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Poly(ethylene-*co*-butyl acrylate). Phase Behavior in Ethylene Compared to the Poly(ethylene-*co*-methyl acrylate)−Ethylene System and Aspects of Copolymerization Kinetics at High Pressures

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ABSTRACT: Cloud point data for poly(ethylene-*co*-butyl acrylate) (EBA)−ethylene and poly(ethylene-*co*-methyl acrylate) (EMA)−ethylene mixtures are presented to 250 °C and 2600 bar as a function of butyl acrylate (BA) content from 5.2, 17.0, 25.2, 40.3, and 100 mol % BA and of molecular weight, and as a function of methyl acrylate (MA) content from 10, 18, 31, 41, and 100 mol % MA. Cloud point pressures initially decrease with increasing BA content at rate of ∼17 bar/mol % BA up to ∼40 mol % BA and then they remain relatively constant with further increases in BA content. The cloud point pressures increase with increasing weight-average molecular weight (M_w), at a rate of ∼4 bar/10000 M_w. However, cloud point pressures for the EMA−ethylene mixtures initially decrease as the MA content increases to ∼20 mol % but then increase rapidly as the MA content is further increased. In fact, it is not possible to dissolve poly(methyl acrylate) in ethylene to 240 °C and 2600 bar, although poly(butyl acrylate) readily dissolves in ethylene at pressures as low as 800 bar at 50 °C. The experimental data are modeled using the SAFT equation of state with two mixture interaction parameters. The EBA copolymers used in this study were synthesized in two different types of continuous-flow reactors at variable-feed compositions, temperatures to 225 °C, and pressures to 2000 bar. The number-average degree of polymerization decreases with increasing temperature, and it is significantly affected by transfer reactions to monomer. The chain transfer to butyl acrylate monomer plays a dominant rule among transfer reactions at 150 °C, as indicated by the decrease in EBA molecular weight with increase in BA content in the copolymer. The molecular weight polydispersity decreases slightly from 3.0 to 2.5 as the BA content in the copolymer increases to 25 mol %.

Introduction

This study compares the cloud point behavior of mixtures of ethylene with poly(ethylene-*co*-butyl acrylate) (EBA) and poly(ethylene-*co*-methyl acrylate) (EMA) copolymers. These data demonstrate the sensitivity of the cloud point to changes in comonomer structure even when the comonomers are from the same chemical family. Data are also presented on the effect of temperature on the degree of copolymerization of ethylene with butyl acrylate (BA) and on the impact of BA content in the copolymer on the weight- and number-average molecular weights of the resultant EBA copolymers. The cloud point data presented in this work define the pressures and temperatures at which the copolymerization can be operated in a single phase to produce EBA copolymers with differing molecular weights and BA contents.

Ethylene is the only solvent used in this study for both types of copolymers. Ethylene has a modest polarizability, which makes it a feeble solvent for nonpolar polymers, such as polyethylene, as compared to larger hydrocarbons such as propane.[1−4] However, ethylene has a significant quadrupole moment, which makes it a good solvent for moderately polar copolymers. Hasch et al.[3] showed that ethylene is a better solvent for EMA copolymers that have ∼20 mol % methyl acrylate (MA) repeat units than it is for nonpolar polyethylene (PE). As the concentration of MA repeat units increases above ∼30 mol %, EMA copolymers become less soluble in ethylene since they now exhibit significant polar character. In this study, the cloud point data reported by Hasch et al.[3] for mixtures of ethylene with EMA copolymers of 10, 31, and 41 mol % MA are extended to temperatures as high as 250 °C. Also, cloud point data are reported for ethylene with an EMA copolymer containing 18 mol % MA.

Ethylene−EMA cloud point data are contrasted with data for the ethylene−EBA system. Both acrylates are expected to have approximately the same dipole moments; however, the dipole moment of *n*-butyl acrylate is distributed over a larger molar volume as compared to methyl acrylate. Since the strength of interactions associated with the dipole moment scales inversely with the square root of the molar volume,[5] the increase in polarity per polar repeat unit is greater for MA as compared to BA. Also, polar interactions scale roughly with inverse temperature, so that the system temperature is expected to have a large effect on the cloud point pressures. Hence, the pressure−temperature shift of the cloud point curve per increase in copolymer acrylate content is expected to be very different for these two ethylene−acrylate copolymers.

Another characteristic difference between EMA and EBA copolymers is that the free volume of the EBA copolymers should be greater than that of the EMA copolymers with equivalent numbers of acrylate groups since poly(butyl acrylate) has a much lower glass transition temperatures (T_g), −56 °C, than does poly-

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(methyl acrylate), 3 °C.[6] Therefore, as long as the temperature is high enough that polar interactions do not control solubility behavior, it should be easier to dissolve EBA copolymers since the EBA−ethylene free volume difference is smaller than that expected with EMA copolymers.

As previously mentioned, it is necessary to ensure that the copolymerization occurs homogeneously if the simplified terminal unit model is used to determine the kinetic parameters for free-radical copolymerization reactions. Very different values are expected for the reactivity ratios, the rate of polymerization, and the copolymer architecture if the copolymerization occurs in a two-phase region.[7] Equation 1, derived by assuming that the reaction takes place in a single phase and at differential monomer conversion, shows that the reactivity ratios for ethylene ($r_E = k_{\text{ethylene−ethylene}}/k_{\text{butyl acrylate−ethylene}}$ where k_{ii} is the homopropagation rate coefficient of monomer i and k_{ij} is the cross-propagation rate coefficient for the addition of monomer j to a free radical terminating in species i) and BA ($r_{BA} = k_{\text{butyl acrylate−butyl acrylate}}/k_{\text{butyl acrylate−ethylene}}$) are needed to predict the backbone composition of the copolymer produced at a given temperature and pressure.

$$F_{BA} = \frac{r_{BA}f_{BA}^{\ 2}}{(r_{BA}f_{BA}^{\ 2} + 2f_{BA}f_E + r_Ef_E^{\ 2})} \tag{1}$$

where F_{BA} is the mole fraction of BA in the backbone of the copolymer, and f_{BA} and f_E are the mole fractions of BA and ethylene in the feed mixture, respectively. Ehrlich and Mortimer reported that r_E varies from 0.03 to 0.30 at temperatures from 70 to 182 °C and pressures between 1000 and 1450 bar.[2] However, it is not apparent that a single phase exists over the entire pressure−temperature range reported by Erhlich and Mortimer for r_E. Moreover, it is difficult to use the instantaneous copolymer equations since the correction to zero conversion is not described in any detail by these authors. Buback and co-workers[8] described in detail the copolymerization of ethylene with BA over an extended range of pressures and temperatures. They reported information on r_E and r_{BA} which is needed to rationally choose the most effective reactor configuration that can be used to produce an EBA copolymer with the desired physical properties. For the copolymerization data reported here, the system pressure and temperature are adjusted to maintain a single phase during copolymerization to produce sufficient quantities of EBA copolymers for use in the cloud point studies. Data are reported for the effect of temperature on the number-average degree of polymerization and also reported is the impact of BA content in the copolymer on the weight- and number-average molecular weights.

Table 1 lists the properties of the poly(ethylene-*co*-methyl acrylate) and poly(ethylene-*co*-butyl acrylate) copolymers used in this study. Both types of copolymers are assumed to be statistically random. Note that two different polyethylenes are used to establish reference cloud point curves since the weight-average molecular weights of the EBA copolymers are roughly twice those of the EMA copolymers. Although the molecular weight polydispersities of these copolymers are fairly large, previous studies have shown that the polar comonomer content has a much larger effect on the cloud point behavior than does polydispersity.[9] Therefore, all experiments are done with unfractionated parent material. Note that the crystallinity of these two types of copolymers is reduced to zero once the concentration of acrylate groups increases above ~15 mol %. Cloud point measurements are performed with the two EBA_{17} and the two EBA_{25} copolymers to determine the impact of molecular weight on the location of the cloud point curve.

Table 1. Physical Properties of the Polymers Used in This Study[a]

	T_g (°C)	T_{melt} (°C)	cryst (%)	acrylate (mol %)	M_W	M_N	M_W/M_N
PE_A	−125	113	37	0	108 500	20 100	5.4
EMA_{10}		82	15	10	74 800	17 000	4.4
EMA_{18}			0	18	185 200	37 800	4.9
EMA_{31}			0	31	99 000	33 000	3.0
EMA_{41}			0	41	96 360	29 900	3.3
PMA	3		0	100	30 700	10 600	2.9
PE_B	119	119	46	0	297 300	57 100	5.2
EBA_5	88	88	33	5.2	209 700	40 700	5.2
EBA_{17A}			0	17.2	56 800	26 200	2.2
EBA_{17B}			0	17.0	282 700	101 700	2.8
EBA_{25A}			0	25.2	268 300	97 500	2.8
EBA_{25B}			0	25.9	403 800	144 500	2.8
EBA_{40}			0	40.3	35 200	13 900	2.5
PBA	−56		0	100.0	59 200	19 900	3.0

[a] Low-density polyethylenes (PE_A and PE_B), poly(methyl acrylate) (PMA), poly(butyl acrylate) (PBA), poly(ethylene-*co*-methyl acrylate) (EMA_x), and poly(ethylene-*co*-butyl acrylate) (EBA_x). The subscript, x, represents the molar amount of acrylate in the backbone.

Experimental Section

Cloud Point Measurements. Described in detail elsewhere are the techniques used to obtain cloud point curves using a high-pressure, variable-volume view cell.[9] Cloud points are obtained at a fixed copolymer concentration of ~5 wt%. Care is taken to remove entrapped air from the cell by purging with ethylene at room temperature and ~6 bar. Ethylene, to within ±0.002 g, is then transferred into the cell, previously loaded with ~0.350 g of solid copolymer. The system pressure is measured to within ±2.8 bar and the system temperature is measured to within ±0.2 °C, but is maintained to within ±0.2 °C below 200 °C and ±0.4 °C above 200 °C. Cloud points are repeated at least twice at each temperature and are typically reproducible to within ±5 bar. The cloud point curves terminate at the highest operating pressure of the experimental apparatus, the crystallization boundary, or 30 °C, which ever comes first.

Ethylene−Butyl Acrylate Copolymerization. The reactor configurations used for the high-pressure copolymerization reactions are described in detail elsewhere[8] and are only briefly described here. Copolymerization reactions are performed with two reaction cells that roughly correspond to a tubular reactor (internal volume 2.5 cm^3) and a continuously stirred tank reactor (CSTR, internal volume 50 cm^3). Both cells are capable of operating to 3000 bar and 300 °C.

Reaction mixture enters the tubular reactor at flow rates regulated between 150 and 500 g/h. The copolymerization reaction is initiated thermally with residence times on the order of 30 s to obtain differential conversions as a result of very low copolymerization rates.

Reaction mixture enters the CSTR reactor at flow rates of 250 and 1000 g/h. The CSTR is equipped with a sapphire window through which UV excimer radiation at a wavelength of 308 nm XeCl can be introduced to generate BA radicals that initiate copolymerization. Thermally initiated copolymerization reactions are also be obtained with the CSTR.

The effluent stream from either of the reactors is routed to another high-pressure cell, with an optical path length of 1 mm bounded by two polycrystalline silicon windows, and positioned in the optical compartment of a Fourier transform spectrometer. Spectra from 1500 to 6500 cm^{-1} are taken at intervals of 2.5 min and are integrated on-line in the regions with specific absorption bands for ethylene, BA, and the

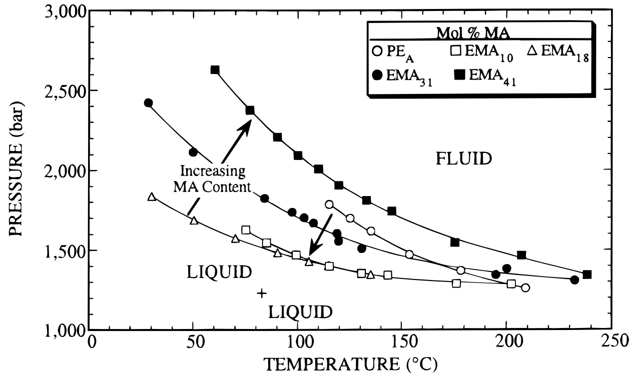

Figure 1. Cloud point curves of EMA−ethylene mixtures. Data at temperatures above 150 °C and the cloud point curve for the EMA$_{18}$−ethylene system are obtained in this study. Data at temperatures below 150 °C were obtained by Hasch and co-workers.[3]

resulting copolymer. The copolymer is then recovered in two stages by first precipitating at 200 bar and 120 °C in an autoclave and then decompressing to ambient pressure in a second autoclave. Reactions are run for ~30 min at monomer conversions typically maintained close to 1%, but always below 4%, yielding a few grams of copolymer. During the reaction, the pressure is maintained to within ±30 bar and the temperature is maintained to with ±1.0 °C.

Materials. The PE$_B$ is synthesized in the continuous-flow reactor as described in detail elsewhere.[10] PBA and PMA, both in toluene (Aldrich Corp.), are recovered from solution using a Rotovap system and are used without subsequent purification. PE$_A$ and the EMA copolymers were kindly donated by the DuPont Corp., who also provided composition and molecular weight information for these copolymers. The EMA molecular weight averages are obtained on the basis of LDPE calibration curves corrected for MA content. For the cloud point measurements, ethylene (CP grade, 99.5% minimum purity, Linde Corp.) is used as-received.

For the copolymerization studies, high-purity ethylene with an oxygen content of less than 5 mass ppm is kindly supplied by BASF AG (Ludwigshafen, Germany). Butyl acrylate (Fluka, purity 99+%, stabilized with 15 mass ppm hydroquinone monomethyl ether (HQME)) is distilled at a reduced pressure over a 30 cm Vigreux column. Small amounts of water-free K$_2$CO$_3$ are added to the BA during distillation to retard the HQME. Oxygen is removed from the BA by gas exchange with nitrogen or by a degasser (Erma, Degasser ERC-3322) directly before use. The purity of the BA is checked before each experiment by comparing the molar absorbtivity at a UV absorbance of 308 nm to the accepted literature value.[11]

Elemental analysis is used to determine the composition of the EBA copolymers, and gel permeation chromotagraphy is used to determine their molecular weight averages on the basis of LDPE calibration curves corrected for BA content. Both analytical techniques for the EBA copolymers are performed at BASF AG.

Experimental Results

Cloud Point Behavior. Figure 1 shows the effect of MA content on the cloud point behavior of EMA−ethylene mixtures. PE$_A$ is used for comparison in this case since its molecular weight characteristics closely match those of the EMA copolymers. Consider, first, the general characteristics of the cloud point curves at low and high temperatures. Below ~150 °C, the cloud point curves diverge from one another and increase rapidly in pressure with decreasing temperature as a consequence of polar interactions between MA repeat units. The dipole moment of an MA repeat unit is expected to be ~1.7 D, the value found for methyl propionate.[12,13] The large dipolar interaction of the MA units outweighs the dipole−quadrupole interactions between the acrylate units and the ethylene, which makes the EMA copolymer difficult to solubilize in ethylene. The PE$_A$−ethylene cloud point curve also exhibits a steep negative slope at temperatures below ~150 °C. In this instance, the shape of the PE$_A$−ethylene curve is due to quadrupolar interactions between the ethylene molecules that increase with decreasing temperature and that make it difficult to maintain nonpolar PE$_A$ in solution.

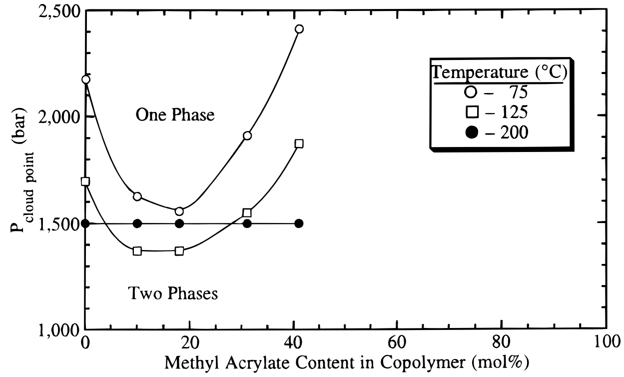

Figure 2. Impact of MA content on the cloud point pressure of EMA copolymers in ethylene. The cloud point pressures for PE at 75 and 125 °C are obtained by extrapolating the cloud point curve to lower temperatures disregarding that PE may crystallize.

At temperatures above ~150 °C, the cloud point curves for PE$_A$ and the copolymers with 10, 31, and 41 mol % appear to converge to within 50 bar of each other. At high temperatures, configuration-dependent polar forces are diminished and the copolymers exhibit more "PE-like" behavior. These three EMA copolymers have weight-average molecular weights that are similar to that of PE$_A$ so the cloud point pressures are expected to be close as long as dispersion forces are the dominant type of intermolecular force in operation.

Figure 2 demonstrates how cloud point pressure is affected as MA units are added to the backbone of PE. At 75 °C, where polar interactions dominate the phase behavior, the initial addition of MA lowers the cloud point pressure considerably since the copolymer becomes slightly polar, which provides favorable interactions with ethylene. The cloud point pressure of the EMA$_{10}$−ethylene system is ~550 bar lower than that of the PE$_A$−ethylene system. Increasing the MA content from 10 to 20 mol % has only a small effect on the location of the cloud point curve. However, when the acrylate content is increased further to 30 and 40 mol %, the cloud point curves increase sharply in pressure. In this temperature region, strong acrylate dipolar interactions dominate weaker dipole−quadrupole interactions and the copolymer is expected to adapt a more coiled configuration to accommodate these interactions. Hence, it becomes more difficult for ethylene to solubilize the copolymer. At 125 °C, the decrease in cloud point pressure with increasing MA content is not as pronounced as it is at 75 °C. This behavior is to be expected since polar interactions between ethylene and MA repeat units are attenuated with increasing temperature. At 200 °C, the cloud point pressure shown in Figure 2 is not affected by MA content. This high-temperature behavior is somewhat surprising since it was not possible to dissolve PMA in ethylene to pressures of 2500 bar at temperatures below 250 °C. And the PMA used in this study has a very modest M_w of 30 700. Therefore, the 200 °C curve in Figure 2 must

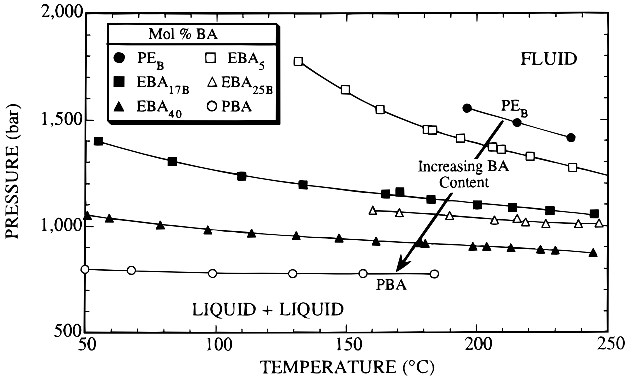

Figure 3. Cloud point curves of EBA−ethylene mixtures obtained in this study.

increase rapidly in pressure as the acrylate content increases above 40 mol %.

Figure 3 shows the effect of BA content on the cloud point behavior of EBA−ethylene mixtures. PE$_B$ is used for comparison in this case since its molecular weight characteristics closely match those of the EBA copolymers. The cloud point curves for the EBA−ethylene system exhibit behavior quite different from the EMA−ethylene curves. Adding BA to the backbone of PE consistently reduces the pressure needed to obtain a single phase at concentrations up to 100 mol % BA. Two factors are likely responsible for the differences between the EBA−ethylene and the EMA−ethylene systems. First, the EBA copolymers are expected to have more free volume than EMA copolymer of similar acrylate content since the glass transition temperature of poly(butyl acrylate) is ~60 °C less than that of poly(methyl acrylate).[6] Note that, as the temperature is decreased, the EBA−ethylene curves do not increase in pressure nearly as rapidly as the curves did for the EMA−ethylene system. For BA contents greater than 17 mol %, the cloud point curves exhibit only slight negative slopes over the 50−250 °C temperature range. Second, the *n*-butyl tails on two BA units are expected to screen the BA groups from interacting effectively with one another which also reduces the impact of the polar group and, therefore, reduces the sensitivity of the cloud point curve to temperature. In addition, the dipole of BA in the backbone does not interact as strongly with the quadrupole of ethylene as does the dipole of MA since the dipole moment of BA is distributed over a larger volume.

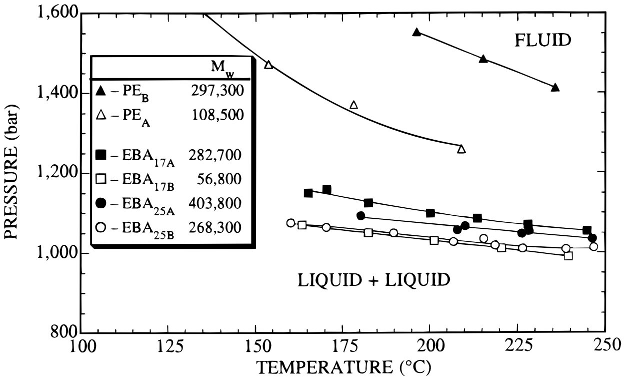

Figure 4. Effect of molecular weight on the cloud point curve of the EBA−ethylene system. The molecular weight polydispersities are 5.3 ± 0.1 for the polyethylenes, 2.5 ± 0.3 for the two EBA$_{17}$ copolymers, and 2.8 for the two EBA$_{25}$ copolymers. Only data in the high-temperature range are presented for the EBA$_{17A}$−ethylene system. The PE$_A$−ethylene data at temperatures below 150 °C are outside the pressure range of the graph.

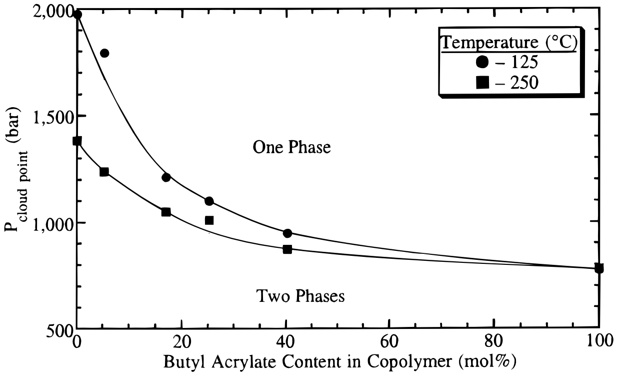

Figure 5. Impact of BA content on the cloud point pressure of EBA copolymers in ethylene. The cloud point pressure for PE at 125 °C is obtained by extrapolating the cloud point curve disregarding that PE may solidify.

Although there is a steady decrease in cloud point pressure with increasing BA content, it is not apparent that the locations of the EBA$_{40}$ and PBA curves are fixed more by BA content or by molecular weight since the weight-average molecular weights for EBA$_{40}$ and PBA are so much lower than those of the other EBA copolymers. To differentiate the effect of molecular weight and backbone composition, cloud point curves were measured for the PE, EBA$_{17}$, and EBA$_{25}$ systems as shown in Figure 4. The largest differences in cloud point pressures in ethylene are observed for the two PEs, which are more nonpolar than either of the two EBA copolymers. Not only are the energetics of mixing nonpolar PE with polar ethylene less favored than mixing polar EBA copolymers with ethylene, the structural differences between the two polyethylene polymers exacerbate this effect. Hasch and co-workers[4] demonstrated that the cloud point pressure of PE dissolved in ethane decreases by ~5 bar/crystallinity% at 155 °C. The PE data in Figure 4 differ by ~22 bar/crystallinity% at 200 °C, probably because ethylene is not as good a solvent as ethane for PE, which means that any structural differences in PE are magnified in ethylene. The impact of molecular weight on the EBA$_{17}$−ethylene system is approximately one-third that of the PE system even though the molecular weights of the two EBA$_{17}$ copolymers fall in the range of 60 000−400 000, where molecular weight typically still has a large effect on cloud point pressure. In this instance, the structural difference between PE and EBA$_{17}$ is provided by BA, which disrupts the steroregularity of the chain backbone and increases the steric hindrance between two interacting EBA$_{17}$ chains. The BA groups also improve the solubility characteristics of this copolymer relative to PE. Evidently, ethylene is a sufficiently good solvent for EBA$_{17}$ that molecular weight differences are now minimized. Likewise, the impact of molecular weight on the EBA$_{25}$−ethylene system is also minimal relative to the PE−ethylene system.

Based on the results shown in Figure 4, it is reasonable, to a first approximation, to compare the impact of BA content on the cloud point pressure even though the weight-average molecular weights of EBA$_{40}$ and PBA are lower than the other EBA copolymers. Figure 5 demonstrates the impact of BA content on cloud point pressure. At 125 °C, the cloud point pressure initially decreases rapidly with the addition of the first 40 mol % BA, but then it decreases only slightly as the BA content increases to 100 mol %. At 250 °C, the decrease

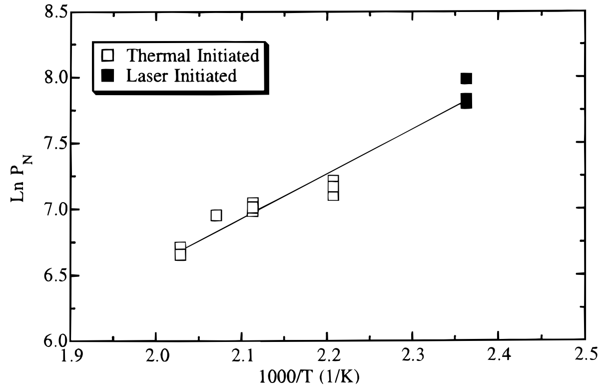

Figure 6. Number-average degree of polymerization (P_N) as a function of temperature at 2000 bar for an EBA copolymer with 11 mol % BA. The data are obtained at 1.5% degree of conversion by two different modes of initiation.

in cloud point pressure is less dramatic with the addition of BA. Note that the cloud point pressures at both temperatures do not exhibit a minimum with increasing BA content as is found with the MA system. Apparently, the polarity increase caused by the addition of BA to the backbone is less substantial than that found with the addition of MA.

Copolymerization Behavior. Figure 6 shows the number-average degree of the polymerization for EBA copolymers containing 11 mol % BA in the backbone, synthesized at 2000 bar, at different temperatures, and at conversions smaller than 1.5%. Buback and co-workers[8] have shown that less than 1 mol % BA is needed in the monomer mixture to obtain EBA copolymers with up to 15 mol % BA. Any unreacted BA that remains in the monomer mixture acts as a cosolvent that effectively lowers the cloud point pressures, based on the results of Rätzsch and co-workers[14] for the poly(ethylene-*co*-vinyl acetate)–ethylene–vinyl acetate system. Therefore, the cloud point pressures needed to obtain a single phase for the EBA copolymers shown in Figure 3 represent the highest pressures since there is no cosolvent in the solution. The cloud point data in Figure 3 verify that the copolymerization data in Figure 6 are obtained well within the one-phase region for an EBA copolymer with 11 mol % BA. As the temperature increases, the degree of polymerization decreases and it appears that the degree of polymerization is insensitive to the method of initiation, either thermal or laser initiated. Buback and co-workers[15] have shown that as long as the generated radical concentration is small, the degree of polymerization for the high-pressure, free-radical polymerization of ethylene, initiated thermally and photochemically, only depends on temperature and pressure and not on the mode of initiation. Therefore, since the data shown in Figure 6 are obtained at low radical concentrations, the high values of the degree of polymerization at low temperatures are not attributed to the use of a laser to generate the free radicals. Hence, the degree of polymerization for the copolymerization of ethylene and BA is significantly affected by transfer reactions to monomer.[11] Knowing the chain transfer constant of ethylene, it can be shown that the chain transfer constant of BA at 200 °C and 2000 bar is significantly larger than that for the homopolymerization of ethylene using the data in Figure 6.[8,11]

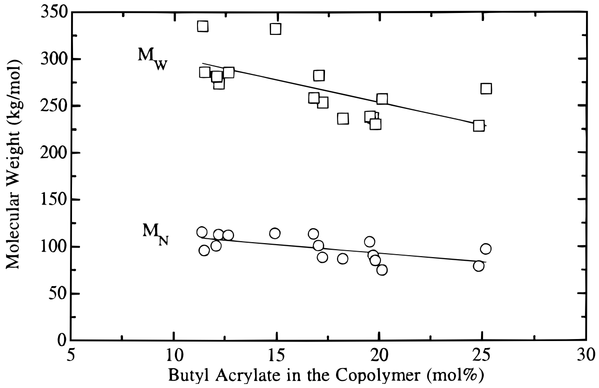

Figure 7. Number-average and weight-average molecular weights for EBA copolymers with up to 25 mol % BA content obtained at 150 °C and 2000 bar.

Figure 7 presents weight-average and number-average molecular weights of EBA copolymers with BA contents of up to 25 mol % synthesized at 150 °C and 2000 bar. As previously described, molecular weight in the range of 50 000–400 000 (M_w) has only a small impact on the cloud point pressure and that impact diminishes as the BA content in the copolymer increases from 0 to 25 mol %. The cloud point data in Figures 3 and 4 clearly show that EBA copolymers represented in Figure 7 are synthesized in the one-phase region. The content of BA in the copolymer is directly related to the amount of BA in the monomer mixture as shown in eq 1 and as previously reported.[8] However, the data in Figure 7 show that the molecular weight of the copolymer drops slightly as the content of BA in the copolymer increases. This behavior implies that chain transfer to monomeric BA at 150 °C plays a dominant role among the possible transfer reactions. The molecular weight polydispersity, which decreases from 3.0 to 2.5 as the BA content in the copolymer increases, also provides another indication that the molecular weight distribution is significantly affected by chain transfer reactions.

Buback and co-workers[8] have shown that the production of high-BA-content copolymers is facilitated by increasing the concentration of BA in the monomer mixture above ~5 mol % and by lowering the temperature as indicated by the variation of reactivity ratios with temperature over the range of 135–225 °C

$$\ln r_E = -1.139 - \frac{917.3}{(T + 273.15)} \tag{2}$$

$$\ln r_{BA} = -3.591 + \frac{2428}{(T + 273.15)} \tag{3}$$

where T is in °C. Note that, with increasing temperature, the reactivity ratio for ethylene increases slowly but the reactivity ratio for BA decreases at a very fast rate. The EBA–ethylene cloud point data indicate the feasibility of producing an EBA copolymer with a high BA content since the pressure needed to maintain a single phase at a given temperature decreases as the BA content in the EBA copolymer increases and, to a lesser degree, as the weight-average molecular weight of the copolymer decreases. In contrast, the feasibility of producing an EMA copolymer with a high MA content is lower since the pressure needed to maintain a single phase at low temperatures increases rather than decreases as the MA content in the copolymer increases. This leads to difficulties in maintaining a single phase and in obtaining reliable kinetic data for EMA copolymers.

Phase Behavior Modeling. Statistical associating fluid theory (SAFT), a perturbation-theory-based equation of state,[16–21] is used to calculate high-pressure copolymer−solvent phase behavior. SAFT considers molecules as covalently bonded chains of segments which may contain sites capable of forming associative complexes. The residual Helmholtz free energy, a^{res}, as determined by SAFT is a sum of four contributions

$$a^{\text{res}} = (a^{\text{hs}} + a^{\text{chain}} + a^{\text{assoc}}) + a^{\text{disp}} \tag{4}$$

where a^{hs} is the Helmholtz free energy contribution of segment−segment, hard-sphere repulsion, a^{chain} is the Helmholtz free energy contribution of connectiveness of the segments (i.e., covalent bonds between segments), a^{assoc} is the Helmholtz free energy contribution for site−site-specific interactions (i.e., hydrogen bonds), and a^{disp} is the Helmholtz free energy contribution of the mean-field, dispersion attraction between segments. Because the systems modeled in this paper do not exhibit hydrogen bonding, the associative term is ignored in subsequent discussions of the SAFT equation. The Helmholtz free energy expressions, for both pure components and mixtures, are given in detail elsewhere[22−24] and are not reproduced here.

For each nonassociating pure component, there are three parameters in the SAFT equation: v^{oo}, the temperature-independent volume of a segment, u^{o}/k, the temperature-independent, nonspecific energy of attraction between two segments, and m, the number of segments in a molecule. Three mixing rules are required for the extension of SAFT to mixtures: one for the temperature-dependent volume of a segment, v^{o}, another for the temperature-dependent energy of attraction between two segments, u, and a third one for the average segment size for the mixture, m. The mixing rule for the volume of a segment is

$$v^{\text{o}} = \frac{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^{\text{o}}}{[\sum_i x_i m_i]^2} \tag{5}$$

where

$$v_{ij}^{\text{o}} = \frac{1}{8}[v_i^{\text{o}1/3} + v_j^{\text{o}1/3}]^3 \tag{6}$$

The mixing rule for the energy of attraction between segments is

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j \left[\frac{u_{ij}}{kT}\right] v_{ij}^{\text{o}}}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^{\text{o}}} \tag{7}$$

where

$$u_{ij} = (u_{ii} u_{jj})^{1/2}(1 - k_{ij}) \tag{8}$$

The parameter k_{ij} is a fitted, binary mixture parameter that corrects the mean-field energy contribution in SAFT. The mixing rule for the average segment size for the mixture is

$$m = \sum_i \sum_j x_i x_j m_{ij} \tag{9}$$

where

$$m_{ij} = {}^1/_2(m_i + m_j)(1 - \eta_{ij}) \tag{10}$$

The parameter η_{ij} is also a fitted, binary mixture parameter as subsequently described.

SAFT has been applied to a variety of (co)polymer−solvent mixtures with varying degrees of success.[25−31] Hasch and McHugh[25] recently demonstrated the utility of the SAFT equation for calculating the phase behavior of poly(ethylene-*co*-methyl acrylate)−solvent mixtures. In this instance, pure component density data were not available for the EMA copolymers they considered. Therefore, it was necessary to calculate pure-component copolymer parameters using mixing rules that combine the properties of PE and PMA. However, the pure component parameters fit to homopolymer pressure−volume−temperature data did not yield reasonable predictions of polymer−solvent cloud point curves. This observation is also consistent with the work of Prausnitz and co-workers,[32] who found that the pure-component parameters of the copolymer must be modified from their fitted values to obtain reasonable cloud points using a different perturbation equation of state. The EBA−ethylene data are modeled using the approach described by Hasch and McHugh.[25] Calculations are only performed for the EBA−ethylene since the EMA−ethylene system has already been described in detail.[25]

For the EBA−solvent calculations, v^{oo} is fixed at 12 cm^3/mol and m is calculated from 0.05096(number-average molecular weight) (M_{n}), the same value and relationship used for PE. The mixing rules for v^{oo} and m are now trivial, as $v^{\text{oo}} = 12$ cm^3/mol and $m = 0.05096M_{\text{n}}$ for all of the EBA copolymers, regardless of backbone composition. The mixing rule shown in eq 7 is used to calculate a value for $(u^{\text{o}}/k)_{\text{EBA}}$ for the EBA copolymers, where now the pure component parameters are $(u^{\text{o}}/k)_{\text{PE}}$ and $(u^{\text{o}}/k)_{\text{PBA}}$. The cross term, $(u^{\text{o}}/k)_{\text{PE−PBA}}$, is calculated using the geometric mean rule. Since a value for $(u^{\text{o}}/k)_{\text{PE}}$ is given in the literature,[22] $(u^{\text{o}}/k)_{\text{PBA}}$ is the remaining unknown term in eq 7. If $(u^{\text{o}}/k)_{\text{PBA}}$ is fit to PBA density data, the value obtained is so large that it is not possible to match calculated and observed EBA−ethylene data regardless of the values used for the mixture parameters. Therefore, $(u^{\text{o}}/k)_{\text{PBA}}$ is determined by fitting the PBA−ethylene cloud point curve rather than fitting pure-component PBA density data.[25] It is important to note that PBA densities calculated with these pseudo-pure-component parameters are ∼30% lower than experimental values. In addition, the method used here requires two adjustable parameters for each copolymer−ethylene cloud point curve, although consistent trends are observed in the mixture parameters as a function of copolymer composition.

SAFT calculations are performed by assuming that the copolymer molecular weight and chemical composition are "monodisperse", as the goal is to determine whether SAFT can capture the main characteristics of the cloud point data. The cloud point curves are obtained by calculating pressure−composition ($P-x$) isotherms at various temperatures. The calculated cloud point pressure is the pressure at 5 wt % copolymer on the $P-x$ isotherm.

The parameters $(u^{\text{o}}/k)_{\text{PBA}}$, $k_{\text{ethylene−PBA}}$, and $\eta_{\text{ethylene−PBA}}$ are determined from a fit of the PBA−ethylene cloud point curve. A value of $(u^{\text{o}}/k)_{\text{PBA}}$ near 200 K is needed to obtain relatively low cloud point pressures at high temperatures, while a positive value of $\eta_{\text{ethylene−PBA}}$ is needed to obtain a cloud point curve with a slightly negative slope. Using these criteria, the best fit of the

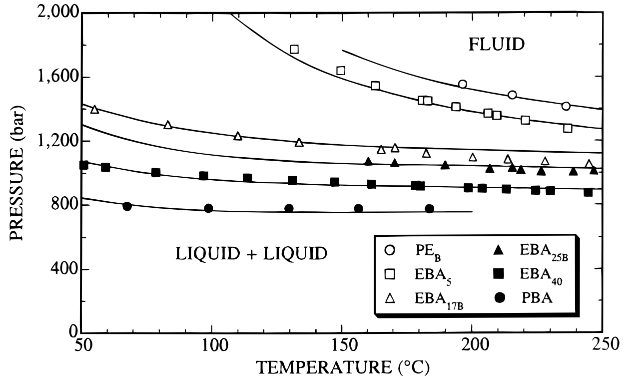

Figure 8. Comparison of experimental and calculated cloud point curves for poly(ethylene-*co*-butyl acrylate)−ethylene systems. The mixture parameters used in these calculations are given in Table 3.

Table 2. SAFT Parameters for PE_A, PE_B, PBA, and EBA_x Copolymers Used in This Study

component	v^{oo} (cm^3/mol)	m	u^o/k (K)
PE_A	12.00	1024	216.15
PE_B	12.00	2910	216.15
EBA_5	12.00	2084	216.81
EBA_{17A}	12.00	1335	218.33
EBA_{17B}	12.00	5182	218.31
EBA_{25A}	12.00	4969	219.35
EBA_{25B}	12.00	7363	219.69
EBA_{40}	12.00	708	221.68
PBA	12.00	1014	229.00

Table 3. Mixture Parameters Determined from Fitting Cloud Point Curves for the EBA−Ethylene System

polymer	k_{ij}	η_{ij}	polymer	k_{ij}	η_{ij}
PE_B	0.055	−0.035	EBA_{25A}	0.035	0.035
EBA_5	0.052	−0.020	EBA_{40}	0.035	0.045
EBA_{17B}	0.035	−0.005	PBA	0.035	0.140

PBA−ethylene curve is obtained with $(u^o/k)_{PBA}$ equal to 229 K, k_{ij} equal to 0.035, and η_{ij} equal to 0.140. Table 2 lists the calculated pure-component parameters for all of the EBA copolymers using the value of u^o/k determined for PBA.

Figure 8 compares calculated and experimental cloud point curves for PE, EBA_5, EBA_{17B}, EBA_{25A}, EBA_{40}, and PBA in ethylene. Table 3 lists the parameters used for these calculations. The cloud point pressures are predicted quantitatively over the entire temperature range with two, temperature-independent, mixture parameters. The value of k_{ij} is equal to 0.035 for all of the copolymers, except for PE_B and EBA_5. A slightly higher value of k_{ij} is needed for PE and EBA_5 which both are rich in nonpolar polyethylene to compensate for polar interactions not accounted for by SAFT. When the copolymer is lean in acrylate, there is only a small amount of polar interaction between the BA repeat groups in the copolymer and the ethylene solvent molecules that favor EBA miscibility. However, simultaneously, there is a larger amount of polar interactions between ethylene solvent molecules that energetically favors the solution to phase separate. As a result, k_{ij} must be increased to a value of 0.052 for the EBA_5−ethylene system, and to 0.055 for the PE_B−ethylene system to capture the negative slope of the cloud point curves.

Figure 9 shows the linear variation of η_{ij} as a function of BA content in the copolymer. The linear relationship between η_{ij} and BA content is not unreasonable as η_{ij} accounts for changes in the packing of unlike molecules, which is expected as the structure of the copolymer changes from that exhibited by semicrystalline PE to that of amorphous PBA.

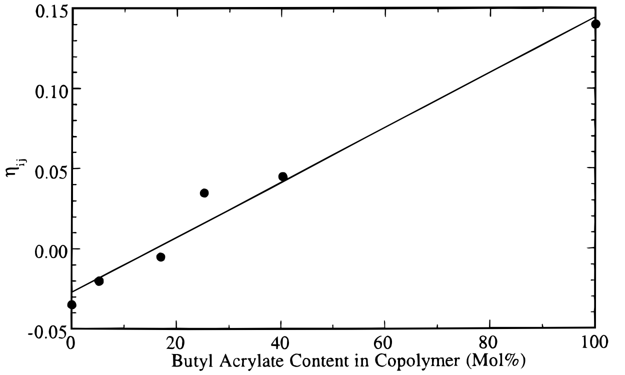

Figure 9. Comparison of η_{ij} as a function of copolymer BA content obtained from the fit of EBA−ethylene cloud point curves.

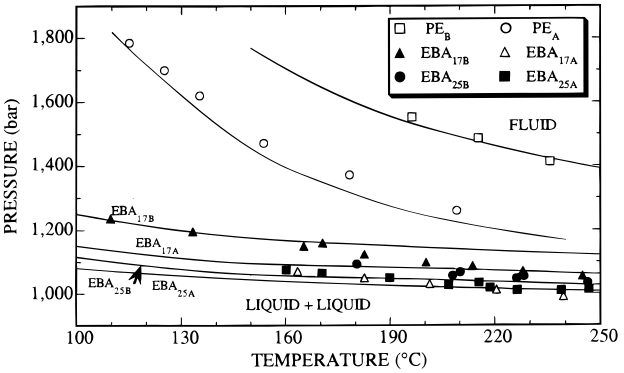

Figure 10. Comparison of experimental and calculated cloud point curves for poly(ethylene-*co*-butyl acrylate)−ethylene systems. The mixture parameters used in these calculations are given in Table 4.

Table 4. Mixture Parameters Needed To Capture the Effect of Molecular Weight on the Phase Diagram for the Polyethylene, EBA_{17}, and EBA_{25} Copolymer Systems

polymer	k_{ij}	η_{ij}	polymer	k_{ij}	η_{ij}
PE_B	0.055	−0.035	EBA_{17A}	0.035	−0.005
PE_A	0.055	0.000	EBA_{25B}	0.035	0.035
EBA_{17B}	0.035	−0.005	EBA_{25A}	0.035	0.035

Figure 10 shows calculated and experimental cloud point curves for the two PEs and two sets of EBA copolymers which contain virtually identical amounts of BA but different molecular weights. Table 4 lists the mixture parameters used for these calculations. Two mixture parameters are used for each calculation, although the parameters are not allowed to vary as a function of molecular weight for the copolymer−solvent mixtures. A different value of η_{ij} is used for the two PEs because of the differences in crystallinity between the two polymers. SAFT does a reasonable job in capturing the effect of molecular weight on the cloud point behavior, but, it does so at the expense of several fitted mixture parameters.

Conclusions

The phase behavior data for the EMA−ethylene and the EBA−ethylene systems presented in this paper demonstrate the sensitivity of the cloud point pressure to copolymer composition and system temperature. Even though BA and MA are members of the same chemical family, their effect on the phase behavior of ethylene−acrylate copolymers is markedly different.

The sensitivity of the cloud point pressure to temperature and MA content in the EMA−ethylene system indicates that there is a fine balance between the energy of copolymer−solvent interactions, that favor miscibility, and solvent−solvent and copolymer−copolymer interactions, that favor phase separation. The EBA−ethylene system is far less sensitive to temperature mainly due to the shielding effect of the butyl tail on polar acrylate interactions.

When operating a copolymerization reaction at high pressures, there is always a concern that the reaction occurs homogeneously. The interrelation between phase behavior and kinetic data is shown for the EBA copolymerizations considered here. Making BA-rich copolymers at high pressures appears feasible since the EBA solubility increases as the amount of BA in the copolymer increases, unlike the trends observed for the EMA copolymers. Increasing MA content initially increases EMA solubility, but the solubility actually decreases dramatically as the MA content is further increased. Making an EMA copolymer with a high MA content could lead to phase separation, which would make it difficult to produce copolymer with the desired physical properties.

At present, reliably predicting high-pressure copolymer−solvent phase behavior is not feasible using only pure-component data. Further refinement of SAFT is needed to address the issue of the nonspecific energy parameter, u^o/k, that appears in the mean-field term. The value of u^o/k obtained from a fit of PBA density data is so large that it is not possible to match calculated and observed PBA−ethylene data regardless of the values used for the mixture parameters. In this work it was necessary to fit $(u^o/k)_{\mathrm{PBA}}$ to the PBA−ethylene cloud point curve which, in turn, is used with a mixing rule to calculate u^o/k for the various EBA copolymers. With this approach, it is possible to fit EBA−ethylene cloud point curves with two mixture parameters that varied in a rational manner with BA content in the copolymer. As noted earlier, however, calculated PBA densities with $(u^o/k)_{\mathrm{PBA}}$ fitted to PBA−ethylene cloud point data are too low by ~30%. More work is needed applying SAFT to other polymer−solvent and copolymer−solvent mixtures to develop reasonable estimates for $(u^o/k)_{\mathrm{polymer}}$ and $(u^o/k)_{\mathrm{copolymer}}$ and to develop correlations that describe the variation of the mixture parameters with copolymer architecture.

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