -density is shown in Figure 4B where 15% error bars were added for illustrative purposes. From a qualitative point of view, when the solvent quality is improved, the PFDA becomes more soluble, the micelles start to break up and the PS-blocks, which were initially protected inside the micelles, are more exposed to CO_2 . The observation of larger aggregates instead of the formation of unimers are in good agreement with results from a recent micellization study of diblock copolymer solutions [33], where a solvent-phobic homopolymer residue as low as 1 wt % within the sample influenced a drastic size increase of polymeric aggregates when the solvent quality was tuned and the micelle-to-unimers transition was approached [33]. Below the micelle-to-unimer transition, the solvent-phobic homopolymer is solubilized inside the micelles and it has no discernable effect on the solution properties of the sample; close to the micelle-to-unimer transition, part of the diblocks having the longest soluble chains are released as unimers and the formation of large aggregates is attributed to the flocculation of particles poorly stabilized by the diblock and rich in solvent-phobic homopolymer. Despite the fact that the PS-*b*-PFDA sample was purified by Soxhlet extraction to minimize the extent of PS homopolymer residue, trace amounts of the homopolymer induced the observed “abnormal” micellization. Consequently, the $g^{(1)}(t)$ behaviour and the population change of PS-*b*-PFDA based aggregates with increasing density likely correspond to the flocculation of PS homopolymer particles poorly stabilized by the increasingly soluble PS-*b*-PFDA diblock copolymer.

Moderate temperature and pressure imposed by the setup prevented studying the micelle-to-unimer transition for PS-*b*-PFDA; however, poly(vinyl acetate)-*b*-PFOA in CO_2 solution has demonstrated a similar size increase close to the micellar transition [13,16,20]. In addition, the micelle-to-unimer transition has been suggested for PS-*b*-PFOA [21], and demonstrated for poly(vinyl acetate)-*b*-PTAN [17], however the formation of large aggregates has not been reported. These results obtained in various diblock- CO_2 systems reemphasize the role of polymer chemistry and characterization to interpret the behaviour of block copolymers in carbon dioxide.

CONCLUSION

Nitroxide-mediated radical polymerization was used to synthesize both PFDA homopolymer and the semifluorinated block copolymer PS-*b*-PFDA. At 25°C, the solvent quality for the PFDA homopolymer was shown to increase with CO₂ density. It was demonstrated that the soluble block copolymers formed micelles in CO₂ with PFDA in the outer shell and PS in the core. Although solubilized in the core of the PS-*b*-PFDA micelles at low CO₂ density, very low amounts of PS homopolymer residue induced the formation of a second population of larger aggregates at higher CO₂ density when the micelle-to-unimers transition is approached.

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