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## Effect of high pressure in free radical terpolymerizations

Unlike the study of two-component vinyl polymers, the much larger field of three-component polymers has received relatively little attention. Likewise the pressure effect has not been examined in these systems, the quantitative work on high pressure multicomponent polymerizations being centred on free radical copolymerizations[1], so that the present contribution has to be regarded as an exploratory investigation.

Terpolymerization reactions were carried out at 50.0°C in stainless steel tubes or PTFE capsules (at high pressure). The distilled monomers, the initiator (lauroyl peroxide), the solvent (acetone) were introduced in the tube and weighed. After isolation and drying, the polymer was analysed by microanalysis. The yield was limited to 5–10% in all experiments to ensure that the mean composition of the terpolymers was close to the instantaneous composition.

We have examined the pressure effect (3000 bar) first on the contour maps for terpolymer composition, and secondly on azeotropy in terpolymerization systems.

### *Pressure effect on the contour maps for terpolymer composition*

Applying the relationship connecting the feed composition with the instantaneous composition of a multicomponent polymer[2,3]:

$$d[M_1]/d[M_2]/\ldots/d[M_n]$$

$$= [M_1]\sum_{i=1}^{n}\frac{[M_i]}{r_{1i}}\Bigg/[M_2]\sum_{i=1}^{n}\frac{[M_i]}{r_{2i}}\Bigg/$$

$$\ldots\Bigg/[M_n]\sum_{i=1}^{n}[M_i]\,\frac{r_{n1}}{r_{ni}}$$

where $r_{ni}$ is the reactivity ratio of monomer $n$ *versus* monomer $i$; we have calculated the terpolymer composition which requires the knowledge of six binary reactivity ratios. The relation between the molar composition of the terpolymers and the corresponding composition of monomer feed is represented in the form of triangular plots[4].

Using the method developed by O'Driscoll[5], we have computed the contour lines for each monomer; these have been drawn with increments of 0.1 in units of mole fraction. As an example, using the reactivity ratios shown in *Table 1* for the system: acrylonitrile ($M_1$)–diethyl fumarate ($M_2$)–styrene ($M_3$) and replacing them in the above equation, we obtained the contour lines at 1 and 3000 bar, respectively, for the three monomers (*Figure 1*). It should be noticed that variations of position in the composition lines may be considerable (especially for styrene) which gives evidence for the influence of pressure on terpolymer composition. This is due to the pressure effect on reactivity ratios (see *Table 1*) related to the differences in activation volumes for homo- and cross-propagation[8].

### *Pressure effect on azeotropy in terpolymerization systems*

*Ternary azeotrope.* A true azeotrope in terpolymerization would occur, when the mole fraction of all three monomers in the polymer initially produced were the same as those in the feed. For example, we have found that two systems present a true ternary azeotrope (*Table 2*). According to the results given in this Table, the coordinates are practically not affected by pressure. This result is rather surprising, since, with the exception of α-methylstyrene, combinations of all other comonomers lead to reactivity ratios which are pressure dependent. This point must be

*Table 1* Pressure effect on the reactivity ratios in the system acrylonitrile (1)–diethyl fumarate (2)–styrene (3)

| | 1 bar | 3000 bar | Reference |
|---|---|---|---|
| $r_{12}$ | 5.5 | 9.2 | 6 |
| $r_{21}$ | 0.15 | 0.10 | 6 |
| $r_{13}$ | 0.02 | 0.05 | 6 |
| $r_{31}$ | 0.65 | 0.53 | 6 |
| $r_{23}$ | 0.06 | 0.15 | 7 |
| $r_{32}$ | 0.15 | 0.25 | 7 |

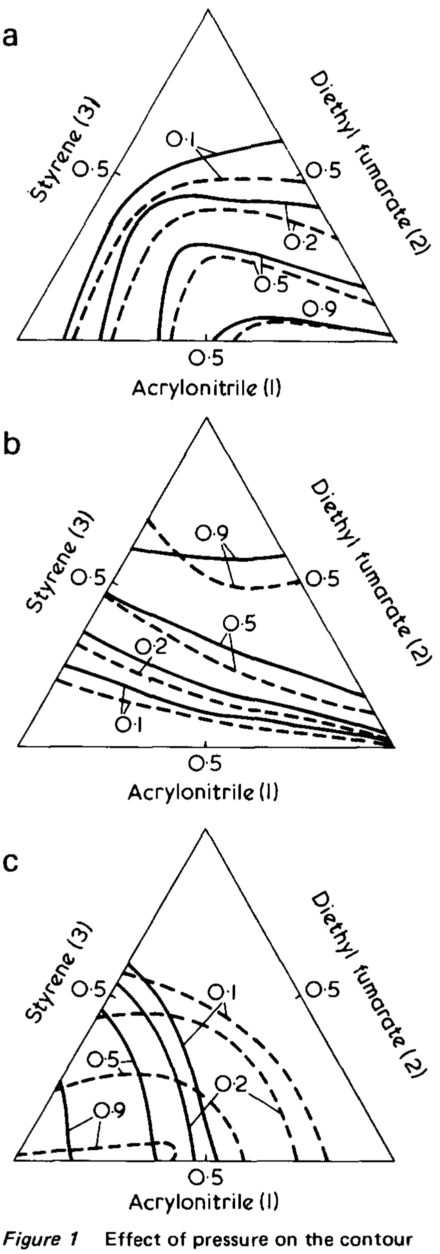

*Figure 1* Effect of pressure on the contour maps for the three monomers of system A. ——, 1 bar; – – – –, 3000 bar

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*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)

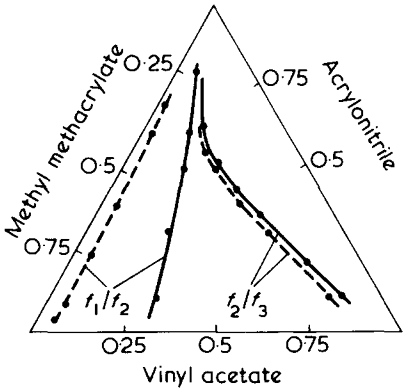

*Figure 2* Effect of pressure on the partial azeotropic lines for system C. ———, 1 bar; – – – –, 3000 bar

carefully examined with other systems.

*Partial azeotropy.* The definition of partial azeotropy is given by Ham[9] 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 terpolymer, 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 method[5] 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.

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# 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.