

NOTE

Heterogeneous Polymer Systems. V. Viscosity Behavior of Polymerizing Solutions of Rubber in Styrene*

In the preceding paper¹ the formation of rubber particles from a polymerizing solution of rubber in styrene by phase inversion of a polymeric oil-in-oil emulsion has been described. A polymeric oil-in-oil emulsion consists of immiscible polymer solutions emulsified by a block or graft copolymer.² In a polymerizing rubber-styrene solution, a polystyrene-styrene solution is, at first, dispersed in a continuous phase of a rubber-styrene solution. As the polymerization proceeds and more and more polystyrene is formed, phase inversion to the opposite type emulsion occurs, and the rubber-styrene solution is dispersed in a continuous phase of polystyrene-styrene solution. The phase inversion region correlates with a decrease in viscosity which has been observed often.^{3,4} When the viscosity of the polymerizing rubber-styrene solution is plotted as a function of the degree of conversion of monomer to polymer, a curve with a characteristic sigmoidal shape is obtained. In this paper it is shown that the shape of the viscosity curve is entirely a result of the two-phase nature of the polymerizing system and is caused by changes in emulsion type and phase compositions.

With most commercial rubbers, the viscosity of a rubber-styrene solution is considerably higher than the viscosity of a solution of molding-grade polystyrene in styrene having the same concentration. Thus, the coexisting phases in a polymerizing rubber-styrene solution differ widely in their individual viscosities and any change of the emulsion type must be reflected in the shape of the viscosity-conversion curve, because the viscosity of an emulsion is determined largely by the viscosity of its continuous phase. In the initial part of the polymerization, the viscosity of the polymeric oil-in-oil emulsion is determined by the high viscosity of the rubber solution, which is the continuous phase. In the phase inversion region, the overall emulsion viscosity decreases, because the less viscous polystyrene solution becomes the continuous phase and becomes viscosity determining. With further increases in conversion, the overall emulsion viscosity increases again, because more polystyrene is formed and its concentration in the viscosity-determining phase increases.

If this explanation is correct, the viscosity behavior is independent of the polymerization per se, and the characteristic sigmoidal curve must be obtained when the changes of the emulsion type and the concentrations of the polymers are brought about by means other than polymerization. Thus, the viscosity variations in a series of samples taken out of a polymerizing rubber-styrene solution should be observable also in a series of samples of the same composition but prepared by directly dissolving the polymeric components in styrene monomer. In order to prepare a series of "simulated samples" using the emulsification technique described elsewhere,⁵ two series of polymer solutions in styrene were made. In one series, polybutadiene rubber was dissolved in styrene in concentrations identical with the concentrations of rubber in the rubber phase of polymerizing rubber-styrene solution at various degrees of conversion. In the other series, polystyrene was dissolved in styrene in concentrations identical with the concentrations of polystyrene in the polystyrene phase at the same degrees of conversion. The necessary phase equilibrium data were obtained in independent experiments. The viscosities of all samples were measured at 25°C at a shear rate of 88 sec⁻¹. The rubber solutions and the polystyrene solutions of corresponding compositions, i.e., of corresponding "simulated degrees of conversion," were then mixed and emulsified by addition of 0.6 wt-% (based on total emulsion) of an AB-type block copolymer of 70 wt-% styrene and 30 wt-% butadiene. The viscosities of the emulsions were measured again at 25°C and at a shear rate

* Part of a paper presented at the Symposium on Polymer Modification of Rubbers and Plastics, Chicago ACS Meeting, Sept. 10-15, 1967.

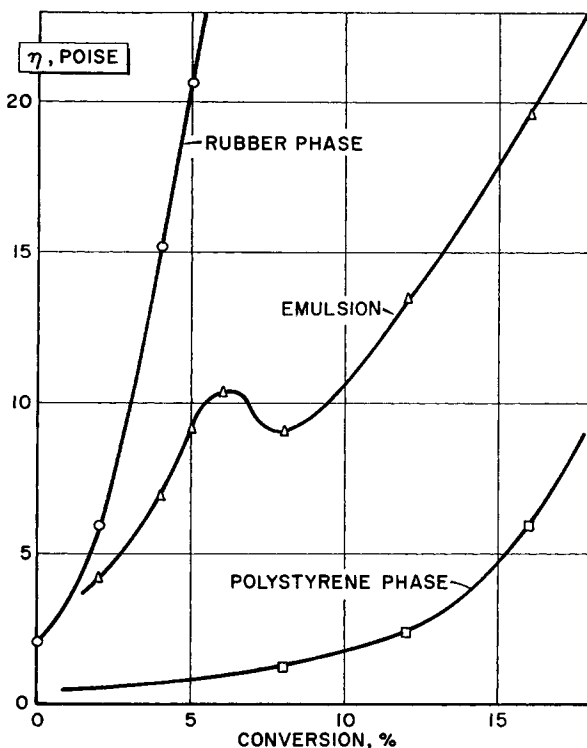


Fig. 1. Viscosity of the polymeric oil-in-oil emulsions and the corresponding oil phases.

of 8.8 sec^{-1} . All viscosity data have been plotted over the "simulated degree of conversion" in Figure 1. (The "simulated degree of conversion" is the degree of conversion which the samples would have if they were made by polymerization of a solution of 6 wt-% polybutadiene rubber in styrene rather than by dissolving the polymers in styrene and emulsifying with the block copolymer.) The viscosity curve of the series of oil-in-oil emulsions shows the same characteristic sigmoidal shape found in polymerizing rubber-styrene solution. In all samples, the emulsion viscosity lies between the viscosities of the individual phases.

Microscopic inspection of the oil-in-oil emulsion confirmed that a phase inversion occurred within the series of simulated samples and that the sigmoidal portion of the viscosity curve fell into the phase inversion region.

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Received July 28, 1969