Phase Separation Conditions in Polystyrene–Styrene–(Butadiene–Styrene) Copolymer Solutions

INTRODUCTION

In 1925, Ostromislensky[1] filed a patent for an invention which "briefly stated consists in dissolving rubber, gutta percha, balata and the like in styrol and polymerizing the solution thus obtained." Ostromislensky reported that the polymerized products had the advantage of "decreased sensitivity to shock, greater malleability, enhanced machining properties and nacreous color effects." Thus was born the material which is now commonly referred to as "high-impact polystyrene." An improved manufacturing process was developed by Amos and his co-workers at Dow Chemical[2,3] which led to superior products and commercialization. The true nature of the physicochemical phenomena occurring during the polymerization of elastomer–styrene solutions was not apparent until the last decade with the publications of Bender[4] and Molau et al.[5] In the manufacture of high-impact polystyrene, an elastomer is dissolved in styrene which is subsequently polymerized. As the polymerization proceeds, the styrene solution, now a ternary system of a solvent and two polymers, becomes thermodynamically unstable and separates into two phases. One phase is essentially a polystyrene–styrene solution and the second, an elastomer–styrene solution. Generally, the former solution is dispersed in the latter. As the polymerization reaction proceeds, the amount of polystyrene relative to the elastomer continues to increase. Eventually, a phase inversion occurs, with the polystyrene–styrene solution becoming the continuous phase and the elastomer becoming the disperse phase. This is the final morphology of the polymerized product. The occurrence of a phase separation due to the incompatibility of polystyrene and the elastomer component in styrene monomer is apparent from Ostromislensky's patent where he reports the development of cloudiness during polymerization and "nacreous" products. There have been a number of investigators of this process through the years. Some have been concerned with the formation of graft copolymers between the elastomer and the styrene which should tend to act as emulsifiers,[6–8] while others have been concerned with the phase inversion.[4,5,9]

In this note, our interest lies in the first stages of polymerization when the first phase separation occurs. The general incompability of ternary polymer solutions of two chemically different polymers in the same solvent was perhaps first pointed out by Dobry and Boyer-Kawenoki[10] who considered a number of systems including polystyrene–natural rubber–benzene. This phenomenon was interpreted by Scott[11] and Flory[12] in terms of the Flory-Huggins theory of polymer solutions in which completely flexible homopolymer chains were randomly placed on a lattice. There was no consideration by the authors of copolymers in ternary solutions of nonrandomness which must occur in such systems in analogy to the behavior of ternary systems of a polymer dissolved in a mixture of two solvents.[13,14]

We are concerned in this note with the character of the incompability or phase equilibrium in polystyrene–elastomer–styrene solutions. Little has appeared in the literature on this subject. The elastomers of most importance seem to be polybutadienes. The question of the variation of the phase equilibrium characteristics with the nature of the elastomer is of considerable interest. Polybutadienes of varying types are commercially available, as are butadiene–styrene copolymers of varying composition. In this note, we will determine the ternary phase equilibrium between polystyrene–styrene and various polybutadienes and butadiene–styrene copolymers.

EXPERIMENTAL

Materials

The polystyrene used in the ternary systems was Dow Styron 678. Its number-average molecular weight was 80,000 and its weight-average molecular weight, 240,000. It is the same polymer used by Ide and White[15] in their work. Seven elastomers were studied. Of these, three were polybutadienes, and four were butadiene-styrene copolymers of varying micro-

TABLE I
Molecular Weight Distributions of Polymers in Ternary-Phase
Equilibrium Study

Designation	Source	Styrene, %	M_n	M_w/M_n	Remarks
PS	Dow Styron 678	100	80,000	3	
BR-1	Firestone Diene 35NF	0	69,000	3.4	alkyllithium polymerized microstructure is 37% cis-1,4, 55% trans-1,4 and 8% 1,2
BR-2	Texas–US Chemical	0	73,000	8.1	emulsion polymerized polymer similar to that used as base rubber in Texas–US Chemical EBR, contains significant branching, microstructure is 10% cis-1,4, 70% trans-1,4– 20% 1,2
BR-3	Phillips cis-4	0	119,000	3.4	Ziegler polymerized 93% cis-1,4 microstructure
SBR-1	Phillips Solprene 301	25	122,000	1.7	alkyllithium polymerized random copolymer
SBR-2	Phillips Solprene 1205	25–30	52,000	1.5	simple block copolymer
SBR-3	Shell Kraton 1101	35	56,000	1.4	mixed block styrene–butadiene–styrene copolymers
SBR-4	Phillips Petroleum Solprene 303	48	102,000	1.6	block copolymer of polystyrene and butadiene–styrene copolymer

structure. The three polybutadienes were polymerized by alkyllithium (BR-1), emulsion (BR-2), and Ziegler methods (BR-3). Table I lists the polymers, their sources, and their molecular weight distribution as determined by gel permeation chromatography. Many of these are the same polymers considered in our earlier papers.[16,17,18]

Procedure

Solutions of different concentration of each of the elastomers and the polystyrene in styrene monomer were prepared. These were mixed together in varying proportions to define specific ternary compositions and maintained at both 20° and 60°C. The solutions were examined about 48 hr later for the presence of distinct layers. A series of solutions with small differences in concentration were used to be sure to pinpoint the phase separation conditions.

RESULTS AND DISCUSSION

Figures 1 and 2 exhibit the phase and equilibrium data for the ternary system polystyrene–styrene–elastomer in the form of triangular phase diagrams. It is generally seen that the compatibility of the ternary system is less than either the polystyrene–styrene or the elastomer–styrene binary. The phase diagrams are qualitatively similar to those found by Dobry and Boyer-Kawenoki and predicted by Scott and Flory.

The compatibility of the copolymers in the ternary system is generally greater than for the polybutadienes. The greater the level of styrene, generally the greater the compatibility. The SBR-3, a styrene–butadiene–styrene mixed block copolymer, shows less solubility than found for more random copolymers of the same composition.

There are differences in the equilibrium data for the three polybutadienes studied. These may be interpreted as due to differences in butadiene microstructure, molecular weight, and perhaps branching. The high cis-1,4-polybutadiene is obviously different from the high trans-1,4 and 1,2-addition polymers. The emulsion-polymerized polybutadiene has more higher molecular weight species, and less compatibility is to be expected.

We have illustrated the course of styrene polymerization in the 60°C ternary phase diagram (Fig. 1). This allows us to interpret how each of the elastomers would probably respond if it
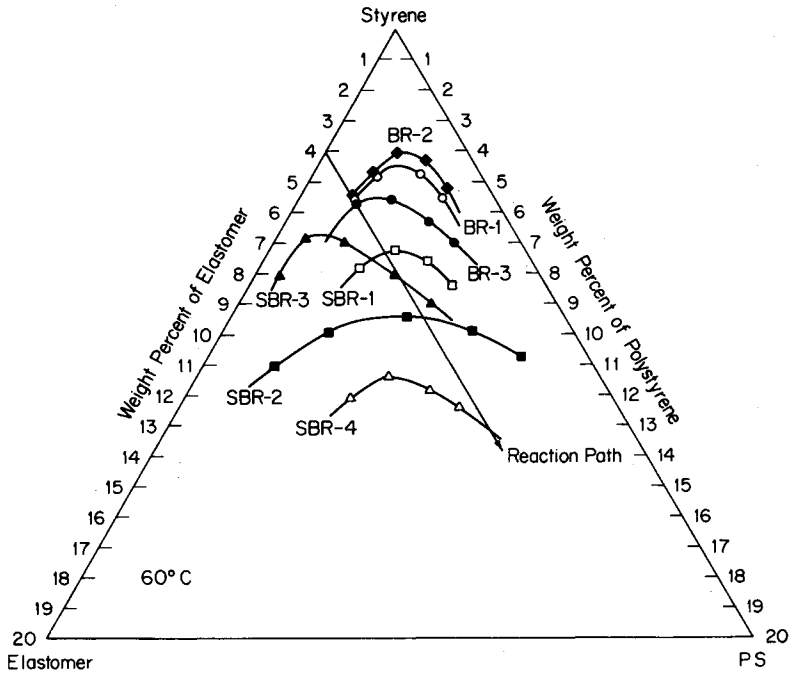
Fig. 1. Ternary equilibrium phase diagram for the system polystyrene–styrene–elastomer for several polybutadienes and butadiene–styrene copolymers at 60°C (see Table I for code of polymers).
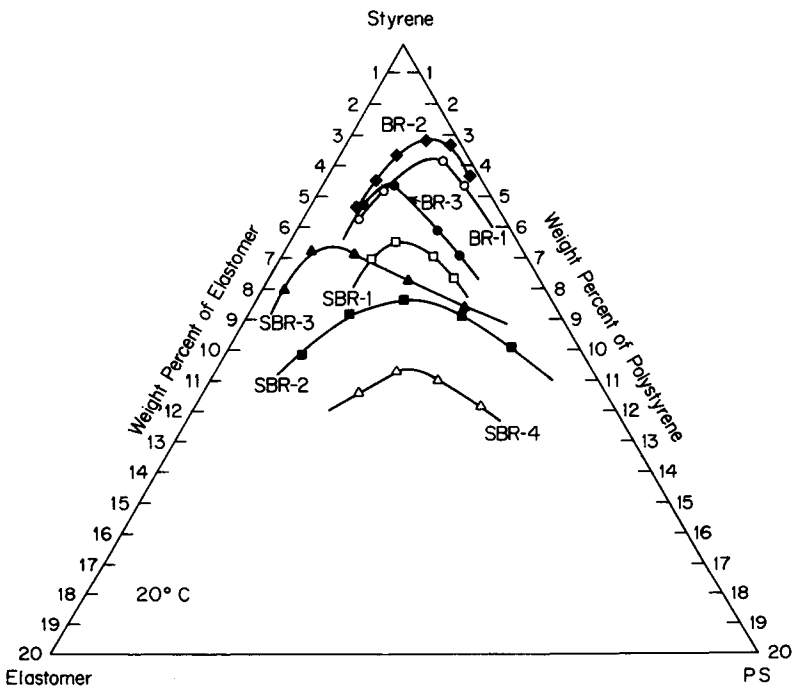

Fig. 2. Ternary equilibrium phase diagram for the system polystyrene–styrene–elastomer for several polybutadienes and butadiene–styrene copolymers at 20°C (see Table I for code of polymers).

were dissolved in styrene to be polymerized to form high-impact polystyrene. Generally, the conversion required to achieve phase separation varies. It increases with increasing styrene content in the copolymers and has its lowest value with the emulsion polybutadiene.

We have not accounted for the increased solubilization of the elastomers caused by the formation of graft copolymers during polymerizations. The SBR-2 and SBR-3 are blocks of polystyrene with a polybutadiene with microstructure similar to BR-1. These show enhanced solubility compared to the BR-1. In poor solutions, various measurements[18,19] suggest that block copolymers tend to form micellar structures. How much such block and graft copolymers would solubilize polybutadiene is a problem of considerable interest.

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