

# Non-rubber Modified Impact Polystyrene by Suspension Polymerization: Bench Scale Studies

H. U. KHAN,\* P. K. GOEL, V. K. GUPTA, B. M. L. WADHERA, and K. K. BHATTACHARYYA

Indian Institute of Petroleum, Mohkampur, Dehradun-248005, India

## SYNOPSIS

Polystyrene (PS) homopolymer is transparent but has low impact strength. High impact PS (HIPS), made by grafting on elastomer, has good impact strength but is not transparent. The operating parameters, namely, polymerization temperature and initiator concentration, during styrene homopolymerization (in suspension) can be modified such that 5–10% of benzene-insoluble PS gel is formed that remains dispersed as very fine to small discrete particles in the continuous PS phase. The resulting polymer retains transparency and impact properties comparable to those of HIPS. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polystyrene (PS) homopolymer is a low cost thermoplastic having good transparency; however, a limitation to its application is its low impact strength. Incorporation of an elastomer by blending, or by grafting PS on the elastomer during polymerization improves the impact strength of PS significantly. Thus rubber-modified impact polystyrene (IPS) finds wider applications. In IPS made by blending, the elastomer phase is dispersed as a cluster in the continuous phase of PS, which imparts some impact resistance.<sup>1,2</sup> High impact PS (HIPS) grafted on elastomer is produced in a two-step process of prepolymerization followed by suspension or mass (in the presence of a solvent) polymerization. During the prepolymerization, 5–15 wt % elastomer disintegrates into fine particles and the PS chains are grafted onto the structural backbone of this elastomer. On further polymerization of styrene, in the second step, this grafted elastomer remains dispersed as fine discrete particles in the continuous PS phase.<sup>3–5</sup> The extent of the impact strength improvement depends upon the elastomer content and its particle size distribution along with the grafting parameters. The limitations of this grafted-HIPS process are the availability of the proper grade of

elastomer and the need for multistage operation. Moreover, due to the incorporation of rubber, the products are translucent.

In our earlier process studies<sup>5,6</sup> on PS homopolymer and graft IPS by suspension polymerization, it was observed that some insoluble PS gels are formed when the initiator concentration and the reaction temperature were at higher levels than those normally applied. Experiments were planned to determine if the operating parameters during the styrene homopolymerization could be controlled such that 5–10% of PS gel would be formed in the early stages of polymerization, and would be dispersed as small particles in the continuous PS phase. Thus, the resultant polymer would have higher impact strength. The results were very encouraging, yielding transparent HIPS. These results were confirmed in bench scale experiments and are reported in this article.

## EXPERIMENTAL

### Materials

Styrene (commercial grade, from Synthetics & Chemicals, Bareilly, India) was distilled at 45°C/10 mbar before use.

Benzoyl peroxide (BPO, E. Merck), 97% containing a minimum of 20% water, was used as received without further purification.

\* To whom correspondence should be addressed.

**Table I Monomer Conversions and PS-Gel Formation During Styrene Polymerization**

Initiator Concentration (wt %)	Conversion (wt %)	Benzene Insoluble PS gel (wt %)
0.11	50	—
0.15	80	—
0.24	98.5	15.42
0.16 + 0.08 <sup>a</sup>	98.5	5-7

<sup>a</sup> Added after 5.0 h from the start of polymerization at 90°C.

Polyvinyl alcohol (PVA-GH-17 of M/S Nippon, Osaka, Japan), surfactant (commercial DET, India), gelatin (commercial edible grade), benzene and toluene (AR grade), methanol (LR grade), and redistilled water (pH 7-8) were used.

### Polymerization

Preliminary experiments were first conducted with variations of temperature-time combinations, initiator concentrations, and the concentration of suspending agents to establish the suitable polymerization procedure for producing the polymer with the desired PS-gel content. The results reported here were obtained following this procedure in the bench scale unit fitted with a 10-L stainless steel reactor.

The reactor was purged with nitrogen, partly filled with 2 L water, and again flushed with nitrogen. Suspending agents consisting of 0.2 wt % PVA, 0.05 wt % DET, and 0.02 wt % gelatin were then added and the stirrer switched on. The monomer (1.0 kg), initiator (BPO, 0.16 wt %), and a small amount of mineral oil (2 wt %) were then fed into the reactor and heating started. The temperature reached 90°C in 30-45 min and polymerization was carried out at this temperature for 6 h. In between, an additional 0.1 wt % PVA and 0.08 wt % initiator (BPO) were added after 3.5 and 5.0 h respectively. Thereafter, the temperature was gradually raised to 100-105°C and maintained for 1 h to complete the polymerization. The pressure in the reactor was 2.0 kg/cm<sup>2</sup> under a blanket of nitrogen. The total time for a run was 8.5-9.0 h including heating and cooling.

The data on monomer conversions with increasing initiator concentrations determined during the preliminary runs are given in Table I.

During polymerization runs, samples (25-30 g) of the reaction mass were pipetted out of the reactor at intervals of 1 and 2 h. The first sample was collected in a previously weighed separating funnel and

the rest in a weighed conical flask. The first sample was almost a thick paste that separated into two layers on standing. The aqueous layer was removed and the organic part repeatedly washed with a known quantity of fresh water. It was then sufficiently diluted with benzene and filtered through Whatman-42 filter paper collecting the benzene insoluble PS gel on the filter paper. This was further washed with benzene to ensure complete removal of the benzene soluble part (PS). The filtrate was then added to methanol to precipitate the PS. This was then filtered and dried to constant weight in an oven at 50°C/5-10 mbar. Monomer conversions were estimated from the weights of the sample, water, and polymer (PS + PS gel) formed.

The samples drawn after 2 h and later were in the form of semisolid to solid beads that soon settled at the bottom of the flask. After decanting the water, the beads were washed well with fresh water to ensure complete removal of the suspension stabilizer. The beads were dissolved in benzene and treated as mentioned above for determining the contents of the soluble PS, the insoluble PS gel, and the conversion. The final product on completion of polymerization was centrifuged and washed with water (5-6 times) for removal of the suspending agents. The beads were dried to constant weight in an air oven at 70-80°C for determining the product yield.

The contents of the soluble PS and PS gel in the product beads were determined in the same way after dissolving in benzene. The data of soluble PS and insoluble PS-gel contents with the progress of polymerization are given in Table II.

### Product Characterization

#### Properties

The viscometric average molecular weight of the soluble PS part was determined in toluene at 30°C

**Table II Conversion and PS-Gel Content with Progress of Polymerization of Styrene**

Duration (h)	Conversion (wt %)	In Benzene	
		Soluble PS (wt %)	Insoluble PS Gel (wt %)
1	25	20.75	4.25
2	39	33.90	5.10
4	61	55.00	6.00
6	85	78.15	6.85
8	97	90.15	6.85

applying the formula  $K = 11.0 \times 10^{-5}$  and  $\alpha = 0.725$  in the Mark-Houwink equation.<sup>7</sup>

The dried final products were extruded and molded to obtain the test specimen to determine the following properties: hardness (ASTM D1706-61), heat distortion temperature (HDT, ASTM D1525-587), Vicat softening point (VsPt, ASTM D648-56), impact strength (Izod, ASTM D246-56), tensile strength (ASTM D638-52 T), percent elongation (ASTM D638-56 T), and light transmission. The results are summarized in Table III. The average values are given at the bottom of the table.

Several commercial PS products,<sup>8</sup> viz., Styron-666 (crystal PS), Styron-777 (medium impact), Styron-475 (high impact), and crystal PS prepared earlier in our laboratory were also characterized in the same way and compared with the average values of PS gel-IPS products. These values are given in Table IV.

### Spectroscopic Analysis

**Microscopic Examination.** One bead from the final product of each of the run was placed on a glass slide, covered with a cover glass, and heated gently. When the bead showed signs of melting, it was pressed gently. These slides were examined under a phase contrast microscope (Num Union Optical Company Ltd., Japan). PS and PS-gel samples obtained in each experiment were also examined by microscope in the same way. Photographs of some of the slides at 750-Å magnification were taken. The photographs for one set of products are shown in Figure 1 (A-C). A photograph of the commercial HIPS-475 is shown in Figure 1(D).

### IR Analysis

Using a Perkin-Elmer spectrophotometer (model 399B), IR spectra were obtained of free PS, PS gel, and the PS gel-IPS samples. The spectras for the PS gel and PS gel-IPS samples were recorded in KBr; and the free PS spectra were obtained from thin film prepared from its solution in chloroform.

### X-Ray Diffraction Analysis

The X-ray diffraction pattern for the PS gel-IPS, the PS gel, and the free PS samples were obtained on a GE X-Rd-6 diffractometer (slow scan 0.4°/min with a chart speed of 6 in./h). For this the samples were ground to a powder after chilling in liquid nitrogen. The diffraction patterns of PS and PS gel-

Table III Properties of PS Gel-IPS

Run	Yield (wt %)	Aqueous Spent		Molecular Weight of PS	Benzene Insoluble PS Gel (%)	HDT (°C)	VsPt (°C)	Impact Strength (kg cm cm <sup>-2</sup> )	Hardness Shore D	Tensile Strength (kg cm <sup>-2</sup> )	Elongation (%)	Transmission (%)
		Spent	Recovered									
1	98.5	87	87	211,000	6.33	76	97.0	21	D/77/1	233	22	76.0
2	97.5	87	87	225,000	6.85	77	99.0	16	D/75.5/1	238	15	74.5
3	98.5	87	87	231,000	5.97	75.5	94.5	15	D/75/1	240	15	74.0
4	98.0	87	87	220,000	6.02	75	96.0	17.2	D/75/1	235	19	75.0 <sup>a</sup>
Av.	98.1	87	87	222,000	6.30	75.9	97.0	17.3	D/75.6/1	236.5	20.5	74.9

<sup>a</sup> Light transmission after 24 h of UV radiation.

**Table IV Properties of PS Gel-IPS Compared with Commercial PS Products**

Properties	PS Gel-IPS	Styron-666	Styron-777	Styron-475	Crystal PS (Our Sample)
Impact strength Izod (kg cm cm <sup>-2</sup> )	17.3	3.27	9.8	17.1	3.0
Tensile strength (kg cm <sup>-2</sup> )	236.0	391.6	336.8	281.8	173.0
Elongation (%)	20.25	2.66	11.5	21.8	1.6
HDT (°C)	75.9	70.0	69.0	67.5	66.75
VsPt (°C)	96.5	102.0	99.0	96.75	—
Benzene insoluble gel (%)	6.3	—	6.4 (elastomer)	10.0	—
Molecular weight	222,000	209,000	237,000	222,000	120,000
Hardness, shore D	D/75.6/1	D/82/1	D/80.5/1	D/79/1	D/84/1
Transmission (%)	75	81	—	—	78
Density (d <sub>4</sub> <sup>15</sup> )	1.008	1.0046	1.0219	1.0069	1.010

IPS from the same experiments are compared in Figure 2. The diffraction patterns of the PS gel from the same experimental product is compared with that of a commercial PS sample reported by Okamura and Higashimura<sup>9</sup> in Figure 3.

#### Stability of Product under UV Radiation

The product (PS gel-IPS) was transparent. To examine whether this transparency is stable, the molded test specimens of the product were impinged with UV radiation (350 mμ) continuously for 24 h. The transparency and the color of the samples were compared before and after irradiation.

## RESULTS AND DISCUSSION

The data in Table I indicate that with increasing concentration of the BPO initiator, the monomer conversion rises, reaching maximum at 98.5% with 0.24 wt % initiator added at the starting time. The resultant product contained around 15.4% benzene insoluble PS gel. This PS-gel content could be reduced to 5–7% without affecting the total conversion when the initiator was added in two lots of 0.16% initially and 0.08% after 5.0 h of polymerization at 90°C. The moldability of the product also appeared difficult with increasing PS-gel content in the polymer; with 5–7% PS-gel content in the PS gel-IPS, the moldability was very good; but with 15.4% PS gel, the moldability was very poor. The data in Table II shows that on conducting the polymerization at 90°C, adding 0.16 wt % initiator at the start, the

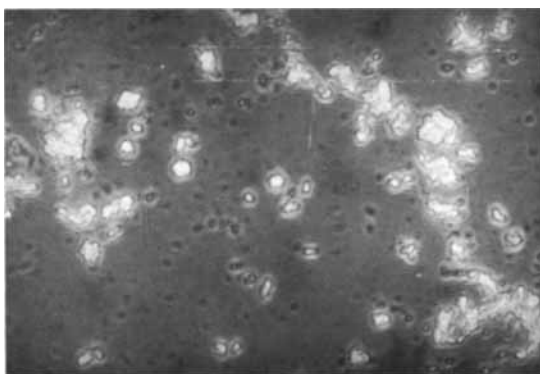
monomer conversion increased gradually up to about 85% in 6.0 h. The formation of PS gel under these conditions also started right from the initial polymerization stage and reached 6–7% at 80–85% monomer conversions. During the last 2.0 h of polymerization, at higher temperatures of 100 and 105°C, the monomer conversion rose to 97–98%, but the PS-gel content did not rise further.

Thus the lower PS-gel content resulted from the controlled addition of initiator in two lots, which maintained the total free radical species at moderate levels and up to the end of polymerization.

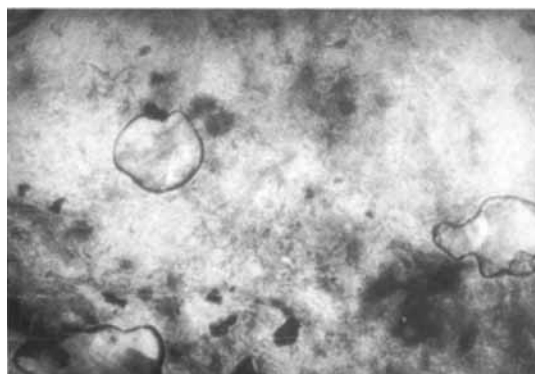
Table III presents the properties of the PS gel-IPS products from five experiments carried out under the identical conditions of the polymerization. It can be seen that the yields, benzene insoluble PS-gel content, and the properties measured (HDT, VsPt, Izod impact strength, shore hardness, tensile strength, percent elongation, and light transmission) match quite closely. The repeatability was within a 95% confidence level. The impact strength of the product was fairly high with the PS-gel content remaining in the narrow range of 6–7%. Light transmission was also fairly high at about 75%.

A test specimen was irradiated with UV rays (350 μm) continuously for 24 h; the color of the specimen as well as the light transmission value remained unchanged as shown in the bottom line of Table III. The average values of the properties of our PS gel-IPS product are compared in Table IV with the properties of different commercial PS products ranging from crystal to grafted high impact grade. These data clearly show that our PS gel-IPS product containing 6–7% PS gel has, in almost all respects,

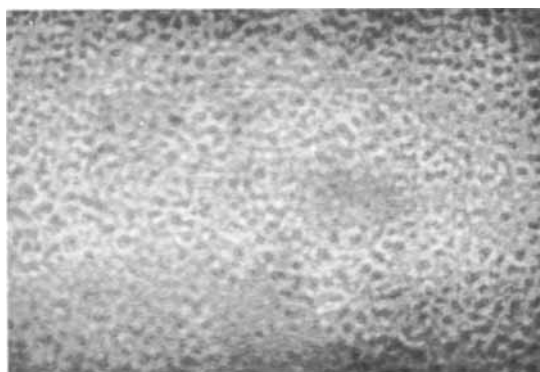
## Photomicrograph of different PS products



(A)



(B)



(C)



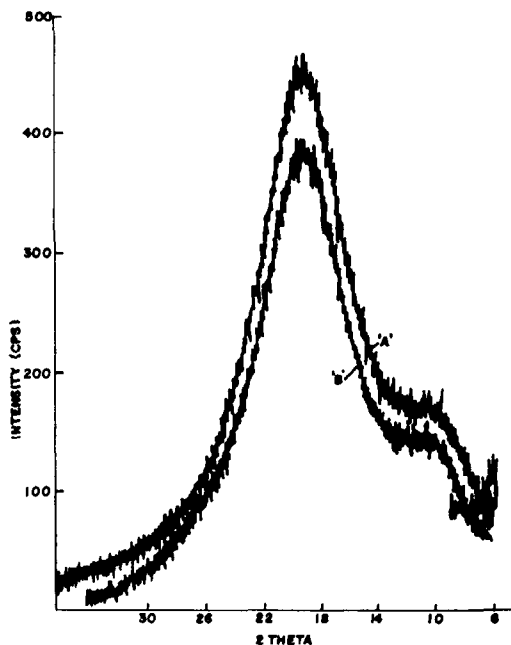
(D)

**Figure 1** Photomicrograph of (A) PS gel-IPS, (B) PS gel, (C) free PS, and (D) HIPS-475 at 750-Å magnification.

superior properties than the several crystal PS samples. The HDT and the percent elongation were even better than that of commercial HIPS, although the other properties of these two products closely matched. A very notable point is that our PS gel-IPS samples were similar to crystal PS in color and transparency, unlike the translucent grafted HIPS. UV radiation did not affect the color and the transparency and thus indicated its stability; this offers a clear advantage of the PS gel-IPS.

The photomicrograph of PS gel-IPS, the separated PS gel, the separated free PS, and that of a

commercial product HIPS-475 are given in Figure 1. These indicated that both the PS gel and the grafted elastomer in impact PS remain dispersed in the PS phase as very small discrete particles; the dispersion of the elastomer, however, appears wider and uniform in the micrograph. The micrograph of the benzene soluble free PS also shows the presence of well-dispersed very fine particles that did not show up clearly in the photograph. Obviously, these very fine particles did not separate out as the benzene insoluble PS gel. These dispersed, very fine, and coarse discrete PS-gel particles probably are the



**Figure 2** X-ray diffractograms of (A) PS gel-IPS and (B) free PS.

contributors to the high impact strength of the gel-IPS. The total gel formation was observed to be in the range of 7–10%.

The IR spectra of PS gel-IPS, the PS gel, and free PS showed that the characteristic peaks due to styrene are present in all of them, although they differ in magnitude.

The X-ray diffraction patterns of PS gel-IPS and free PS samples given in Figure 2 show their similarity in the region of interest ( $6\text{--}30^\circ$ ); and for both samples the diffraction maxima centered at  $4.57\text{--}4.59\text{ \AA}$ . However, the two samples differ in angular width of the diffraction maxima that for PS gel-IPS is around 5–6% more than the free PS sample. This suggests that the crystalline domain in PS gel-IPS is lower by 5–6% in comparison with the free PS. The diffraction pattern for PS gel (Fig. 3) suggests that in addition to  $4.57\text{-\AA}$  diffraction maxima, there are several sharper and weaker crystalline peaks and the pattern does not match completely with that of the commercial PS sample, although the essential characteristics of PS are clearly observed. The results of one run given in Table II (column 4) show that the formation of PS gel begin soon after the start of polymerization and continued to grow steadily up to about 7%, until styrene conversion was around 85%. Thereafter the PS-gel formation seemed to be negligible, although the second lot of BPO initiator was added and the reaction temperature was raised to  $100\text{--}105^\circ\text{C}$  in the last stage. Of

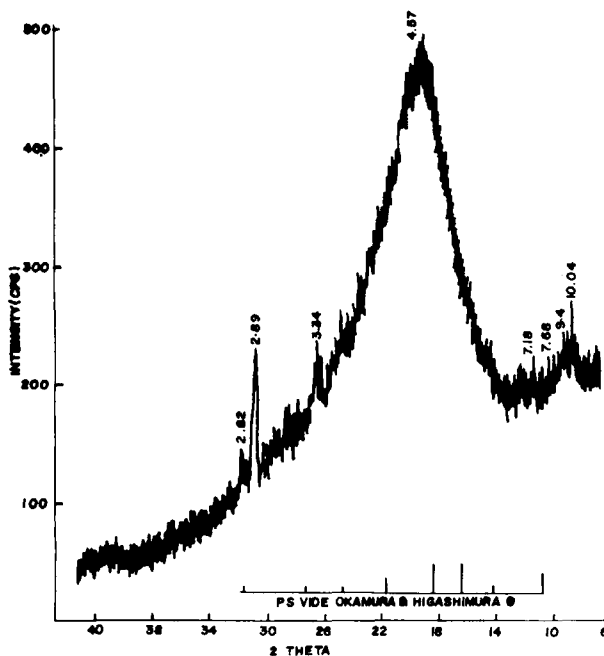
course this excludes the very fine PS-gel particles that remained in the benzene soluble PS mass. This indicated that PS-gel formation occurred when the concentration of free radicals of both primary and growing chains were very high, and these had enough mobility within the monomer-polymer globules to react toward crosslinking, most probably through hydrogen abstraction leading to very high molecular weight PS gels.

It would be realistic to think that these PS gels have a wide range of molecular weights and those with lower molecular weights do not easily separate out as benzene insolubles. These lower PS-gel molecules appear to remain as very fine particles in the benzene soluble PS mass [Fig. 1(C)]. The PS gels get dispersed in the continuous phase immediately due to the relatively higher temperature and the applied shear. After 80–85% monomer conversion, the monomer-polymer globules attain a fairly rigid shape and mobility of the residual radicals becomes too low to lead to further PS-gel formation.

These results thus indicated that PS gel containing PS homopolymer could be attractive for many end use applications.

## CONCLUSION

The polymerization of styrene in aqueous suspension under controlled high temperature and concentra-



**Figure 3** X-ray diffractograms of PS gel with a commercial PS sample.

tion of the initiator leads to the formation of 5–7% benzene insoluble PS gel that remain dispersed in the PS mass. This PS product containing PS gel is transparent and its properties are comparable to those of commercial HIPS products.

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