

SYNTHESIS AND LIGHT SCATTERING OF FLUORINATED AND SILOXANE-BASED POLYMERS IN COMPRESSED CARBON DIOXIDE

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Traditionally, the macroscopic solubility of a polymer in compressed carbon dioxide (CO₂) is visually determined, but the behavior of the individual chains is neglected. In this work, the mass and the second virial coefficient (A_2), a thermodynamic parameter corresponding to the extent of the polymer-polymer versus the polymer-solvent interactions, were determined for samples of poly(1H,1H-perfluorooctyl methacrylate) (PFOMA), poly(Zonyl TM), and poly(dimethylsiloxane) (PDMS) in compressed CO₂ using high pressure static light scattering at various temperatures and pressures. In addition, dynamic light scattering was used to determine the size of the chains in solution.

INTRODUCTION

As the negative impact of extensive water and traditional organic solvent use becomes more apparent, researchers look for environmentally friendly solvent alternatives. Carbon dioxide is nontoxic, nonflammable, easily recycled, and relatively inexpensive. A convenient advantage of the utilization of scCO₂ as compared to other SCFs, is its readily accessible critical temperature and pressure ($T_{\text{critical}} = 31 \text{ }^\circ\text{C}$; $P_{\text{critical}} = 73.8 \text{ bar}$) [1].

Amorphous fluoropolymers and polysiloxanes both exhibit appreciable solubility in compressed CO₂. The most commonly used method to determine their solubility is cloud point measurements. To knowledgeably use these species in applications, however, it is necessary to have an understanding of the interactions with the solvent. The extent of solubility of individual polymer chains in any solvent is dependent upon the relative strengths of the polymer-polymer, solvent-solvent, and polymer-solvent interactions. The net interaction between two polymer chains serves to classify the solvent as a “good,” “theta (?),” or “poor” solvent for a particular polymer at specified conditions. This interaction is known through the determination of the second virial coefficient, A_2 .

The chain size of PDMS has been investigated with small angle neutron scattering (SANS) in CO₂ as a function of temperature and pressure [2-5], and the researchers concluded that a theta temperature and pressure could be determined. The acrylate analog of PFOMA has also been preliminarily investigated with SANS in CO₂ to determine chain size and A_2 [6]. Light scattering in CO₂ has been performed on poly(*t*-butyl methacrylate)-*b*-PFOMA [7] and poly(vinyl acetate)-*b*-poly(Zonyl TA-N) [8] with a focus on micellar phase transitions. A systematic study to determine A_2 over an applicable temperature and pressure regime, however, has not previously been conducted.

MATERIALS AND METHODS

PFOMA was synthesized by atom transfer radical polymerization of 1H,1H-perfluorooctyl methacrylate (FOMA) (provided by 3M) in *a,a,a*-trifluorotoluene using methyl 2-bromopropionate, CuCl, Cu(0), and dRf₆bpy [9]. Poly(Zonyl TM) (provided by DuPont)

was synthesized in CO₂ by free radical polymerization with AIBN, and was subsequently fractionated by supercritical fluid extraction in CO₂ [10]. PDMS was purchased from Polymer Standards Service or synthesized by living anionic polymerization. Carbon dioxide (SFC/SFE grade) was kindly provided by Air Products and used as received.

Instrumentation. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n , with respect to polystyrene standards (Polymer Laboratories, Inc.) using toluene as the eluent. ¹H NMR spectra for determination of molecular weights were obtained on a Bruker Avance 400. Fluoropolymer spectra were run in 1,1,2-trichlorotrifluoroethane with a capillary of chloroform-d for the lock.

Dynamic and static light scattering experiments were performed with a spectrometer equipped with an argon ion laser (Coherent Innova 70C) operating at $\lambda = 514$ nm and a BI-9000AT digital auto correlator. Two variable volume high pressure cells (<450 bar), designed and manufactured at the University of North Carolina, were implemented for measurements conducted in CO₂. When the refractive index of CO₂ = 1.2, the cells possess wave vector (Q) ranges of 0.10 to 0.28 Å⁻¹ (over three separate windows) and 0.10 to 0.27 Å⁻¹ (for one single window) for cells with volumes of 8.8 to 58.1 mL and 10.6 to 52.6 mL, respectively.

RESULTS AND CONCLUSION

The mass, size, and second virial coefficients for amorphous fluoropolymers and siloxane-based polymers can be determined by light scattering in compressed CO₂. Determination of the solubility properties of these species is important for intelligent application to surfactant systems as well as processes such as “dry” photolithography [11].

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