Cloud-Point Behavior of Poly(ethylene-*co*-20.2 mol %-1-Butene) (PEB_{10}) in Ethane and Deuterated Ethane and of Deuterated PEB_{10} in Pentane Isomers

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High-pressure phase behavior data are reported for statistically random poly(ethylene-*co*-20.2 mol %-1-butene) (PEB_{10}) in ethane and deuterated ethane from ambient temperature to 155 °C and pressures to 130 MPa. The two cloud-point curves exhibit negative slopes in pressure−temperature ($P-t$) space with the PEB_{10}-deuterated ethane curve at higher pressures than the curve in ethane. Data are also reported for statistically random deuterated PEB_{10} (d-PEB_{10}) in *n*-pentane, isopentane, neopentane, and cyclopentane. Solvent quality orders as cyclopentane > *n*-pentane ≥ isopentane > neopentane, which is also the same ordering of the solvent critical temperatures. The d-PEB_{10}−cyclopentane cloud-point curve has a steep positive $P-t$ slope of ≈ 0.28 $MPa\cdot°C^{-1}$ near 200 °C. The d-PEB_{10}−*n*-pentane and isopentane curves also have positive $P-t$ slopes of ≈ 0.16 $MPa\cdot°C^{-1}$ at temperatures between (≈ 100 and 200) °C and pressures to ≈ 15 MPa. The curve for the d-PEB_{10}−neopentane system is virtually flat at a fixed pressure of ≈ 20 MPa from (200 to ≈ 30) °C, where the curve changes abruptly to a positive slope of ≈ 1.65 $MPa\cdot°C^{-1}$. The positive-slope portion of this cloud-point curve represents solid + liquid to fluid transitions where the neopentane is the solid phase not the d-PEB_{10}, which is amorphous.

Introduction

Radiation scattering techniques, such as small angle neutron scattering (SANS) and dynamic light scattering (DLS), are being used to characterize intra- and intermolecular interactions of a polymer in supercritical fluid (SCF)[1,2] and liquid solvents[3–5] at high pressures. These techniques complement more conventional phase behavior studies performed to map the $P-t$ behavior of polymer−solvent mixtures. The macroscopic phase behavior studies provide information on the location of the single-phase region where these radiation techniques can be applied. Information on the radius of gyration of a single chain in a solution at high polymer concentration can be obtained with SANS using an isotopic labeling technique that requires the mixing of protonated and deuterated polymer in a deuterated solvent at prescribed concentrations. SANS and DLS data have been reported for poly(ethylene-*co*-20.2 mol %-1-butene) (PEB_{10}) in a variety of SCFs.[1,2,6–8] For these radiation scattering studies, experimental phase behavior information is needed for PEB_{10} and deuterated PEB_{10} (d-PEB_{10}) in different solvents.

DiNoia showed that the cloud-point curves for PEB_{10} in pentane and d-pentane exhibit positive slopes and intersect the liquid−liquid−vapor curve for each mixture at ≈ 110 °C.[1] In this instance, the slopes of both cloud-point curves are similar to those reported for binary mixtures of PE in pentane[9–12] and for poly(isobutylene) in alkane solvents.[13] The slope of the curve with deuterated pentane is slightly higher than that with protonated pentane, which means it takes slightly higher pressures to obtain a single phase with the deuterated solvent. Differences in cloud-point pressures are expected since replacing hydrogen with deuterium affects the magnitude of the intermolecular pair potential energies and the interchange energy of mixing a polymer segment with a solvent. Rabinowich[14] shows that the magnitude of dispersion interactions decreases when a deuterium is substituted for hydrogen since the shorter C−D bond length compared to a C−H bond reduces the segment volume and the segment polarizability. In addition, Bates and co-workers[15,16] also show that isotopic labeling causes nonideal behavior for mixtures of high molecular weight polymers.

The high-pressure phase behavior data reported here for PEB_{10} in ethane and deuterated ethane demonstrate the effect of solvent deuteration on the cloud-point curve for mixtures with a protonated polymer. The high-pressure phase behavior data reported for d-PEB_{10} in cyclopentane, *n*-pentane, isopentane (2-methyl butane), and neopentane (2,2-dimethyl propane) demonstrate the effect of the molecular structure of the solvent on location of the cloud-point curve. Table 1 shows selected physical properties for the protonated solvents used in this study.

Experimental

Described elsewhere are details on the apparatus and techniques used to obtain polymer−solvent cloud-point data.[17,18] The main component of the experimental apparatus is a high-pressure, variable-volume cell (Nitronic 50, 7.0 cm o.d., 1.5 cm i.d., and ≈ 15 cm^3 working volume). Solid polymer is first loaded into the cell to within ± 0.0001 g, and then the cell is carefully purged with gaseous solvent (or with vapor if the solvent is a liquid) three times at pressures less than 0.3 MPa to remove trace amounts of air. The solvent of interest is then added to the cell, to within ± 0.01 g, using a high-pressure bomb or using a syringe if the solvent is a liquid at room

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Table 1. Critical Properties of the Solvents Used in This Study[26]

solvent	t_c/°C	P_c/MPa	V_c/cm^3·mol^{-1}
ethane	32.2	4.87	146
n-pentane	196.5	3.37	304
isopentane (2-methyl butane)	187.3	3.38	306
neopentane (2,2-dimethyl propane)	160.6	3.20	307
cyclopentane	238.5	4.51	260

temperature. The solution in the cell is stirred using a stir bar controlled by a magnet located beneath the cell. The contents of the cell are projected onto a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-024-000-55) placed directly against the sapphire window. The solution temperature is measured to within ± 0.1 °C with a type K thermocouple (calibrated against a NIST certified thermometer) immersed directly in the solution and is held constant to within ± 0.3 °C. The system pressure is measured with a Heise pressure gauge (model CM-57303) with an uncertainty of ± 0.2 MPa for pressures to 60 MPa and with a pressure transducer (Viatran model 245) with an uncertainty of ± 0.4 MPa for pressures up to 300 MPa. The mixture in the cell is compressed to a single phase, and the pressure is then slowly decreased until a second phase appears. Fixed polymer concentrations of (4.3 and 4.8) wt % are used for PEB_{10} in ethane and d-ethane, respectively, since data close to the mixture-critical concentration are used for the SANS studies.[1,3–5,7] Fixed polymer concentrations of ≈ (0.15 to 1.9) wt % are used for d-PEB_{10} in *n*-pentane, isopentane, neopentane, and cyclopentane since very dilute solution data are needed for DLS studies. The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. These cloud points have been compared in our laboratories to those obtained with a laser light source where the phase transition is the condition of 90 % reduction in transmitted laser light through (15 to 20) mm of solution at noncritical concentrations. Both methods gave identical results within the reproducibility of the data. Cloud points are reproduced two to three times to within approximately ± 0.4 MPa.

Materials. Ethane (99.0 % minimum purity), *n*-pentane (99.0 % minimum purity), and cyclopentane (99.0 % minimum purity) were obtained from Sigma-Aldrich Chemical Co., isopentane (99.5 % minimum purity) from Fluka, and neopentane (99.0 % minimum purity) from ChemSampCo, LLC. Fully deuterated ethane (d-ethane) (99.8 % minimum purity - D, 99 %) was obtained from CDN Isotopes. These solvents were used without further purification. Pamela Wright and Lewis Fetters of Exxon Research and Engineering Company provided the PEB_{10} and d-PEB_{10} copolymers used in this study. The statistically random PEB_{10} copolymers were produced from anionic polymerization of polybutadiene that was subsequently saturated with hydrogen or deuterium as described elsewhere.[19–21] The PEB_{10} and d-PEB_{10} copolymers have weight-average molecular weights of 232 500 and 245 000, respectively, and number-average molecular weights of 230 200 and 222 700, respectively. The 20.2 mol % 1-butene content corresponds to an average of 10 ethyl branches per 100 backbone carbon atoms.

Results and Discussion

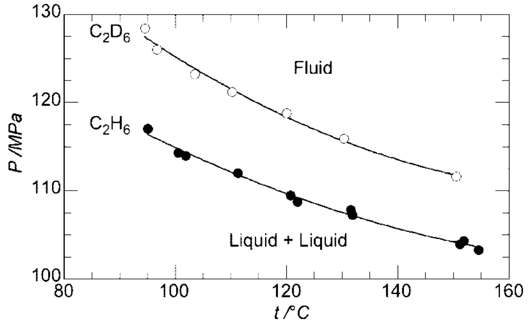

Figure 1. Deuterium isotope effect on the phase behavior of PEB_{10} (●, 4.3 wt %) in ethane and PEB_{10} (○, 4.8 wt %) in d-ethane.

Table 2. Cloud-Point Data for PEB_{10} in Ethane and d-Ethane at Various Weight Fractions x of PEB_{10}

$x = 0.043$ in ethane		$x = 0.048$ in d-ethane	
t/°C	P/MPa	t/°C	P/MPa
94.5	128.4	95.1	117.0
96.7	126.0	100.5	114.3
103.5	123.2	101.9	113.9
110.2	121.2	111.2	112.0
120.0	118.8	120.7	109.5
130.3	115.9	122.0	108.8
150.5	111.6	131.5	107.8
		131.9	107.2
		151.1	103.9
		151.9	104.3
		154.5	103.3

Figure 1 shows that the cloud-point curves for PEB_{10} in ethane and in d-ethane both exhibit a negative slope. The cloud-point pressures with d-ethane are ≈ 10 MPa higher than those for ethane at the same temperature, which shows the impact of deuteration on the solvent quality of ethane. These data demonstrate that ethane, whether deuterated or not, is a very weak supercritical fluid solvent for these high molecular weight PEB_{10} polymers. Table 2 lists the cloud-point data for PEB_{10} in ethane and in d-ethane.

The phase behavior of d-PEB_{10} in cyclopentane, *n*-pentane, isopentane, and neopentane is shown in Figures 2, 3, 4, and 5, respectively. The cloud-point data for d-PEB_{10} in these solvents are presented in Tables 3 to 6a. Solvent quality orders from highest to poorest as cyclopentane > *n*-pentane ≥ isopentane > neopentane, which is also the same ordering of the solvent critical temperatures of these solvents as shown in Table 1. Figure 2 shows the phase behavior of the d-PEB_{10}—cyclopentane system. Only a limited amount of data are obtained with this high-quality solvent since the elevated temperatures needed to locate the phase boundary can cause the degradation of d-PEB_{10}. In this case, the cloud-point curve has a positive slope of ≈ 0.28 MPa·°C^{-1}.

The d-PEB_{10}—*n*-pentane and isopentane cloud-point curves, shown in Figures 3 and 4, respectively, exhibit positive slopes of ≈ 0.16 MPa·°C^{-1} at temperatures between ≈ (100 and 200) °C and pressures to ≈ 15 MPa. The cloud-point curve for the

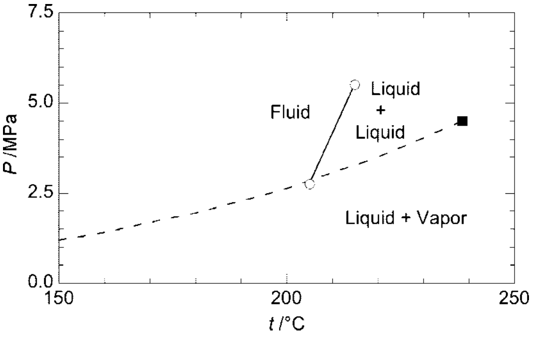

Figure 2. Phase behavior of d-PEB_{10} (○, 0.15 wt %) in cyclopentane. The cyclopentane vapor pressure curve[24] (dashed line) ends at the cyclopentane critical point (■).

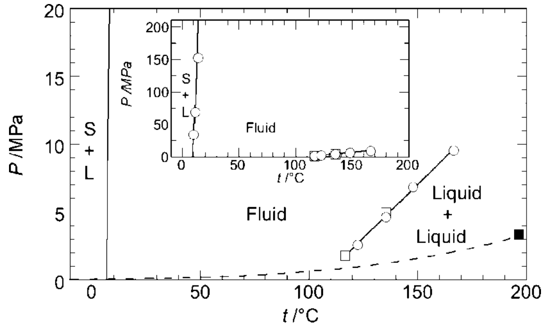

Figure 3. Phase behavior of d-PEB$_{10}$ (□, 1.8 wt %; ○, 0.5 wt %) in *n*-pentane. S + L represents the solid + liquid region. The inset graph shows the S + L → Fluid boundary, and the *n*-pentane vapor pressure curve[25] (dashed line) ends at the *n*-pentane critical point (■).

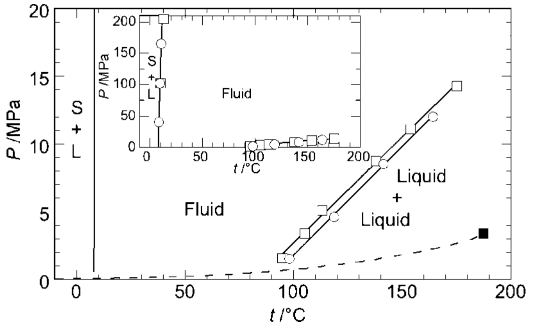

Figure 4. Phase behavior of d-PEB$_{10}$ (□, 1.9 wt %; and ○, 0.5 wt %) in isopentane. S + L represents the solid + liquid region. The inset graph shows the S + L → Fluid boundary, and the isopentane vapor pressure curve[25] (dashed line) ends at the isopentane critical point (■).

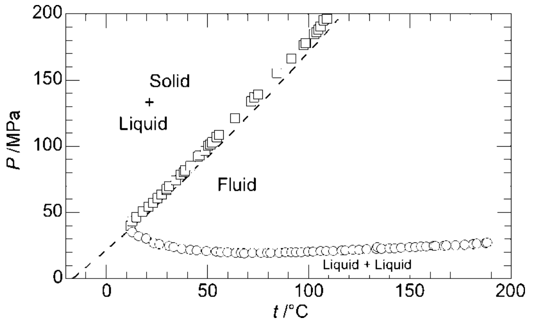

Figure 5. Phase behavior of 0.3 wt % d-PEB$_{10}$ (○, Fluid → Liquid + Liquid transitions; □, Solid + Liquid → Fluid transitions) in neopentane (2,2-dimethyl propane). The Solid + Liquid → Fluid data represent the boundary where solidification of neopentane occurs. The dashed line is the equation of the melting curve for neopentane reported by Woznyj et al.[22]

Table 3. Cloud-Point Data for d-PEB$_{10}$ in Cyclopentane at a PEB$_{10}$ Weight Fraction Equal to 0.0015

t/°C	*P*/MPa
215	5.5
205	2.8

d-PEB$_{10}$–neopentane system, shown in Figure 5, is virtually flat at a fixed pressure of ≈ 20 MPa from (200 to ≈ 30) °C where the curve changes abruptly to a positive slope of ≈ 1.65 MPa·°C^{-1}. Note that this slope is approximately 6 to 10 times greater than the slopes observed for the cloud-point curves for the other polymer–pentane mixtures. In this instance, the positive-slope portion of the d-PEB$_{10}$–neopentane cloud-point curve represents a solid + liquid → fluid transition where neopentane is the solid phase, not d-PEB$_{10}$, which is amorphous. At this freezing phase transition (Figure 5, Table 6b), frost quickly develops on the internal surface of the view window. When starting in the d-PEB$_{10}$–neopentane solid + liquid region, a single phase could easily be obtained by decreasing the pressure. At a given heating rate the neopentane solid-to-liquid transition occurs over a much smaller temperature interval than is typically observed for a solid polymer-to-liquid transition. Figure 5 also shows that the d-PEB$_{10}$–neopentane solid + liquid → fluid phase boundary is very close to the melting curve for pure neopentane.[22] Note that the extrapolation of the d-PEB$_{10}$–neopentane solid + liquid → fluid phase boundary to ambient pressure superposes onto the normal melting point of neopentane (−16.5 °C),[23] which further suggests that the solid phase is neopentane not d-PEB$_{10}$.

Table 4. Cloud-Point Data for d-PEB$_{10}$ in *n*-Pentane at Various Weight Fractions *x* of d-PEB$_{10}$

x = 0.005				*x* = 0.018			
solid–liquid		liquid–liquid		solid–liquid		liquid–liquid	
t/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa
13.9	220.6	122.5	2.6			116.7	1.8
13.8	151.7	135.3	4.6			135.3	5.0
11.3	68.9	147.8	6.8				
10.0	34.6	166.4	9.5				

Table 5. Cloud-Point Data for d-PEB$_{10}$ in Isopentane at Various Weight Fractions *x* of d-PEB$_{10}$

x = 0.005				*x* = 0.019			
solid–liquid		liquid–liquid		solid–liquid		liquid–liquid	
t/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa
10.6	165.3	98.0	1.5	10.1	102.2	94.8	1.6
9.7	102.3	118.6	4.6	13.1	204.9	105.1	3.4
8.4	40.6	141.3	8.6			113.1	5.1
		163.9	12.0			137.7	8.8
						153.8	11.1
						175.0	14.3

Table 6a. Cloud-Point Data at Low Pressures for d-PEB$_{10}$ in Neopentane at a d-PEB$_{10}$ Weight Fraction Equal to 0.003

t/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa
12.8	35.3	63.9	19.6	108.6	20.9	155.6	24.3
16.0	32.4	66.4	19.5	112.2	21.1	158.1	24.5
19.6	30.3	68.2	19.4	116.4	21.4	161.7	24.7
23.5	27.1	72.3	19.4	118.2	21.5	162.7	24.7
26.3	26.3	76.3	19.4	121.7	21.7	166.9	25.0
31.0	25.0	79.6	19.5	125.0	22.0	168.1	25.1
33.4	23.8	85.4	19.8	128.7	22.3	172.5	25.3
37.2	22.6	88.5	19.9	133.3	22.6	177.0	25.7
41.6	21.7	91.5	20.0	135.9	22.9	181.2	26.2
44.7	21.3	93.8	20.1	139.8	23.1	182.9	26.4
49.5	20.8	96.2	20.2	142.4	23.3	187.5	27.1
54.2	20.4	99.6	20.4	145.6	23.5	188.2	27.2
56.5	20.2	102.3	20.6	149.9	23.9		
60.0	20.0	106.0	20.8	152.6	24.1		

Table 6b. Solidification Boundary Data for a d-PEB$_{10}$ in Neopentane Solution at a d-PEB$_{10}$ Weight Fraction Equal to 0.003[a]

t/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa	*t*/°C	*P*/MPa
12.2	40.0	31.2	70.0	50.4	100.4	97.5	176.5
13.0	43.7	34.4	74.3	51.4	101.4	98.6	177.9
15.0	46.3	36.6	78.6	54.5	106.9	102.7	184.8
18.1	51.0	38.5	80.3	55.6	108.7	103.9	186.2
20.8	54.2	39.0	81.9	63.6	121.4	104.8	188.2
23.0	57.6	41.5	85.5	71.5	133.8	105.8	190.3
25.3	60.7	45.2	92.4	73.0	136.9	107.4	195.1
27.4	63.6	46.2	93.1	75.0	138.9	109.0	196.2
29.8	67.2	48.8	96.5	84.5	155.1		
29.9	68.0	49.0	96.5	91.4	166.2		

[a] This solidification boundary corresponds to the freezing of neopentane.

Conclusions

The high-pressure phase behavior data reported for nonpolar PEB_{10} in ethane and deuterated ethane (d-ethane) demonstrate that d-ethane is a poorer solvent than ethane likely due to the reduced dispersion interactions with d-ethane due to the shorter C−D bond length compared to a C−H bond that reduces the segment volume and the segment polarizability.[14] The trend in the solvent quality reduction of d-ethane relative to ethane for PEB_{10} is also similar to that observed for d-pentane relative to pentane.

The other sets of high-pressure phase behavior data reported here for d-PEB_{10} in pentane isomers demonstrate the effect of solvent molecular structure on solvent quality. For these polymer−pentane isomer mixtures, the increase in solvent quality follows the same ordering as the magnitude of the critical temperatures with cyclopentane being the highest quality solvent and neopentane being the poorest quality solvent.

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