

Phase Behavior and Viscosities of Linear and Star Methacrylate Copolymers in a Supercritical Fluid

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ABSTRACT

Recent literature studies on the architectural effects of star polymers on the resultant solution behavior compare the behavior of star polymers with their linear analogue polymers dissolved in liquid solvents. These studies report data on the second virial coefficient, the radius of gyration, and the upper critical solution temperature with incompressible good quality, theta quality, and poor quality liquid solvents at ambient pressure. Star (sPS) and linear polystyrene (lPS) are mostly used for these studies since these polymers are available with narrow molecular weight distribution. Interestingly greater solubility was found for sPS in a poor liquid solvent while lPS has a greater solubility in a good solvent. However, the solvent quality for a liquid is sufficiently high to mask the potential differences in the solution behavior of a star and linear analogue polymer. Rather than use an incompressible fluid with sPS and lPS, this talk reports the differences in lauryl methacrylate (LMA) -*co*- methyl methacrylate (MMA) copolymers in propane, a highly compressible, supercritical fluid solvent that magnifies the impact of polymer architecture on solubility and solution viscosity. The synthesized star copolymers in this talk are first fractionated with supercritical fluids to obtain purified samples with narrow molecular weight distributions. A high-pressure, variable-volume view cell and a high-pressure, rolling-ball viscometer are used for the solution behavior and viscosity determination, respectively, at temperatures to 250°C and pressures to 250 MPa. Conclusions are presented on the impact of the amount of LMA in each copolymer arm and the molecular weight of the linear and star copolymers on the observed solution and viscosity behavior.

INTRODUCTION

Over the past few decades the advent of new chemistries has led to the creation of polymers with unique, well-defined architectures, such as star polymers with a fixed number of branches or, in other words, arms. Star polymers, with low to moderate molecular weight arms, have a globular structure that does not promote chain entanglements. Star polymers can be synthesized from a large range of homopolymer, block, and copolymer arms that can also contain functionalized groups. Once the star polymer is synthesized the functional groups can be readily modified to adjust their physical properties for specific applications in the areas of catalysis, coatings, lubrication, membrane formation, and drug delivery. Despite their increasingly mature applications, some fundamental physical properties, such as phase behavior and viscosities, are still lacking and an accurate prediction of these properties over wide ranges of temperatures and pressures remains a challenge.

The present study reports the phase behavior for star polymer with poly(lauryl methacrylate-*co*-methyl methacrylate) (LMA-MMA_x where x represents the mole percent MA) arms in supercritical propane. The star polymer is first fractionated to recover "free" LMA-MMA_x

arms from the parent solution and to obtain star polymer fractions with low molecular weight polydispersity indices. Experiments are performed with the "free" LMA-MMA_x arms and the star polymers to elucidate the impact of the star morphology and molecular weight on the phase behavior in supercritical propane and the viscosity in liquid hydrocarbons.

MATERIALS AND METHODS

Star polymers and the LMA-MMA_x copolymer arms are synthesized using reversible addition-fragmentation-transfer (RAFT) method [1]. The star polymers are donated by Afton Chemical Corporation and are fractionated prior to use. The molecular weight and molecular weight distribution are obtained with gel permeation chromatography (GPC, columns calibrated with IPS standards and tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at ~ 313 K (40°C)). LMA to MMA mole ratio in the copolymer arms and other chemical structure information are obtained using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy.

Fractionation of the parent polymer is performed to extract the free arms not attached to the star polymers and to reduce the polymer molecular weight distribution. Figure 1 shows a schematic diagram of the fractionation system, described in detail elsewhere [2]. Typically 10 to 20 grams of polymer are charged to a column interspersed with stainless steel packing. Propane is pressurized (Newport Scientific Inc., Model 46-13421-2) to ~70 MPa, and charged to a surge tank. The propane is then throttled through an in-line pressure regulator to obtain the desired operating pressure, to within ± 0.5 MPa, delivered to a preheat column, and to the polymer column maintained at a fixed temperature, to within ± 1.0 K. The SCF solvent, loaded with extract, exits the column and is throttled to atmospheric pressure, which causes the extract to precipitate into a preweighed, side-arm beaker.

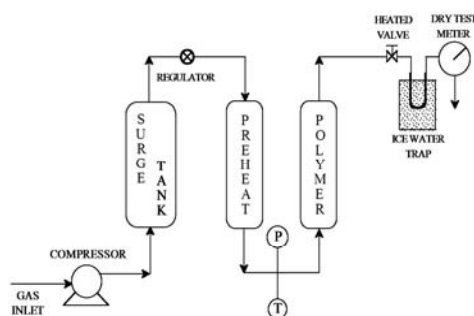


Figure 1. Schematic diagram of high-pressure fractionation system used in this study.

High-pressure phase behavior is performed using a variable-volume, view cell shown in Figure 2 and described in detail elsewhere [3, 4]. Phase equilibrium data are determined for mixtures with polymer at 5.0 ± 0.5 wt% in propane. The mixture in the cell is projected on a video monitor using a camera (Olympus Corporation, Model STC-N63CJ) connected to a borescope (Olympus Corporation, Model F100-024-000-55) placed against a sapphire window secured at one end of the cell. The mixture is isothermally compressed to a single phase and the pressure is then decreased incrementally and held constant for approximately 10 minutes. If the mixture remains clear, the pressure is decreased further until the mixture begins to get hazy (P_{hazy}). The pressure is further decreased, stepwise, until the mixture becomes so opaque that the piston is not visible (P_{opaque}). The cloud-point pressure is the midpoint between P_{hazy} and P_{opaque} .

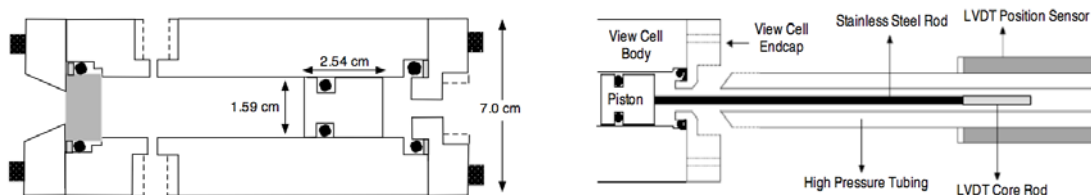


Figure 2. Variable-volume view cell for high-pressure phase behavior determination.

A windowed, variable-volume, rolling ball viscometer is used for the high-pressure viscosity determination. Figure 3 shows the schematic diagram of the viscometer and details on the apparatus and technique can be found elsewhere [5].



Figure 3. Schematic diagram of high-pressure, variable-volume, rolling ball viscometer.

RESULTS

Figure 4 shows the GPC chromatograms for one of the parent star polymer-oil mixtures, which has a polymer peak centered at $\sim 417,000$, an LMA-MMA_x arm peak centered at $\sim 46,000$, and an oil solvent peak. In this study, the temperatures (T) and pressures (P) for effective fractionation are based on the conditions needed to dissolve the oil solvent and the star polymers in propane, the fractionation solvent. Figure 5 shows the P-T conditions needed to dissolve ~ 5 wt% oil solvent in propane and in CO₂, two typical fluids used for supercritical fractionation. The P-T traces of the fluid \rightarrow liquid + liquid boundaries exhibit the same characteristics observed for other propane-saturated hydrocarbon and CO₂-saturated hydrocarbon binary mixtures. The oil solvent easily dissolves in propane and the dissolution pressure increases with an increase in temperature. In contrast, the solvent-CO₂ phase transition pressure increases dramatically at temperatures below 325 K. These results suggest that propane can extract the oil solvent at lower pressures, while higher pressures are needed for CO₂ to effectively remove the oil solvent from the parent star polymer polymers. Therefore, in this study, supercritical propane is used for fractionation. Figure 6 shows the GPC chromatograms for the star polymers after extracting the oil solvent. It is obvious that only the star polymer peak and LMA-MMA_x arm peak exist. Further fractionation results will be presented in the poster to remove the LMA-MMA_x arm and reduce the molecular weight distribution of the star polymer.

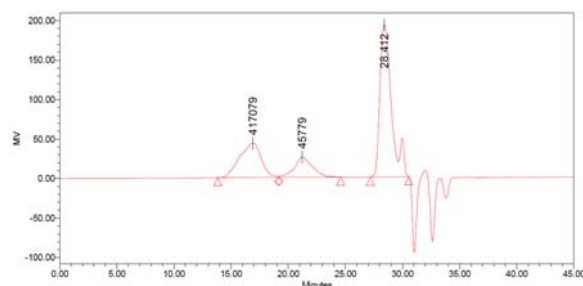


Figure 4. GPC chromatograms of parent star polymer-oil mixtures.

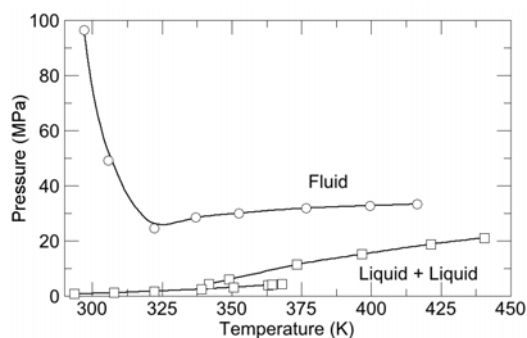


Figure 5. Phase diagram of ~5 wt% oil solvent in propane (□) and PN solvent in CO₂ (○) obtained in this study. Solid lines are used to guide the eyes.

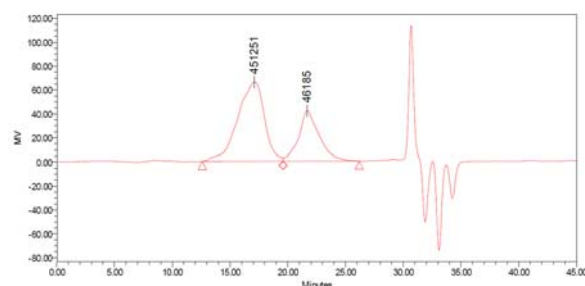


Figure 6. GPC chromatograms of parent star polymer without oil solvents.

Figure 7 shows the phase behavior of typical arms in propane. Four linear homopolymer and copolymers, PLMA ($M_w = 80,000$), LMA-MMA₃₅ ($M_w = 45,000$), LMA-MMA₅₀ ($M_w = 28,000$), and LMA-MMA₅₀ ($M_w = 130,000$), are used to represent typical arms to investigate the effects of polymer backbone structure and molecular weight on the phase behavior. Figure 7 also shows the cloud-point curve for ~5 wt% PLMA ($M_w = 250,000$) in propane from Liu *et al.* [6] for comparison to the data in the present study. The cloud-point pressures from Liu *et al.* are only slightly higher than those exhibited by the PLMA ($M_w = 80,000$)-propane system, suggesting that the effect of M_w has already reached a point of saturation on the phase behavior for this binary mixture.

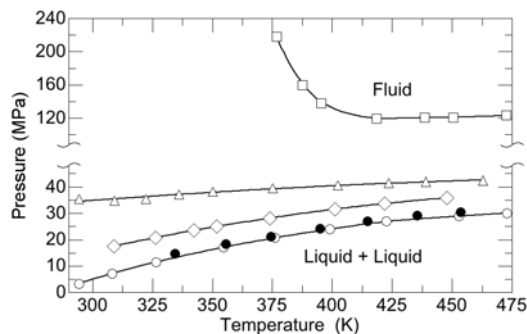


Figure 7. Cloud-point curves for ~5 wt% PLMA ($M_w = 80,000$) (○), LMA-MMA₃₅ ($M_w = 45,000$) (◇), LMA-MMA₅₀ ($M_w = 28,000$) (△), and LMA-MMA₅₀ ($M_w = 130,000$) (□) in propane obtained in this study and PLMA ($M_w = 250,000$) (●) in propane from Liu *et al.* [6]. Solid lines are used to guide the eyes.

Polymer backbone architecture has a more significant effect on the phase behavior for the polar polymer-nonpolar solvent, binary mixture considered here than does polymer M_w . Consider first the phase behavior of the LMA-MMA_x copolymer-propane mixtures. The cloud-point curves for PLMA, LMA-MMA₃₅ ($M_w = 45,000$), and LMA-MMA₅₀ ($M_w = 28,000$) shift to higher pressures as MMA is incorporated randomly into the backbone of the polymer. Note also that the shift to higher pressures is opposite to that expected based on polymer M_w , indicating that polymer-solvent interactions have a larger effect on the conditions needed to dissolve these polymers than does molecular weight. The polarity of the ester group, per molar volume, is reduced in LMA due to the size of the non-polar dodecane tail, relative to MMA, with a short methyl tail. In fact, PMMA, with an M_w of only 15,000, does not dissolve in propane even to temperatures to 473 K and pressures to 200 MPa verifying that MMA-rich copolymers are harder to dissolve in nonpolar propane compared to LMA-rich copolymers. Figure 4 also shows the cloud-point curve for LMA-MMA₅₀ ($M_w = 130,000$) in propane obtained in this study. In this instance the curve exhibits a sharp increase in pressure at temperatures less than ~400 K. It is likely that the cloud-point curves for the other LMA-MMA_x copolymers also exhibit sharp increases in pressure at temperatures colder than 300 K, which is outside the range for the apparatus used in this study. As the copolymer molecular weight increases, the size asymmetry with propane increases and the number of propane-MMA interactions per unit volume also increases. Hence, the cloud-point curve shifts to higher pressures, due primarily to a size disparity, and to higher temperatures, due primarily to a mismatch in energetics.

The star polymers used in this study have a unique structure, with a polymer core and with LMA-MMA_x copolymer arms. The phase behavior of star polymers in propane will be presented in the poster. The architectural effect on the phase behavior for the star polymers will be also be presented in detail in the poster.

Figure 8 shows a preliminary results for the viscosity data of n-octane and a star polymer-octane mixture with ~5 wt% star polymer at the temperature of 296 K and pressures to 120 MPa. More details about the viscosity data and the architectural effects on the viscosities will be presented in the poster.

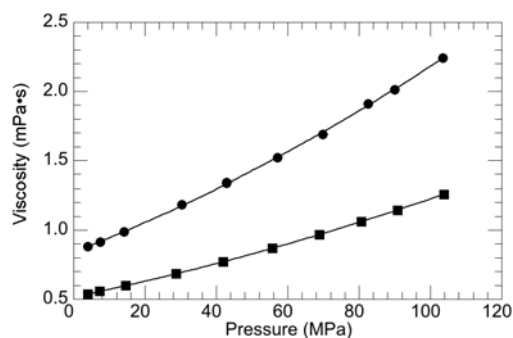


Figure 8. Viscosity data of n-octane (■) and ~5 wt% star polymer-octane mixtures (●) at the temperature of 296 K and pressures to 120 MPa.

CONCLUSION

The star polymers investigated in this study have a unique structure with a core and copolymer arms. Such a unique structure affects the phase behavior and viscosities compared with its linear analogue. In this study, phase behavior and viscosities are determined for the star polymer and its linear copolymer arms in hydrocarbon solvents at high pressures. The architectural effects for the star polymer will be highlighted in the poster.

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