

Table 2 Pressure effect on azeotropes in terpolymerization systems

System	P (bar)	f_1	f_2	f_3
A	1	0.36(0.40)	0.14(0.06)	0.52(0.54)
	3000	0.38	0.13	0.49
B	1	0.39(0.36)	0.17(0.18)	0.44(0.46)
	3000	0.40	0.17	0.43

The values in brackets refer to the *calculated* values of Wittmer *et al.*¹⁰. There is satisfactory agreement between these values and our experimental data. A, acrylonitrile (1)—diethyl fumarate (2)—styrene (3). B, acrylonitrile (1)—methyl methacrylate (2)— α -methylstyrene (3)

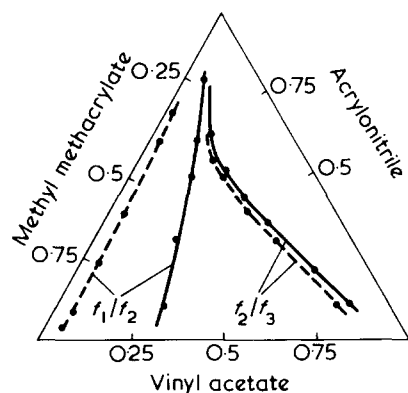


Figure 2 Effect of pressure on the partial azeotropic lines for system C. —, 1 bar; ----, 3000 bar

carefully examined with other systems.

Partial azeotropy. The definition of partial azeotropy is given by Ham⁹ as:

$$f_1/f_2 = F_1/F_2; f_2/f_3 = F_2/F_3;$$

$$f_3/f_1 = F_3/F_1$$

where f_1 and F_1 are the molar fractions of monomer 1 in the feed and terpoly-

mer, respectively.

By means of a computer program generating the points defining the azeotropic line for a given monomer, we have calculated the lines of partial azeotropy. The calculation is compared with O'Driscoll's graphic method⁵ using the contour maps. Figure 2 shows partial azeotropic lines for the system, vinyl acetate (M_1)—acrylonitrile (M_2)—methyl methacrylate (M_3). We can see that partial azeotropy is greatly affected by pressure. This is also the case for the first system (not shown here) given in Table 1 for which, as indicated in Table 2, the coordinates of the ternary azeotrope are not changed by pressure, but partial azeotropic lines are modified by pressure.

In conclusion, the pressure effect in terpolymerization systems can be important with regard to composition and partial azeotropy. However, in the investigated azeotropic systems, the coordinates of the ternary azeotrope are insensitive to pressure. The latter

point should be checked for other ternary systems.

Acknowledgements

The authors are greatly indebted to the Service de Microanalyse, Centre de Recherches sur les Macromolécules, Strasbourg, for their valuable assistance in analysing the polymers.

S. Aieche and G. Jenner

Laboratoire de Chimie Organique Appliquée,
Institut de Chimie, B.P. 296/R8,
67008 Strasbourg,
France
(Received 20 April 1978; revised 26 May 1978)

References

- 1 Weale, K. 'Chemical Reactions at High Pressures'. London, 1967
- 2 Ham, G. *J. Polym. Sci. (A)* 1964, 2, 2735
- 3 Tomescu, M. and Pusztai, K. *Rev. Roum. Chim.* 1975, 20, 677
- 4 Slocombe, R. *J. Polym. Sci.* 1957, 26, 9
- 5 O'Driscoll, K. *J. Polym. Sci. (C)* 1968, 25, 47
- 6 Jenner, G. and Aieche, S. *J. Polym. Sci. (A)* 1978, in press
- 7 Dellsperger, W. and Weale, K. *Polym. Prepr.* 1970, 11, 645
- 8 Yala, T., Jenner, G. and Deluzarche, A. *Bull. Soc. Chim. (France)* 1973, p. 609
- 9 Ham, G. *J. Macromol. Sci. (B)* 1966, 1, 93
- 10 Wittmer, P., Hafner, F. and Gerrens, H. *Makromol. Chem.* 1967, 104, 101

ERRATUM

'Moderated copolymerization: 3. Concentration changes in copolymerization with chain transfer: general equations, with special reference to moderated copolymerization' by C. H. Bamford and S. N. Basahel, *Polymer* 1978, 19, 943–947. Page 946, equation (27) should read:

$$C_B = \frac{1}{r_B[B]_0} \left[\frac{(r_A[A]_0^2 + 2[A]_0[B]_0 + r_B[B]_0^2) \ln \left\{ 1 - \frac{\Delta(A+B)}{[S]_0} \left(\frac{1}{\bar{P}_n} - \frac{1}{P_n^0} \right) \right\}}{([A]_0 + [B]_0) \ln \left\{ 1 - \frac{\Delta(A+B)}{[A]_0 + [B]_0} \right\}} - r_A C_A [A]_0 \right]$$

We apologize for this error.