

Dehydrochlorinated Poly(vinyl Chloride-*g*-Styrene).

I. Effect of Synthesis Conditions

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Synopsis

Dehydrochlorinated poly(vinyl chloride) (DHPVC) was graft copolymerized with styrene monomer using benzoyl peroxide (Bz_2O_2) as free radical initiator, in vacuum. The effect of synthesis conditions such as time, initiator concentration, the ratio of monomer to polymer, and temperature on various grafting parameters was studied. On the whole, a maximum of 47 wt % polystyrene (PSt) in the graft (DHPVC-*g*-PSt) was obtained. PSt contents of graft copolymers determined by gravimetry, chlorine analysis, and UV spectroscopy have been compared. A "grafting from" mechanism has been proposed for the graft copolymerization.

INTRODUCTION

Poly(vinyl chloride-*g*-styrene) (PVC-*g*-PSt) has been prepared by anionic,^{1,2} cationic,³⁻⁶ and free radical⁷ techniques. The free radical chain transfer method is widely used for the preparation of the graft copolymer. Minoura et al.⁸ have synthesized PVC-*g*-PSt by transfer reaction using a persulfate initiator in the latex state. Moszner and Hartmann⁹ grafted PVC with styrene in the presence of $TiCl_3$, thus providing an active site for the initiation of grafting. Cooper¹⁰ synthesized PVC-*g*-PSt thermally in the presence of oxygen by free radical reactions without the addition of initiator. PVC-*g*-PSt was also obtained by heating PVC swollen in the vapors of styrene, at 110–30°C for 2–8 h.¹¹

An important method of the graft copolymer formation is the chemical modification of PVC to provide more active side groups at random positions along the length of the polymer chain to form a multifunctional initiator for grafting reactions. Nitric and nitrous side groups were formed along the backbone polymer chain by treating PVC with a mixture of nitric acid and P_2O_5 . Grafting of styrene or butadiene was then initiated from these reaction sites at 70°C, using a free radical initiator.^{12,13} Peroxy groups along the polymer chain were created by ozonolysis of the backbone of the polymer. PVC was first dehydrochlorinated to give unsaturated groups within the chain which were peroxidized by ozone treatment. The peroxidized polymer was treated with styrene to form poly(vinyl chloride-*g*-styrene).¹⁴

Activation of the polymer molecule as initiator is another synthetic route to the graft copolymer. Partially dehydrochlorinated PVC, by virtue of its unsaturated groups, has been directly grafted by swelling the dehydrochlorinated polymer in monomer–initiator solution and copolymerizing the aqueous suspension.¹⁵ However, no extensive study has been carried out on the grafting of styrene to dehydrochlorinated PVC.

The present work is aimed at grafting styrene to dehydrochlorinated PVC (DHPVC) using benzoyl peroxide (Bz_2O_2) as free radical initiator, and studying

the effect of synthesis conditions on PSt content of the graft copolymer (DHPVC-*g*-PSt).

EXPERIMENTAL

Materials

DHPVC prepared by refluxing a solution of PVC in pyridine (41.7 g/L) at 120°C for 135 min was used for the graft copolymerization. Characterization data of this dehydrochlorinated product are as follows: extent of dehydrochlorination (x , %) 3.62; $[\eta]$ (dL/g) 0.81; \bar{M}_v (viscometry) 70.3×10^3 ; \bar{M}_n (GPC) 37.9×10^3 ; \bar{M}_v (GPC) 92.8×10^3 ; \bar{M}_w (GPC) 109.3×10^3 ; heterogeneity index (H) 2.8; ultraviolet spectroscopic analysis number (N) of polyenes having conjugated double bonds (n) of: 2, 4.22; 3, 1.77; 4, 0.54; 5, 0.19; 6, 0.15; 7, 0.10; total number of polyenes (T_n) 6.97; total number of double bonds (D_n) 18.48; percentage of double bonds (P_n) 1.20. Details of the preparation characterization and properties of DHPVC have been given in preceding papers.¹⁶⁻¹⁸

Styrene (Eastman Kodak Co.) was washed several times with 5% NaOH solution to remove the inhibitor. It was then washed thoroughly with distilled water to eliminate all traces of alkali, dried with fused CaCl_2 (20 g/100 mL styrene) and distilled under reduced pressure (30°C/0.5 mm Hg).

Bz_2O_2 was purified by dissolving in chloroform at room temperature and recrystallizing from methanol.

Tetrahydrofuran (THF) was purified by refluxing over sodium borohydride and distilling from metallic sodium in nitrogen atmosphere.

Petroleum ether (40–60°C) and methanol were distilled once and used as the precipitant.

Cyclohexane was used as received (A.R., BDH).

Graft Copolymerization

Grafting was carried out in a 50-mL round-bottomed flask fitted with a stopper having a long neck with a constriction for sealing purpose, and side tube attached to the vacuum pump connector (Fig. 1).

A weighed amount of purified DHPVC and a Teflon® coated magnetic stirring bar were placed at the bottom of the flask. The mouth of the flask was fitted with the stopper tube. The upper end of the stopper tube was closed by a rubber septum, and vacuum was applied to the flask through the side tube. The monomer–initiator solution was injected into the flask through the rubber septum, using a hypodermic syringe. The stopper tube was sealed in vacuum. The polymer was swelled in the monomer–initiator solution for about 15 min. The reaction flask was immersed in an oil bath and heated at the required temperature with continuous stirring. After the desired time period, the reaction was terminated by the addition of an excess of petroleum ether. The reaction mixture was filtered, and the residue was washed several times with petroleum ether and dried to constant weight under vacuum at 50°C. The product thus obtained was purified by dissolving in THF and reprecipitating with petroleum ether under vigorous stirring.

The product obtained after graft copolymerization was a mixture of DHPVC-*g*-PSt, PSt, and DHPVC as well. Homo PSt was separated from the grafted product by Soxhlet extraction of the crude mixture with cyclohexane

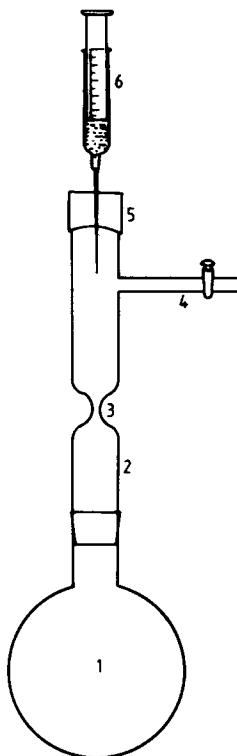


Fig. 1. Graft copolymerization apparatus: (1) reaction flask; (2) stopper tube; (3) constriction for sealing; (4) vacuum connector; (5) rubber septum; (6) hypodermic syringe.

until no more PSt could be detected in the cyclohexane soluble fraction (48 h). The remaining portion, which contains mainly DHPVC-*g*-PSt, was washed with methanol. The slightly discolored residue free of homopolymer was then dried in vacuum at 50°C.

PSt content of the graft copolymer and grafting efficiency (GE) were calculated from the relations used in determining the composition of grafts in the cationic synthesis of poly(vinyl chloride-*g*-isobutylene)¹⁹:

$$\text{PSt in graft (wt \%)} = \frac{\text{grafted PSt weight}}{\text{graft copolymer total weight}} \times 100$$

$$\text{grafting efficiency (\%)} = \frac{\text{grafted PSt weight}}{\text{grafted PSt weight} + \text{homo PSt weight}} \times 100$$

Estimation of Grafting Parameters

Gravimetry

The grafting parameters were calculated from the weight of the sample before and after grafting.

Chlorine Estimation

This method gives only wt % PSt in the graft copolymer. It was evaluated by chlorine estimation using Bomb combustion method.²⁰ Percent chlorine in

various compositions of DHPVC-*g*-PSt was calculated, wt % PSt in these graft copolymer samples was determined gravimetrically, and a calibration curve was obtained by plotting percent chlorine versus wt % PSt in graft (Fig. 2). From the experimental results of percent chlorine and this calibration curve, wt % PSt in the graft copolymers was obtained.

Ultraviolet Spectroscopy

Composition of the graft copolymer was determined also by ultraviolet (UV) spectroscopic analysis. Absorption of THF solutions (0.05 g/dL) of the graft copolymers was measured at 260 m μ (static UV). Weight percent polystyrene was then calculated from the relations used in the determination of composition of grafts in the grafting of PSt from chlorosulfonated polyethylene²¹:

$$c_1 = \frac{(A/b - a_2c_0)}{(a_1 - a_2)}$$

$$\% \text{ PSt} = (c_1/c_0) \times 100$$

where A = solution absorbance, b = cell path length (1 cm), a_1 = absorptivity of PSt (25.2 dL/g-cm), a_2 = absorptivity of DHPVC (10.0 dL/g-cm), c_0 = total solution concentration (g/dL), c_1 = calculated PSt concentration (g/dL). Absorptivities a_1 and a_2 were determined experimentally.

RESULTS AND DISCUSSION

Effect of Synthesis Conditions on Grafting

Effect of Reaction Time

The effect of reaction time on grafting is shown in Table I and Figure 3. The rate of styrene conversion increased continuously on increasing the reaction time;

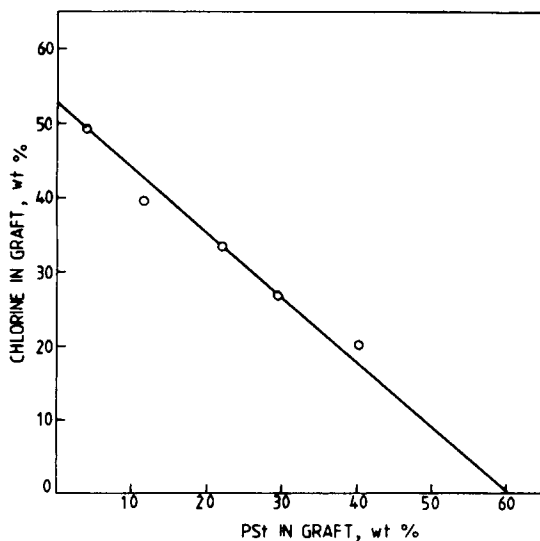


Fig. 2. Plot showing relationship between % chlorine and % grafting.

TABLE I
Effect of Reaction Time on Styrene Grafting^a to Dehydrochlorinated PVC^b

Sample no.	Reaction time (h)	Styrene conversion (%)	PSt in graft (wt %)	GE (%)
A ₁	1	2.3	—	—
A ₂	2	3.7	4.0	7.9
A ₃	4	11.0	11.4	8.2
A ₄	7	15.8	22.0	12.1
A ₅	10	18.4	26.5	13.5
A ₆	16	27.4	44.2	19.7
A ₇	19	28.8	45.0	19.5

^a Results were obtained gravimetrically.

^b DHPVC = 0.5 g, Bz₂O₂ = 2.0×10^{-4} mol/g DHPVC, styrene = 14.0×10^{-2} mol/g DHPVC, and temperature = 65°C.

yet the grafting reaction started only after an induction period. Grafting did not occur up to 1 h of the reaction, but after 2 h the graft having 4 wt % PSt was obtained. PSt content increased upon further increase in reaction time. The increase in the rate of styrene conversion during the "induction period" may be due to homopolymerization (PSt formation) by traces of scavenging impurities and/or chain transfer to monomer. Some "grafting onto" may also take place. "Grafting onto" is basically a chain transfer step which not only links the growing chain to a preformed polymer, but it also produces an independent initiating species, which in turn gives rise to sufficient quantities of homopolymer.

A large amount of graft copolymer formation beyond the "induction period" indicates predominance of "grafting from" over "grafting onto." The difficulty with "grafting onto" is reduced interpenetration (incompatibility) between the growing polymer and preformed polymer. This is not the case with "grafting from" because a monomer is much easier to diffuse to an active site on a backbone than a growing polymer.

Polystyrene content of the graft copolymer and grafting efficiency increased on increasing the reaction time, continuously for 16 h. However, upon further increase in reaction time, PSt content and GE remained almost unchanged. The

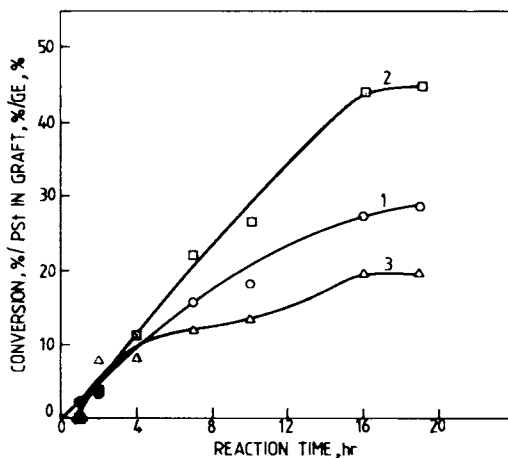


Fig. 3. Effect of reaction time on grafting: (1) conversion (%); (2) PSt in graft (%); (3) grafting efficiency (%).

TABLE II
Effect of Bz_2O_2 Concentration on Styrene Grafting to Dehydrochlorinated PVC^a

Sample no.	Bz_2O_2 concn (mol $\times 10^4$ /g DHPVC)	Styrene conversion (%)	PSt in graft (wt %)	GE (%)
B ₁	0.54	10.6	46.3	55.7
B ₂	1.08	15.4	47.0	39.2
A ₄	2.00	15.8	22.0	12.1
B ₃	4.12	22.0	5.4	1.8
B ₄	8.20	29.8	7.0	1.7
B ₅	16.60	31.2	—	—

^a DHPVC = 0.5 g, styrene = 14.0×10^{-2} mol/g DHPVC, time = 7 h, and temperature = 65°C.

fact that the maximum GE and PSt incorporation occurred at about the same conversion level indicates that, beyond this maximum, GE is determined primarily by the rate of chain transfer to monomer.

Effect of Initiator (Bz_2O_2) Concentration

The effect of concentration of Bz_2O_2 on grafting was studied in the range of 0.54 – 16.60×10^{-4} mol/g DHPVC. The results are summarized in Table II and Figure 4. The rate of styrene conversion increased on increasing the concentration of Bz_2O_2 , whereas both GE and PSt content decreased continuously. At Bz_2O_2 concentration of 16.60×10^{-4} mol/g DHPVC there was no grafting (Fig. 4). Probably, the chain transfer to monomer is the predominant reaction upon increase in the concentration of Bz_2O_2 which results in an increase in the rate of homopolymer formation.

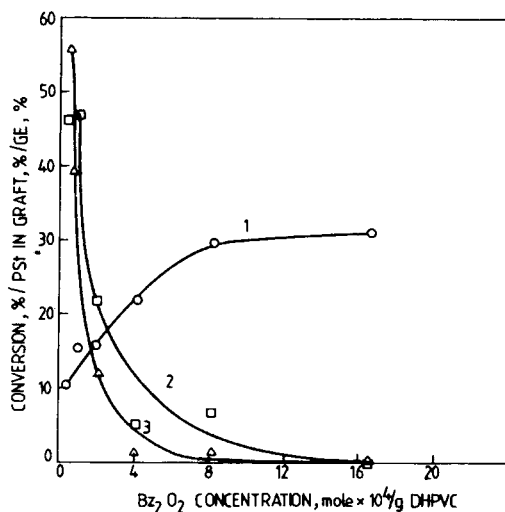


Fig. 4. Effect of Bz_2O_2 concentration on grafting: (1) conversion (%); (2) PSt in graft (%); (3) grafting efficiency (%).

TABLE III
Effect of the Ratio of Styrene to DHPVC, on Styrene Grafting to Dehydrochlorinated PVC^a

Sample no.	Ratio of styrene to DHPVC (mol $\times 10^2$ /g DHPVC)	Styrene conversion (%)	PSt in graft (wt %)	GE (%)
B ₂	14.0	15.4	47.0	39.2
C ₁	24.5	10.6	46.2	31.8
C ₂	31.5	9.9	40.5	20.9
C ₃	45.5	7.6	40.0	18.0

^a DHPVC = 0.5 g, Bz₂O₂ = 1.08×10^{-4} mol/g DHPVC, time = 7 h, and temperature = 65°C.

Effect of the Ratio of Styrene to DHPVC

The effect of the ratio of styrene to DHPVC, on grafting, was studied in the range of $14.0\text{--}45.5 \times 10^{-2}$ mol/g DHPVC. The results are presented in Table III.

A continuous decrease in the rate of styrene conversion, PSt content of the graft copolymer, and grafting efficiency was observed on increasing the amount of styrene in the reaction (Fig. 5). The decrease in the PSt content and GE may be due to increase in the rate of chain transfer to monomer (homopolymer formation) upon increase in the amount of styrene in the reaction. Polystyrene thus formed perhaps is of low molecular weight, which may be partially soluble in the nonsolvent, leading to a decrease in the observed conversion.

Effect of Reaction Temperature

The effect of reaction temperature on grafting, in the range 55–75°C, is presented in Table IV.

Styrene conversion rate increased continuously on increasing the reaction temperature, whereas PSt content of the graft copolymer increased upon increase

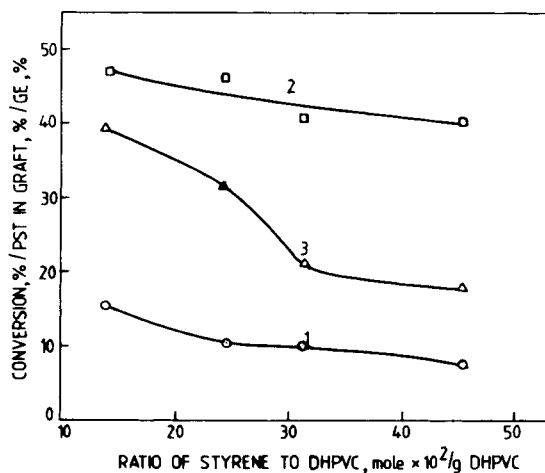


Fig. 5. Effect of ratio of styrene to DHPVC on grafting: (1) conversion (%); (2) PSt in graft (%); (3) grafting efficiency (%).

TABLE IV
Effect of Reaction Temperature on Styrene Grafting to Dehydrochlorinated PVC^a

Sample no.	Reaction Temp (°C)	Styrene conversion (%)	PSt in graft (wt %)	GE (%)
D ₁	55	5.4	29.3	23.5
D ₂	60	7.1	32.6	20.0
C ₂	65	9.9	40.5	20.9
D ₃	75	10.3	29.0	12.0

^a DHPVC = 0.5 g, Bz₂O₂ = 1.08 × 10⁻⁴ mol/g DHPVC, styrene = 31.5 × 10⁻² mol/g DHPVC, and time = 7 h.

in the temperature only up to 65°C and then decreased. Grafting efficiency remained almost unchanged or increasing the temperature up to 65°C and then decreased rapidly (Fig. 6).

Increase in the PSt content of the graft copolymer on increasing the temperature may be due to the formation of high molecular weight PSt branches. A rapid decrease in PSt content and GE above 65°C reflects the increase in the rate of chain transfer to monomer at higher temperatures, forming homopolystyrene. Since transfer is a higher activation energy process than propagation, it becomes less predominant at lower temperatures. Similar results were obtained by Kennedy and Davidson¹⁹ in the polymerization of isobutylene from PVC backbones and by Kennedy and Charles²² in the grafting of PSt from chlorobutyl rubber using alkyl aluminum coinitiators.

Graft Copolymer Composition

PSt contents of the graft copolymers were determined gravimetrically. Selected samples have also been characterized by UV spectroscopy and chlorine analysis before and after grafting. A comparison of the PSt contents obtained

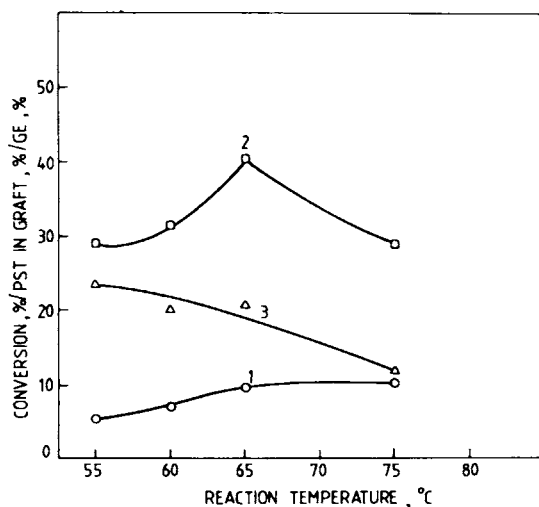


Fig. 6. Effect of reaction temperature on grafting: (1) conversion (%); (2) PSt in graft (%); (3) grafting efficiency (%).

TABLE V
Comparison of Gravimetric, UV, and Chlorine Analyses for Wt % PSt in DHPVC-*g*-PSt

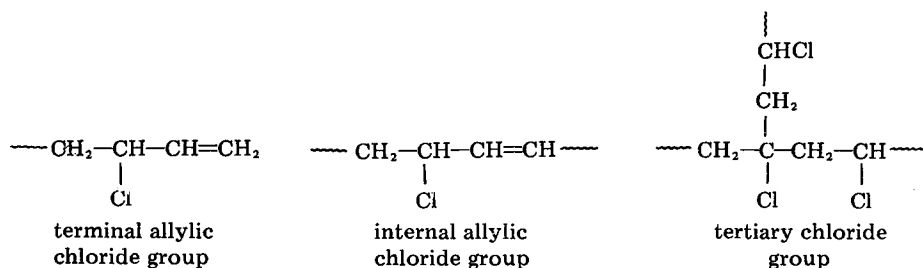
Sample no.	Gravimetry	Ultraviolet spectroscopy	Chlorine analysis ^a
B ₃	5.4	5.6	6.5
A ₄	22.0	24.0	25.0
D ₃	29.0	30.0	30.0
C ₃	40.0	40.8	41.0
B ₂	47.0	48.0	48.5

^a Based on 52.89 wt % chlorine in dehydrochlorinated PVC.

by gravimetric, UV, and chlorine analyses is shown in Table V. These three methods of analyses gave more or less identical results. The decrease in the values obtained by the gravimetric method is probably due to unavoidable polymer losses during the experiments. The chlorine analysis method is a reliable procedure for the determination of PSt content of DHPVC-*g*-PSt. Despite this, the PSt contents were determined gravimetrically because of the convenience.

Mechanism of Graft Copolymerization

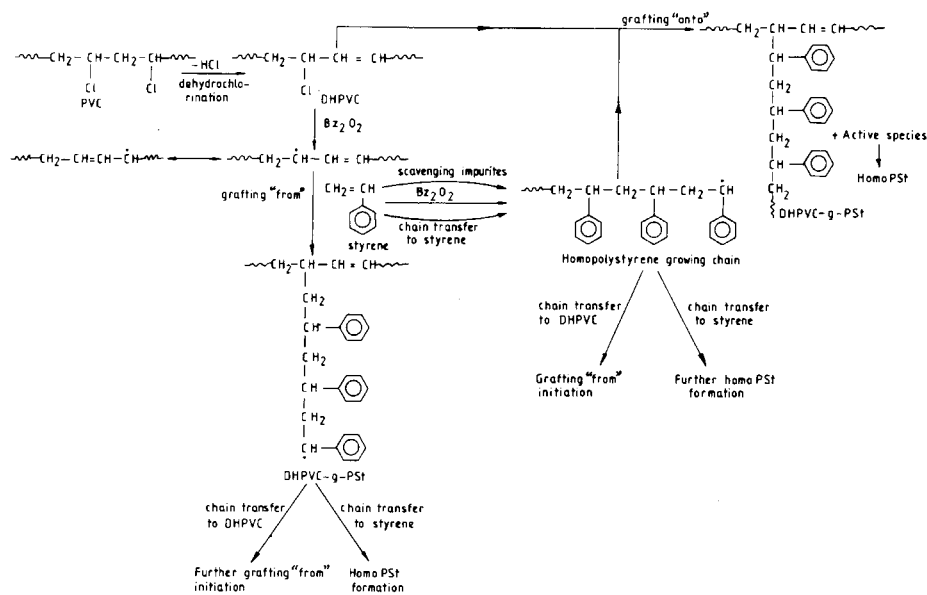
Kennedy and Davidson²³ in the cationic polymerization of isobutylene from PVC demonstrated that "PVC contains, in addition to the 'normal' secondary chlorines, labile allylic and/or tertiary chlorines as well. The thermal instability of PVC has been attributed to the presence of a small but critical amount of labile structures":



The labile chlorine atoms in PVC in conjunction with suitable catalyst provide initiation sites for grafting.

Partial dehydrochlorination of PVC generates new double bonds, and thus increases the availability of allylic chlorine atoms in the backbone. These labile chlorine atoms are removed by benzoyl peroxide initiator, thus generating active sites on the backbone where grafting of styrene is carried out. Chain transfer to styrene, some impurities and/or "grafting onto" during the reaction lead to homopolystyrene formation. Homo PSt is also formed by direct initiation of styrene by Bz₂O₂ initiator present in the grafting system. The reaction mechanism is proposed to take place as shown in Scheme I.

In view of the above results and discussion, it seems likely that the grafting taking place in the present study falls under the "grafting from" category.



Scheme I.

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