



Prediction of the liquid–liquid phase equilibria for polydisperse polyethylene solutions under conditions of high temperature and pressure



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ABSTRACT

In the present study, the liquid–liquid (LL) phase equilibria for the hexane + polydisperse polyethylene (PE) and the ethylene + hexane + polydisperse PE systems were simulated using the Sanchez–Lacombe equation of state, in order to investigate the effects of the addition of ethylene and the polydispersity of PE on the LL phase equilibria of the PE solution. In the calculation, the polydispersity of PE was represented as a mixture of 16 types of monodisperse PE. The interaction parameter between hexane and PE was determined by fitting to the LL phase boundary curve of the hexane + polydisperse PE binary system in the previous work, and it depended on the molecular weight of PE. The interaction parameter between ethylene and PE was used, as also determined from the LL phase boundaries for the ethylene + hexane + polydisperse PE system in the present work. And, the parameter of the ethylene–hexane pair that was based on the value reported in the literature was used.

The simulated results indicated that the critical PE weight fraction increased as the feed ethylene content increased. On the other hand, although the addition of ethylene greatly increased the LL phase boundary, the ethylene content had only a small influence on the PE content of both separated LL phases and their molecular weight distributions for the LL phase equilibria. The effect of the polydispersity of PE was notable on the PE weight fractions in the separated phases.

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1. Introduction

Polyethylene (PE) is one of the most utilized polymers, and is used for a variety of commodities such as wrapping materials. During the PE production process, many types of olefin comonomers are added to enhance the functionality of PE. Among the polymerization methods, solution polymerization at high temperature and pressure has become a standard method for the easy addition of comonomers. For the process design and operation of a reactor and separator, a knowledge of the liquid–liquid (LL) phase boundary for the ethylene (monomer of PE) + comonomer + solvent + PE system is important, and many experimental and theoretical studies have reported the LL

phase boundaries of this system [1–11]. Many polydisperse PEs are industrially produced. When PE has polydispersity, the LL phase boundary curve and the LL phase equilibrium curve are not in accord, even in a solvent + PE binary system [12]. Therefore, the LL phase equilibria for PE solutions at high temperature and pressure are indispensable data. However, the available studies on the LL phase equilibria of PE solutions are quite limited.

In our previous work [13], the LL phase equilibria for a hexane + polydisperse PE system were experimentally measured at 473 K, and both the compositions and molecular weight distributions (MWDs) of the PE-rich and the hexane-rich phases were determined. Moreover, the LL phase boundary at 473 K that was also measured in the previous work was correlated using the Sanchez–Lacombe equation of state (S-L EOS), wherein the interaction parameter between hexane and PE was determined, and the characteristic parameter, ρ^* , of PE was also determined in order to express the critical point at 473 K as well as the LL phase boundary

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curve. The predictions of the LL phase equilibria were subsequently carried out and the results were compared with both the experimental phase equilibrium compositions and the MWDs of each phase. The predicted results approximated the experimental results in the hexane-rich phase, and the predicted and experimental results qualitatively agreed in the PE-rich phase.

The present work was focused on the ethylene + hexane + polydisperse PE system, and the LL phase boundary was measured and correlated to adjust the interaction parameter of the ethylene – PE pair. The LL phase equilibria were then simulated to clarify the effect of the addition of ethylene into the hexane + polydisperse PE system. Moreover, the effect of the polydispersity of PE on both the LL phase boundary and phase equilibria were also investigated.

2. Experimental

The polydisperse PE used in the present work was the same as that used in the previous work [13], and was supplied by Sigma–Aldrich Co. The number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w), and polydispersity index (\bar{M}_w/\bar{M}_n) were 7.07 kg/mol, 30.0 kg/mol, and 4.24, respectively, and were determined using the results from the gel permeation chromatography in previous work. The MWD of the polydisperse PE used is described in Fig. 1. Hexane was also purchased from Sigma–Aldrich Co., and its purity was >99 mol%. Ethylene with purity >99.9 vol% was purchased from Sumitomo Seika Co. All chemicals were used without further purification. The specifications of the chemicals used in the present work are summarized in Table 1.

The LL phase boundary of the ethylene + hexane + polydisperse PE was measured via a synthetic method using a variable-volume optical cell. A detailed explanation of the apparatus and procedure for the LL phase boundary measurement is provided in our previous papers [9–11], and, therefore, these are only briefly described here. A particulate PE with a certain weight was introduced directly into the cell, and the inside of the cell was evacuated. Ethylene was then introduced into the cell using a small sample cylinder via a freeze-thaw method. Finally, hexane was added into

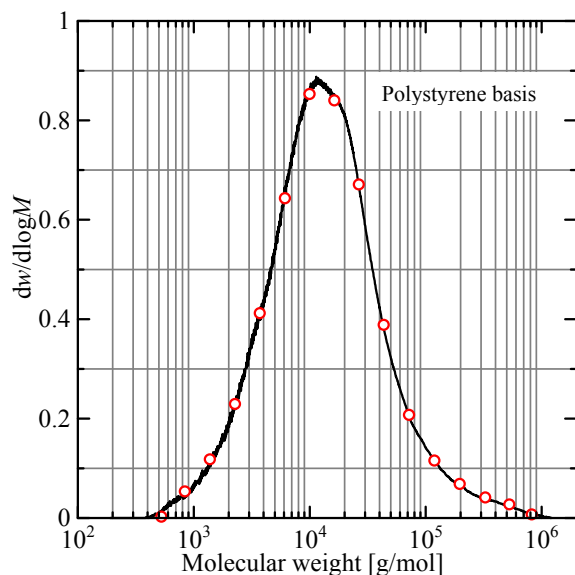


Fig. 1. MWD of polydisperse PE used. Solid line shows the MWD obtained via GPC analysis. Open circles show the representative 16 pseudo-components used for the calculations via S-L EOS.

Table 1
Specifications of chemicals used in the present work.

Chemical name	Purity	Source	CAS No.
ethylene	>99.9 vol%	Sumitomo Seika Co.	74-85-1
hexane	>99 mol%	Sigma–Aldrich Co.	110-54-3
polyethylene	–	Sigma–Aldrich Co.	9002-88-4

the cell using an HPLC pump. The uncertainty of the amounts of ethylene and the hexane introduced was estimated to be within ± 2 and ± 10 mg, respectively. As the total amounts of components introduced were generally about 5 g, the uncertainty of the feed weight fraction of each component was estimated to be within ± 0.002 .

The LL phase boundary is generally determined by identification of the phase transition at which a transparent liquid phase changes to a cloudy phase by decreasing the pressure at a constant temperature and feed composition. However, the phase transition points were difficult to recognize at high PE weight fractions because the transition from a transparent phase to a cloudy phase proceeded in a gradual manner. In the present work, a method for identifying the boundary between transparent and cloudy phases was mainly used, and the results at a high-feed PE weight fraction were compared with the results obtained by observing the elimination of the interface of the separated LL phases by carefully increasing the pressure in a step-by-step manner.

3. Calculation model

The Sanchez–Lacombe (S-L) EOS was used to correlate the LL phase boundary and to simulate the LL phase equilibria. The S-L EOS is expressed as follows [14,15]:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (1)$$

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad r = \frac{MP^*}{RT^*\rho^*} \quad (2)$$

where P^* , ρ^* and T^* are characteristic parameters of the S-L EOS, and r is the segment number—the number of lattice sites occupied by molecules. M and R are the molecular weight and universal gas constant, respectively. For m -component mixtures, the mixing rules of the characteristic parameters are given by the following equations:

$$P^* = \sum_{i=1}^m \phi_i P_i^* - \frac{1}{2} \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j \Delta P_{ij}^* \quad (3)$$

$$\Delta P_{ij}^* = P_i^* + P_j^* - 2(1 - k_{ij}) \sqrt{P_i^* P_j^*} \quad (4)$$

$$T^* = P^* \sum_{i=1}^m \left(\frac{\phi_i T_i^*}{P_i^*} \right) \quad (5)$$

$$\frac{1}{r} = \sum_{i=1}^m \left(\frac{\phi_i}{r_i^0} \right) \quad (6)$$

$$\varphi_i^0 = \frac{(\varphi_i P_i^* / T_i^*)}{\sum_{j=1}^m (\varphi_j P_j^* / T_j^*)} \quad (7)$$

$$\varphi_i = \frac{(w_i / \rho_i^*)}{\sum_{j=1}^m (w_j / \rho_j^*)} \quad (8)$$

where w_i indicates the weight fraction of the i -th component and k_{ij} in Eq. (4) represents the binary interaction parameter.

In the calculations for polymer solutions including polydisperse polymer, the polymer is often regarded as a mixture of monodisperse polymers with different molecular weights [16–18]. In our previous work [13], the same polydisperse PE as that in the present work was regarded as a mixture composed of 16 types of monodisperse PEs with different molecular weights for theoretical studies. And reasonable results were obtained for both the LL phase boundary and LL phase equilibria. In the present work, therefore, the same model and calculation procedure were also applied to investigate and its effects of the ethylene addition and the polydispersity of PE on the phase behavior of the hexane + polydisperse PE. The main features of the calculation methods containing parameter fitting are as follows:

1. The polydispersity of PE was represented by treating polydisperse PE as a mixture of 16 types of monodisperse PEs with different molecular weights, as described above.
2. With respect to the binary interaction parameter, k_{ij} , in Eq. (4), the $k_{C_6-PE_i}$ between hexane and PE depended on the molecular weight of the PE. The $k_{PE_i-PE_j}$ of PEs with different molecular weights was set to zero regardless of the molecular weight of the PE, which was similar to the previous work [13,19]. On the other hand, the $k_{C_2-PE_i}$ between ethylene and PE was determined by correlating the LL phase boundary curve for the ethylene + hexane + PE system at 473 K measured in the present work, and it did not depend on the molecular weight of the PE for simplicity.
3. The k_{ij} between ethylene and hexane, $k_{C_2-C_6}$, was cited from the literature [6].
4. The characteristic parameter sets, T^* , P^* and ρ^* of ethylene and hexane were cited from the literature [14,20]. On the other hand, the parameter set determined by Kiran et al. [3] was used for all PEs, with the exception of ρ^* . The ρ^* was determined along with the $k_{C_6-PE_i}$ by the correlation of the LL phase boundary and the critical point for the hexane + polydisperse PE system in the previous work [13], because the reproducibility of the critical point, as well as the phase boundary, is important for the accuracy of the phase equilibrium calculation.

The molecular weights and weight fractions of 16 pseudo-

components, and the \bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n of the mixture of them are listed in Table 2. Moreover, the relationship between $\log M$ and $dw/d\log M$ is shown in Fig. 1 along with the MWD of the original polydisperse PE, as obtained by GPC analysis. In the creation process for the 16 pseudo-components, the experimental logarithmic basis of the molecular weights between the maximum and minimum values were divided into 16 sections at almost equal intervals, and the molecular weights of each section were then estimated as the representative molecular weights. The deviations between created and experimental \bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n were 0.4, 1.5, and 1.9%, respectively. As for the characteristic parameters of each component and the binary interaction parameters, k_{ij} , the values used for calculation are listed in Tables 3 and 4, respectively.

The LL phase-boundary calculations were carried out at a certain feed PE concentration with a temperature of 473 K, and the MWD of the PE in the original phase was kept at the same MWD of the feed PE in the calculation. On the other hand, the composition and MWD of PE in the newly generated phase and the phase boundary pressure were determined using the Newton–Raphson method with the convergence condition of equality for the chemical potentials of each component in both the original and newly generated phases, μ_i^O and μ_i^N (Eq. (9)), and with unity of the sum of the mole fraction of each component in the newly generated phase.

$$\left| 1 - \frac{\mu_i^O}{\mu_i^N} \right| \leq \varepsilon \quad (9)$$

In the present study, the value of ε was set from 10^{-10} to 10^{-12} .

As for the LL phase equilibrium calculation, the flash algorithm was generally used to obtain the equilibrium compositions and amounts of the components of both phases at a certain feed composition, temperature and pressure. A brief explanation of the algorithm is described here. The mass balance in the system is represented by the following equation for the LL equilibrium state.

$$n^F z_i = n^{L1} x_i^{L1} + n^{L2} x_i^{L2} \quad (10)$$

where n indicates the molar number, and z and x show the mole fractions of the feed and separated liquid phases, respectively. The superscripts, F, L1 and L2, represent the feed and the liquid phases of lower and heavier densities, respectively. When the molar ratio of the L1 phase to the sum of both phases, α , and the equilibrium ratios of each of the components, K_i , are represented by Eqs. (11) and (12), respectively, the mass balance of Eq. (10) can be rewritten as Eq. (13):

$$\alpha = \frac{n^{L1}}{n^{L1} + n^{L2}} = \frac{n^{L1}}{n^F} \quad (11)$$

$$K_i = \frac{x_i^{L1}}{x_i^{L2}} \quad (12)$$

Table 2
16 pseudo-components of polydisperse PE for calculations by the S-L EOS.

No.	M [10^3 g/mol]	Content [wt%]	No.	M [10^3 g/mol]	Content [wt%]
1	0.533	0.3323	11	72.793	4.4830
2	0.849	1.0532	12	120.488	2.5000
3	1.396	2.5212	13	199.293	1.4672
4	2.298	4.9360	14	331.156	0.8805
5	3.760	8.7834	15	534.139	0.5387
6	6.192	13.9101	16	831.452	0.1122
7	10.093	18.0739		\bar{M}_n [10^3 g/mol]	7.098
8	16.506	17.9141		\bar{M}_w [10^3 g/mol]	29.54
9	26.846	14.1462		\bar{M}_w/\bar{M}_n	4.161
10	44.103	8.3474			

Table 3
Characteristic parameters of the S-L EOS for ethylene, hexane and PE.

Substance	P^* [MPa]	ρ^* [kg/m^3]	T^* [K]
ethylene	335 ^a	648 ^a	285 ^a
hexane	298 ^b	775 ^b	476 ^b
polyethylene	359 ^c	1200 ^d	521 ^c

^a Sato et al. [20].

^b Sanchez and Lacombe [14].

^c Kiran et al. [3].

^d previous work [13].

Table 4The values of the binary interaction parameters, k_{ij} , in S-L EOS.

Binary pair	k_{ij}	Source	Ref.
ethylene-hexane	0.0515	VLE	[6]
ethylene-PE	-0.1706	LL boundary	This work
hexane-PE	0029-6.0 × logM[kg/mol]	LL boundary and critical point	[13]

Table 5Experimental phase boundaries for the ethylene + hexane + PE system at 473 K.^a

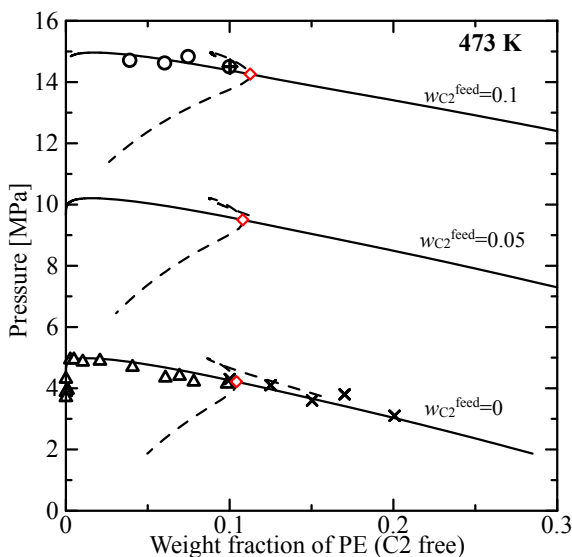
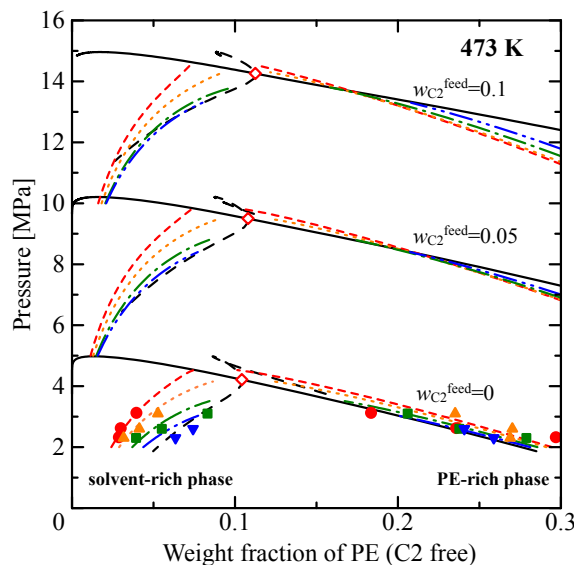
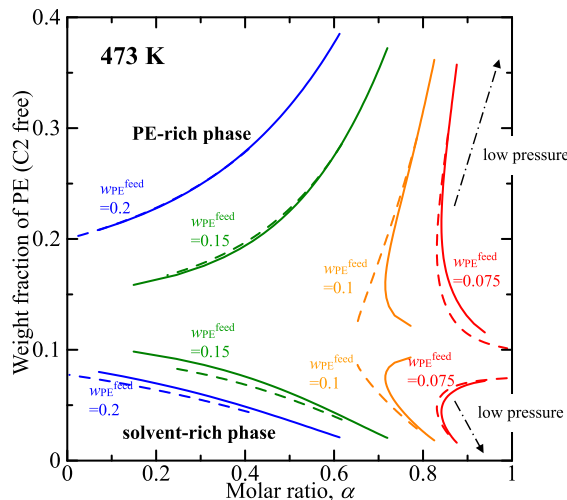
Feed composition [weight fraction basis]				Pressure [MPa]
Ethylene	Hexane	PE	PE (ethylene free)	
0.1037	0.8610	0.0353	0.0394	14.96
0.0972	0.8481	0.0548	0.0607	14.60
0.1139	0.8196	0.0664	0.0750	14.81
0.1008	0.8090	0.0901	0.1002	14.48 (14.50 ^b)

^a Standard uncertainties for weight fraction, temperature and pressure are 0.002, 0.2 K and 0.2 MPa, respectively.^b The value determined by identifying the disappearance of the interface of the separated liquid phases.

$$z_i = \alpha x_i^{L1} + (1 - \alpha)x_i^{L2} = \{1 + (K_i - 1)\alpha\}x_i^{L2} \quad (13)$$

Therefore, the mole fractions of each phase are shown as follows using the feed mole fraction, molar ratio and equilibrium ratio.

$$x_i^{L2} = \frac{z_i}{1 + (K_i - 1)\alpha}, \quad x_i^{L1} = K_i x_i^{L2} = \frac{K_i z_i}{1 + (K_i - 1)\alpha} \quad (14)$$

In the present study, K_i and α were set to the variables, and they were determined using the convergence condition of Eq. (9) (replacing μ_i^0 and μ_i^N with μ_i^{L1} and μ_i^{L2}) with unity of the summations of mole fractions for both liquid phases.**Fig. 2.** LL phase boundaries and shadow curves for the hexane + PE and ethylene + hexane + PE systems at 473 K and at the feed ethylene (C2) weight fraction from 0 to 0.1. Open circles and triangles are experimental LL phase boundaries that are determined by identifying the phase transitions. Cross and diagonal crosses show the experimental LL phase boundaries determined by identifying the disappearance of the interface of the separated liquid phases. Solid and dashed lines are the correlated LL phase boundaries and shadow curves, respectively. The open diamonds represent the calculated critical points. Both experimental and calculated results at the feed ethylene weight fraction of 0 are cited from the previous work [13].**Fig. 3.** Calculated LL phase equilibria and correlated LL phase boundaries and shadow curves for the ethylene + hexane + PE systems at 473 K and at the feed ethylene (C2) weight fraction from 0 to 0.1. Black solid and dashed lines are the correlated LL phase boundaries and shadow curves, respectively. Dashed (red), short dashed (orange), long and short dashed (green), and long and two short dashed (blue) lines are the predicted LL phase equilibrium lines at the feed PE weight fractions of 0.075, 0.1, 0.15, and 0.2 (C2 free basis), respectively. The open diamonds represent the correlated critical points. Closed circle (red), triangle (orange), tetragon (green) and inverted triangle (blue) show the experimental LL phase equilibria for the hexane + PE binary system at the feed PE weight fractions of 0.075, 0.1, 0.15 and 0.2, respectively. Both experimental and calculated results at the feed ethylene weight fraction of 0 are cited from the previous work [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)**Fig. 4.** Calculated relationships between the molar ratio defined as Eq. (11) and the weight fraction of PE for the ethylene (C2: weight fraction of 0.1) + hexane + PE and the hexane + PE systems at 473 K. Solid and dashed lines represent the calculated results of the ternary and binary systems, respectively. The upper and bottom sides of the figure show the results of the PE-rich and solvent-rich phases, respectively.

4. Results and discussion

4.1. Experimental LL phase boundary

The experimental results of the LL phase boundaries at the ethylene weight fraction of 0.1 and 473 K are listed in Table 5 and shown in Fig. 2. In the table, both the results, which were obtained by the determination of the phase transition from a transparent phase to a cloudy phase and by detecting the disappearance of the LL interface in the step-by-step pressurization, are listed. The phase-transition pressures measured by both methods showed good agreement at a PE weight fraction of 0.09, which was the highest PE concentration in the measurement. The phase-separation pressures measured at a PE weight fraction ranging from 0.035 to 0.09 were almost constant, as opposed to those of the hexane + PE system [13]. The addition of a 0.1 weight fraction of ethylene raised the phase boundary pressure about 10 MPa. These

effects of ethylene addition are well known as the anti-solvent effect of a low-boiling-point compound.

4.2. Correlation of the LL phase boundary and the effect of ethylene addition

The correlated results of the phase boundary curve of the ethylene + hexane + PE system at 473 K are shown in Fig. 2 along with the experimental results. As described in the calculation model shown in “3. Calculation model” section, the binary interaction parameter between ethylene and PE, k_{C2-PE} , was adjusted to obtain a good correlation, and the determined value is listed in Table 4. The correlated results successfully reproduced the experimental LL phase boundary with an average absolute relative deviation of 1.1%. The calculated LL phase boundary for an ethylene weight fraction of 0.05 is also described in Fig. 2 to further clarify the effect of the addition of ethylene. The phase boundary pressure

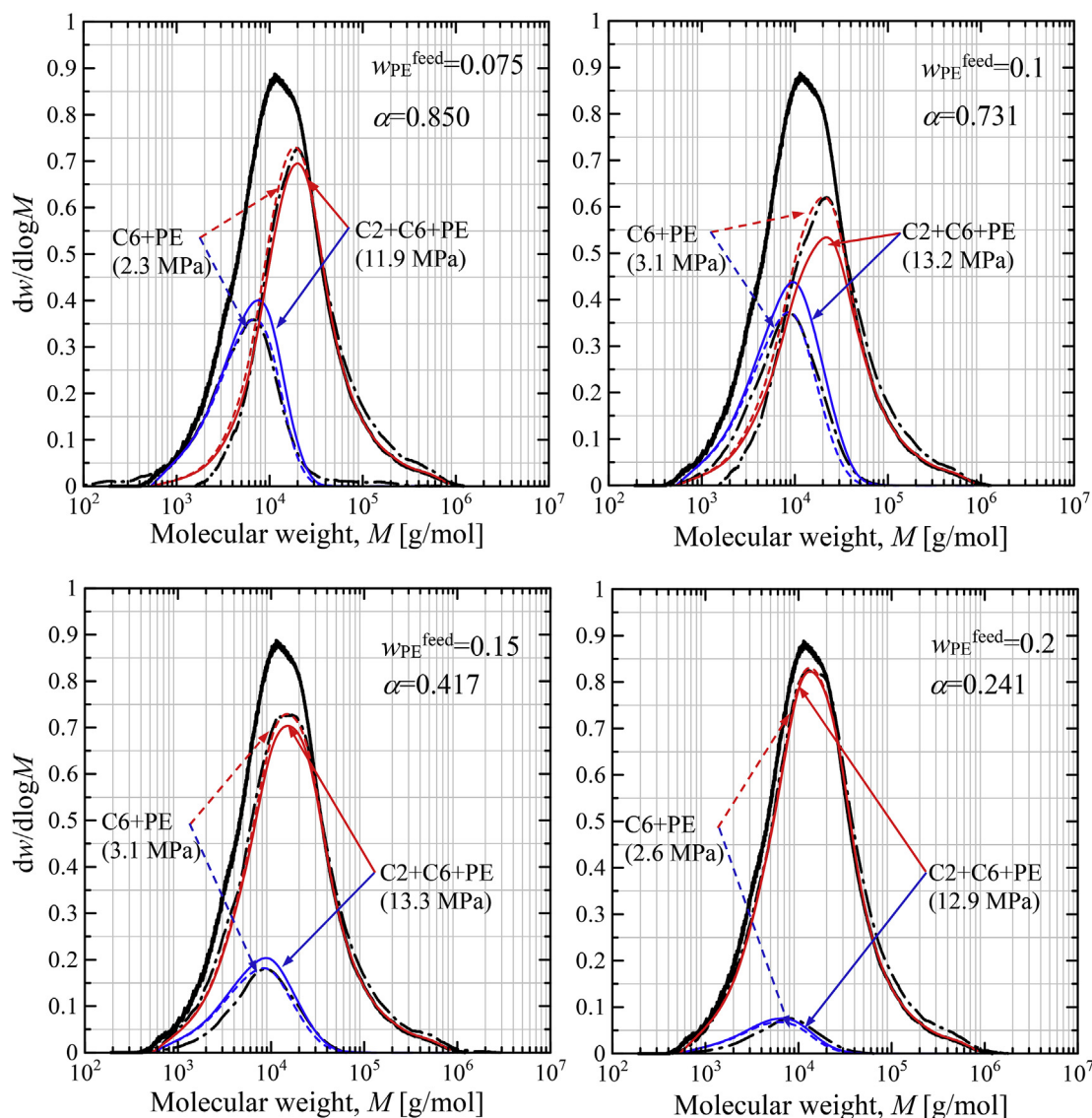


Fig. 5. Simulated MWDs of PEs in the separated two LL phases at each feed PE weight fraction and molar ratio for the ethylene (C2: weight fraction of 0.1) + hexane + PE and the hexane + PE systems at 473 K. Solid and dashed lines show the ternary and binary systems, respectively. The red and blue lines show the results of the PE-rich and the solvent-rich phases, respectively. Black solid lines show the MWD of the original PE. Black long and short dashed lines indicate experimental MWDs for the hexane + PE system obtained by the GPC analyses [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

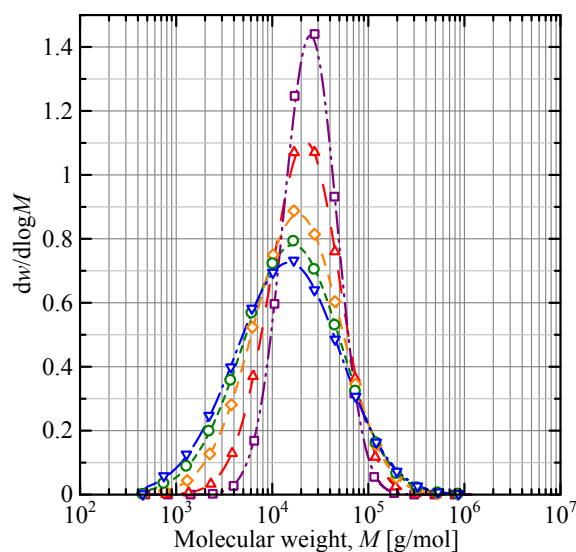


Fig. 6. The MWDs of polydisperse PE obtained by the Hosemann-Schramek distribution function. \bar{M}_w of all MWDs is 3.0×10^4 g/mol. The long and the two dashed (purple), long dashed (red), dashed (orange), short dashed (green), and long and dashed (blue) lines show the \bar{M}_w/\bar{M}_n of 1.5, 2, 3, 4, and 5, respectively. Symbols show the pseudo 16 components constituting the polydisperse PE used for the calculations (Details are shown in Supplementary material). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

increase was approximately linear with increases in the ethylene weight fraction of at least up to 0.1, and a slope of about 1 MPa per 0.01 of ethylene weight fraction. As for the calculated critical point that is represented as the cross-point of the phase boundary curve and shadow curve, the critical PE composition was moved to a higher PE weight fraction as the ethylene weight fraction increased.

4.3. Simulation studies of the effect of ethylene addition on the LL phase equilibria

Calculations of the LL phase equilibria were carried out to clarify the effect that the addition of ethylene exerted on the LL phase equilibria for the PE solutions at high temperature and pressure. The characteristic and interaction parameters used were determined by the correlations as listed in Tables 3 and 4. The calculated results for the phase equilibrium curve at 473 K and the ethylene weight fractions from 0 to 0.1 are shown in Fig. 3 along with the experimental LL phase equilibria for the hexane + PE system measured in our previous work [13]. The flash calculations for the LL phase equilibria were carried out at the ethylene free basis PE weight fractions of 0.075, 0.1, 0.15, and 0.2. The calculated critical PE weight fractions existed between 0.1 and 0.11 of the ethylene free basis in the range of ethylene weight fraction from 0 to 0.1. Therefore, the LL phase equilibrium curves of the feed PE weight fractions of 0.075 and 0.1 were connected to the LL phase boundary curve, and those of 0.15 and 0.20 were connected to the shadow curve at each LL phase separation pressure for the solvent-rich phase. On the other hand, in the PE-rich phase, the behaviors of connection for the LL phase equilibrium curves with the LL phase boundary curves were opposite to those in the solvent-rich phase. Both the LL phase equilibrium curves of solvent- and PE-rich phases intersected with the phase equilibrium and the shadow curves for the ethylene + hexane + PE system, although these could not be observed for the hexane + PE binary system.

The LL phase boundary pressures were drastically increased by the addition of ethylene. Therefore, it was difficult to evaluate the

effect of the ethylene addition on the LL phase equilibria of the PE solution by comparing the results between the hexane + PE and ethylene + hexane + PE systems at the same pressure. In the present work, the results between binary and ternary systems were compared at the same molar ratio, α , estimated from Eq. (11). The relationship between molar ratio and the PE weight fraction at each feed PE weight fraction is shown in Fig. 4. In the figure, the side of high PE content (upper side of Fig. 4) shows the results of the PE-rich phase, and the lower PE content (bottom side of Fig. 4) indicates the results of the solvent-rich phase. The effect of ethylene was small for both the PE-rich and the solvent-rich phases at lower pressure regardless of the feed PE weight fraction. In the high-pressure region, which was near the phase-boundary pressure, a degree of difference was apparent between the binary and ternary systems, and the large difference in the PE weight fraction of 0.1 was due to the vicinity of the critical point. Moreover, the MWDs of the PEs were compared between the binary and ternary systems at the same molar ratio and feed PE weight fractions. The comparisons of the simulated MWDs of PEs between binary and ternary systems are shown in Fig. 5. The experimental MWDs of PEs for the binary hexane + PE systems obtained in the previous work [13] are also included in the figure to present the accuracies of the calculations. Note that, the values of the $dw/d\log M$ of the experimental MWDs were rescaled to equal the maximum $dw/d\log M$ to that of the calculated result because the mass of each phase couldn't be determined experimentally. The calculated MWDs of the binary systems approximately corresponded with the experimental MWDs regardless of the feed PE weight fractions. And the MWDs of the PEs from both systems were also similar, and therefore, a significant effect from the addition of ethylene couldn't be found. The probable reason that the ethylene effect was small for the LL phase equilibria was because the main component of both separated phases was hexane—regardless of the 0.1 weight fraction of the ethylene addition.

4.4. Simulation study of the effect of the polydispersity of PE on the LL phase equilibria

The PEs with different MWDs were created using the three-parameter Hosemann–Schramek distribution function in order to investigate the effect of the polydispersity of PE on the LL phase equilibria. The distribution function that was used was as follows [6,21]:

$$w(M) = \alpha \delta^{(\kappa+1)/\alpha} \Gamma^{-1} \left(\frac{\kappa+1}{\alpha} \right) M^\kappa \exp(-\delta M^\alpha) \quad (15)$$

where w and M are the weight fraction and molecular weight, respectively. Γ represents the Gamma function, and α , κ and δ are the parameters that determine the shape of the MWD. Moreover, the average molecular weights can be expressed by the Gamma function based on three parameters, as follows:

$$\bar{M}_n = \Gamma \left(\frac{\kappa+1}{\alpha} \right) \Gamma^{-1} \left(\frac{\kappa}{\alpha} \right) \delta^{-1/\alpha} \quad (16)$$

$$\bar{M}_w = \Gamma \left(\frac{\kappa+2}{\alpha} \right) \Gamma^{-1} \left(\frac{\kappa+1}{\alpha} \right) \delta^{-1/\alpha} \quad (17)$$

$$\bar{M}_z = \Gamma \left(\frac{\kappa+3}{\alpha} \right) \Gamma^{-1} \left(\frac{\kappa+2}{\alpha} \right) \delta^{-1/\alpha} \quad (18)$$

In the present work, five different types of MWDs were created, and all MWDs had the same \bar{M}_w (3×10^4 g/mol), although the polydispersity of each MWD was different: $\bar{M}_w/\bar{M}_n = 1.5, 2, 3, 4$ and

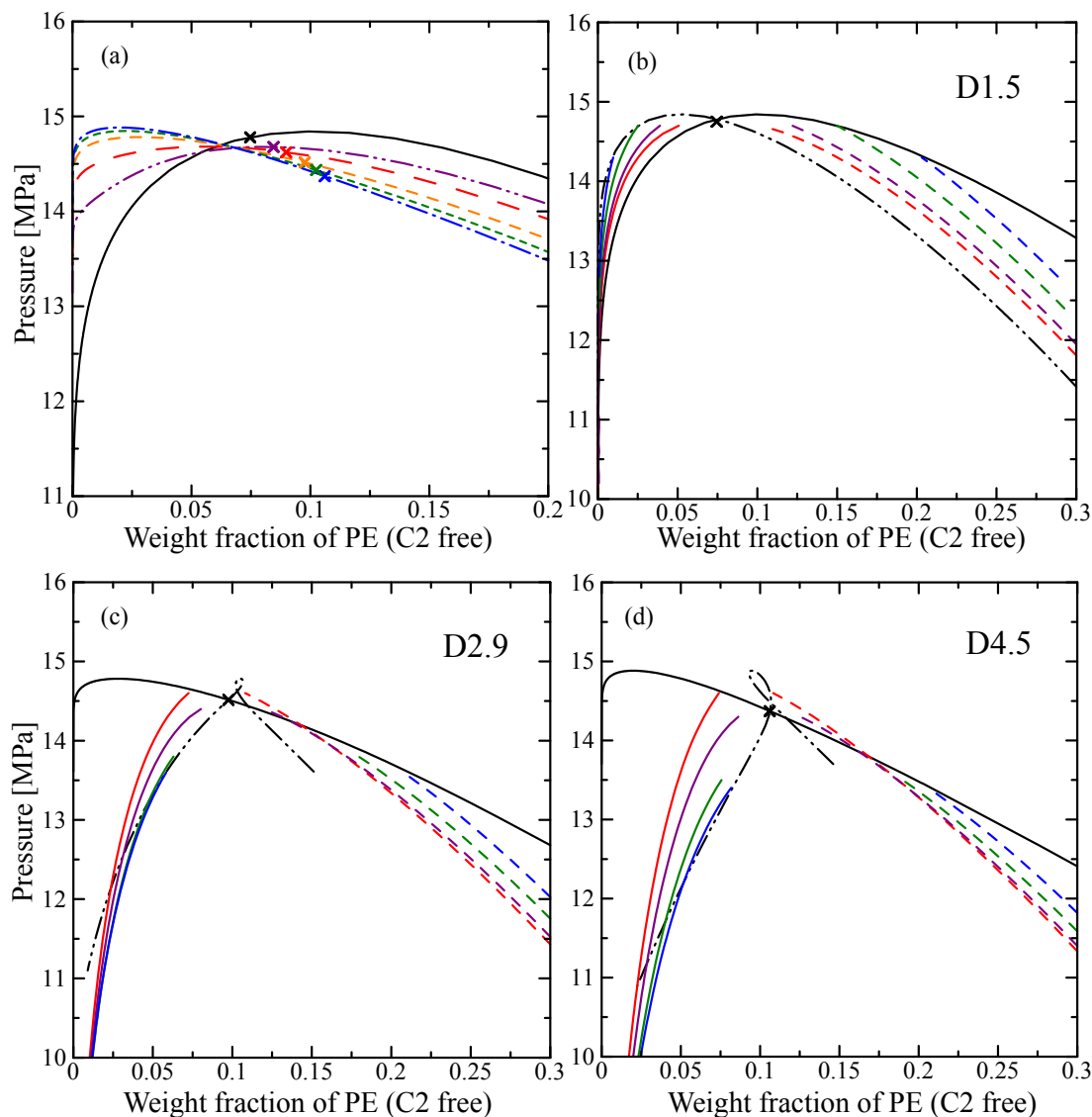


Fig. 7. Calculated LL phase boundary curves, shadow curves and the LL phase equilibrium curves for the ethylene + hexane + PE systems at 473 K and at the feed ethylene weight fraction of 0.1. (a): LL phase boundary curves for each polydisperse PE solution. Solid (black), long and two short dashed (purple), long dashed (red), dashed (orange), short dashed (green) and long and short dashed (blue) lines indicate the phase boundaries for the PEs of monodisperse, D1.5, D2.0, D2.9, D3.8 and D4.5, respectively. (b)–(d): LL phase equilibrium lines for each polydisperse PE solution of D1.5, D2.9 and D4.5, respectively. Solid, and long and two short dashed lines are the LL phase boundary and shadow curves, respectively. Red, purple, green and blue dashed lines are the calculated LL phase equilibrium lines at the feed PE weight fractions (C2 free basis) of 0.075, 0.1, 0.15, and 0.2, respectively. The diagonal cross symbols represent the calculated critical points. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5. The MWDs created by the distribution function are shown in Fig. 6. In the calculation of the LL phase boundaries and phase equilibria, the polydispersities of each MWD were represented as the mixture of 16-pseudo monodisperse PEs, as described in “3. Calculation model” section. The values of pseudo components are also illustrated in Fig. 6, and the numerical data are listed in Supplementary material. The \bar{M}_w of all mixtures composed of 16-pseudo components were about 2.9×10^4 g/mol regardless of polydispersity. Moreover, the \bar{M}_w/\bar{M}_n of the mixtures approximately reproduced the values of the original MWDs. As for the MWDs having large polydispersity, slight deviations between the values of the original MWDs and pseudo component mixtures, which might be due to the method to create the representative molecular weights and their contents, were found. In the present work, therefore, each pseudo component mixtures created using the MWDs obtained from the Hosemann-Schramek distribution

function were named: D1.5, D2.0, D2.9, D3.8 and D4.5, respectively.

The simulated LL phase boundary curves, shadow curves and LL phase equilibrium curves for the ethylene + hexane + PE systems at 473 K and at an ethylene weight fraction of 0.1 are shown in Fig. 7. As for the LL phase-boundary curves, the PE weight fraction at the highest phase boundary pressure was decreased with an increase in polydispersity. However, the difference in the values of the highest phase boundary pressures was small regardless of the polydispersity, because the values for \bar{M}_w of each MWD were the same. On the other hand, the critical PE weight fraction increased as the polydispersity increased (Fig. 7(a)). As for the LL phase equilibrium curves, the PE weight fraction increased as the feed PE weight fraction in the PE-rich phase was increased regardless of polydispersity at sufficiently low pressure compared with the phase boundary curve. On the other hand, the behavior of the phase equilibrium curves of the solvent-rich phase differed depending on

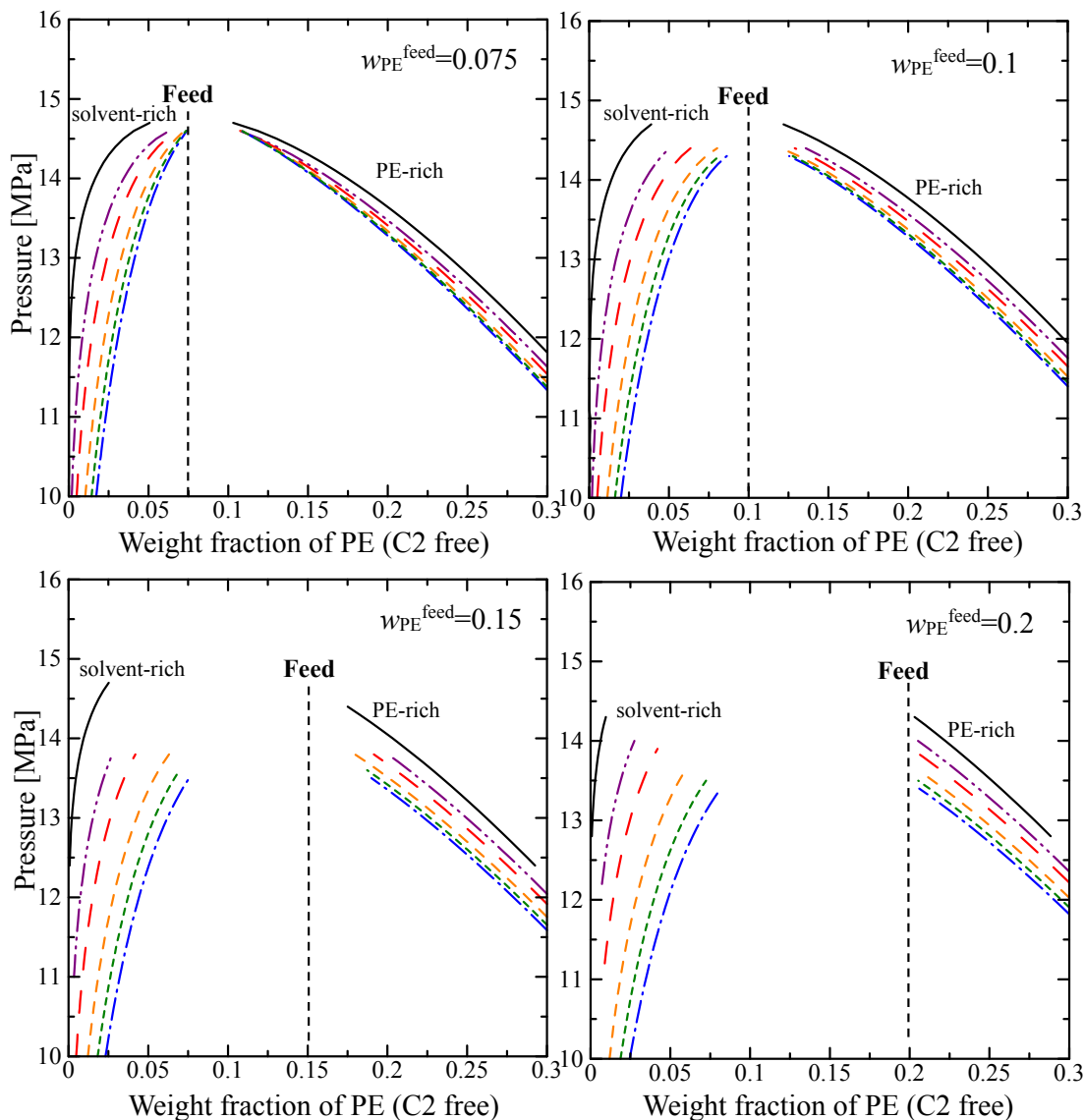


Fig. 8. Simulated of the effect of the MWD of PE on the LL phase boundary curves at 473 K and at the feed ethylene weight fraction of 0.1. Solid (black), long and two dashed (purple), long dashed (red), dashed (orange), short dashed (green), and long and dashed (blue) lines show the results of the polydisperse PE solutions of monodisperse, D1.5, D2.0, D2.9, D3.8 and D4.5, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polydispersity. As shown in Fig. 7, the PE weight fraction in solvent-rich phase decreased with increasing the feed PE weight fraction for D1.5. In an opposite fashion, the PE weight fraction increased as the feed PE weight fraction increased in the cases of D2.9 and D4.5. Namely, the relationships between the feed PE weight fraction and the LL phase equilibrium curve differed based on polydispersity. This difference seemed to be based on the relationship between the phase boundary curve and shadow curve. The simulated polydispersity dependencies of the LL phase equilibrium curves at each feed PE weight fraction are illustrated in Fig. 8. The same tendency was obtained at either feed PE weight fraction. The PE weight fraction increased with increases in polydispersity in the solvent-rich phase, and decreased with increases in polydispersity in the PE-rich phase. The reason of these tendencies is considered that the larger amount of low-molecular-weight PE can exist in the solvent-rich phase for high polydispersity of PE. As shown in Fig. 6, it is obvious that the amount of low-molecular-weight PE included in PE with high-polydispersity is larger than that of PE with low-

polydispersity. In addition to the discussion about PE weight fraction in the separated phases, the effect of polydispersity on the MWDs of PE at 473 K and 13 MPa at ethylene weight fraction of 0.1 is shown in Fig. 9. As shown in the figure, the maximum molecular weights of PEs dissolved in the solvent-rich phase were quite similar at the same temperature, pressure and feed PE weight fraction regardless of the polydispersity.

5. Conclusions

In the present work, the effects of the ethylene addition and the polydispersity of PE on the LL phase boundary and the LL equilibria for the ethylene + hexane + PE system were investigated using the Sanchez–Lacombe equation of state. The binary interaction parameters between PE and solvent molecule that were determined from the correlations of the LL phase boundary of PE solution were used. The effect of the ethylene addition on the LL phase equilibria was small compared with that on the LL phase boundary curves. On

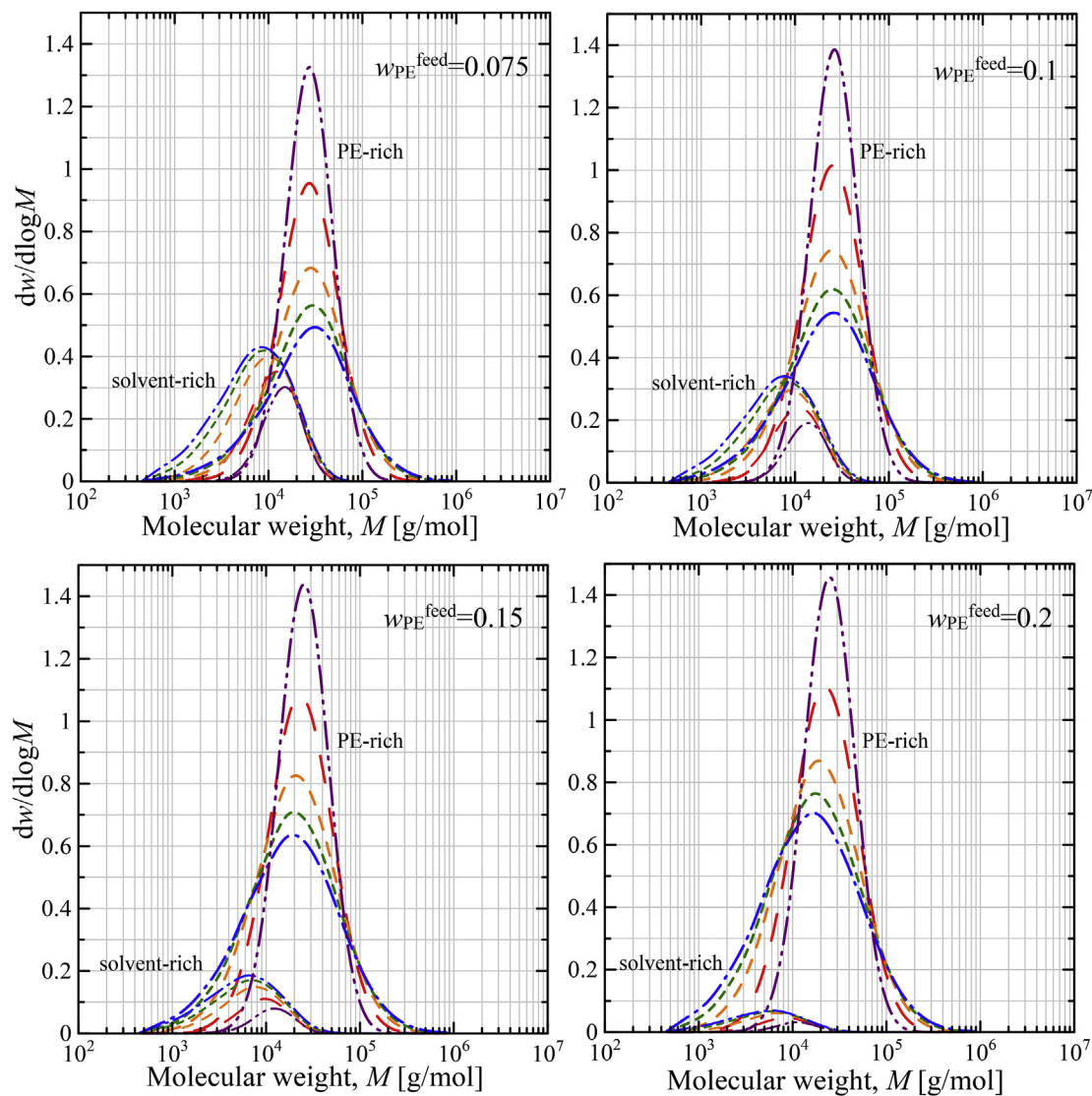


Fig. 9. Simulated MWDs of PEs in the separated LL phases for the ethylene + hexane + PE systems at 473 K and 13 MPa, and at the feed ethylene weight fraction of 0.1. Long and two dashed (purple), long dashed (red), dashed (orange), short dashed (green), and long and dashed (blue) lines show the results of the polydisperse PE solutions of D1.5, D2.0, D2.9, D3.8 and D4.5, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

