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Studies on Mechanism of Grafting of Polystyrene on Elastomer Backbone

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ABSTRACT

The mechanism of grafting of polystyrene on a polybutadiene (PB) backbone during the preparation of impact-resistant polystyrene was studied by withdrawing samples during propolymerization from beginning of the reaction to about 25% conversion. Good separation of the "elastomer and graft" fraction of the polymer from the free polystyrene part could be achieved by using 0.24 volume fraction of methanol in (MEK + benzene) + methanol solvent-nonsolvent. IR analysis of the grafted fraction showed that the microstructure of the elastomer remained unaltered. The unsaturation of the samples studied through the bromine number as well as by the perbenzoic acid number was also found to remain unchanged. Formation of free polystyrene started with the onset of polymerization and was faster. During prepolymerization, 80% of styrene converted constantly to form free polystyrene and 20% went into the grafted polymer. The results indicate that grafting is initiated through proton abstraction at the α -carbon of butadiene, most probably by initiator radicals. The grafted polystyrene chains possibly are shorter than free polystyrene chains.

INTRODUCTION

Impact polystyrene is produced by grafting styrene chains on an elastomer. The mechanism of this grafting has been studied by several workers [1-3]; however, the question of whether the polystyrene chains grow on the ethylenic double bonds or on the α -carbons of butadiene species of the elastomer has not been satisfactorily resolved. If the attachment is on the carbon atoms of the double bonds, the unsaturation of the elastomer should decrease. Bucknell [1] and Crompton and Reid [2] reported the loss of 7 and 10% unsaturation, respectively, in the grafted polymer. On the other hand, Ballova et al. [3] found no such change in the unsaturation and were of the opinion that the grafting occurs at the α -carbon of butadiene after extraction of a proton.

The polymer product contains grafted polystyrene as well as free polystyrene. For investigation of the grafted polymer, these have to be separated. Bucknell [1] separated the grafted polystyrene from free polystyrene by solvent-nonsolvent treatment; Blanchette and Nielson [4] used a turbidometric titration method.

In the course of our studies on impact polystyrene, investigations were also carried out to study the progress of grafting during pre-polymerization along with any possible change of unsaturation so that some confirmed view on the mechanism can be expressed. For this purpose samples were taken at different grafting stages during pre-polymerization and the grafted polymer was separated and analyzed. The conditions for good separation of the grafted polystyrene from the free polystyrene were also established.

EXPERIMENTAL

Five parts of polybutadiene elastomer (PB) were dissolved in 95 parts of distilled styrene at 60°C and polymerized under controlled conditions of temperature and agitation in the presence of a peroxide initiator in a 10-L stainless steel reactor. Four samples of the product, each about 10 g, were withdrawn at different levels of styrene conversion. The samples were taken at intervals starting after about 10 min from the onset of polymerization until about 25% styrene conversion. Each sample was weighed in stoppered flasks, dissolved completely in a minimum quantity of benzene, and precipitated with an excess of methanol. The precipitate was dried at 45-50°C under vacuum until constant weight was reached. The conversion of styrene was calculated from the weight of the precipitate. These precipitated samples were dissolved in a mixture of benzene and MEK (for each 1 g of sample 20.0 mL of benzene and 15.0 mL of MEK were used [4]) and fractionated. A number of polymer fractions were separated from the solution on adding measured amounts of methanol, each fraction corresponding to the volume fraction of methanol present in

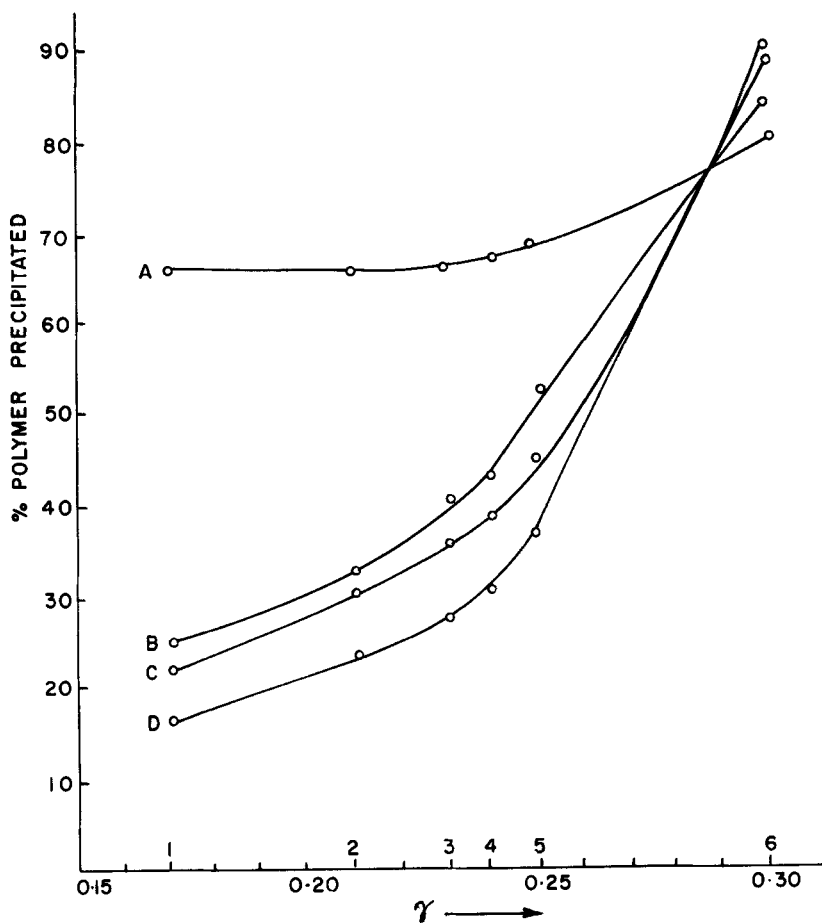


FIG. 1. Percent of fraction separated against the methanol volume fraction of total solvent nonsolvent. The numbers 1 to 6 indicate the γ values of 0.17, 0.21, 0.23, 0.24, 0.25, and 0.30, respectively. A = 2.93%, B = 9.52%, C = 16.55%, D = 24.87%.

the solvent-nonsolvent mixture. These volume fractions of methanol, γ , were 0.17, 0.21, 0.23, 0.24, 0.25, and 0.3. [$\gamma = x/(x + y)$, where x is the milliliters of methanol and y is the milliliters of MEK + benzene]. Figure 1 shows the fractionation data of the four prepolymer samples. It was found that the precipitation rose slowly up to $\gamma = 0.23$ and was quite rapid after $\gamma = 0.25$. IR analysis of the fractions below $\gamma = 0.23$ showed that these did not contain any free polystyrene, whereas the two fractions obtained with methanol volume fractions of 0.25 and 0.3 contained only free polystyrene and no grafted product.

TABLE 1. Microstructures and Unsaturation of PB-Styrene Graft at Different Conversions (Columns 1 to 4 indicate the percentage of total charge taken for polymerization)

No. of sample	Total polymer content (MI) (%)	Styrene conversion (%)	Elastomer + graft separated from MI by adding methanol to $\gamma = 0.24$ (%)	Microstructure of rubber + graft by IR analysis		Microstructure of rubber part of graft (styrene free)		Rubber + graft calculated from IR data (Columns 2, 5, 6, 7) (%)	Unsaturation			
				trans-1,4 (%)	trans-1,2 (%)	trans-1,4 (%)	trans-1,2 (%)		Bromine number	Perbenzoic acid number		
											Styrene (%)	trans-1,4 (%)
1	2	-	3	4	5	6	7	8	9	10	11	12
1. Pure polybutadiene	-	-	-	-	84	16	0	84	16	0	242	270

2.	5.625	0.625	5.00	0.625	84	16.00	0.00	84.00	16.00	5.0	240	-
3.	6.071	1.071	5.00	1.071	83.1	16.90	0.00	83.10	16.90	5.0	-	273
4.	7.150	2.150	5.35	1.800	81.5	16.25	2.25	83.40	16.60	5.115	-	270
5.	8.118	3.118	5.48	2.640	77.8	16.10	6.10	82.85	17.15	5.325	246	-
6.	11.818	6.818	6.05	5.768	72.1	14.00	13.90	83.74	16.26	5.807	-	288
7.	23.642	18.642	7.90	15.740	55.5	10.00	34.50	84.70	15.30	7.633	235	278
8.	25.823	20.823	8.18	17.643	54.0	11.05	34.95	83.10	16.90	7.687	-	265
9.	27.607	22.607	9.40	18.207	46.3	9.40	44.30	83.10	16.90	8.98	245	269
10.	Final beads	-	9.80	90.200	43.4	7.60	49.00	83.50	16.50	-	-	-

Fractionation at $\gamma = 0.24$ showed that the fractionation was sharp. Thus this 0.24 methanol volume fraction in this solvent-nonsolvent system was found to give satisfactory separation of the grafted polystyrene along with the elastomer from the free polystyrene in these prepolymer samples.

In another experiment carried out under similar conditions, eight samples were withdrawn at different conversion levels of prepolymerization and purified. The percentage precipitate (methanol insoluble) obtained from each sample is given in Column 1 of Table 1; styrene conversion (Column 2) was found by subtracting the 5% elastomer taken in the charge from the amount of methanol insolubles. The "elastomer and graft" fractions contained in these methanol insolubles were separated by dissolving them in a MEK + benzene mixture and then adding methanol corresponding to $\gamma = 0.24$. The amounts of such graft fractions thus separated are given in Column 3. Subtracting the values of Column 3 from Column 1, the amounts of styrene converted to homopolymer were obtained and are given in Column 4. Columns 5, 6, and 7 give the microstructure of the "elastomer and graft" fractions (of those given in Column 3) as determined by IR following the method suggested by Binder [5]. From these data, the contents of trans-1,4-PB and 1,2-PB (styrene free bases) in the "elastomer and graft" fractions were calculated and are given in Columns 8 and 9. The styrene percentage in the grafted fractions are given in Column 7; the rest (100 - % styrene in Column 7) was the elastomer amounting to 5% of the total charge. Based on this % styrene from IR, the corresponding amounts of "elastomer and graft" fractions were calculated (Column 10) for comparison of the data. These calculated values were in good agreement with those given in Column 3, taking into account the sample size and the inaccuracies involved in the methods of separation and analysis.

After the samples were withdrawn at the prepolymer stage, the charge was suspended in double the volume of demineralized water containing polyvinyl alcohol as stabilizer. The polymerization was continued with the free radical initiator for 6 h at 80°C and finally for 2 h at 100°C. The polymer beads were washed well with water and dried under vacuum at 50°C. About 10 g of the beads were taken and extracted with ethyl acetate to remove the free polystyrene. The insoluble "elastomer and graft" was then treated with petroleum ether to remove any free elastomer; however, no free elastomer could be detected in the petroleum ether extract. The analysis of the grafted fraction of this final bead polymer is given at the bottom of Table 1.

In addition to this fractionation and analysis of the microstructure of the grafted fractions, the unsaturation of these fractions was also examined by determining their bromine number and the perbenzoic acid numbers. For bromine number a known weight of the grafted fraction was dissolved in carbon tetrachloride and reacted with potassium bromide-bromate solution. After addition of potassium iodide solution, the liberated iodine was titrated against sodium thiosulfate. The perbenzoic acid number was determined as follows: A known

weight of the sample was dissolved in benzene, an excess of perbenzoic acid added, and the mixture left for 24 h to oxidize the olefinic bonds to epoxides. This was then titrated iodometrically. Simultaneously, blank determinations were also made in both cases. Finally, the bromine numbers and perbenzoic acid numbers were calculated for the elastomer part only. The results are given in the last two columns of Table 1.

DISCUSSION

The formation of grafted polystyrene was detected when the styrene conversion was about 2%. Free polystyrene was found to be formed (Table 1, Column 4) right from the beginning and continued in the same manner during polymerization. Grafted polystyrene formation might have commenced earlier but missed detection as the quantity was very small. The results, however, distinctly showed that free polystyrene formation was faster than graft polymerization. Figure 2 adds further evidence to this and also leads to interesting deductions. In Fig. 2 the distribution of polystyrene in the graft and in the free polystyrene is plotted against the total conversion of styrene up to nearly the end of the graft formation stage. The straight line shows that all along this graft formation stage, only about 20% of the converted styrene entered into the graft formation and the rest (80%) was converted to free polystyrene. In other words, the free polystyrene formation was 4 times faster than the grafting.

At around 23% styrene conversion the "elastomer and graft" fraction constituted about 9.4% of the reaction mass. The grafted fraction separated from the beads after complete conversion was also found to be around 9.8% (i.e., contained 4.8% styrene in the graft). This showed that the amount of grafted polymer formed at about 23-24% styrene conversion had remained the same (on further polymerization to complete styrene conversion and no more grafted polymer had formed). In other words, under the experimental conditions the formation of the grafted polymer reached saturation at about 23-24% styrene conversion level during the prepolymerization stage. The total grafted fraction in the polymer amounted to 9.8%; this contained 5% elastomer. Thus the grafted polymer fraction contained almost equal amounts by weight of the elastomer and the grafted polystyrene. A similar observation was also made by other workers [6, 7].

The IR analysis of polybutadiene used in this study showed that it contained 84% trans-1, 4-PB and 16% 1,2-PB. The microstructure (determined by IR) of all the grafted fractions separated from the prepolymer as well as the final polymer samples given in Table 1, indicates that the amount of trans-1,4 and 1,2 in PB remained unchanged during polymerization. On extracting the "elastomer and graft" fraction of the final polymer with petroleum ether and adding methanol to this extract, no precipitation was observed; this showed

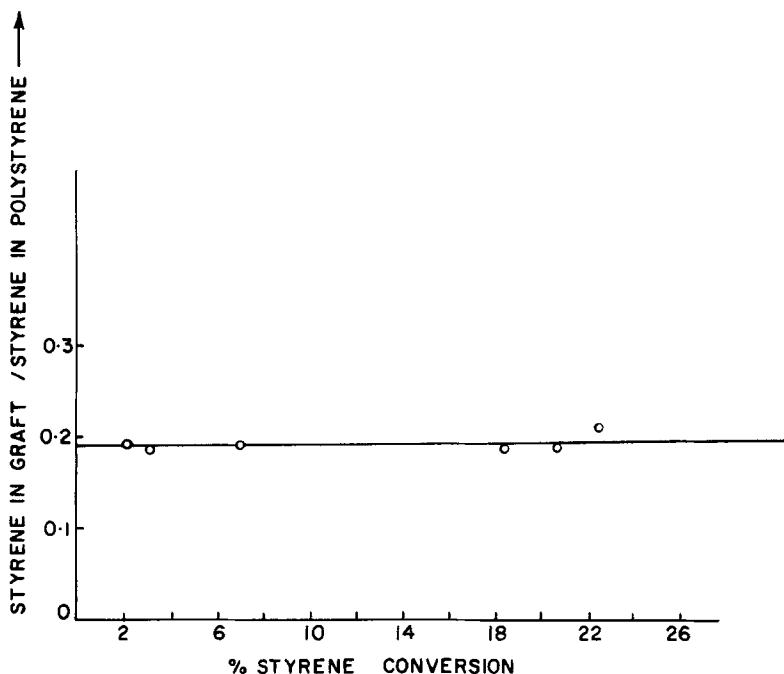


FIG. 2. Distribution of styrene in the graft and free polystyrene during prepolymerization.

that no free elastomer was present in the separated graft fractions and all the elastomer had reacted to form the grafted polystyrene. It follows, therefore, that in the system under study the polystyrene chains get grafted on all the elastomer molecules in such a way that the structure of PB molecules containing the trans-1,4- and 1,2-butadiene units remain unchanged.

The unsaturation in the polybutadiene contained in the grafted fraction was checked by both bromine number and perbenzoic number determinations. The values given in Columns 11 and 12 of Table 1 show that the unsaturation in the elastomer remained unchanged after grafting. The bromine numbers determined were slightly lower than the theoretical value of 290. This may be due to several factors such as accessibility of reagent sample size, solvent used, and duration of reaction which have been reported to affect the measurement. However, if a few double bonds were affected during grafting, these were not detectable. These results lend support to the postulated mechanism [3] that the grafting of polystyrene occurred through the abstraction of proton from the α -carbon atom of the butadiene unit. The slower rate of grafting compared with free polystyrene formation

also conforms to this view. If the radicals on the elastomer chains were grafted by uncoupling of the electrons at the double bonds of the butadiene moiety, it should be fast; if it occurred through proton extraction, it would be slow. The observed much slower rate of grafting shows proton extraction to be the case. Extraction of protons can occur by the radical end of the growing polystyrene chains or by the initiator radicals. The occurrence of grafting in the early stages of polymerization, when the concentration of free radicals is high, and the absence of grafting after the prepolymerization stage, when the formation of styrene chains continues to remain the same, show that the proton extraction by initiator molecules is more probable. The absence of grafting after prepolymerization may be due to inhibitions which create radical centers by water or other chemical agents present; it may also be due to the inaccessibility of the free radicals to the grafted elastomer existing in highly viscous discrete particles surrounded by free polystyrene and adsorbed suspending agents.

Equal amounts by weight of butadiene and styrene in the grafted fraction show that the number of styrene molecules would be about half of the butadiene molecules. With 84% of trans linkages present, where proton extraction can occur, formation of short grafted polystyrene chains seems to be more probable than a very few long polystyrene chains. This can better explain the reduction of accessibility of the radicals for further grafting.

CONCLUSION

These investigations on graft polymerization of styrene on 5% polybutadiene showed that from the onset of polymerization free polystyrene (homopolymer) is formed and possibly also graft polystyrene. As polymerization progresses along with graft formation, 20% of the converted styrene was found to go into the graft and 80% to form free polystyrene. Formation of grafted polymer was found to be completed at the prepolymerization stage at about 23-24% styrene conversion. The grafted polymer fraction contained the same weight percentage of polystyrene as that of the elastomer. The grafted fraction could be satisfactorily separated from the free polystyrene by the (MEK + benzene) and methanol solvent-nonsolvent system. Sharp separation was obtained on using a 0.24 methanol volume fraction in the total solvent-nonsolvent added.

The microstructure and the unsaturation of the PB-elastomer in the grafted polystyrene fraction were found to remain unchanged during the formation of the grafted polymer (prepolymerization) as well as in the final polymer. These results lend support to the mechanism postulating that the initiation of the grafting reaction occurs through the abstraction of a proton at the α -carbon of the butadiene unit, most probably by the initiator radicals. It also appeared more

probable that the graft contains a number of short polystyrene chains rather than only one or two long chains per elastomer molecule.

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