

has its maximum pressure near the critical temperature of the solvent, barring crystallization of polymer, is closed at the top (along the pressure axis). The size of the dome of immiscibility evidently increases as the size of the solvent molecule is reduced. The pressure maximum for a polymer with a hypothetical amorphous polymethylene of infinite molecular weight would be presumably in the neighborhood of 1500 atm. Whereas the critical points on the critical locus may be referred to as lower and upper critical solution temperatures, the term upper critical solution pressure is perhaps more descriptive, since the critical locus extends over a great temperature range at a pressure which varies only slowly. This locus is best described as a fluid-liquid locus. It must be distinguished, of course, from the very important gas-liquid locus which extends presumably over a range of several hundred degrees centigrade at most between the critical point of the pure solvent and the upper critical end point (UCEP).³ Every point on the fluid-liquid locus for polymer of infinite molecular weight satisfies Flory's definition of a critical point.

Physically, the critical phenomena and shapes of the critical loci described here may be attributed to the high coefficients of thermal expansion and thermal compressibility of the solvents near or above their critical points. In the more familiar case where an UCST is not the result of these conditions, such as with polystyrene-cyclohexane near room temperature, the slope of the critical locus, $(dP/dT)_c$, can be by one or two orders of magnitude greater and opposite in sign.¹⁸

We are indebted for discussions to Dr. D. C. Chappellear and to Professor J. S. Rowlinson who also pointed out the relevance of his work on the LCST to the solubility of polymers in gases. We are also grateful to Messrs. R. A. Isaksen and C. Crofoot for preparing the polyethylene fractions.

References

1. Ehrlich, P., and E. B. Graham, *J. Polymer Sci.*, **45**, 246 (1960).
2. Symcox, R. O., and P. Ehrlich, *J. Am. Chem. Soc.*, **84**, 531 (1962).
3. Freeman, P. I., and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).
4. Rowlinson, J. S., *Liquids and Liquid Mixtures*, Academic Press, New York, and Butterworths, London, 1959, Chaps. 5 and 6.
5. Rzasa, M. J., and D. L. Katz, *Petroleum Transactions, AIME*, **189**, 119 (1950).
6. Trementozzi, Q. A., *J. Polymer Sci.*, **23**, 887 (1957).
7. Reamer, H. H., B. H. Sage, and N. W. Lacey, *Ind. Eng. Chem.*, **41**, 482 (1949).
8. Parks, W., and R. B. Richards, *Trans. Faraday Soc.*, **45**, 203 (1949).
9. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, chaps. 12 and 13.
10. Richards, R. B., *Trans. Faraday Soc.*, **42**, 10 (1946).
11. Delmas, G., D. Patterson, and T. Somcynsky, *J. Polymer Sci.*, **57**, 79 (1962).
12. Baker, C. H., W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubbley, and R. E. Readon, *Polymer*, **3**, 215 (1962).
13. Longuet-Higgins, H. C., *Discussions Faraday Soc.*, **15**, 73 (1953).
14. Hildebrand, J. H., and R. L. Scott, *The Solubility of Nonelectrolytes*, Reinhold, New York, 1950, p. 107.
15. Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford, 1952, p. 78.