

# Graft Copolymerization of Poly(vinyl Chloride) with Styrene. I. Synthesis and Characterization

K. K. SHARMA and I. K. VARMA, *School of Materials Science and Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110029, India*

## Synopsis

Graft copolymerization of poly(vinyl chloride) (PVC) partially dehydrochlorinated by heating in nitrobenzene was investigated using styrene as monomer and anhydrous  $\text{AlCl}_3$  as cationic initiator in the temperature range of 0–35°C. Effect of monomer, catalyst, and PVC concentration on % graft-on was also evaluated. Introduction of labile sites in PVC by partial dehydrochlorination in nitrobenzene resulted in an increase in % graft-on. Intrinsic viscosity of PVC-*g*-polystyrene in THF initially increased with an increase in % graft-on. At higher % graft-on a decrease in  $[\eta]$  was observed.

## INTRODUCTION

Graft copolymerization of poly(vinyl chloride) (PVC) with various vinyl monomers has been investigated extensively in the past with an aim to improve impact strength, tensile strength, and thermal stability.<sup>1</sup> Reactive chlorine atoms in PVC provide potential sites for grafting which may be carried out by using irradiation techniques or radical or ionic polymerization.

Allylic chlorines and tertiary chlorines in PVC may be removed by conventional Friedel–Crafts catalysts leading to the formation of carbonium ions on the backbone. In the presence of suitable monomers grafting can be initiated at these sites. Removal of labile sites from the PVC backbone is expected to improve thermal properties of the polymer.

Alkylaluminum compounds have been reported to be effective grafting agents with halogenated polymers such as PVC, neoprene, chlorobutyl rubber, etc. Trialkylaluminum and dialkylaluminum monohalides have been used to graft styrene, isobutene, and chloroprene on PVC.<sup>2–7</sup> Plesch<sup>8</sup> has reported the synthesis of graft copolymers of PVC with styrene using  $\text{AlCl}_3$  and  $\text{TiCl}_4$ . However, the product was not well characterized because of large amounts of homopolymer formed and degradation of PVC which accompanied grafting reaction. Solomon et al.<sup>9</sup> have also used  $\text{AlCl}_3$  as initiator for grafting *N*-vinylcarbazole onto PVC.

In this paper we report the graft copolymerization of styrene onto PVC using  $\text{AlCl}_3$  as initiator and nitrobenzene as solvent. The effect of concentration of catalyst, styrene, and PVC on % grafting was investigated. Dehydrochlorination of PVC in the presence of nitrobenzene has been reported in the literature.<sup>10</sup> It is quite likely that allylic chlorine generated during PVC degradation may offer additional sites for cationic graft copolymerization of styrene. Therefore, the effect of heating PVC in nitrobenzene in the temperature range of 80–110°C on the extent of grafting reaction was also evaluated. The graft copolymers were characterized by chlorine estimation, intrinsic viscosity evaluation, and IR spectroscopy.

## EXPERIMENTAL

### Materials

PVC was purified by precipitation using tetrahydrofuran as solvent and methanol as precipitant.<sup>11</sup> Styrene (LR Grade, Wilson Ltd., Bombay) was washed with 10% NaOH to remove the inhibitor, then washed with water. It was finally dried over  $\text{CaCl}_2$  and distilled under reduced pressure. The fraction boiling at  $39^\circ\text{C}$  at 14 mm was collected. Nitrobenzene (LR Grade, BDH) was dried over fused  $\text{CaCl}_2$  before distillation. Anhydrous  $\text{AlCl}_3$  was used as such.

### Graft Copolymerization

The graft copolymerization was carried in nitrogen atmosphere. A weighed quantity of PVC was taken in a round-bottomed three-necked flask fitted with a condenser and a nitrogen inlet tube. The desired amount of nitrobenzene was then added and the contents were left overnight for swelling. The contents were then heated in nitrogen atmosphere at the desired temperature ( $80\text{--}110^\circ\text{C}$ ) for 75 min. By this treatment PVC was dissolved completely and a homogeneous solution was obtained. A mercury-sealed stirrer was attached to the flask and nitrogen was continuously bubbled through the solution. A known quantity of  $\text{AlCl}_3$  was added to the solution. After the solution had attained the desired temperature, styrene monomer was introduced. The contents were mixed thoroughly, and the reaction was carried for a known interval of time. Contents of the flask were then poured into an excess of distilled water to decompose aluminum complex. The solid residue thus obtained was dissolved in THF and polymer was precipitated in an excess of methanol. Graft copolymer was freed from polystyrene by extracting the latter in benzene for several hours. The residual polymer was washed with methanol and dried under vacuum at  $30\text{--}35^\circ\text{C}$ .

The % chlorine in the original PVC and various polymer samples obtained after graft copolymerization with styrene was estimated by using the Stepanov method.<sup>12</sup>

For estimation of % graft-on, the following procedure was used. First, the % chlorine in various compositions of PVC-*g*-polystyrene was calculated and a calibration chart was prepared by plotting % chlorine versus % graft-on. From the experimental values of % chlorine obtained in the various samples and this calibration chart, the % graft-on was obtained.

### Characterization of Graft Copolymers

The graft copolymers were characterized by recording the IR spectra of polymers in KBr pellets using a WEB Carl Zeiss Jena UR-10 infrared spectrophotometer. Intrinsic viscosity of the polymers was determined in THF at  $30^\circ\text{C}$ , using an Ubbelohde suspension-level viscometer.

TABLE I  
Effect of Initial Heating of PVC on % Graft-on (Rates of Dehydrochlorination of PVC at Various Temperatures are also Given)

Amount of PVC taken = 50 g/l. Amount of styrene taken = $48.1 \times 10^{-2}$ mole/l. Amount of initiator taken = $37.5 \times 10^{-2}$ mole/l. Temperature of graft copolymerization = 35°C Reaction time = 15 hr			
Temp. of heating PVC in nitrobenzene for 75 min, °C	$d\text{HCl}/dt$		% Graft-on
	(mole acid/ l. sec) $\times 10^6$	(mole acid/ g sec) $\times 10^7$	
80	—	—	16.0
90	0.40	0.08	20.5
100	0.60	0.12	27.5
110	1.60	0.32	34.5

## RESULTS AND DISCUSSION

The extent of grafting may be influenced by the availability of labile sites in the polymer backbone; concentration of initiator, monomer, and PVC; and duration and temperature of the grafting reaction. The effect of these parameters on the graft copolymerization of PVC with styrene was investigated.

### Effect of Initial Dehydrochlorination of PVC on % Graft-on

Dehydrochlorination of PVC in nitrobenzene was carried in nitrogen atmosphere at four different temperatures (i.e., 80, 90, 100, and 110°C) before carrying out the graft copolymerization. A polymer concentration of 50 g/l. was used. The dehydrochlorination was carried for a period of 75 min, and evolved acid was estimated at regular intervals of time, as described earlier.<sup>11</sup> The rates of dehydrochlorination at various temperatures were evaluated and are given in Table I. No acid was evolved at 80°C. However, as the temperature was further increased, the amount of acid evolved also increased.

PVC solution thus obtained was used for carrying out graft copolymerization with styrene at 35°C for 15 hr. The results of % graft-on as determined by chlorine estimation are given in Table II. These results indicate that as the extent of dehydrochlorination was increased in PVC, the % graft-on also increased. In cationic graft copolymerization of PVC,  $\text{AlCl}_3$  might extract a labile chlorine from PVC, thereby generating a carbonium ion which may be stabilized

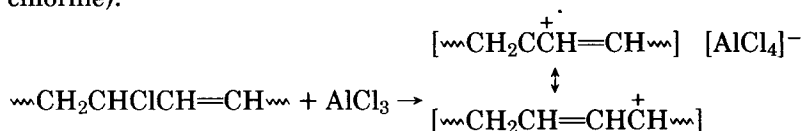
TABLE II  
Effect of Monomer Concentration on % Graft-on of PVC Heated Initially at 90°C for 75 min

Amount of PVC taken = 50 g/l. Amount of initiator taken = $37.5 \times 10^{-2}$ mole/l. Temperature of grafting reaction = 0°C Reaction time = 1 hr	
Concn. of monomer, mole $\times 10^2$ /l.	% Graft-on
48.1	28.0
74.5	25.6
104.8	15.0

TABLE III  
Effect of PVC Concentration on % Graft-on of PVC Initially Heated at 90°C for 75 min

Amount of styrene taken = $74.5 \times 10^{-2}$ mole/l. Amount of initiator taken = $37.5 \times 10^{-2}$ mole/l. Reaction time = 15 hr at 35°C or 1 hr at 0°C		
Concn. of polymer, g/l.	% Graft-on at	
	35°C	0°C
10	0.8	22.0
25	8.0	24.5
50	18.5	25.6

by resonance (in case of allylic chlorine) or by hyperconjugation (in case of tertiary chlorine):



It is quite likely that from initial dehydrochlorination of PVC in nitrobenzene, additional labile sites are generated thus increasing the % graft-on. The graft copolymerization taking place at 80°C where no acid was evolved indicates the existence of active sites in PVC. This was further confirmed by heating PVC in nitrobenzene at 60°C for 5 hr and copolymerizing with styrene ( $74.5 \times 10^{-2}$  mole/l.) using  $\text{AlCl}_3$  ( $37.5 \times 10^{-2}$  mole/l.) as initiator at 0°C. The % graft-on was found to be lower (20.5%) than a sample which was heated initially at 90°C and then graft copolymerized under similar conditions (% graft-on = 25.6%).

### Effect of Styrene Concentration on % Graft-on

The effect of monomer concentration on % graft-on was investigated by taking PVC degraded in nitrobenzene at 90°C for 75 min. Three monomer concentrations were used, i.e.,  $48.1 \times 10^{-2}$ ,  $74.5 \times 10^{-2}$ , and  $104.8 \times 10^{-2}$  mole/l. The grafting was carried at 0°C for 1 hr. The results indicate a decrease in % graft-on (Table II) on increasing styrene concentration in the solution. This may be due to an increase in homopolymer formation by proton transfer to styrene monomer. Such transfer may take place either with a growing graft copolymer chain or with the reactive carbonium ion on PVC backbone.

TABLE IV  
Effect of Initiator Concentration on % Graft-on of PVC Heated Initially at 90°C for 75 min

Amount of PVC taken = 50 g/l. Amount of styrene taken = $74.5 \times 10^{-2}$ mole/l. Temperature of graft copolymerization = 0°C Reaction time = 1 hr	
Initiator concn., mole $\times 10^2$ /l.	% Graft-on
7.5	22.0
18.7	24.0
37.5	25.6
56.2	9.0

### Effect of Polymer Concentration on % Graft-on

Investigations were carried at three different polymer concentrations, i.e., 10, 25, and 50 g/l. Graft copolymerization was carried at 35°C for 15 hr or at 0°C for 1 hr. The results of % graft-on at various polymer concentrations are given in Table III. It is obvious from these results that grafting was influenced by PVC concentrations, and an increase in amount of PVC taken resulted in an increase in % graft-on. This effect was more pronounced when grafting was carried out at higher temperatures. This behavior may be due to the availability of more reactive sites on the polymer. At higher temperatures  $\text{AlCl}_3$ -catalyzed dehydrochlorination of PVC might result in the generation of more reactive sites.

### Effect of Catalyst Concentration on % Graft-on

The amount of catalyst was varied between  $7.5 \times 10^{-2}$  and  $56.2 \times 10^{-2}$  mole/l. An increase in catalyst concentration resulted in an increase in % graft-on up to a concentration of  $37.5 \times 10^{-2}$  mole/l. (Table IV). Further increase in catalyst concentration resulted in a decrease in grafting.

### Effect of Temperature on % Graft-on

The reaction was carried at four different temperatures, i.e.,  $35 \pm 1$ ,  $22 \pm 1$ ,  $5 \pm 1$ , and  $0 \pm 2^\circ\text{C}$ . An increase in % graft-on was observed on decreasing the reaction temperature (Table V). Negative temperature dependency in cationic polymerizations is well documented. This observation confirms the mechanism of grafting in the presence of  $\text{AlCl}_3$ . Similar results have been obtained by Kennedy et al.<sup>13</sup> in the graft copolymerization of styrene onto chlorinated EPM using  $\text{Et}_2\text{AlCl}$  as cationic initiator.

### Effect of Reaction Time on % Graft-on

The effect of reaction time on % graft-on was investigated by conducting the reaction at 0°C for 60, 120, and 180 min (Table VI). There was no increase in % graft-on when the reaction time was increased.

TABLE V  
Effect of Reaction Temperature on % Graft-on of PVC Initially Heated at 90°C for 75 min in Nitrobenzene

Concentration of PVC = 50 g/l. Concentration of initiator = $37.5 \times 10^{-2}$ mole/l. Concentration of styrene = $74.5 \times 10^{-2}$ mole/l.		
Reaction temperature, °C	Reaction time, hr	% Graft-on
35	15	18.5
22	10	20.3
5	1	21.0
0	1	25.6

TABLE VI  
Effect of Reaction Time on % Graft-on of PVC Initially Heated at 90°C for 75 min in Nitrobenzene

Concentration of PVC = 50 g/l. Concentration of initiator = $37.5 \times 10^{-2}$ mole/l. Concentration of styrene = $74.5 \times 10^{-2}$ mole/l. Temperature of graft copolymerization = 0°C	
Reaction time, min	% Graft-on
60	25.6
120	25.6
180	24.5

### Intrinsic Viscosity of PVC-*g*-Polystyrene

The intrinsic viscosities of grafted polymer samples were determined in THF at 30°C (Table VII). Most of the samples used for this work were prepared by carrying the graft copolymerization at 35°C, and only a sample with 25.6% graft-on was prepared at 0°C. The  $[\eta]$  of this sample is found to be slightly lower than that of the sample having 25% graft-on.  $\text{AlCl}_3$ -catalyzed dehydrochlorination of PVC might have taken place at 35°C. Conjugated double bonds thus introduced in the backbone along with grafted chains may have resulted in a rigid material with higher  $[\eta]$ .

An increase in intrinsic viscosity was observed with an increase in % graft-on up to 25%. This may be attributed to the extension of PVC chains as a result of deposition of polystyrene grafts. However, as the % graft-on is increased, a distortion of conformation of the two incompatible polymer chains might take place, resulting in the shrinkage of the grafts. This contraction of the overall structure might be responsible for a reduction in the  $[\eta]$  of the grafted polymers. Infrared spectra of various PVC-*g*-polystyrene samples were recorded for characterization. In Figure 1 the IR spectrum of sample with 8.0% graft-on is given. Similar spectra were obtained for other samples. The presence of styrene in the sample is indicated by the appearance of peaks in the 1500–1600  $\text{cm}^{-1}$  region, along with the typical bands of PVC. An absorption band at 615  $\text{cm}^{-1}$  was observed which has been attributed to the C–Cl bond in grafted PVC samples by Taminka et al.<sup>14</sup>

On the basis of these observations it can be concluded that graft copolymerization of PVC can be carried out using  $\text{AlCl}_3$  as an initiator. The extent of grafting is influenced by the availability of labile sites on PVC, and partial

TABLE VII  
Intrinsic Viscosity of Various PVC-*g*-polystyrene Samples in THF at 30°C

Sample no.	% Graft-on	Intrinsic viscosity, ml/g
1	0	103
2	0.8	114
3	8.0	118
4	17.5	124
5	18.5	124
6	25.0	136
7	25.6	128
8	31.0	116

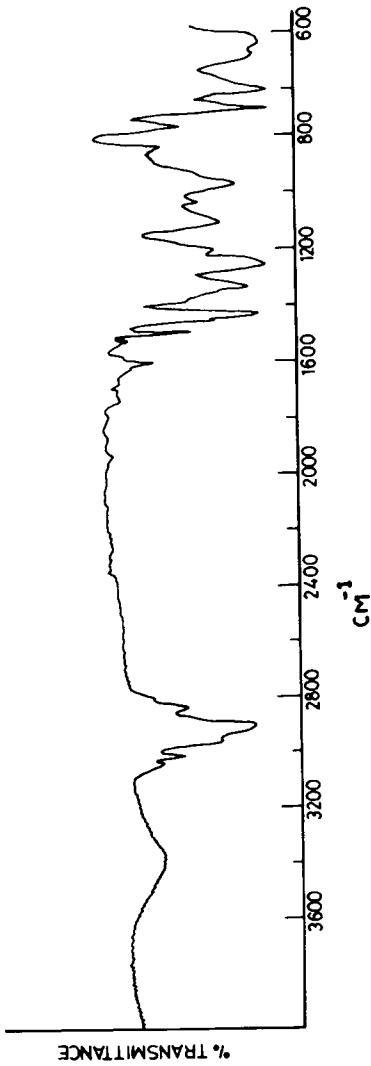


Fig. 1. Infrared spectrum of PVC-*g*-polystyrene (8.0% graft-on).

dehydrochlorination of polymer prior to grafting reaction enhances the % graft-on. Formation of homopolymer under these conditions can be explained by a chain transfer reaction between a growing graft copolymer ion and styrene monomer.

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