

# Radiation-Induced Graft Polymerization of 4-Vinyl Pyridine to Styrene–Butadiene–Styrene Triblock Copolymer

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## Synopsis

The radiation-induced graft polymerization of 4-vinyl pyridine to styrene–butadiene–styrene triblock copolymer (SBS) was investigated. Relations between the rate of grafting and the dose rate when SBS was irradiated in 4-vinyl pyridine–methanol solution, and between the rate of grafting and 4-vinyl pyridine concentration of 4-vinyl pyridine–methanol solution have been investigated. An experiment that had been carried out on SBS immersed in various 4-vinyl pyridine concentration of 4-vinyl pyridine–methanol solutions showed that the extent of swelling of SBS by the various 4-vinyl pyridine–methanol solutions increased with increasing 4-vinyl pyridine concentration. The largest rate was found at 20 vol % 4-vinyl pyridine–methanol solution. The rate was smaller at the volume percent of 4-vinyl pyridine higher or lower than 20 vol %. On the assumption that the theory of homogeneous homopolymerization could be applied to this grafting reaction, the value of  $k_p^2/k_t$  was obtained, where  $k_p$  and  $k_t$  are the propagation and termination constant, respectively. The value of  $k_p^2/k_t$  greatly decreased with increasing adsorbed concentration of vinyl pyridine–methanol solution. This decrease of  $k_p^2/k_t$  was explained by the fact that 4-vinyl pyridine and methanol adsorbed in SBS acted as a plasticizer which increased the molecular motion of the polymer. The solvent effect on the graft polymerization was also investigated. The result was explained by solubility parameter. When the chosen solvent had better solubility with the polymer, the degree of grafting was smaller. That was connected with the extent of the polymer chain mobility.

## INTRODUCTION

There are several methods of carrying out radiation-induced graft polymerization. The mechanism of radiation-induced graft polymerization has been studied by a number of investigators.<sup>1–5</sup>

The polymers, such as polyethylene,<sup>2,3</sup> cellulose,<sup>4</sup> Teflon,<sup>2</sup> etc., have partial crystallinity.<sup>4</sup> In this paper complete amorphous polymer styrene–butadiene–styrene triblock copolymer (SBS) was used as the polymer and 4-vinyl pyridine as the monomer. SBS is a complete amorphous polymer and it can be swollen/or dissolved easily in various 4-vinyl pyridine–methanol solutions. Measurements were carried out to determine the relationship between the rate of grafting and 4-vinyl pyridine concentration of various 4-vinyl pyridine–methanol solutions, and the relationship between the rate of grafting and the dose rate when SBS was irradiated in 20 vol % 4-vinyl

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pyridine-methanol solution. A discussion of the mechanism of graft polymerization was presented and the effect of solvent was also discussed.

## EXPERIMENTAL

### Materials

Methanol and ethanol were dried with soda lime and then distilled. Benzene was extracted several times with 80 mL of concentrated sulfuric acid per liter of benzene, until it became colorless, and then was distilled. 4-Vinyl pyridine was distilled under 5 mm Hg/54°C to eliminate impurities and kept under nitrogen gas. Styrene-butadiene-styrene triblock copolymer (SBS) was Kraton 1101 of Shell Company. The characteristics of Kraton 1101 are listed in Table I. SBS was dissolved in benzene, precipitated by methanol, and then dried in an oven. This procedure was repeated three times to make SBS free of antioxidant.

### Film Casting

SBS was dissolved in benzene and then the solution was poured onto a clean surface of Teflon. After benzene was evaporated, a film was obtained with a smooth surface and thickness of about 0.05 mm.

### Procedure for Swelling

Strips of SBS sheet measuring approximately  $3 \times 0.5$  cm were washed in acetone, vacuum-dried, and then immersed in various 4-vinyl pyridine-methanol solutions and were equilibrated at 25°C for 48 h. This time interval was greater than that of the attainment of equilibrium swelling. The equilibrated samples were removed from the 4-vinyl pyridine-methanol solutions, wiped dry with absorbent paper, and weighed quickly. The degree of swelling of SBS samples was calculated from the equations

$$\% \text{ swelling} = \frac{W_{\text{eq}} - W_i}{W_i} \times 100$$

where  $W_{\text{eq}}$  and  $W_i$  are the equilibrated and initial sample weights, respectively. The results are shown in Table II.

TABLE I  
Molecular Characteristics of Kraton 1101

Total molecular weight	$102 \times 10^3$
Polystyrene (%)	30
Terminal PS block ( $\bar{M}_w$ )	$17 \times 10^3$
Central PB block ( $\bar{M}_w$ )	$68 \times 10^3$
Microstructure	
PB 1,4-trans (%)	42
PB 1,4-cis (%)	49
PB 1,2 (%)	9

TABLE II  
Swelling Percent of SBS Immersed in 4-Vinyl Pyridine–Methanol Solution at 25°C

Vinyl pyridine in solution (vol %)	Methanol in solution (vol %)	Swelling of SBS
0	100	0.38
10	90	7.00
20	80	11.20
30	70	14.64
40	60	17.30
50	50	18.90
60	40	—
70	30	Partially soluble
100	0	Completely soluble

In order to determine the composition of the liquid sorbed by SBS, samples of SBS equilibrated with the various methanol–vinyl pyridine solutions were placed in liquid nitrogen and irradiated at  $8 \times 10^5$  rad/h to a total dose of approximately 4 Mrad. The sorbed vinyl pyridine is completely polymerized by this procedure and thus rendered nonvolatile, while the methanol is unaffected and remains volatile. After irradiation the samples were vacuum-dried at 40°C to constant weight. The difference in weight between the equilibrated samples before and after irradiation is the amount of methanol sorbed by the SBS. From these data various concentration terms were calculated (see Table III).

### Procedure for Graft Polymerization

Strips of SBS film were immersed in 4-vinyl pyridine–methanol and 4-vinyl pyridine–ethanol–water solution of known composition. After standing for at least 24 h at 25°C, the solution were sparged with nitrogen for 10 min, and then irradiated at 25°C in a 3000-Cu Co<sup>60</sup> source with various dose rates for various time intervals. After irradiation, the film was washed with an ultrasonic cleaner for 10 min, extracted with hot methanol for at least 48 h to remove homopolymer, dried in a vacuum oven, and weighed. The degree of grafting in weight percent was calculated by the equation,

$$\% \text{ graft} = \frac{W_f - W_i}{W_i} \times 100$$

where  $W_f$  and  $W_i$  are the final and initial weights of film, respectively.

## RESULTS AND DISCUSSION

### The Degree of Swelling of SBS

When SBS was immersed in various 4-vinyl pyridine–methanol solutions, the monomer gradually diffused into the polymer. Table II shows the degree of swelling of SBS after immersed in various solutions. The degree of swelling of SBS increased with increasing 4-vinyl pyridine concentration of 4-vinyl

pyridine-methanol solution. When the solution contained only 4-vinyl pyridine, SBS film was dissolved. When the solution contained only methanol, the degree of swelling was 0.38, because methanol is a nonsolvent for SBS and 4-vinyl pyridine is a good solvent for SBS. Due to the partial solubility of SBS film in high 4-vinyl pyridine concentration of 4-vinyl pyridine-methanol solutions, we only examined 4-vinyl pyridine concentration from 10 to 50 vol % in 4-vinyl pyridine-methanol solutions.

### Rate of Grafting and Monomer Concentration

SBS films were immersed in various 4-vinyl pyridine-methanol solutions at room temperature to absorb 4-vinyl pyridine to a certain concentration in the polymer. Then the swollen polymer in 4-vinyl pyridine-methanol solutions was irradiated with  $\gamma$ -rays from a  $\text{Co}^{60}$  source. The dose rate was 0.125 Mrad/h. Figure 1(a) shows the relationship between the 4-vinyl pyridine concentration of various pyridine-methanol solutions and the degree of grafting for various irradiation times. The degree of grafting was largest at the 4-vinyl pyridine concentration of about 20 vol % and was smaller at both the lower and higher concentrations.

The values of the rate of grafting, which is defined as the increase of the degree of grafting per unit time, are plotted in Figure 1(b) against the concentration of 4-vinyl pyridine with methanol. This curve shows the relationship between the rate of grafting and the monomer concentration. The rate of grafting was the largest at the 4-vinyl pyridine concentration of about 20 vol % and was smaller at both the lower and higher concentrations.

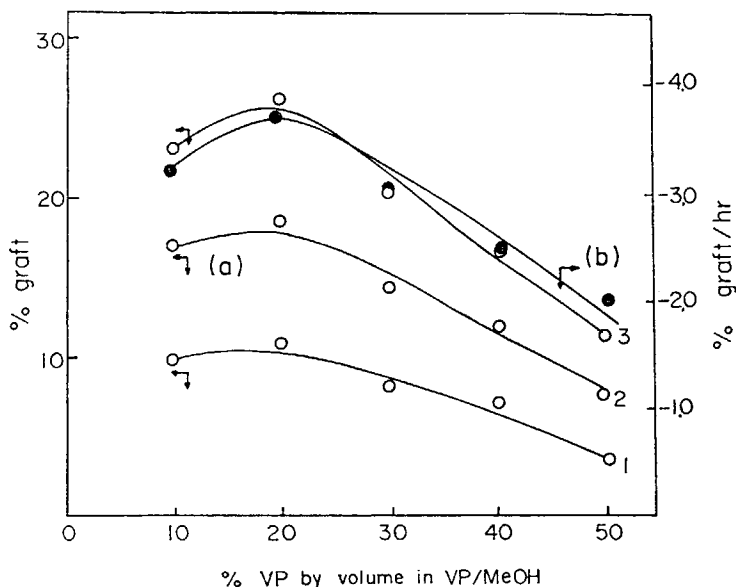


Fig. 1. Plots of (a) the degree of graft for the irradiation times of (1) 4, (2) 6, (3) 8 h and (b) the degree of graft per hour under irradiation at 0.125 Mrad/h.

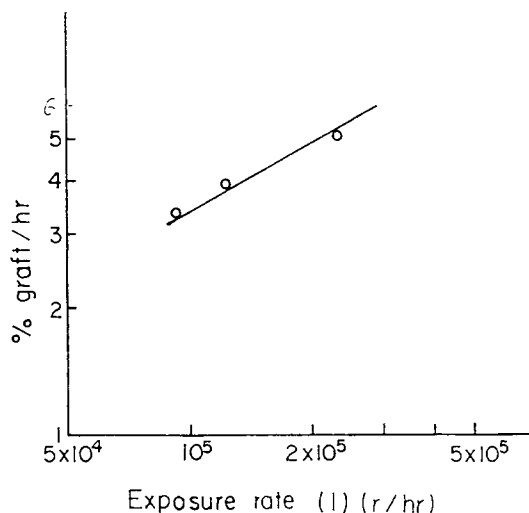


Fig. 2. Relation between the rate of grafting and exposure rate. The polymer was irradiated in VP/MeOH = 20/80 (v/v).

### Rate of Grafting and Dose Rate

Figure 2 shows the relationship between the rate of grafting and the dose rate when the polymer was irradiated in 4-vinyl pyridine-methanol solution. The rate of grafting is seen to be proportional to the half power of the irradiation dose rate.

### Consideration of Kinetics of Graft Polymerization

In order to understand the reaction mechanism in graft polymerization, it is important to analyze the results in terms of reaction kinetics. It is interesting to determine the specific rate of graft polymerization and the  $k_p^2/k_t$  values for the various 4-vinyl pyridine-methanol-SBS system. In order to perform the necessary calculation, it is necessary to determine the extent of swelling of the SBS by the various 4-vinyl pyridine-methanol solutions, and the concentration of the adsorbed solutions. These data are shown in Table III. From these values and the grafting data, the  $k_p^2/k_t$  values were calculated.

These calculations were made by applying the theory of homogeneous homopolymerization to the graft polymerization reaction, and were based on the following assumption: (1) 4-vinyl pyridine was uniformly absorbed in the polymer; (2) the grafting reaction homogeneous took place in the matrix; (3) the monomer concentration in the polymer was kept at a constant value; and (4) the grafting reaction was not diffusion-controlled. The applicability of these assumptions will be examined in detail later. The initiation of polymerization is the production of free radicals in the polymer. According to the

TABLE III  
Swelling of SBS by Methanol-Vinyl Pyridine Solution at 25°C

Vinyl pyridine in outside solution (vol %)	Swelling (%)	Methanol in sorbed solution (wt %)	$\rho_p$ (g/L)	$[M]^a$ (mol/L)	$[M]_m^b$ (mol/L)	$[M]_t^c$ (mol/L)
10	7.0	33.33	877.40	0.386	0.633	1.019
20	11.2	42.86	844.28	0.495	1.218	1.713
30	14.6	45.00	808.45	0.652	1.749	2.401
40	17.3	45.45	797.15	0.701	1.916	2.617
50	18.9	48.00	780.23	0.743	2.250	2.968

<sup>a</sup> $[M]_v$  = the concentration of 4-vinyl pyridine (mol/L) of SBS-4-vinyl pyridine-methanol.

<sup>b</sup> $[M]_m$  = the concentration of methanol (mol/L) of SBS-4-vinyl pyridine-methanol.

<sup>c</sup> $[M]_t = [M]_v + [M]_m$ .

theory for the stationary state reaction kinetics<sup>6,7</sup>

$$R_p = k_p [M]_v (R_i/k_t)^{1/2} \quad (1)$$

where  $R_p$  is the number of moles of 4-vinyl pyridine grafted per second per liter of SBS film containing 4-vinyl pyridine and methanol,  $[M]_v$  is the concentration of 4-vinyl pyridine in moles per liter of SBS-4-vinyl pyridine-methanol,  $k_p$  is the rate constant for propagation,  $k_t$  is the rate constant for termination, and  $R_i$  is the rate of initiation of the graft polymerization.  $R_i$  is given by

$$R_i = G\phi\rho_p/(6.023 \times 10^{25}) \quad (2)$$

where  $G$  is the  $G$  value of production of free radicals in SBS,  $\rho_p$  is the mass of SBS (g/L) of SBS-4-vinyl pyridine-methanol, and  $\phi$  is the rate of absorption of  $\gamma$ -ray energy by SBS in SBS-4-vinyl pyridine-methanol film calculated by the equation

$$\phi = \text{rad/g h} \times 100 \text{ erg/rad} \times 1 \text{ eV}/1.6 \times 10^{-12} \text{ erg} \times 1 \text{ h}/3600 \text{ s} \quad (3)$$

Equation (1) can be written as

$$k_p^2/k_t = \frac{R_p^2}{[M]_v^2 R_i} \quad (4)$$

This equation was used in calculating  $k_p^2/k_t$  from the measured values of  $R_p$ ,  $[M]_v$ , and  $R_i$ . So it was necessary to determine the extent of swelling of SBS by the various 4-vinyl pyridine-methanol solutions and the concentration of absorbed 4-vinyl pyridine in SBS.

The rate of initiation was calculated by eq. (2) and a  $G$  value of 1.5 for poly(butadiene-styrene) containing 30% styrene obtained by Witt,<sup>8</sup> was used in the calculation. The specific rate of graft was calculated from the conver-

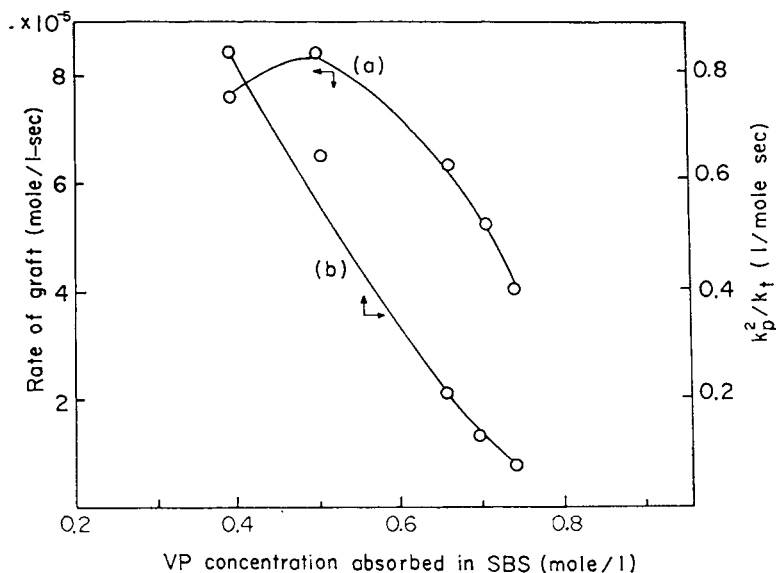


Fig. 3. Plots of (a) rate of grafting  $R_p$ , and (b)  $k_p^2/k_t$  as functions of vinyl pyridine concentration  $[M]_c$ .

sion rate of grafting in %/h by the equation

$$R_p = \frac{\% / h \times \rho_p}{100} \times \frac{1 \text{ mol}}{105 \text{ g}} \times \frac{1 \text{ h}}{3600 \text{ s}} \quad (5)$$

where  $\rho_p$  is grams of SBS per liter of SBS-4-vinyl pyridine-methanol and 105 g is the molecular weight of 4-vinyl pyridine. Figure 1(b) was replotted in the form shown in Figure 3(a). This figure shows the relations between the specific rate of grafting and concentration of 4-vinyl pyridine absorbed in SBS. Table IV gives the value of  $R_p$  obtained experimentally and the value of  $k_p^2/k_t$  calculated by using eq. (4).

The value of  $k_p^2/k_t$  is plotted against the concentration of 4-vinyl pyridine absorbed in SBS in Figure 3(b). The value of  $k_p^2/k_t$  decreased rapidly as the concentration of 4-vinyl pyridine absorbed in SBS increased.

TABLE IV  
Determination of Various Kinetic Terms in the Graft Polymerization of Vinyl Pyridine to SBS

Vinyl pyridine in outside solution (vol %)	Grafting rate (%/h)	$R_p \times 10^5$ (mol/L s)	$R_i \times 10^8$ (mol/L s)	$k_p^2/k_t$ (mol/L s)
10	3.33	7.73	4.74	0.846
20	3.83	8.55	4.56	0.654
30	3.00	6.42	4.37	0.222
40	2.50	5.27	4.30	0.131
50	2.00	4.13	4.21	0.073

Now the assumptions made in the foregoing analysis will be examined. Assumptions (1)–(3) will be accepted in view of the facts that the thickness of the film used was thin, and the polymer was easily swollen in the solution. The monomer concentration in the polymer was kept at a constant value.

The case where the graft polymerization rate is independent of films thickness and varies with the half power of the initiation rate is the diffusion-free reaction.<sup>9</sup> Odian<sup>9</sup> has considered that the diffusion-free is the case when one or both of the following conditions exist: (1) the polymer film thickness is small; and (2) the polymerization rate is slow in comparison to the diffusion rate, i.e.,  $R_i$ , and  $k_p^2/k_t$  are small while diffusion coefficient is large. In this paper, Figure 2 shows that rate of grafting was proportional to the half power of the irradiation rate. The film thickness used was very small. Therefore, assumption (4) can be considered as being not diffusion controlled.

### Molecular Motion of the Polymer and the Rate of Grafting

The foregoing treatment has shown that the value of  $k_p^2/k_t$  changed rapidly as the adsorbed concentrations of the vinyl pyridine and methanol changed. Since  $k_p^2/k_t$  is a measure of determination and propagation of active centers at the end of the growing chains, its value is easily affected by the molecular motion of the chain. In the case of graft polymerization, this motion of grafted branch is, in turn, influenced by the molecular motion of the polymer. That the value of  $k_p^2/k_t$  changes with the concentration suggests that the adsorbed concentration has a large effect on the molecular motion of the polymer.

Table II shows that the degree of swelling of SBS after immersed in various 4-vinyl pyridine–methanol solutions increased as the concentration of 4-vinyl pyridine in 4-vinyl pyridine–methanol solutions increased. When the composition of the solution was completely 4-vinyl pyridine, the SBS film was dissolved. Therefore, 4-vinyl pyridine can be regarded as a good solvent for SBS. When SBS was swollen by 4-vinyl pyridine–methanol solution, the segment motion of SBS became easier than that of unswollen SBS, and the active centers of propagation chain end could be easily determined, i.e., the higher was the degree of swelling of SBS by 4-vinyl pyridine–methanol the smaller was the  $k_p^2/k_t$ . As shown in Tables III and IV, the value of  $k_p^2/k_t$  greatly decreased with increasing adsorbed concentration of vinyl pyridine–methanol solution. The adsorbed 4-vinyl pyridine–methanol solution can be considered as plasticizer.

The foregoing discussion is limited to SBS swollen by 4-vinyl pyridine–methanol solution. In fact, the irradiation-induced heterogeneous type graft polymerization includes the graft copolymerization occurring in the polymer, as well as the homopolymerization, which occurs mostly in the solvent, and increases the viscosity of total systems. It is important to choose a proper solvent. When the solvent system is a better solvent for homopolymer, the polymer molecular motion becomes easier; the viscosity of total system increases slowly; the active centers of propagation chain end in the polymer branch have higher mobility; and the termination constant will be higher, i.e., the rate of grafting or/and the degree of grafting will be smaller. On the other hand, if the solvent system is a poorer solvent for homopolymer, the termination rate of active center of propagation chain end in the polymer branch



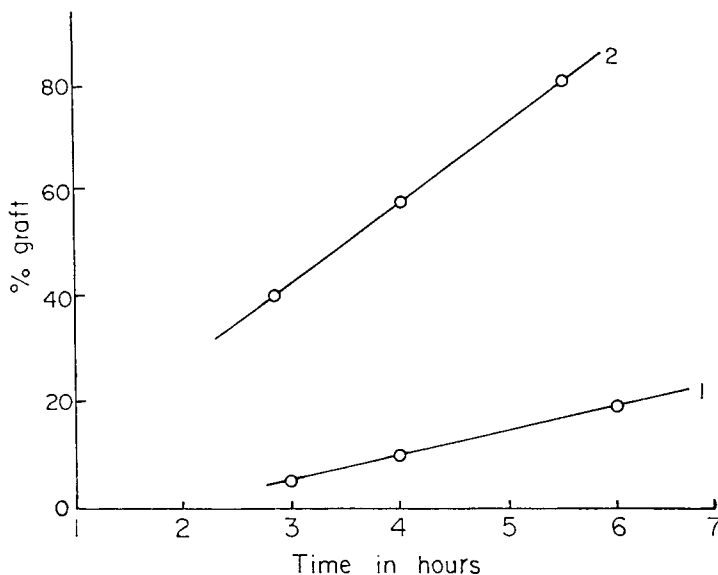


Fig. 4. Grafting of vinyl pyridine to SBS under irradiation at 0.125 Mrad/h, 20% (vol) vinyl pyridine with different solvent: (1) MeOH and (2) EtOH/H<sub>2</sub>O = 1/1 (v/v).

chain will be smaller and the rate of grafting and/or the degree of grafting will be larger.

Figure 4 shows the effect of solvent on the degree of grafting. From the values of solubility parameter in Table V, methanol is a nonsolvent for SBS and a good solvent for poly(4-vinyl pyridine); ethanol-water (1/1 v/v) mixed solvent is also a nonsolvent for SBS. For poly(4-vinyl pyridine), the solubility effect of ethanol-water is less than methanol. Therefore, under the same conditions the chain mobility of poly(4-vinyl pyridine) in methanol is larger than that in ethanol-water mixed solvent and the viscosity of poly(4-vinyl pyridine)-methanol system is smaller than that of the poly(4-vinyl pyridine)-ethanol-water system.

In the irradiation-induced graft polymerization, the SBS-4-vinyl pyridine-methanol system viscosity is smaller than the viscosity of SBS-vinyl pyridine-ethanol-water system. Therefore, the active centers of propagation chain end in the grafted polymer chain branch are easy to be determined, and the degree of grafting is smaller for SBS-vinyl pyridine-methanol system.

TABLE V  
The Solubility Parameters of Polymer and Solvent

	Solubility parameter $\delta[(\text{cal}/\text{cm}^3)^{1/2}]$
SBS	8.48
Methanol	14.50
4-Vinyl pyridine	11.00
Water + ethanol (1 : 1)	18.05

From the above discussion, we can conclude that the degree of grafting of irradiation-induced graft polymerization is affected by the molecular chain mobility, and this is related to the solubility of molecules in the graft polymerization system. If the grafted monomer has a better solubility with the polymer, the degree of grafting will be smaller. When the solvent system is a good solvent for the grafted polymer or homopolymer, the degree of grafting will be small.

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