

## LETTERS TO THE EDITORS

**Phase Separation in Rubber-Poly(methyl Methacrylate)-Solvent Systems**

The phenomenon of phase separation (polymer incompatibility) which almost invariably ensues on mixing solutions of concentration exceeding 1-2% of two polymers in the same solvent is well recognized; experimental data<sup>1,2</sup> and theoretical treatments<sup>3,4</sup> have been reported. This note reports measurements on rubber-poly(methyl methacrylate) systems for two solvents; benzene, which is a good solvent for both polymers, and *n*-butyl acetate, which is a good solvent for poly(methyl methacrylate) but poor for rubber. Some observations using interpolymers are also presented.

Graduated stoppered tubes containing known amounts of the polymers and solvent were rotated end-over-end at room temperature until solution was complete. The tubes were then allowed to stand at 25°C. until the inter-phase boundary was sharply defined (2-6 days). After noting the relative volumes of the phases, weighed portions of each phase were treated with excess 60/80 petroleum ether to precipitate the poly(methyl methacrylate). The rubber in

the rubber-rich (upper) layer was similarly estimated by precipitation with nitromethane. This method failed to precipitate the rubber from the lower layer so an indirect estimate was made from the total amount of rubber present and the relative volumes of the phases. The results for rubber (osmotic  $\bar{M}_n$ ,  $3 \times 10^6$ ) with two poly(methyl methacrylates), I and II ( $\bar{M}_n$   $1.6 \times 10^6$ ,  $3 \times 10^5$ , respectively), in benzene, and for the same rubber sample with poly(methyl methacrylates), II and III ( $\bar{M}_n$   $1 \times 10^6$ ), in *n*-butyl acetate are given in Figures 1 and 2.

For the benzene systems, some measurements were made on mixtures containing small amounts (5-10%) of 70/30 rubber/poly(methyl methacrylate) interpolymers prepared by mastication.<sup>5</sup> The presence of interpolymers caused a marked reduction in the speed of phase separation though the position of the binodal was unaltered (Fig. 1). Larger amounts of interpolymers interfere with the precipitation analysis method. In some systems containing >10% interpolymers the appearance of a small amount of a third phase was noted. Phase separation also occurs in systems of rubber with poly(methyl methacrylate)-rich interpolymers and

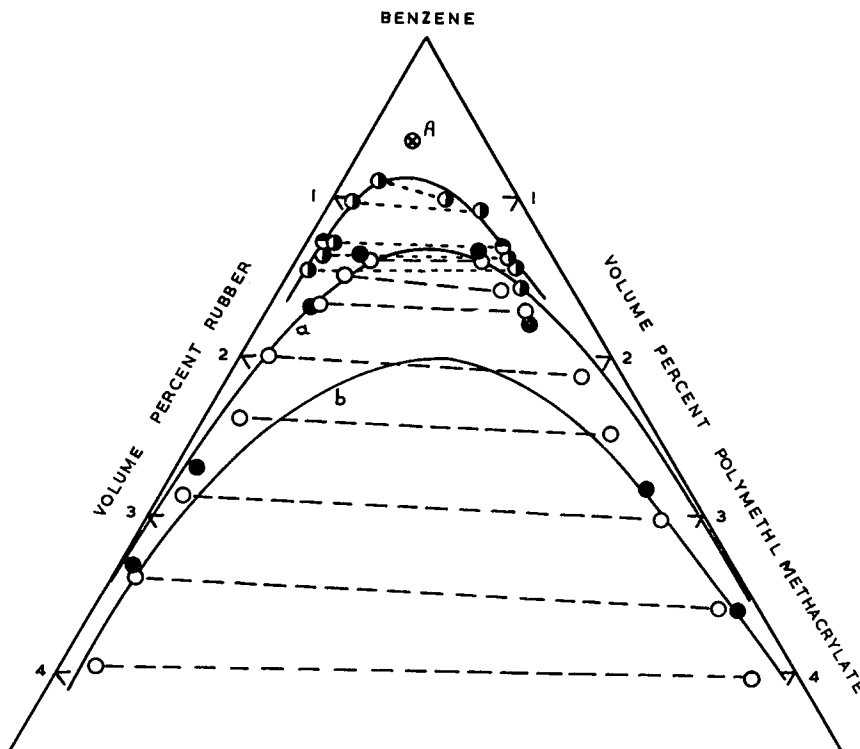


Fig. 1. Phase diagrams for rubber-poly(methyl methacrylate)-benzene systems. Rubber-poly(methyl methacrylate) I: (●) experimental points; (⊗) experimental points with 5% interpolymers; (- -) tie lines; (—) experimental binodal. Rubber-poly(methyl methacrylate) II: (○) experimental points; (●) experimental points with 5% interpolymers; (- -) tie lines; (a) binodal for  $m\chi_{12} = 154$ ; (b) binodal for  $m\chi_{12} = 100$ .

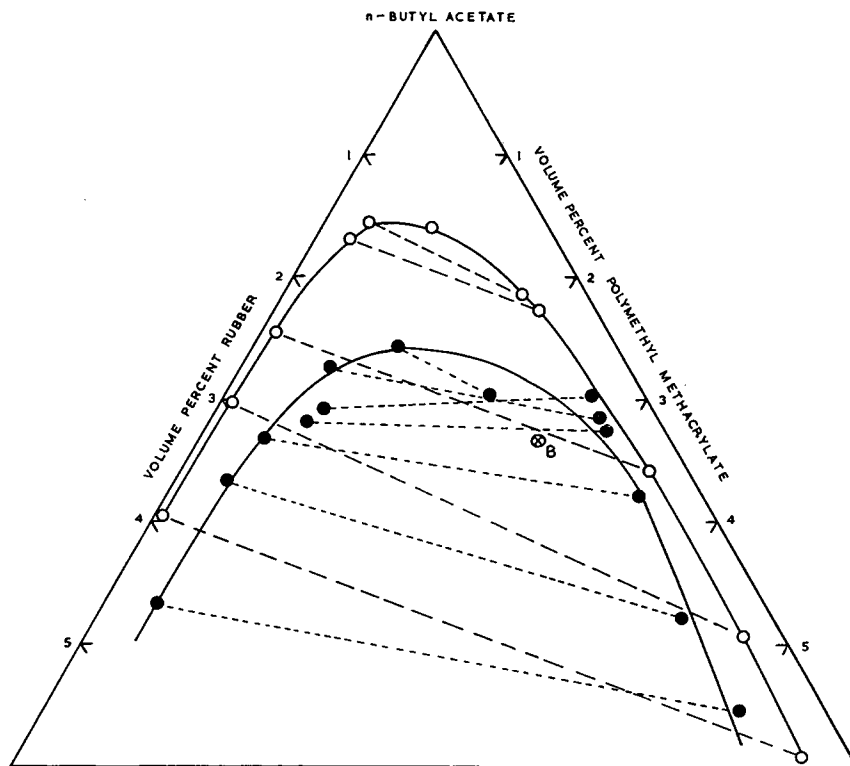


Fig. 2. Phase diagrams for rubber-poly(methyl methacrylate)-*n*-butyl acetate systems. Rubber-poly(methyl methacrylate) II: (O) experimental points; (---) tie lines. Rubber-poly(methyl methacrylate) III: (●) experimental points; (---) tie lines. All full lines are smoothed curves through experimental points.

of poly(methyl methacrylate) with rubber-rich interpolymers, though attempts to study such systems quantitatively were vitiated by the simultaneous occurrence of fractionation with respect to composition of the interpolymer.

The chain lengths of the rubber ( $m_1$ ) and poly(methyl methacrylate) II ( $m_2$ ) are approximately equal and also, as benzene is a good solvent for both polymers,  $\chi_{01} \approx \chi_{02}$ . This system approximates, therefore, to the symmetrical case of Scott<sup>3</sup> and this is confirmed by the nearly horizontal tie lines. For such systems the critical miscibility point is given by

$$\phi_{0c} = 1 - (2/m\chi_{12}); \quad \phi_{1c} = \phi_{2c} = 1/m\chi_{12} \quad (1)$$

and the binodials by

$$\ln x - m\chi_{12}(1 - \phi_0)x = \ln y - m\chi_{12}(1 - \phi_0)y \quad (2)$$

where

$$x = \phi_1/(\phi_1' + \phi_2'), \quad y = 1 - x \\ \phi_1' = \phi_2'', \quad \phi_0' = \phi_0'' = \phi_0, \quad \phi_2' = \phi_1''$$

$\phi_0$ ,  $\phi_1$ , and  $\phi_2$  are the volume fractions,  $\chi_{12}$  the polymer-polymer interaction parameter,  $m = m_1 = m_2$ , and primes and double primes denote the two phases. From Figure 1 for the rubber/poly(methyl methacrylate) II system,  $\phi_{1c} = \phi_{2c} = 0.0065$ , hence  $m\chi_{12} = 154$  and  $\chi_{12} \approx 0.038$ . The binodial calculated from (2) using this value is shown in Figure 1; the experimental points fit fairly well. Also shown for comparison is the binodial calculated for  $m\chi_{12} = 100$ .

For the rubber/poly(methyl methacrylate) I system (Fig. 1), where  $m_1 \neq m_2$ , the binodial is no longer symmetrical but the tie lines are still nearly horizontal. Scott<sup>3</sup> has shown that for this case the critical point is given approximately by

$$\phi_{0c} \approx [1 - (1/2\chi_{12})](m_1^{-1/2} + m_2^{-1/2})^2 \\ \phi_{1c} \approx [(1/2\chi_{12})m_2^{1/2}/(m_1^{1/2} + m_2^{1/2})](m_1^{-1/2} + m_2^{-1/2})^2 \quad (3)$$

Substituting values for  $m_1$ ,  $m_2$ , and  $\chi_{12}$ , we obtain  $\phi_{0c} \approx 0.9935$ ,  $\phi_{1c} \approx 0.00417$  (point A in Fig. 1). The agreement with experiment is probably quite satisfactory in view of the possible errors in  $m_1$  and  $m_2$ .

For the *n*-butyl acetate systems where  $\chi_{01} \neq \chi_{02}$  a symmetrical binodial with horizontal tie lines would not be expected, but ( $\chi_{01} - \chi_{02}$ ) must still be small so that deviations from symmetry should only be slight. However, for the rubber/poly(methyl methacrylate) II system (Fig. 2) there is a large departure of the tie lines from horizontal in this solvent as compared with those for the same system in benzene. This effect is probably due to polar interactions between the poly(methyl methacrylate) and butyl acetate. For the rubber/poly(methyl methacrylate) III system in *n*-butyl acetate the expected large increase in miscibility due to the reduced molecular weight of the poly(methyl methacrylate) is observed. Here again the tie lines are markedly nonhorizontal, a feature which may be due to polar effects as well as the difference in chain length of the two polymers. The critical point calculated from expression (3) is marked as B in Figure 2. The agreement with experiment is prob-

ably as good as can be expected in view of the assumptions made and the experimental error in  $m_1$  and  $m_2$ .

### References

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## The Radiation-Induced Polymerization of Alkyl Vinyl Ethers

It is generally accepted that the polymerization of alkyl vinyl ethers by free-radical catalysts is "difficult."<sup>1</sup> Under forcing conditions substantial conversions can be achieved, but the products are polymers of low molecular weight.<sup>2</sup> Alkyl vinyl ethers are more readily polymerized by ionic catalysts such as boron trifluoride etherate,<sup>2</sup> silver perchlorate,<sup>3</sup> iodine,<sup>3</sup> and triphenyl methyl chloride.<sup>3</sup> Even ionic catalysts tend to give low molecular weight material at normal temperatures. According to Schildknecht, only at low temperatures and with cationic catalysts can high polymers be obtained.<sup>2</sup>

More recently, Lal<sup>4</sup> has described the stereospecific polymerization of isobutyl vinyl ether at  $-78^\circ$  with titanium tetrachloride/aluminum trialkyl systems, to which a coordinate anionic mechanism has been attributed.<sup>5</sup> The radiation-induced polymerization of alkyl vinyl ethers, other than octadecyl vinyl ether,<sup>6</sup> has not hitherto been described.

We were led to study the effects of radiation on alkyl vinyl ethers following our experience with the low temperature radiation-induced polymerization of isobutene,<sup>7</sup> to which a cationic mechanism was attributed.<sup>8,9</sup>

The alkyl vinyl ethers were fractionally distilled through a 20-plate column packed with glass helices, the middle fraction being used, after outgassing and filtering, for polymerization in vessels cleaned as previously described.<sup>9</sup> Irradiations were with Cobalt 60  $\gamma$ -rays at 320–5200 rad/min. and with 2 Mev electrons from the scanned beam of a Van de Graaff generator at an instantaneous dose rate of ca  $10^8$  rad/min. The conversions were followed dilatometrically and the final value confirmed gravimetrically. Limiting viscosity numbers of the polymers in benzene solutions were determined at  $25^\circ\text{C}$ . using a suspended level dilution viscometer.

Though many attempts were made to produce polymerized ethyl vinyl ether at  $-78.5^\circ$ , no significant yield was obtained either with  $\gamma$ -rays or electrons. Exposure to  $\gamma$ -

rays at room temperature, however, led to the formation of rubber-like transparent high polymers with limiting viscosity numbers in the range 0.5–0.6 dl./g. This contrasted markedly with the behavior of isobutene which polymerized readily when irradiated at  $-78.5^\circ$  or lower, but not at room temperature.<sup>7</sup>

Closer examination of the  $\gamma$ -ray initiated room temperature reaction revealed induction periods, i.e., a slow initial rate of polymerization of the ethyl vinyl ether, followed by a period of acceleration, leading rapidly to about 90% conversion. The curve in Figure 1 illustrates the usual pattern. Similar curves were obtained with  $\gamma$ -irradiated *n*-butyl vinyl ether and isobutyl vinyl ether. This type of behavior has frequently been encountered with both catalyzed and radiation-induced free-radical polymerization and has been attributed to diffusion control of the termination rate in the gel state.<sup>10</sup> The radiation-induced conversions of isobutene, on the other hand, showed no induction periods and were essentially linear with dose.<sup>9</sup>

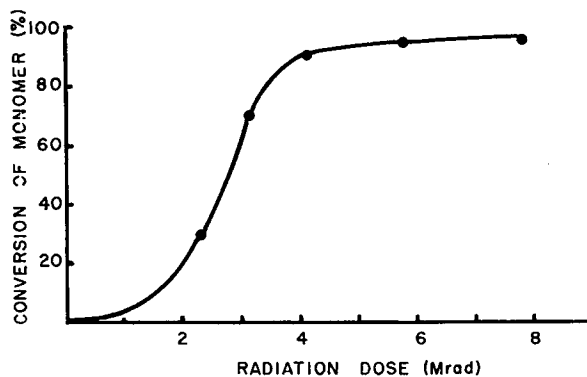


Fig. 1. Radiation-induced polymerization of ethyl vinyl ether (dose rate 1080 rad/min.).

The polymerization of ethyl vinyl ether differed also from that of isobutene in its dependence on intensity. Yields were much inferior with high dose-rate electron irradiation, whereas the conversion of isobutene was essentially independent of dose rate.<sup>9</sup>

Many of the characteristics of the radiation-induced polymerization of isobutene which have been previously cited in support of an ionic mechanism<sup>9</sup> thus failed to apply in the case of alkyl vinyl ethers. The kinetic behavior of the latter accords with bi-molecular termination<sup>10</sup> and a gel effect<sup>11</sup> and is suggestive rather of a free-radical mechanism. We have sought confirmatory evidence of this mechanism, but the work has been hindered by a strong variability of the induction periods, which implies that residual impurities were initially present, despite rigorous precautions, or that inhibitors or retarders were formed during irradiation. (The marked effect of traces of impurities in retarding polymerization of the lower alkyl vinyl ethers has been previously emphasized.<sup>2</sup>) Polymers isolated during the induction periods were liquids of low molecular weight (limiting viscosity numbers  $<0.1$  dl./g.) resembling those resulting from slow polymerization under heat, light, or peroxides.<sup>2</sup>

The implication of this work, coupled with the results reported by Lal<sup>4</sup> and by Fee et al.,<sup>8</sup> is that various catalytic agencies serve to polymerize alkyl vinyl ethers and that it is