

# Phase behaviour of copolymer–copolymer–solvent mixtures at high pressures

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Cloud-point data to 250°C and 2600 bar are presented for ternary mixtures consisting of either butane or butene with two (co)polymers chosen from polyethylene (PE), poly(ethylene-*co*-10 mol% methyl acrylate) (EMA<sub>10</sub>), EMA<sub>19</sub>, EMA<sub>31</sub>, EMA<sub>41</sub>, poly(ethylene-*co*-10 mol% vinyl alcohol) (EVOH<sub>10</sub>) and poly(ethylene-*co*-acrylic acid) (EAA<sub>3,9</sub>). The cloud-point curves for ternary mixtures with butane are at higher temperatures than either of the two binary cloud-point curves. The temperatures needed for a single phase increase substantially as the difference in chemical architecture of the two copolymers increases. The cloud-point curves for ternary mixtures with butene are at lower temperatures than the same ternary mixtures with butane. The cloud-point curve for the ternary mixture of 1:2.4 EMA<sub>41</sub>:EVOH<sub>10</sub> in butane is also at higher temperatures than either of the curves for the two binary mixtures even though the hydroxyl groups in EVOH<sub>10</sub> are expected to form hydrogen bonds with the acrylate groups in EMA<sub>41</sub>. Small amounts of EAA<sub>3,9</sub> cause the PE–butene cloud-point curve to shift by more than 50°C to higher temperature and, likewise, small amounts of PE also cause the EAA<sub>3,9</sub>–butene curve to shift to higher temperatures. Pressure has little effect on the location of the cloud-point curves for all of the systems considered. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Studies on the kinetics of ethylene-based copolymerization show that the composition of the copolymer backbone can be a very sensitive function of the comonomer feed concentration<sup>1</sup>. As a consequence, small variations in the feed concentration can result in the formation of copolymer chains of differing composition in the reactor. It has also been established that the temperatures and pressures needed to dissolve an ethylene-based copolymer in a given solvent are very sensitive to backbone composition, especially if the comonomer is polar<sup>2–9</sup>. Therefore, variations in feed concentration could ultimately lead to the formation of a second phase in the reactor. In this paper, high-pressure phase behaviour data are presented for ternary mixtures of two different ethylene-based copolymers in a given solvent to demonstrate the sensitivity of the location of the phase boundary to the difference in the backbone architecture of the two copolymers and to the quality of the solvent.

To the best of our knowledge, there are no data on polymer–polymer–solvent mixtures at high pressures available in the literature. However, several phase behaviour studies at ambient pressure have been reported for polymer–polymer–solvent mixtures where the two polymers are incompatible and the liquid solvent is good for one of the polymers and poor for the other polymer<sup>10–19</sup>. In general, the authors of these studies report that phase separation occurs owing to repulsive interactions between the two incompatible polymers and the poor quality of the solvent for one of the polymers. Since polymer–polymer

interactions can lead to phase separation, it is worthwhile to summarize briefly a few of the many modelling and experimental studies available on the phase behaviour of polymer–polymer blends. Flory–Huggins theory predicts that the contribution of the combinatorial entropy to the free energy is negligible for blends of high-molecular-weight polymers<sup>19–21</sup>. Therefore, two polymers are expected to form a miscible blend only if the enthalpic contribution to the free energy is negative, which will occur when there are specific interactions such as hydrogen bonding or strong polar interactions between the monomer units of both polymers. Bernstein *et al.*<sup>22</sup> demonstrated that polar interactions are needed to form miscible blends of poly(vinylidene fluoride) (PVF<sub>2</sub>) with a variety of poly(-acrylate)s and poly(methacrylate)s. In addition, these blends will phase separate if the temperature is raised above the lower critical solution temperature (LCST)<sup>22</sup> since the strength of polar interactions decreases with increasing temperature<sup>23</sup>. While many other researchers<sup>24–34</sup> have also shown that polar polymers can form miscible blends, a fine balance of interactions between repeat units must exist to form miscible blends. For instance, LCST-type phase behaviour has been observed for blends of poly(styrene-*co*-acrylonitrile) (SAN) with poly(methyl methacrylate), poly(ethyl methacrylate) and poly(*n*-propyl methacrylate) (PnPMA)<sup>32</sup>. It is interesting that these miscible blends form only within a limited range of acrylonitrile content in SAN even though many poly(methacrylate)s are not miscible with homopolymers of either styrene or acrylonitrile<sup>32,35</sup>. Similar studies<sup>19,36</sup> show that the compatibility of blends of partially chlorinated polyethylene with poly(vinyl chloride)

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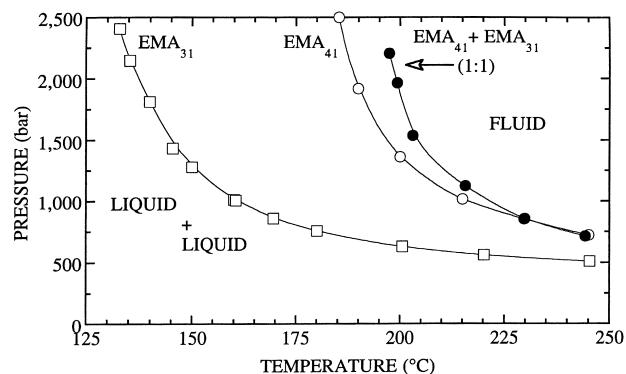
**Table 1** Properties of polyethylene, poly(ethylene-co-methyl acrylate) (EMA<sub>x</sub>), poly(ethylene-co-vinyl alcohol) (EVOH<sub>10</sub>) and poly(ethylene-co-acrylic acid) (EAA<sub>3,9</sub>) used in this study

	MA (mol%)	$M_w$	$M_w/M_n$	Crystallinity (%)
Polyethylene	0	112 700	4.6	42
EMA <sub>10</sub>	9.8	74 800	4.4	20
EMA <sub>19</sub>	19.2	140 300	3.5	10
EMA <sub>31</sub>	31	108 900	3.3	0
EMA <sub>41</sub>	41	110 400	2.6	0
EVOH <sub>10</sub>	9.9	> 50 000	unknown	unknown
EAA <sub>3,9</sub>	3.9	123 100	5.9	36

and poly(ethylene-co-vinyl acetate) increases as the concentration of chlorine or acetate functional groups in the copolymers increases.

Although Flory–Huggins theory predicts that the contribution of combinatorial entropy to the free energy is negligible, polymer equations of state<sup>37,38</sup> predict that LCST behaviour is generally anticipated for polymer–polymer mixtures, which means that the calculated phase behaviour is greatly influenced by the difference in thermal expansion coefficients of the two polymers<sup>20</sup>. For example, LCST-type phase behaviour is exhibited with blends consisting of high-molecular-weight polymers as long as the pure-component thermal expansion coefficients for the two polymers differ by more than ~4%, even if the interaction parameter is close to zero. The application of pressure usually causes the LCST of a polymer blend to increase, similar to its effect on the LCST of polymer–solvent mixtures<sup>39–42</sup>. It is evident from these modelling studies that free volume considerations cannot be neglected when interpreting the phase behaviour of polymer blends.

In this paper, cloud-point data to 250°C and 2600 bar are presented for ternary mixtures consisting of either butane or butene with two (co)polymers chosen from polyethylene (PE), poly(ethylene-co-10 mol% methyl acrylate) (EMA<sub>10</sub>), EMA<sub>19</sub>, EMA<sub>31</sub>, EMA<sub>41</sub>, poly(ethylene-co-10 mol% vinyl alcohol) (EVOH<sub>10</sub>) and poly(ethylene-co-acrylic acid) (EAA<sub>3,9</sub>). Table 1 lists the physical properties of the copolymers used in this study. Data are presented with various binary mixtures of EMA<sub>x</sub> copolymers to demonstrate how the difference in polarity of the two EMA<sub>x</sub> copolymers can increase the temperature needed to obtain a single phase. The results obtained with non-polar butane are compared with those obtained for butene to highlight the impact of solvent polarity on the phase behaviour, since butene has a modest dipole and quadrupole which will interact favourably with the polar MA repeat units in these copolymers. One set of data is presented for EMA<sub>41</sub> with EVOH<sub>10</sub> in butane to determine whether hydrogen bonding between the MA groups and the hydroxyl groups favours the formation of a single phase. The weight-average molecular weight of the EVOH<sub>10</sub> is expected to be at least 50 000 although the exact value is not known. Nevertheless, based on low-pressure studies<sup>10–19</sup>, the ternary phase behaviour is expected to be fixed more by the chemical architecture rather than the molecular weight or molecular weight polydispersity of the copolymer. EAA<sub>3,9</sub>–PE–butene mixtures are presented to show how a small amount of hydrogen bonding between repeat units in the copolymer can have a large impact on the temperatures needed to obtain a single phase.



**Figure 1** Cloud-point curves of EMA<sub>31</sub>, EMA<sub>41</sub> and a 1:1 EMA<sub>31</sub>–EMA<sub>41</sub> mixture in butane. The weight ratio of EMA<sub>31</sub> to EMA<sub>41</sub> is on a butane-free basis. The EMA<sub>31</sub>–butane and EMA<sub>41</sub>–butane data were obtained by Pratt *et al.*<sup>44</sup>

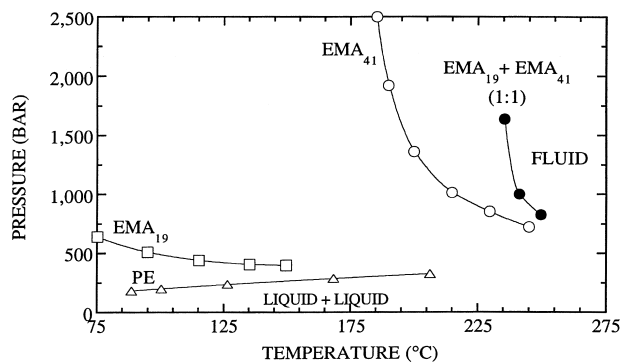
## EXPERIMENTAL

A high-pressure, variable-volume view cell was used to obtain cloud-points as described in detail elsewhere<sup>3,9</sup>. Copolymer concentrations were fixed at ~5 wt% for the binary polymer–solvent mixtures and at 8 to 10 wt% for the ternary copolymer–copolymer–solvent mixtures considered here. Cloud-point pressures are reproducible to within  $\pm 10$  bar. The lowest temperatures of the cloud-point curves presented in this work occurred at either the highest operating pressure of the experimental apparatus or at the crystallization boundary.

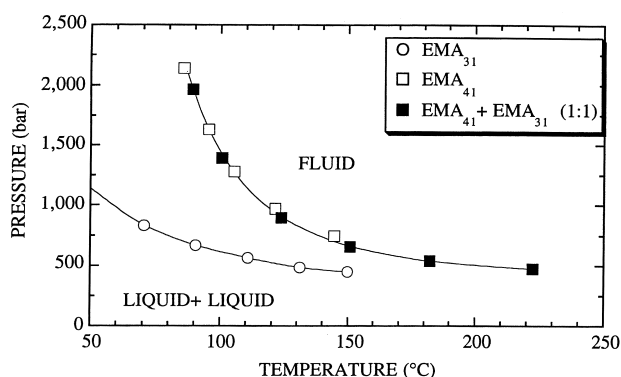
The polyethylene, poly(ethylene-co-methyl acrylate) and poly(ethylene-co-acrylic acid) were donated by Du Pont. The poly(ethylene-co-vinyl alcohol) was obtained from Polymer Sciences. Butane and 1-butene, with minimum purities of 99%, were obtained from MG Industries and were used as received.

## RESULTS AND DISCUSSION

Figure 1 shows cloud-point curves of EMA<sub>31</sub><sup>(44)</sup>, EMA<sub>41</sub><sup>(44)</sup> and a 1:1 EMA<sub>31</sub>–EMA<sub>41</sub> mixture in non-polar butane. In all three cases cloud-point pressures increase as the temperature is decreased. Non-polar, dispersion-type interactions are not expected to be strongly temperature-dependent between two butane molecules and between the non-polar ethylene repeat units in either of these EMA copolymers. Hence, the temperature sensitivity of the cloud-point curves in Figure 1 is a consequence of polar interactions between methyl acrylate repeat units, which scales with inverse temperature<sup>7,8</sup>. Interestingly, the EMA<sub>41</sub>–EMA<sub>31</sub>–butane cloud-point curve is not located



**Figure 2** Cloud-point curves of PE, EMA<sub>19</sub>, EMA<sub>41</sub> and a 1:1 EMA<sub>19</sub>-EMA<sub>41</sub> mixture in butane. A 1:1 mixture of PE and EMA<sub>41</sub> in butane does not form a single phase until temperatures as high as 238°C and pressures of 2200 bar. The weight ratio of EMA<sub>19</sub> to EMA<sub>41</sub> is on a butene-free basis. The EMA<sub>41</sub>-butene data were obtained by Pratt *et al.*<sup>44</sup>

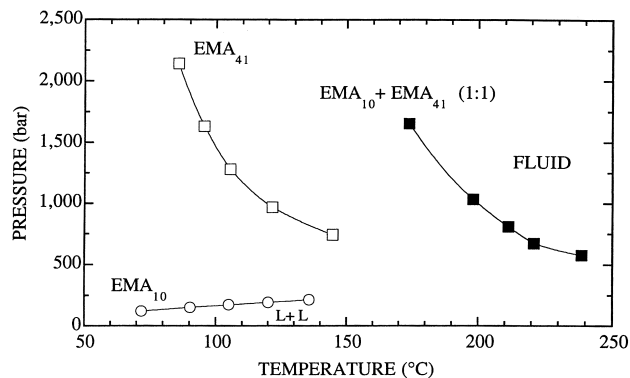


**Figure 3** Cloud-point curves of EMA<sub>31</sub>, EMA<sub>41</sub> and a 1:1 EMA<sub>31</sub>-EMA<sub>41</sub> mixture in butene. The weight ratio of EMA<sub>31</sub> to EMA<sub>41</sub> is on a butene-free basis. The EMA<sub>31</sub>-butene and EMA<sub>41</sub>-butene data were obtained by Pratt *et al.*<sup>44</sup>

between the cloud-point curves of either binary pair, but is at slightly higher temperatures. This behaviour is somewhat surprising since these two copolymers differ by only 10 mol% methyl acrylate content.

Figure 2 shows cloud-point curves of polyethylene (PE), EMA<sub>19</sub>, EMA<sub>41</sub><sup>(44)</sup> and a 1:1 EMA<sub>19</sub>-EMA<sub>41</sub> mixture in non-polar butane. In this instance, the cloud-point curve for the EMA<sub>19</sub>-EMA<sub>41</sub>-butane mixture also does not fall between the curves of the EMA<sub>19</sub>-butane and the EMA<sub>41</sub>-butane systems, but rather it is located at temperatures 40°C higher at a fixed pressure of 1500 bar. The cloud-point curve for the 1:1 EMA<sub>19</sub>-EMA<sub>41</sub> mixture is much steeper and it is at approximately 30°C higher temperature than the 1:1 EMA<sub>31</sub>-EMA<sub>41</sub> mixture curve at 1500 bar. Although it only takes moderate pressures to dissolve PE in butane, it is not possible to obtain a single phase for 1:1 mixtures of PE with EMA<sub>41</sub>, even at 238°C and 2200 bar. The results in Figures 1 and 2 demonstrate that the phase behaviour of copolymer-copolymer-solvent mixtures is very sensitive to the difference in chemical architecture of the two copolymers. These data are also consistent with the results from low-pressure phase behaviour and modelling studies mentioned earlier which suggest that a very small difference in the intermolecular potential energies of the two polymers leads to phase separation.

Figure 3 shows cloud-point curves of EMA<sub>31</sub><sup>(44)</sup>, EMA<sub>41</sub><sup>(44)</sup> and a 1:1 EMA<sub>31</sub>-EMA<sub>41</sub> mixture in butene which is slightly polar. In this instance, the cloud-point



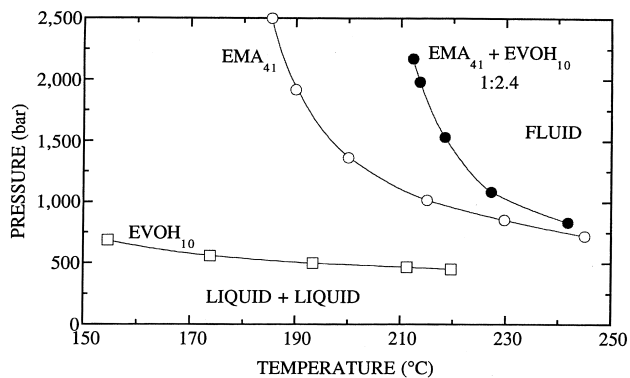
**Figure 4** Cloud-point curves of EMA<sub>10</sub>, EMA<sub>41</sub> and a 1:1 EMA<sub>10</sub>-EMA<sub>41</sub> mixture in butene. The weight ratio of EMA<sub>10</sub> to EMA<sub>41</sub> is on a butene-free basis. The EMA<sub>41</sub>-butene data were obtained by Pratt *et al.*<sup>44</sup>

curve for the ternary EMA<sub>31</sub>-EMA<sub>41</sub>-butene mixture superposes onto the cloud-point curve of the binary EMA<sub>41</sub>-butene system. Notice that the binary EMA<sub>31</sub>-butene and EMA<sub>41</sub>-butene curves are at lower temperatures and are not as steep as the companion curves in butane shown in Figure 1. More than likely the ternary cloud-point curve is close to the binary EMA<sub>41</sub>-butene curve because the polarity of butene provides favourable energetic interactions with the polar MA repeat units that are at roughly the same content in these two copolymers.

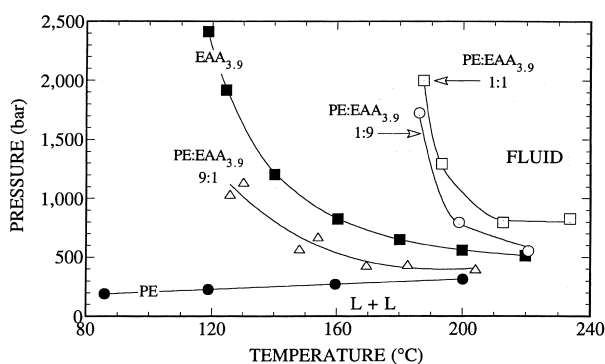
Figure 4 shows cloud-point curves of EMA<sub>10</sub>, EMA<sub>41</sub><sup>(44)</sup> and a 1:1 EMA<sub>10</sub>-EMA<sub>41</sub> mixture in butene. The cloud-point curve of the EMA<sub>10</sub>-butene binary mixture is located at very low pressures since EMA<sub>10</sub> is comprised of 90 mol% non-polar ethylene repeat units. The cloud-point curve for the 1:1 EMA<sub>10</sub>-EMA<sub>41</sub> mixture is at much higher temperatures than the cloud-point curve of the EMA<sub>41</sub>-butene system. For example, at 1500 bar, the cloud-point curve of the 1:1 EMA<sub>10</sub>-EMA<sub>41</sub>-butene mixture is ~80°C higher than the curves for the binary EMA<sub>41</sub>-butene mixture and the ternary EMA<sub>31</sub>-EMA<sub>41</sub>-butene mixture. These data show that the single-phase region of EMA<sub>x</sub>-EMA<sub>y</sub>-solvent mixtures is reduced as the chemical difference between the two EMA copolymers increases, even in a relatively good solvent for these copolymers.

On the basis of studies with propane as the solvent, ethanol is expected to be an excellent cosolvent for EMA<sub>x</sub>-butane mixtures as long as the amount of alcohol in solution is modest<sup>40-42</sup>. The strong cosolvent effect of ethanol is a consequence of ethanol-MA hydrogen bonding especially at low ethanol concentrations. However, the cloud-point curve for the 1:2.4 EMA<sub>41</sub>-EVOH<sub>10</sub> mixture in butane shown in Figure 5 is at higher temperatures than either of the two binary mixture curves. This result is somewhat surprising since methyl acrylate and hydroxyl groups hydrogen bond with one another with an interaction energy that is significantly greater than polar or dispersion energies. The attenuation of the impact of the hydroxyl groups in EVOH<sub>10</sub>, relative to ethanol, is probably due to the difficulty of packing hydroxyl groups tethered to a long-chain, non-polar, hydrocarbon polymer in close proximity to the acrylate groups. Also, there is a larger number of methyl acrylate groups in EMA<sub>41</sub> which means that all of the MA groups are not hydrogen-bonded to a hydroxyl group.

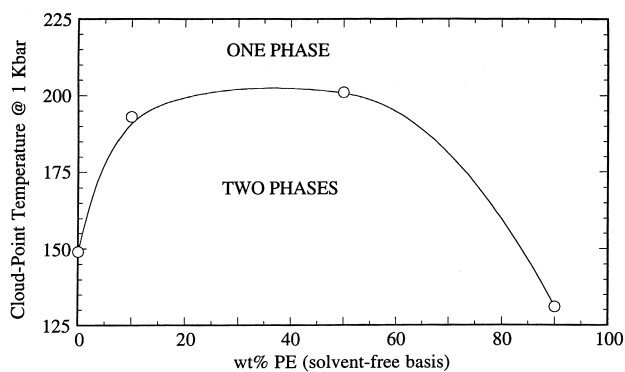
Figure 6 shows cloud-point curves for PE-EAA<sub>3,9</sub>-butene mixtures at various PE-to-EAA<sub>3,9</sub> weight ratios. The cloud-point curve of PE in butene is located at pressures that



**Figure 5** Cloud-point curves of EMA<sub>41</sub>-EVOH<sub>10</sub> mixtures in butane. The weight ratio of EMA<sub>41</sub> to EVOH<sub>10</sub> in the EMA<sub>41</sub>-EVOH<sub>10</sub> is 1:2.4. The weight ratio of EMA<sub>41</sub> to EVOH<sub>10</sub> is on a butane-free basis. The EMA<sub>41</sub>-butane data were obtained by Pratt *et al.*<sup>44</sup>



**Figure 6** Cloud-point curves of PE-EAA<sub>3,9</sub> mixtures in butane at various weight ratios of PE to EAA<sub>3,9</sub>. The weight ratios of PE to EAA<sub>3,9</sub> are on a butane-free basis. The EAA<sub>3,9</sub>-butene data were obtained by Lee *et al.*<sup>3</sup>



**Figure 7** Change in cloud-point temperature at 1000 bar with respect to concentration of polyethylene (PE) in EAA<sub>3,9</sub>-polyethylene-butene mixtures

are less than 250 bar and the curve has a positive slope with respect to temperature. Conversely, the EAA<sub>3,9</sub>-butene cloud-point curve shows a negative slope with respect to temperature and it increases abruptly in pressure at temperatures less than 160°C due to interchain and intrachain acrylic-acid dimerization. Figure 6 also shows that a small amount of EAA<sub>3,9</sub> added to a PE-butene mixture reduces the single-phase region at temperatures below 120°C. As more and more EAA<sub>3,9</sub> is added to the PE-butene mixture, the cloud-point curve shifts to higher temperatures, it reaches a maximum with the 1:1 PE:EAA<sub>3,9</sub> mixture, and the cloud-point temperature decreases slowly and approaches the value found for the binary EAA<sub>3,9</sub>-butene mixture.

The data in Figure 6 are replotted in Figure 7 to show explicitly the change in cloud-point temperature with respect to the amount of PE in the PE-EAA<sub>3,9</sub>-butene mixtures. Since the PE-butene cloud-point curve is located at pressures lower than 250 bar for temperatures between 80 and 200°C, the change in the cloud-point temperature is plotted as a function of PE concentration and not EAA<sub>3,9</sub> concentration. Figure 7 shows that, at fixed pressure of 1000 bar, the cloud-point temperature of PE-EAA<sub>3,9</sub>-butene mixtures has a convex shape with respect to percentage of PE in solution. A 50°C shift to higher temperatures is seen for the cloud-point curves of the ternary mixtures relative to the EAA<sub>3,9</sub>-butene case.

## CONCLUSIONS

The phase behaviour of copolymer-copolymer-solvent mixtures depends to a large extent on small differences in backbone architecture if the solvent is only a modest-quality solvent for either copolymer. If the solvent is a good solvent for each copolymer, then the cloud-point curve for each of the binary mixture will reside between the curves for each of the ternary mixture as long as the difference in copolymer chemical architecture is modest. If there is a large difference in chemical architecture between the two copolymers, the cloud-point curve for the ternary mixture can be as much as 100°C higher in temperature.

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## REFERENCES

1. Brackemann, H. and Buback, M., *Makromol. Chem.*, 1989, **190**, 3073.
2. Ratzsch, M. T., Wagner, P., Wohlfarth, C. and Heise, D., *Acta Polym.*, 1982, **33**, 463.
3. Lee, S.-H., LoStracco, M. A., Hasch, B. M. and McHugh, M. A., *J. Phys. Chem.*, 1994, **98**, 4055.
4. Lee, S.-H. and McHugh, M. A., *Polymer*, 1997, **38**, 1317.
5. Luft, G. and Subramanian, N. S., *Ind. Eng. Chem. Res.*, 1987, **26**, 750.
6. Luft, G. and Wind, R. W., *Chem. Ing. Tech.*, 1992, **64**, 1114.
7. Hasch, B. M., Meilchen, M. A., Lee, S.-H. and McHugh, M. A., *J. Polym. Sci., Part B: Polym. Phys.*, 1991, **30**, 1365.
8. Hasch, B. M., Lee, S.-H. and McHugh, M. A., *Fluid Phase Equilibria*, 1993, **83**, 341.
9. Meilchen, M. A., Hasch, B. M. and McHugh, M. A., *Macromolecules*, 1991, **24**, 4874.
10. Dobry, A. and Boyer-Kawenoki, F., *J. Polym. Sci.*, 1947, **2**, 90.
11. Tong, Z., Einaga, Y., Miyashita, H. and Fujita, H., *Macromolecules*, 1987, **20**, 1888.
12. Berek, D., Lath, D. and Durdovic, V., *J. Polym. Sci., Part C*, 1967, **16**, 659.
13. Narasimhan, V., Lloyd, D. R. and Burns, C. M., *J. Appl. Polym. Sci.*, 1979, **23**, 749.
14. Narasimhan, V., Huang, R. Y. M. and Burns, C. M., *J. Polym. Sci., Polym. Phys. Edn*, 1983, **21**, 1993. (see also references 4 to 27 therein).
15. Lau, W. W. Y., Burns, C. M. and Huang, R. Y. M., *J. Appl. Polym. Sci.*, 1984, **29**, 1531.
16. Robled-Muniz, J. G., Tseng, H. S., Lloyd, D. R. and Ward, T. C., *Polym. Eng. Sci.*, 1985, **25**, 934.
17. Narasimhan, V., Huang, R. Y. M. and Burns, C. M., *J. Polym. Sci., Polym. Symp.*, 1986, **74**, 265.
18. Tseng, H. S., Lloyd, D. R. and Ward, T. C., *J. Polym. Sci., Part B: Polym. Phys. Edn*, 1987, **25**, 325.
19. Walsh, D. J., Higgins, J. S. and Rostami, S., *Macromolecules*, 1983, **16**, 388.

20. McMaster, L. P., *Macromolecules*, 1973, **6**, 760.
21. Patterson, D., *Polym. Eng. Sci.*, 1982, **22**, 64.
22. Bernstein, R. E., Cruz, C. A., Paul, D. R. and Barlow, J. W., *Macromolecules*, 1977, **10**, 681.
23. Prausnitz, J. M., Lichtenthaler, R. N. and Azevedo, E. G., *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd edn. Prentice-Hall, Englewood Cliffs, NJ, 1986.
24. Walsh, D. J. and Cheng, G. L., *Polymer*, 1984, **25**, 495.
25. Paul, D. R., Barlow, J. W., Bernstein, R. E. and Wahrmund, D. C., *Polym. Eng. Sci.*, 1978, **18**, 1225.
26. Wahrmund, D. C., Bernstein, R. E., Barlow, J. W. and Paul, D. R., *Polym. Eng. Sci.*, 1978, **18**, 677.
27. Aubin, M. and Prud'homme, R. E., *Macromolecules*, 1980, **13**, 365.
28. Ziska, J. J., Barlow, J. W. and Paul, D. R., *Polymer*, 1981, **22**, 918.
29. Woo, E. M., Barlow, J. W. and Paul, D. R., *Polymer*, 1985, **26**, 763.
30. Jager, H., Vorenkamp, E. J. and Challa, G., *Polym. Commun.*, 1983, **24**, 290.
31. Walsh, D. J. and McKeown, J. G., *Polymer*, 1980, **21**, 1330.
32. Fowler, M. E., Barlow, J. W. and Paul, D. R., *Polymer*, 1987, **28**, 1177.
33. Aubin, M., Bedard, Y., Morrissette, M. F. and Prud'homme, R. E., *J. Polym. Sci., Polym. Phys. Edn*, 1983, **21**, 223.
34. Woo, E. M., Barlow, J. W. and Paul, D. R., *J. Polym. Sci., Polym. Symp.*, 1984, **71**, 137.
35. Suess, M., Kressler, J. and Kammer, H. W., *Polymer*, 1987, **28**, 957.
36. Walsh, D. J., Higgins, J. S., Rostami, S. and Weeraperuma, K., *Macromolecules*, 1983, **16**, 391.
37. Rostami, S. and Walsh, D. J., *Polym. Eng. Sci.*, 1987, **27**, 315.
38. Walsh, D. J. and Rostami, S., *Macromolecules*, 1985, **18**, 216.
39. Zeman, L., Biro, J., Delmas, G. and Patterson, D., *J. Phys. Chem.*, 1972, **76**, 1206.
40. LoStracco, M. A., Lee, S.-H. and McHugh, M. A., *Polymer*, 1994, **35**, 3272.
41. Hasch, B. M., Meilchen, M. A., Lee, S.-H. and McHugh, M. A., *J. Polym. Sci., Polym. Phys. Edn*, 1993, **31**, 429.
42. Meilchen, M. A., Hasch, B. M., Lee, S.-H. and McHugh, M. A., *Polymer*, 1992, **33**, 1922.
43. McHugh, M. A., *NATO ASI Series E*, 1994, **273**, 599.
44. Pratt, J. A., Lee, S.-H. and McHugh, M. A., *J. Appl. Polym. Sci.*, 1993, **49**, 953.