

## High-Impact Polystyrene. I. The Latex-Suspension Method

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### Synopsis

High-impact polystyrene is prepared in a novel one-step method in which the starting elastomer is present as a latex but the finished resin is recovered as suspension beads. The reaction is initiated by either oil-soluble or water-soluble catalysts. Evidence is presented to show that polymerization begins when the system is still in the latex phase, even when an oil-soluble suspension catalyst is used exclusively.

### INTRODUCTION

High-impact polystyrene (HIPS) is conventionally prepared by bulk-suspension or emulsion techniques. Bulk-suspension polymerization is a two-stage process<sup>1</sup> in which SBR or polybutadiene is dissolved in styrene monomer and partially polymerized with the aid of catalysts. This prepolymer (~15% to 30% conversion) is then added to water containing a suspending agent and the polymerization is completed.

There is a certain critical degree of conversion<sup>2-4</sup> in the bulk stage which must be reached before transfer to the suspension stage; otherwise, product will be formed having large microgel particles present ( $>10 \mu$ ) which will contribute to poor surface or "fish-eyes" in the sheeted product. This critical degree of conversion is the point at which phase inversion occurs. That is, when one begins to polymerize a homogeneous solution of rubber dissolved in styrene monomer, polystyrene homopolymer forms a discontinuous phase within the continuous solution phase of styrene monomer, unreacted elastomer, and grafted elastomer. During the early stage of the reaction, there is a pronounced increase in the viscosity of the system until a monomer conversion of 10% to 15% is reached. At this point, there is a dramatic decrease in viscosity and the phenomenon of phase inversion sets in. The discontinuous phase becomes the monomer-swollen, grafted elastomer and the continuous phase is now a solution of styrene monomer/styrene homopolymer. The reaction is continued in the bulk phase for an additional 10% to 15% conversion. During this time, sufficient shear force must be applied to the system through agitation to reduce the swollen grafted rubber microgel particle size to something less than 10 microns and to gain uniform dispersion.

This paper describes a novel latex-suspension, one-step method of producing HIPS. A mixture of the latex, monomer, catalyst, suspending agent, additives, and water is heated to reaction temperature. The elastomer from the latex phase enters the suspension phase during the course of the polymerization and the product appears as beads. This technique has several advantages over existing art. It is a simpler, more economical process than the widely used bulk-suspension technique in that (a) it is not necessary to shred and dissolve the bulk rubber, (b) it eliminates a transfer step from the prepolymer or bulk stage to the suspension system, and (c) it eliminates the necessity of carrying the bulk stage past a certain critical degree of conversion in order to ensure that the resulting microgel particle size be less than 10  $\mu$ . It is also advantageous in that it is possible to use higher rubber levels than is possible in the bulk-suspension system. The present technique is an improvement over the existing emulsion method of preparing HIPS; it eliminates the coagulation step and yields product in the form of easy-to-handle beads rather than a fine powder.

## EXPERIMENTAL

### Procedure

The latex-suspension method of preparing HIPS is a simple one-step process in which the starting elastomer is in the form of a latex and the finished product is in the form of suspension beads. Typical reactions are run in 5-liter baffled resin kettles which are fitted with propeller or paddle stirrers, water-cooled condensers, and nitrogen inlet tubes. The styrene, latex, and demineralized water are added in random order, and to these are added the suspending agent, catalyst, and antioxidant, if desired. A nitrogen blanket is maintained throughout each reaction. Reactions are kept at 65°C for the specified lengths of time (0–5 hr) before being heated to the designated reaction temperature where they are maintained for at least 2 hr after the formation of hard beads. The product is then filtered, washed with water, and dried.

### Reagents

The styrene, benzoyl peroxide, and potassium persulfate are commercially available grades. They were used without further purification.

Pliolite 5353 latex (Goodyear) is a 75/25 butadiene/styrene copolymer characterized<sup>5</sup> by a broad particle-size distribution (3000–5000 Å), a 10% benzene gel, and an ML-4-212 Mooney viscosity value of 125. SR-5472 is an experimental polybutadiene latex provided by Firestone. It has<sup>6</sup> a mass-average particle size of 1025 Å, a 1.7% toluene gel content, and an ML-4-212 Mooney viscosity value of 65. The elastomeric content of each latex was considered to be equivalent to its total solids content. (Actually, part of the latter is emulsifier and other additives.) All percentages in formulations are based upon the sum of the styrene and elastomer contents.

Wingstay T, a hindered phenol antioxidant, is made by Goodyear.

The Elvanol 50-42 poly(vinyl alcohol) which was used as the suspending agent was supplied by du Pont.

Koppers 501 HIPS was obtained from the Sinclair-Koppers Company.

## RESULTS AND DISCUSSION

### Kinetics

The object of this study was to determine whether polymerization begins in the latex stage or if it does not commence until after the conversion from latex to suspension occurs. This 22-liter run contained SR-5472 PBD at a styrene/elastomer starting ratio of 9/1. Reaction temperature was 93°C.

Samples removed from a stirred solution at timed intervals show a change from a latex to a two-phase system with a clear aqueous lower layer after about  $\frac{1}{2}$  hr at 93°C. The beads continued to grow in the upper layer until approximately  $3\frac{1}{2}$  hr at 93°C at which time they gradually began sinking, but were still suspended in water. By 6 hr at 93°C, the beads were more dense and sank to the bottom of the sample vial. This is shown in Figure 1. Phase separation began about  $\frac{1}{2}$  hr after the reaction temperature had reached 93°C and 3 hr after initial heat-up had started. By the time the reaction had been heating for 1 hr, i.e., long before the system had changed from a latex to a suspension, polymerization of the styrene had begun. At this stage, infrared analysis of the reaction solids showed the solid portion of the polymer to be 98% PBD and 2% polymerized styrene. (Had no polymerization occurred, the solid portion would have been as-

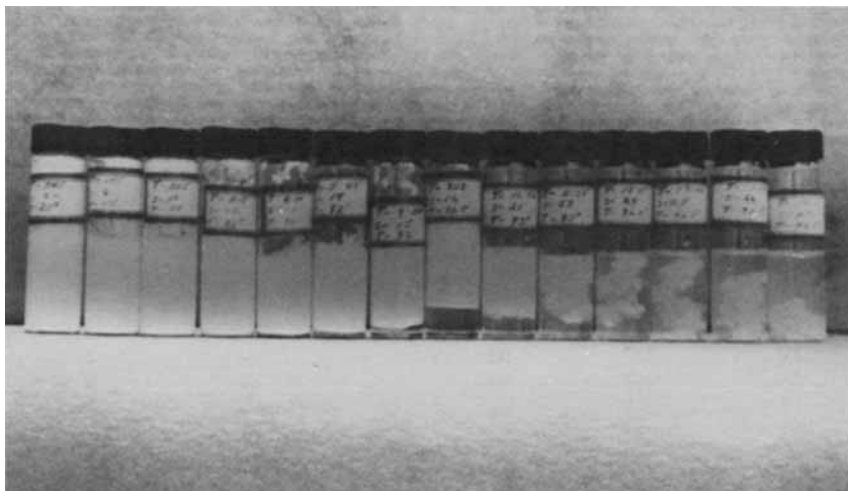


Fig. 1. Phase change in HIPS formation as a function of time. Change from a latex to a two-phase system is shown by the physical appearance of aliquots withdrawn at the following elapsed times from the start of reaction (left to right): 0, 60, 120, 150, 165, 180, 195, 213, 285, 360, 420, 455, 480, and 510 min.

sumed to be 100% PBD.) Kinetic data are tabulated in Table I and shown graphically in Figure 2.

### Catalyst

With the latex-suspension method, it is possible to obtain product in the form of suspension beads under a variety of catalyst conditions: (a) oil-soluble catalysts such as benzoyl peroxide can be used to prepare resin, (b) a low-temperature, oil-soluble catalyst as the above can be used in conjunction with a high-temperature, oil-soluble catalyst such as *t*-butyl peracetate to give impact polystyrene (part II of this series), (c) a water-soluble catalyst can be used in conjunction with an oil-soluble catalyst to produce suspension beads of HIPS, and (d) a water-soluble catalyst such as potassium persulfate can be used alone in this system to produce suspension beads without the necessity of an emulsion coagulation step.

Catalyst concentration has a marked effect on the impact resistance of the experimental resin; lowering the catalyst concentration generally in-

TABLE I  
Kinetic Study of Latex-Suspension HIPS Formation:  
Time vs. Percentage of Styrene in the Reaction Solids

Sample no.	Time, min	Reaction temp., °C	Polymerized styrene, %	PBD, %
1	-10	25	—	—
2	0	25—heating started	0	100
3	15	29	—	—
4	30	35	—	—
5	45	40	—	—
6	60	48	2	98
7	75	54	—	—
8	90	62	—	—
9	105	71	—	—
10	120	78	9.3	90.7
11	135	85	—	—
12	150	93	49.4	50.6
13	165	93	69.4	30.6
14	180	93	74.1	25.9
15	195	93	76.5	23.5
16	213	93	81.2	18.8
17	227	93	—	—
18	240	93	—	—
19	255	93	—	—
20	273	93	—	—
21	285	93	86.2	13.8
22	315	93	—	—
23	360	93	87.9	12.1
24	420	93	88.4	11.6
25	455	93	89.3	10.7
26	480	93	89.0	11.0

creases the impact resistance. In Table II, a series of experiments is described in which Minijector notched Izod values drop from 4.4 ft-lb/in. to 1.1 ft-lb/in. as the benzoyl peroxide concentration is increased from 0.10% to 0.55%. (The Minijector is a laboratory-scale injection molder manufactured by Newbury Industries, Newbury, Ohio. Notched Izods on the experimental HIPS determined on Minijector-molded parts are consistent within themselves but of higher magnitude than those obtained on samples molded in a commercial injection molder.) In addition to the styrene and peroxide, these formulations contain 7% latex solids Pliolite 5353 SBR, 0.20% suspending agent, 0.20% antioxidant, and suspension water. The reactions were run at 85°C.

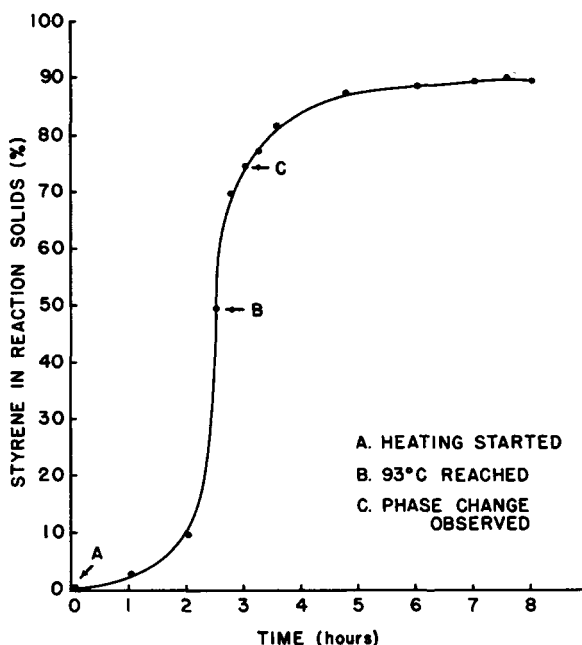


Fig. 2. Kinetic study of latex-suspension HIPS formation.

TABLE II  
The Effect of Catalyst Concentration on the Impact Resistance  
of Latex-Suspension HIPS Containing 7% Pliolite 5353 SBR

Benzoyl peroxide, %	Minijector Izod, ft-lb/in.
0.10	4.0
0.15	2.6
0.20	1.9
0.25	2.7
0.35	1.4
0.45	1.1
0.55	1.1
Koppers 501 HIPS control	1.1

TABLE III  
The Use of a Mixed Catalyst System in Preparing Latex-Suspension  
HIPS Containing 7% Pliolite 5353 SBR

Benzoyl peroxide, %	Potassium persulfate, %	Minijector Izod, ft-lb/in.
—	0.40	1.0
0.05	0.35	1.1
0.10	0.30	0.9
0.15	0.25	1.1
0.20	0.20	1.5
0.25	0.15	1.0
0.35	0.05	1.9
0.40	—	1.5
Koppers 501 HIPS control		0.9

The effects of oil-soluble, water-soluble, and mixed catalyst systems on HIPS containing 7% Pliolite 5353 SBR are shown in Table III. The total catalyst concentration was held constant at 0.40% (based on total solids) while the benzoyl peroxide/potassium persulfate ratio was varied. Izod values obtained throughout the series compare well with a value of 0.90 ft-lb/in. obtained for a control sample of Koppers 501 HIPS. It is especially noteworthy that run (1) containing as the only catalyst 0.40% potassium persulfate, a water-soluble, oil-insoluble catalyst, produced fine suspension beads. Potassium persulfate is generally considered to be an emulsion catalyst.

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