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Critical Polymer Concentrations of Polyethylene Solutions in Pentane

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Critical polymer concentrations of polyethylene solutions in pentane were measured using a variable-volume view cell apparatus. The molecular weights of the polyethylene samples were 27 700 and 41 700 with polydispersity indexes $M_w/M_n = 2.00$ and 3.70, respectively. The phase separation pressures (cloud point) of the polymer solutions were repeatedly measured in the polymer concentration range 0.3−11.0 mass %. Two types of phase separation patterns (dew-point and bubble-point types) were observed, depending on the polymer concentration. The critical polymer concentration was determined by locating a merging point of the two types of phase separation branches. The critical polymer concentrations for the two polyethylene solutions were 6.90 ± 0.1 ($M_w = 27\,700$) and 3.95 ± 0.05 ($M_w = 41\,700$) mass %, respectively.

Introduction

Critical polymer concentration refers to the polymer concentration at which the binodal and spinodal curves merge.[1,2] Experimental assessment of the critical polymer concentration is of great practical, as well as theoretical importance, since the mode of phase separation and the associated dynamics (i.e., kinetics) of phase separation are significantly different if the system enters the spinodal or the metastable region upon a pressure (or temperature) quench.[3,4] However, at the critical polymer concentration, the unstable region that is characterized by spinodal decomposition is entered for any depth of penetration into the region of immiscibility. At concentrations below and above the critical polymer concentration, the system may or may not be able to undergo phase separation by spinodal decomposition—this depends on the depth of penetration and the magnitude of the metastable gap. A consequence of different modes of phase separation is the transient microstructures that develop. If the phase separation is by spinodal decomposition, as would be the case at the critical polymer concentration, phase separation proceeds by first forming a cocontinuous interconnected morphology which in time coarsens. In phase separation at off-critical concentrations, solutions first enter the metastable region and phase separation starts to proceed by the nucleation and growth mechanism. At concentrations lower than the critical one, the polymer-rich phase nucleates in the polymer-lean phase, and at concentrations higher than the critical one, the polymer-lean phase nucleates in the polymer-rich phase. The time evolutions of these phases differ, depending upon the mode of phase separation and the quench depth that has been imposed on the system.[1−4]

Knowing the location of the critical polymer concentration is thus of significance for rational selection of polymer solution concentrations to achieve the desired morphological features or specific modification of the resulting polymer products that may be produced by, for example, precipitation, as in particle formation from polymer solutions in near-critical or supercritical fluids. Indeed, knowledge of the critical polymer concentration could be applied and would be of great value in the pressure-induced particle formation technologies, such as the rapid expansion of supercritical solution (RESS) process. The RESS process has been used to produce many types of polymer particles, fibers, and films.[5]

In this study, the critical polymer concentrations of polyethylene solutions in pentane were experimentally determined by using a variable-volume view cell apparatus. The equipment was used to determine the phase separation boundary for a particular mixture under isothermal conditions. The visual observation indicated that the phase separation patterns could be divided into two types, depending on the polymer concentrations of the solutions: one being a bubble-point type phase separation and the other being a dew-point type phase separation. The critical polymer concentration is located between these two types of phase separation branches in the pressure−concentration projection. Therefore, the measurements were repeated by altering the polymer concentration until the merge point of the two types of phase separation branches could be estimated.

Experimental Methods

Materials. Polyethylene samples with two different molecular weights of $M_w = 27\,700$ and 41 700 with the polydispersity indexes $M_w/M_n = 2.00$ and 3.70, respectively, were purchased from the Pressure Chemical Co. (Pittsburgh, PA), and pentane (purity > 99%) was obtained from Aldrich Chemical Co. All the chemicals were used without further purification.

Apparatus and Procedure. The variable-volume view cell apparatus used in the present study consists of a cylinder type view cell (stainless steel 316, 1.89 cm i.d., 6.35 cm o.d., 12.06 cm length, maximum volume 26.71 cm^3)

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equipped with a window and a movable piston, a pressure generator (HIP 81-5.75-10), and a borescope camera (Olympus F100-024-000-55) with a video monitor. The pressure in the cell was measured using a pressure transducer with an accuracy of ±0.25 bar while the temperature was controlled to ±0.2 K.

Measured masses of polyethylene sample and pentane were charged into the view cell to generate a polymer solution with a known concentration. The solutions of polymer concentrations in the range 0.3−11.0 mass % were investigated in this study. The cell was heated to the desired temperature, and the polymer solution was pressurized by the movable piston to form a clear single phase. The cell content was agitated using a magnetic stirrer during the heating and pressurization steps to maintain a homogeneous condition inside the cell. After the system pressure and temperature became stable, the pressure was slowly reduced by moving the piston backward. The pressure at which the cell content became cloudy (cloud point) was recorded as a phase separation pressure.

At the phase separation pressures, two different phase separation patterns were observed, depending on the polymer concentration. At low polymer concentrations, small polymer drops (polymer-rich phase) initially formed and the heavy polymer-rich phase fell down to the bottom of the cell. This pattern is called a “dew-point type” phase separation. Therefore, a down-flow pattern was observed upon phase separation. This type of phase separation pattern is expected when the polymer concentration is lower than the critical polymer concentration.[1,2,6] When the polymer concentration is higher than the critical polymer concentration, dispersed bubbles (solvent-rich phase) form and the light bubbles rise up to the top of the cell. This is called a “bubble-point type” phase separation. Hence, an up-flow pattern was observed upon phase separation. On the basis of the observations of these two different phase separation patterns, it was possible to determine whether the polymer concentration in the solution is lower or higher than the critical polymer concentration.

At a fixed polymer concentration, the measurements of cloud point pressures and the observations of the phase separation patterns were performed at various temperatures. The experiments were continued with polymer solutions at different polymer concentrations. The polymer concentration was typically changed in 1.0 mass % intervals from low to high concentrations. It was determined visually whether the type of phase separation pattern was dew-point or bubble-point type. The branches of dew-point and bubble-point type phase separations were plotted in the pressure−concentration diagram, with the merging point of the two branches corresponding to the critical polymer concentration. To locate the critical polymer concentration, measurements were repeated by changing the polymer concentration in narrow intervals in the vicinity of the merging point of the two branches. The minimum concentration increment used in the experiments was 0.1 mass %. Finally, the critical polymer concentration was calculated by averaging the two most adjacent concentrations at which each dew-point and bubble-point type phase separation occurred. Figure 1 illustrates the above experimental procedure for the determination of the critical polymer concentration.

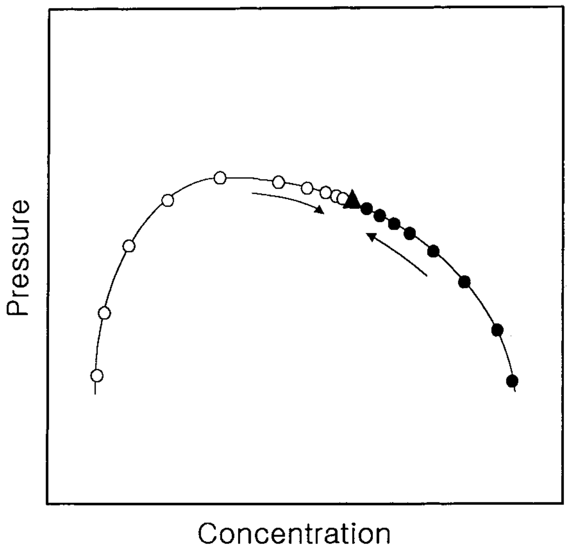

Figure 1. Illustration of the determination of the critical polymer concentration by narrowing down the measurement of phase separation patterns in the vicinity of the critical polymer concentration. The curve represents the binodal boundary. ○, dew-point type branch; ●, bubble-point type branch; ▲, critical polymer concentration.

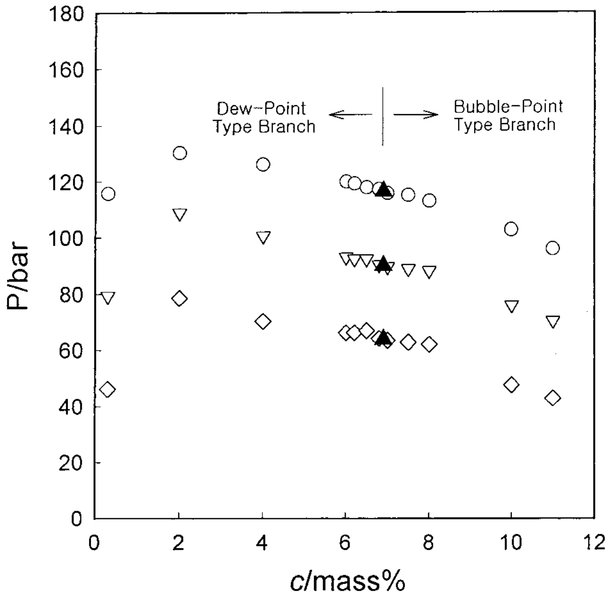

Figure 2. Pressure−concentration phase diagram (binodal boundary) for polyethylene (M_w = 27 700) solutions in pentane at various temperatures. The critical polymer concentration is 6.90 mass %. ◇, 403 K; ▽, 423 K; ○, 443 K; ▲, critical polymer concentration.

Results

Table 1 shows the experimental data of the phase separation pressures for polyethylene (M_w = 27 700 and 41 700) solutions in pentane as a function of polymer concentration (c) at different temperatures. The maximum uncertainty of the phase separation pressure data was ±1.5%. In this table, the types of phase separation patterns were also described for each data point. The critical polymer concentrations (CPCs) were calculated by arithmetic averaging of the two adjacent dew-point (DP) and bubble-point (BP) concentrations shown in the table. The critical polymer concentrations for the polyethylene solutions of molecular weights 27 700 and 41 700 were found to be 6.90 ± 0.1 and 3.95 ± 0.05 mass %, respectively (see Table 1). Observation of the phase separation patterns indicated that the distinction between the two types of phase separations became unclear as the concentration approached the critical polymer concentration. This is due

Table 1. Phase Separation Pressures for Polyethylene (M_w = 27 700 and 41 700) Solutions in Pentane as a Function of Polymer Concentration, *c*, at 403, 423, and 443 K for the Phase Separation Patterns DP = Dew-Point Type, BP = Bubble-Point Type, and CPC = Critical Polymer Concentration

T/K	*c*/mass %	*P*/bar	phase separation pattern
		M_w = 27 700	
403	0.3	46.2	DP
	2.0	78.6	DP
	4.0	70.3	DP
	6.0	66.2	DP
	6.2	66.2	DP
	6.5	66.9	DP
	6.8	64.1	DP
	6.9		CPC
	7.0	63.4	BP
	7.5	62.7	BP
	8.0	62.0	BP
	10.0	47.5	BP
	11.0	42.7	BP
423	0.3	79.3	DP
	2.0	108.9	DP
	4.0	100.6	DP
	6.0	93.1	DP
	6.2	92.4	DP
	6.5	92.4	DP
	6.8	90.3	DP
	6.9		CPC
	7.0	89.6	BP
	7.5	88.9	BP
	8.0	88.2	BP
	10.0	75.8	BP
	11.0	70.3	BP
443	0.3	115.8	DP
	2.0	130.3	DP
	4.0	126.2	DP
	6.0	120.0	DP
	6.2	119.3	DP
	6.5	117.9	DP
	6.8	117.2	DP
	6.9		CPC
	7.0	115.8	BP
	7.5	115.1	BP
	8.0	113.1	BP
	10.0	102.7	BP
	11.0	95.8	BP
		M_w = 41 700	
403	0.3	97.2	DP
	1.0	113.1	DP
	1.5	112.4	DP
	2.0	109.6	DP
	3.0	108.9	DP
	3.5	111.7	DP
	3.7	109.6	DP
	3.9	111.7	DP
	3.95		CPC
	4.0	111.7	BP
	4.3	108.2	BP
	4.5	109.6	BP
	5.0	108.9	BP
	6.0	102.0	BP
	7.0	101.3	BP
423	0.3	124.8	DP
	1.0	137.9	DP
	1.5	137.9	DP
	2.0	133.7	DP
	3.0	135.1	DP
	3.5	137.2	DP
	3.7	135.1	DP
	3.9	136.5	DP
	3.95		CPC
	4.0	136.5	BP
	4.3	131.7	BP
	4.5	133.7	BP
	5.0	131.0	BP
	6.0	127.5	BP
	7.0	127.5	BP
443	0.3	153.7	DP
	1.0	160.0	DP
	1.5	160.6	DP
	2.0	157.9	DP
	3.0	159.3	DP
	3.5	158.6	DP
	3.7	157.2	DP
	3.9	156.5	DP
	3.95		CPC
	4.0	158.6	BP
	4.3	155.1	BP
	4.5	156.5	BP
	5.0	153.7	BP
	6.0	150.3	BP
	7.0	149.6	BP

to the density similarity of the two phases that were formed upon phase separation, which hinders a prompt "rise" of the light phase and a "fall" of the heavy phase. In this study, it was possible by visual observation to differentiate the two types of phase separation when the concentration was changed by 0.1 mass % in the vicinity of the critical polymer concentration.

Figures 2 and 3 display the pressure−concentration diagrams of the polyethylene solutions in pentane with the polymer molecular weights 27 700 and 41 700. In these figures, each data set for each particular temperature corresponds to the binodal boundary. Thus, the pressure range above each boundary identifies the one-phase homogeneous region. In these figures, the binodal shows a maximum pressure (binodal maximum) at a particular polymer concentration. The concentrations corresponding to the maximum pressure of the binodal were about 2 and 1 mass % for the 27 700 (Figure 2) and 41 700 (Figure 3) molecular weight polyethylene samples, respectively. The concentration at which the binodal maximum occurred was independent of temperature under the experimental conditions investigated in this study. The critical polymer concentrations for these two polymer samples were higher than the concentrations corresponding to the maximum in the binodal curves. Similar trends are typically observed in polydisperse polymer systems where the molecular weight distributions are relatively broad.[3,4] Figure 4 shows the binodal curves for the two molecular weight polymer systems at 443 K. This figure depicts another feature, that is the shift in the location of the binodal maximum and the critical polymer concentration to lower polymer concentrations with increasing molecular weight of the polymer sample.

It is interesting to compare the critical polymer concentrations determined in the present study with the critical polymer concentrations reported for polyethylene samples of higher molecular weight in pentane which were determined by pressure-quench and time- and angle-resolved light scattering techniques.[2,4] Carrying out controlled pressure quenches in the region of immiscibility and monitoring the time evolution of the angular distribution of the scattering light intensities help identify the binodal and spinodal boundaries from the characteristic fingerprint patterns associated with nucleation and growth and spinodal decomposition. For a polyethylene sample with the molecular weight 108 000 and the polydispersity index

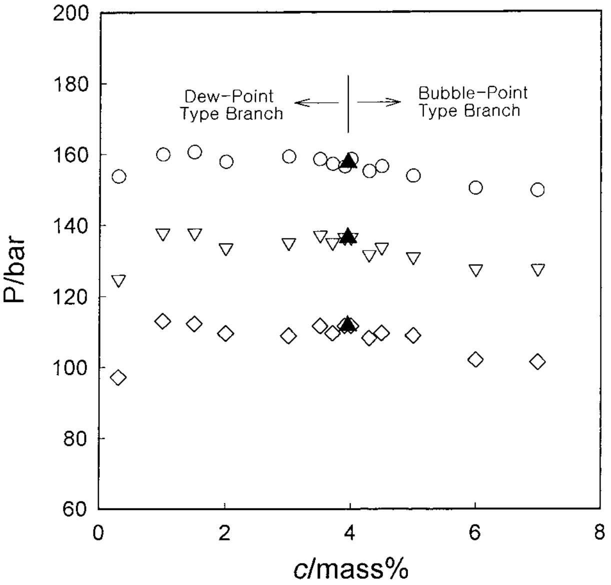

Figure 3. Pressure−concentration phase diagram (binodal boundary) for polyethylene (M_w = 41 700) solutions in pentane at various temperatures. The critical polymer concentration is 3.95 mass %. ◇, 403 K; ▽, 423 K; ○, 443 K; ▲, critical polymer concentration.

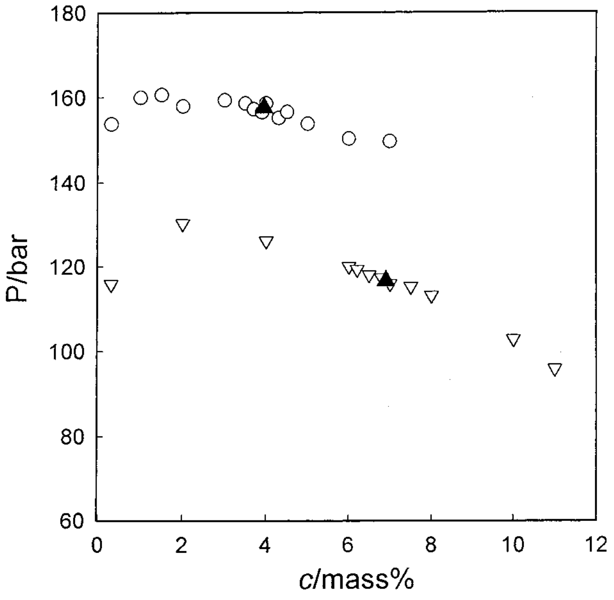

Figure 4. Pressure−concentration phase diagram (binodal boundary) for two different molecular weight polyethylene (M_w = 27 700 and 41 700) solutions in pentane at 443 K: ▽, 27 700; ●, 41 700; ▲, critical polymer concentration.

1.32, the binodal and spinodal curves merge near the apex of the binodal (about 140 bar) at about 2 mass % polymer at 423 K.[4] Whereas for polyethylene of molecular weight 121 000 with a polydispersity index of 4.43, the critical polymer concentration at 423 K is at a much higher polymer concentration, around 5 mass % polymer, even though the apex of the binodal (about 150 bar) in this broader molecular weight distribution sample is also around 2 mass % polymer.[2] The results for the lower molecular weight polymer samples obtained by the present new approach are all consistent in that with increasing molecular weight the critical concentration shifts to lower concentrations if the molecular weight distributions are narrow or similar, while the demixing pressures corresponding to the apex of the binodal become higher. With increasing polydispersity, the critical polymer concentration shifts to higher concentrations.

The focus of this study was on the measurement of critical polymer concentrations of polyethylene solutions in pentane by visual observation. The overall results indicate that the experimental technique used in the present investigation provides a reliable methodology for determination of the critical polymer concentration with a reasonable accuracy.

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