Effect of molecular weight distribution on the liquid–liquid phase separation behavior of polydispersed polyethylene solutions at high temperatures

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A B S T R A C T

The phase behaviors of the hexane + polydispersed polyethylene (PE) systems were measured to clarify the effect of the molecular weight distribution (MWD) of PE on liquid–liquid (LL) phase boundaries. The weight fraction for the PE portion of a maximum LL phase separation pressure in the LL phase boundary decreased as the polydispersity of PE increased. Moreover, depression of the phase separation pressure from the maximum phase separation pressure on the higher PE weight fraction side was more drastic as the polydispersity of the PE increased. The LL phase boundaries were correlated using the Sanchez–Lacombe equation of state (S–L EOS). For the correlations, the polydispersed PEs were regarded as mixtures of 16 types of monodispersed PEs with different molecular weights, and the characteristic parameters of the S–L EOS, P^*, ρ^* and T^*, were assigned the same values for all monodispersed PEs even though the molecular weights differed. However, the interaction parameters of the hexane–PE pairs depended on the molecular weight of the PE and the temperature. The correlated results capably reproduced the effect of the MWD of the PE on the LL phase boundaries for the hexane + polydispersed PE systems.

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1. Introduction

Polyethylene (PE) is one of the most widely utilized polymers in industry. Solution polymerization is frequently applied in PE production because PE obtained by this method has excellent characteristics, and many olefin comonomers can be added without difficulty. In solution polymerization, the viscosity of the solution increases with increasing molecular weight of PE. Therefore, solution polymerization is mainly used for production of PEs with relatively low molecular weight, such as linear low-density polyethylene. Solution polymerization also has the great disadvantage of requiring a large amount of energy to separate products from a reaction solvent and residual monomers in an evaporator. As a result, the separation process, in which a high-temperature liquid–liquid separator is placed prior to the evaporator to reduce energy costs, has received much attention [1]. Data on phase behavior are critically important to the development and operation of the separation process. Therefore, much research has been reported on the phase behaviors of PE solutions at high temperatures and pressures. In particular, the effects of the concentration of ethylene (monomer) and the molecular weight of PE have been studied [2–12]. The liquid–liquid (LL) phase boundaries shifted to a lower temperature as the ethylene content and the molecular weight

of PE increased. In addition to experimental research, correlation and prediction methods for the phase boundaries of PE solutions have been investigated using equations of state (EOS), such as the Sanchez–Lacombe (S–L) [9,10,13–15] and Statistical Associating Fluid Theory (SAFT) [16–20].

Industrial PE usually has a molecular weight distribution (MWD), and, therefore, knowledge of the effect of the MWD of PE on the phase behavior of polymer solutions is quite important. Experimental and numerical studies of polydispersed PE solutions have been reported by Heidemann's group [21–23] and others [8,24–27]. However, there are few systematic studies of phase behavior of the polydispersed PE solutions, compared with those of the monodispersed PE solutions. In the present study, therefore, the phase behaviors of the hexane + polydispersed PE systems were measured at high temperatures. All polydispersed PEs used in the present study had roughly identical weight average molecular weights, although their polydispersities were quite different, which clarified the polydispersity effect on the phase behavior. The experimental results were correlated by the S–L EOS [13,14] with consideration of the polydispersity of PE.

2. Experimental

2.1. Materials

Three types of polydispersed PE, with different average molecular weights and MWDs, were purchased from Sigma–Aldrich Co.

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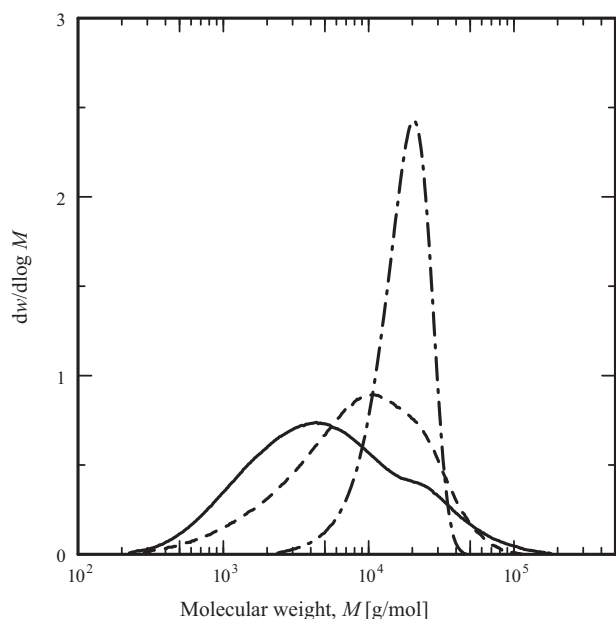 *E-mail address:* mharuki@hiroshima-u.ac.jp (M. Haruki).

Fig. 1. Molecular weight distribution obtained by GPC. Lines: (–··) PE1; (– – –) PE2; (–––) PE3.

Fig. 2. Schematic diagram of the experimental apparatus. 1: hand pump; 2: silicone oil reservoir; 3: pressure gauge; 4: pressure damper; 5: thermostatic water bath; 6: linear scale and displacement meter; 7: linear variable differential transformer; 8: cartridge heaters; 9: aluminium block; 10: polymer solution; 11: sapphire window; 12: free piston; 13: optical cell body; 14: magnetic stirring bar; 15: sample injection port; 16: thermal insulator; 17: temperature indicator; 18: monitor and video recorder; 19: CCD camera; 20: temperature controller; 21: HPLC pump; 22: solvent flask.

These PEs were made in a high pressure radical process based on the ICI process. Hexane with a purity >99 mol% was also purchased from Sigma–Aldrich Co. *o*-Dichlorobenzene with a purity >98 mol% was purchased from Kishida Chemical Co. for preparation of the polymer samples used in measurement, and for the solvent used as the moving bed of the gel permeation chromatography (GPC) analysis.

2.2. Characterization of polyethylene

Two types of polydispersed PEs were prepared using the three commercial polydispersed PEs to adjust the molecular weight and MWD. The molecular weights and MWDs of the PEs were determined by a GPC (Polymer Laboratories Co., PL-GPC210) equipped with a PLgel 10 μm MIXED-B in a LS column (Agilent Technologies Co.) at 413 K, using *o*-dichlorobenzene as a solvent for the moving bed. Molecular weights were calibrated using monodispersed polystyrene standards. The MWDs of the PEs are shown in Fig. 1, along with that of the nearly monodispersed PE used in previous work [8,11]. The weight and number average molecular weights of each PE sample are listed in Table 1. As described in the table, the nearly monodispersed PE with polydispersity index (PI) of 1.21 is called PE1, and the polydispersed PEs with PIs of 2.94 and 4.01 are called PE2 and PE3, respectively, in the following sections.

2.3. Apparatus and procedure

A schematic diagram of the experimental apparatus, which was designed based on the synthetic method, is shown in Fig. 2. The apparatus mainly consisted of a variable-volume optical cell, a
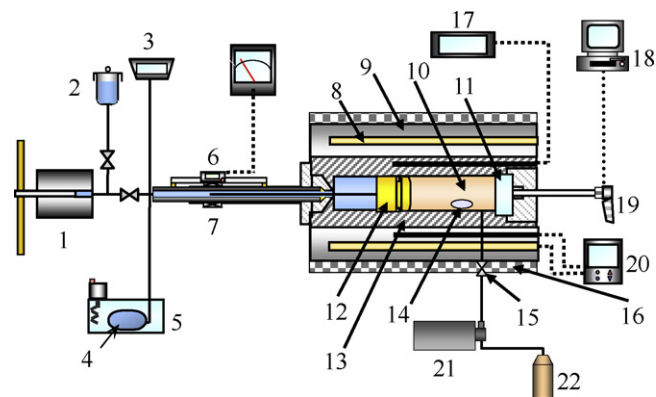
hand pump and an observation system. The internal volume of the cell could be varied from 6 to 20 cm³ by changing the position of the free piston. Because polymer solutions tend to be in a metastable state, the polymer solution was thoroughly mixed with a Teflon-coated magnetic stirring bar to avoid supersaturation. The temperature of the cell was measured using a platinum resistance thermometer (Hart Scientific, Model 1502). The uncertainty of the temperature measurement was ±0.02 K. The pressure in the cell was controlled with a hand pump and was measured with a digital gauge (Heise Gause, F.S. 100 MPa), which had been calibrated against a dead weight tester (Pressurement Ltd., 0.01–110 MPa, uncertainty ±0.025%). The pressure difference between the sides of the free piston was predetermined and did not exceed 0.1 MPa in most cases. While the uncertainty of the pressure gauge was ±0.015 MPa, the uncertainty of the measured LL phase separation pressure, by visual observation inside the optical cell with a charge coupled device camera (ELMO Co., CN42H), was estimated to be within ±0.12 MPa. The uncertainty of the liquid–vapor (LV) and liquid–liquid–vapor (LLV) phase separation pressures was estimated to be much less than that of the LL phase separation, within ±0.05 MPa, because the LV and LLV phase separation were quite clear compared with the LL phase separation.

In the experiment, particulate PE was weighed with an electronic balance (uncertainty ±0.03 mg) and was introduced directly into the cell. The inside of the cell was then evacuated, and hexane was added into the cell using an HPLC pump (JASCO Co., PU-980). The uncertainty of the amount of hexane added was estimated to be within ±10 mg. As the total amounts of the components introduced were generally about 5 g, the uncertainty of the feed weight fraction was estimated to be within ±0.001 for each component. After the sample in the cell reached the desired temperature and formed a homogeneous liquid phase at high pressure, the pressure was slowly reduced while the temperature was held constant. The LL phase separation pressure was the pressure at which the transparent phase became cloudy. On the other hand, the newly vaporized phase was observed as the top phase in the LV and LLV phase separations.

2.4. Results and discussion

The experimentally determined phase boundaries for the hexane + PE2 and hexane + PE3 systems are listed in Tables 2 and 3, respectively. The relationships between the phase separation pres-

Table 1
Characteristics of polyethylene samples used.

Symbol	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_z$ (g/mol)	$\bar{M}_w/\bar{M}_n$
PE1[a]	14.9×10^3	18.1×10^3	20.7×10^3	1.21
PE2	4.46×10^3	13.1×10^3	25.1×10^3	2.94
PE3	2.72×10^3	10.9×10^3	35.3×10^3	4.01

[a] Hydrogenated polybutadiene purchased from Scientific Polymer Products Inc.