VINYL POLYMERISATION

X. The Ternary System: Polymer Fraction 1/Fraction 2/Solvent

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Abstract

The ternary system Poly (methyl methacrylate) Fraction 1/Fraction 2/n-butyl bromide has been studied. A viscometric method is proposed for the estimation of the individual polymer concentration in the two conjugate phases in equilibrium.

Introduction

The phase diagrams of ternary systems of the type Polymer Fraction 1/Fraction 2/Solvent are relevant to fractionation by preferential solution in a single solvent and are also of interest as they form a part of the phase diagram of the systems: non-solvent/solvent/two polymer fractions;[1, 8] the latter is of great importance in fractionation. From a purely theoretical point of view, satisfactory fitting of experiment with the theory in this aspect forms the most stringent test for the latter, especially since it is in the phase separation-regions, the lack of agreement between theory and experiment is most glaring. Flory,[2] Tompa[3,4] and others[5] have discussed the application of Flory-Huggin's[1] theory to the general case of ternary systems. For binary systems the agreement between the theoretical and the experimental curves was not good. Besides, it was felt that a study of systems of two fractions of same polymer and a solvent is of interest for our understanding of the effect of heterogeneity on various parameters.[6] In this article we report the work on the ternary system: poly (methyl methacrylate) fraction 1/poly (methyl methacrylate) fraction 2/n-butyl bromide. Although work on the viscosities of polymer solutions is extensive, little attention has been paid to the use of viscosity as a tool for the analyses of phases containing more than one polymer fraction. We propose a simple scheme of viscometric analysis of the two phases.

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EXPERIMENTAL

The precipitation apparatus and the polymer fractions used were the same as for the binary systems. For getting the ternary phase diagram, at any given temperature, uniform mixtures of the poly (methyl methacrylate) fractions were prepared by dissolving known amounts of each fraction in benzene separately. mixing the two solutions and reprecipitating the polymer by pouring the mixed solution into excess of n-hexane. Fractions 1 and 2 correspond to 11 A and 2 A—the designations given while fractionating. Starting with known amounts of the dried mixtures, the precipitation temperatures (T_p) were determined (as for the binary systems) for different volume fractions of total polymer v_2^0, for each of the mixture samples. T_p versus v_2^0 curves (Fig. 1) were constructed. From these curves, the binodial curve for the ternary system at any temperature can be constructed by drawing a line corresponding to the required temperature parallel to the v_2^0 axis. This line would cut the T_p versus v_2^0 curves for, the various mixtures at two points, each of which would be on the boundary of the isothermal phase diagram. For example, the dotted line in Fig. 1, parallel to the v_2^0 axis, represents one such line corresponding to 19° C.
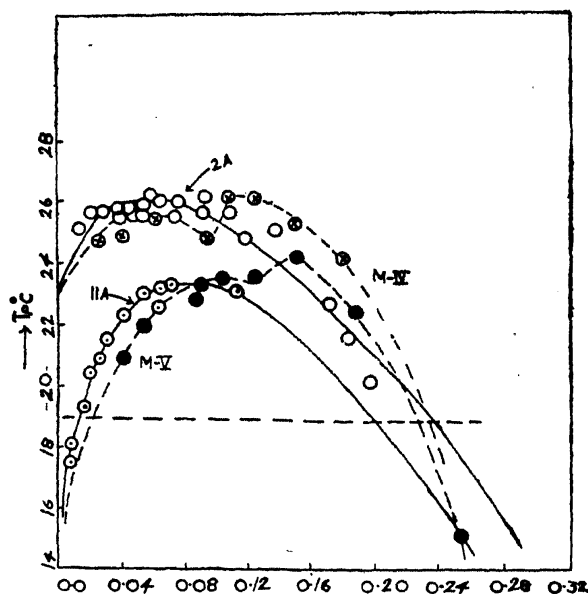

FIG. 1. T_p versus v_2^0 curves for mixtures of poly (M.M.A) fractions 2 A/11 A/n-butyl bromide. Molecular weights: Fr. 2 A = 11·560 × 10⁵; Fr. 10 A = 1·581 × 10⁵. M. IV and M.V. refer to mixtures of 11 A and 2 A.

For getting the concentration of the individual fractions in the two phases in equilibrium, the following relation between the intrinsic viscosities

of the pure 1 and 2 fractions η_1 and η_2 and the viscosity of $1 + 2$ mixture, η_M, was used.

$$\eta_1\,C_1 + \eta_2\,C_2 = \eta_M.C_0. \tag{1}$$

C_1 and C_2, the concentrations of 1 and 2 and C_0, the concentration of the total polymer. η_1, η_2 and η_M were measured in benzene at 30° C. The validity of the above equation has been checked with three different mixtures and the agreement between observed η_M and calculated η_M is found to be accurate to $\pm 3\%$ (Table I).

TABLE I

Viscometric estimation of poly (methyl methacrylate) fractions 11 A and 2 A in a known mixture of the two

Weight of mixture taken = 0·0456 gm.　　　　　　Solvent: benzene.
Weight of 11 A in the mixture = 0·0236 gm.　　　　Temperature: 30° C.
Weight of 2 A in the mixture = 0·0221 gm.　　　　　Flow time of solvent :

η_1 of fraction 11 A in benzene at 30° C. = 0·805.　　165·3 secs.
η_2 of fraction 2 A in benzene at 30° C. = 2·109.

Concentration gm. dl^{-1}	Time (secs.)	η_r	$\ln\eta_r/C$	η_p/C	dl. gm.$^{-1}$
1·140	558·4	3·378	1·068	2·086	From $\ln\eta_r/C$ *vs.* C=1·370
0·912	459·8	2·782	1·122	1·954	From η_{sp}/C *vs.* C=1·420
0·760	398·7	2·412	1·158	1·858	Average η_M=1·395
0·570	330·3	1·998	1·214	1·751	η_M Calculated =1·436
0·456	290·8	1·759	1·238	1·664	..
0·380	267·9	1·621	1·271	1·634	..

For determining the tie lines, first a weighed amount of the mixture was dissolved in a weighed amount of solvent, in a closed test-tube (with a drying bulb attached), and kept in a thermostat at the required temperature. The solution was stirred with a magnetic stirrer for 3–4 hours for equilibration, at the temperature of study. When the precipitated phase settled completely, as much of the dilute phase as possible was removed using a pipette kept at a temperature slightly above the equilibration temperature. The contents were quickly transferred into a weighed weighing bottle and the weights of the dilute phase, and the mixture of the dilute and concentrated phases left in the test-tube (the wet residue) were determined. The

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solvent was evaporated off from either phase and the total amounts of the polymer in them were determined. The individual concentrations C_1 and C_2 in the " dilute phase " and the 'wet residue " were determined by viscometry. The tie lines were plotted on the ternary phase diagram by joining the points representing the composition of the dilute phase and that of the gross composition of the original phase. The accuracy of estimation was indicated by the fact that the line joining the dilute phase to the gross composition, as anticipated, passed through the point corresponding to the wet residue (see dotted lines on Fig. 2).

FIG. 2. Ternary phase diagram of poly (M.M.A.) fractions, 2 A/11 A/n-butyl bromide.
⊙ dilute phase;   ⊗ gross composition;
⊙ wet residue;   ⊗ points from Fig. 1.
.. ● .. lines are the tie lines.

RESULTS AND DISCUSSION

Figure 1 shows the T_p versus $v_2{}^0$ curves for the pure fractions 2 A and 11 A and their mixtures. Figure 2 shows the ternary phase diagram along with the tie lines at 19° C; ⊙; ⊗ and representing the dilute phase, the gross composition and the ' wet residue ' respectively and ⊗, the points obtained from Fig. 1 corresponding to 19° C. In Table II the compositions of the ⊗ points on the ternary phase diagram as read off from the T_p versus v_{20} curves (Fig. 1) are shown. Table III shows the results of analyses of mixtures for tie lines. It may be seen that the shape of the ternary phase diagram is as anticipated. It is seen that whatever may be the composition

of the initial solution subjected to phase separation at 19° C., the dilute phase contains predominantly the lower molecular weight fraction 11 A. When

TABLE II

Evaluation of points on the binodial of the ternary system from Fig. 1 poly (methyl methacrylate) Fr. 2 A/Fr. 11 A/n-butyl bromide

Temperature = 19° C.

Mixture	Weight % of 2 A in the mixture	$v_2^{0\prime}$	Composition of dilute phase (volume fraction)			$v_2^{0\prime\prime}$	Composition of concentrated phase (volume fraction)		
			Solvent	11 A	2 A		Solvent	11 A	2 A
2A	100·00	0·000	1·000	0·000	0·000	0·236	0·764	0·000	0·236
IV	66·66	0·000	1·000	0·000	0·000	0·240	0·760	0·080	0·160
V	33·33	0·024	0·976	0·016	0·008	0·226	0·774	0·151	0·075
11 A	0·00	0·016	0·984	0·016	0·000	0·196	0·804	0·196	0·000

$v_2^{0\prime}$ = Volume fraction of total polymer in dilute phase.

$v_2^{0\prime\prime}$ = Volume fraction of total polymer in concentrated phase.

TABLE III

Construction of the lines for the poly (methyl methacrylate)/11 A/2 A/n-butyl bromide system

	Total polymer (gm.)	Weight of fraction 2 A (gm.)	Weight of fraction 11 A (gm.)	Volume fraction of 2 A	Volume fraction of 11 A
Mixture No. V					
Original solution ..	0·0965	0·0322	0·0643	0·011	0·022
Dilute phase (2·3533 gm.) ..	0·0060	0·0000	0·0060	0·000	0·003
Wet residue (0·5430 gm.) ..	0·0900	0·0320	0·0580	0·062	0·112
Mixture No. I					
Original solution ..	0·0346	0·0167	0·0179	0·006	0·007
Dilute phase (2·4106 gm.) ..	0·0110	0·0000	0·0110	0·000	0·005
Wet residue (0·4980 gm.) ..	0·0236	0·0167	0·0069	0·036	0·015

Mixture of polymers from dilute phase and wet residue were analysed for 11 A and 2 A by viscometry in benzene at 30° C.

the ratio of fraction 2 A : 11 A is 2 : 1 (mixture IV) practically all the polymer goes into the concentrated phase. When the ratio of 2 A : 11 A is 1 : 2 only 11 A comes into the dilute phase. Thus, the solvent n-butyl bromide could, at this temperature, efficiently extract a low molecular weight fraction from a heterogeneous polymer, even in solutions of high concentration ($\sim 10\%$ by weight), as compared to the concentration of solutions (2 to 1%) at which fractionations with solvent-non-solvent mixtures are done. It is concluded that the viscometric method is sufficiently accurate for the analysis of conjugate phase compositions and the simple apparatus and techniques used above can give the complete ternary phase diagram which may be useful in problems of fractionation and study of the effect of heterogeneity of a polymer sample on fractionation.

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