Graft Copolymerization of Styrene onto Ethylene-Vinyl p-Nitrobenzoate Copolymer by Chain Transfer Reaction

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Synopsis

The effect of steric hindrance on the attack of growing polymer radicals to the reaction sites on a trunk polymer was examined in the graft copolymerization of styrene onto a trunk polymer with pendant aromatic nitro groups by chain transfer reaction of growing polymer radicals to the pendant nitro groups. The nitro groups on ethylene-vinyl p-nitro benzoate copolymer (EVNB) are more effectively utilized in the graft copolymerization than those on the vinyl p-nitro benzoate homopolymer (PVNB) previously used as a trunk polymer, because the nitro groups are distributed less frequently on the trunk polymer in the former than in the latter. This was also confirmed by the higher chain transfer constant of growing polystyrene radicals to EVNB compared to that of PVNB.

INTRODUCTION

Aromatic nitro compounds inhibit or retard the free radical polymerization of vinyl monomers depending on the type of monomers. We have carried out the free radical polymerization of vinyl monomers in the presence of the polymers containing aromatic nitro groups as side chain and obtained highly branched graft copolymers by addition of growing polymer radicals to the oxygen atoms of the pendant nitro groups.[1-5]

However, the chain transfer constants of growing polymer radicals to the pendant nitro groups of the trunk polymers are less than half of those to their model compounds.[2,3] This difference is attributed to the difficulty of the bulky growing polymer radicals to diffuse into the random coil of trunk polymer and to attack the nitro groups inside the random coil of the trunk polymer, when the chain transfer occurs to the nitro groups on the trunk polymer. Accordingly, the graft efficiency is decreased by the steric hindrance of the branches already formed with increasing graft content.[2,3] The latter effect will be diminished and the nitro groups will be utilized more efficiently for graft polymerization by decreasing the nitro group content in the trunk polymer.

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In the present study, we carried out graft copolymerization of styrene onto ethylene-vinyl *p*-nitrobenzoate copolymer (EVNB) as a trunk polymer, whose content of vinyl *p*-nitrobenzoate was 28.6 mol%, to clarify the effect of steric hindrance of the branches already formed on the attack of growing polymer radicals on the pendant nitro groups on the trunk polymer.

EXPERIMENTAL

Ethylene-Vinyl *p*-Nitrobenzoate Copolymer

Ethylene-vinyl *p*-nitrobenzoate copolymer (EVNB) was prepared by the esterification of ethylene-vinyl alcohol copolymer with *p*-nitrobenzoyl chloride at 60°C for one hour using pyridine as a solvent. The ethylene-vinyl alcohol copolymer used was obtained by the hydrolysis of ethylene-vinyl acetate copolymer with a vinyl acetate content of 28.6 mol% (a commercial product of Mitsui Petrochemical Co., Ltd.) in tetrahydrofuran (THF) with sodium methoxide. The esterification was repeated twice to obtain a fully esterified product. The number-average molecular weight ($\bar{M}_n$) of ethylene-vinyl acetate copolymer was 1.57×10^5 as determined with a Hewlett-Packard 502 high-speed membrane osmometer using toluene as a solvent. The number-average degree of polymerization ($\bar{P}_n$) of EVNB was calculated as 3.52×10^3 from the $\bar{M}_n$ and vinyl acetate content of ethylene-vinyl acetate copolymer.

Graft Copolymerization

Predetermined amounts of EVNB, styrene, and azobisisobutyronitrile (AIBN) were placed in glass ampoules containing 50 mL DMF or $CHCl_3$. After degassing several times at liquid nitrogen temperature, the ampoules were sealed and the grafting reaction was carried out at 60°C. After a predetermined reaction period, the contents were poured into methanol, and the precipitate was filtered and dried. Nongrafted polystyrene was removed by extraction with cyclohexane. The graft copolymer obtained was then hydrolyzed with an aqueous hydrogen iodide solution (57%) at 140°C for 4 hr under nitrogen to isolate the grafted polystyrene. The molecular weights of the grafted and nongrafted polystyrenes were determined with a Hewlett-Packard Model 302B vapor pressure osmometer. GPC curves of the graft copolymer, nongrafted polystyrene, and the reaction products consisting of the graft copolymer and nongrafted polystyrene were obtained with a Toyo Soda high-speed liquid chromatograph HLC-802 UR using chloroform as a solvent.

Determination of Rate of Initiation

In a four-necked flask equipped with a reflux condenser, a thermometer, and a dropping funnel, predetermined amounts of EVNB, styrene, and AIBN were dissolved in 50 mL DMF. 10 mg 1,1-diphenyl-2-picrylhydrazyl (DPPH) was added to the flask. After the reaction was started, an aliquot of the solution was pipetted out at predetermined intervals, and after suitable dilution, the concentration of remaining DPPH was determined spectrophotometrically from the absorbance at 520 nm with a Hitachi Model 101 spectrophotometer.
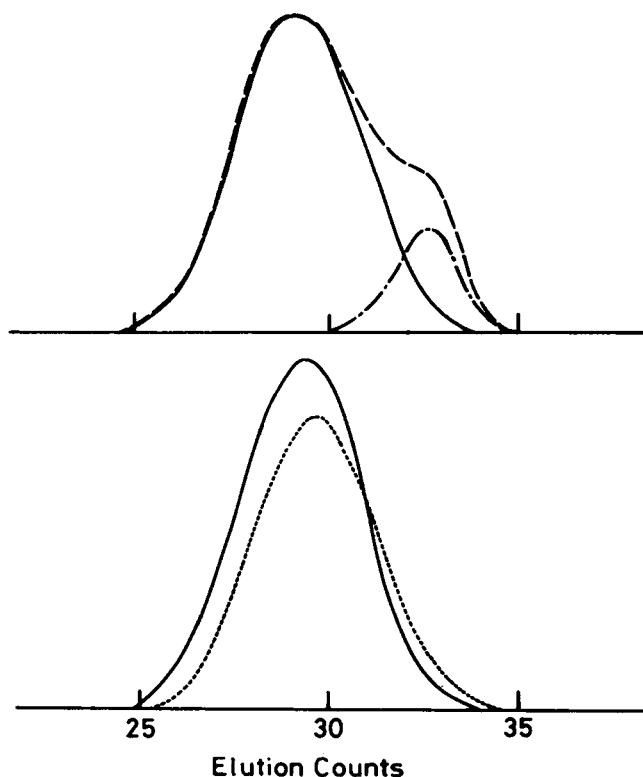
25   30   35

Elution Counts

Fig. 1. GPC curves of graft copolymer (—), styrene homopolymer (·····), trunk polymer EVNB (---), and a mixture of graft copolymer and homopolymer (———) in polymerization of styrene in the presence of EVNB. Per cent grafting, 24.9%, graft efficiency, 48.1%.

RESULTS AND DISCUSSION

Graft Copolymerization

The change of GPC curve of the trunk polymer EVNB by grafting is shown in Figure 1. A peak and a shoulder appear in the GPC curve for a reaction product consisting of graft copolymer and nongrafted polystyrene. After graft copolymer was separated from nongrafted polystyrene by extracting the mixture with cyclohexane, the GPC curves for graft copolymer and nongrafted polystyrene were recorded, and the high-molecular weight portion of the GPC curve for the mixture was assigned to the graft copolymer and the low-molecular weight one to nongrafted polystyrene. The GPC curve for the trunk polymer EVNB expands to higher molecular weight by grafting polystyrene.

Table I shows the results of the graft copolymerization carried out at 60°C for various periods of time. In Table I, [X] is the concentration of nitro groups and [M] is that of monomer styrene. As the reaction time was increased from 6 to 48 h, the per cent grafting increased from 8.9 to 34.9%. No induction period was observed. Therefore, EVNB acts as a retarder in the polymerization of styrene as expected from the result for poly(vinyl p-nitrobenzoate) (PVNB).[2] The molecular weight for nongrafted polystyrene was larger than

TABLE I
Effect of Reaction Time on Graft Copolymerization
of Styrene onto Ethylene-Vinyl p-Nitrobenzoate Copolymer

Reaction time hr	Total conversion %	Per cent grafting %	Graft efficiency %	$\bar{M}_n \times 10^{-3}$		No. of nitro groups per branch	No. of PSt branches per trunk polymer
				Grafted PSt	Nongrafted PSt		
6	5.2	8.9	52.6	—	1.75	—	—
15	7.8	16.7	47.4	1.95	2.38	44	23
24	11.4	24.9	48.1	1.83	2.80	28	36
48	17.4	34.9	44.3	1.86	2.82	20	50

$[X] = 6.89 \times 10^{-2}$ mol/L; $[M] = 7.92 \times 10^{-1}$ mol/L; $[AIBN] = 1.11 \times 10^{-2}$ mol/L; DMF, 50 mL; 60°C.

TABLE II

Effect of Azobisisobutyronitrile Concentration on Graft Copolymerization of Styrene onto Ethylene-Vinyl p-Nitrobenzoate Copolymer

$[AIBN] \times 10^2$ mol/L	Total conversion %	Per cent grafting %	Graft efficiency %	$\overline{M}_n \times 10^{-3}$		No. of nitro groups per branch	No. of PSt branches per trunk polymer
				Grafted PSt	Nongrafted PSt		
0.56	5.4	8.6	35.0	2.97	2.62	131	7.7
1.11	5.6	12.9	50.5	2.82	2.34	83	12.2
1.67	6.2	15.2	54.4	2.24	2.17	56	18.0

$[X] = 6.92 \times 10^{-2}$ mol/L; mol/L; $[M] = 7.92 \times 10^{-1}$ mol/L; $CHCl_3$, 50 mL; 60°C; 15 h.

TABLE III

Effect of Amount of Trunk Polymer on Graft Copolymerization
of Styrene onto Ethylene-Vinyl p-Nitrobenzoate Copolymer

$[X] \times 10^2$ mol/L	Total conversion %	Per cent grafting %	Graft efficiency %	$\overline{M}_n \times 10^{-3}$ Nongrafted PSt
0	10.0	—	—	5.29
1.73	7.5	17.2	13.0	3.49
3.46	6.8	10.7	25.7	3.13
6.92	5.2	8.9	52.6	1.75

[M] = 7.92×10^{-1} mol/L; [AIBN] = 1.11×10^{-2} mol/L; DMF, 50 mL; 60°C; 6 h.

that of grafted polystyrene. This tendency is very similar to the results of the graft polymerization of styrene onto PVNB[2] and poly(p-nitrophenyl acrylate) (PNA).[3]

The number of nitro groups of the trunk polymer EVNB per polystyrene branch decreased from 28 for 24 h to 20 for 48 h. These values are smaller than 30 and 23 obtained for PVNB as a trunk polymer under similar conditions.[2] This result indicates that the nitro groups on EVNB are used more efficiently than those on PVNB for the attack of growing polymer radicals to the pendant nitro groups.

When the amount of the trunk polymer EVNB, namely the concentration of nitro groups, was increased in the reaction systems, the graft efficiency increased, but the total conversion, percent grafting, and the molecular weight of nongrafted polystyrene decreased (Table II), as previously observed for other polymers with aromatic nitro groups as trunk polymers.[2-4] The increase in the graft efficiency with increasing amount of the trunk polymer is attributed to the more frequent occurrence of the reaction between growing polystyrene radicals and the nitro groups on the trunk polymer. However, the increase in the concentration of the nitro groups reduces the average molecular weight of growing polymer radicals and that of grafted polystyrene, resulting in lower total conversion and per cent grafting.

As the initiator concentration was increased, the total conversion, the per cent grafting, and the graft efficiency increased, but the molecular weights of grafted and nongrafted polystyrenes decreased (Table III). These results are different from those using PVNB[2] and PNA[3] as trunk polymers, in which the per cent grafting and the graft efficiency decreased with increasing initiator concentration. This is attributed to the higher reactivity of the nitro groups on EVNB with the primary radicals produced by the decomposition of AIBN or the growing polymer radicals with relatively low molecular weight.

Determination of Rate of Initiation

The rate of initiation (R_i) was determined from the inhibition period by measuring the decrease in the absorbance at 520 nm during the course of polymerization in the presence of trunk polymer EVNB and DPPH as reported previously.[2,3] The rate of initiation (R_i) is related to the inhibition

TABLE IV
Rates of Initiation and Propagation, and Initiation Efficiency for
Polymerization of Styrene in the Presence of
Ethylene-Vinyl p-Nitrobenzoate Copolymer

$[X] \times 10^2$ mol/L	$\dfrac{[X]}{[M]} \times 10^2$	Conversion %	$R_i \times 10^7$ mol/L sec	$R_p \times 10^6$ mol/L sec	Nongrafted PSt $\bar{P}_n$	Initiation efficiency f
0	0	10.0	1.12	3.68	50.8	0.71
1.73	2.18	7.5	1.08	2.75	33.5	0.68
3.46	4.37	6.8	1.06	2.49	30.0	0.67
6.92	8.73	5.2	1.05	1.91	16.8	0.67

[M] = 7.92×10^{-1} mol/L; [AIBN] = 1.11×10^{-2} mol/L; [DPPH] = 4.52×10^{-4} mol/L; DMF, 50 mL; 60 °C; 6 h.

period by the following equation:

$$R_i = -\frac{d[\text{DPPH}]}{dt} = \frac{[\text{DPPH}]}{\text{inhibition period}} \tag{1}$$

The values of R_i obtained for the systems containing various amounts of EVNB are given in Table IV together with the rate of propagation and the initiation efficiency f calculated from $R_i = 2k_d f(C)$, in which k_d, the rate of decomposition of AIBN in the polymerization of styrene in DMF at 60 °C, is assumed to be 7.10×10^{-6} s^{-1}.[6] The values of f decrease from 0.71 to 0.65 with increasing amount of trunk polymer as observed previously.[2,3] This is attributed to the increase in viscosity of the reaction system accompanied by the increase in the primary termination reactions of radicals formed by the decomposition of the initiator.

Determination of Chain Transfer Constant to EVNB

In order to examine the reactivity of nitro groups on EVNB to growing polystyrene radicals, the chain transfer constant of polystyrene radicals to EVNB was determined by various methods and compared with those already obtained for PVNB[2] and isopropyl p-nitrobenzoate (IPNB)[2] as a model compound.

A simple rate equation has been derived by Kar et al.[7] for the polymerization of vinyl monomers:

$$\frac{1}{R_p} = \frac{C_x[X]}{R_i[M]} + \frac{1}{R_{p_o}} \tag{2}$$

where [M] and [X] are the concentration of monomer and retarder, R_n and R_{po} the rates of polymerization in the presence and absence of retarder, respectively, and $C_x (= k_x/k_p)$ is the chain transfer constant to the retarder, where k_p is the rate constant for propagation and k_x is the rate constant for chain transfer to the nitro compound or the nitro group of the trunk polymer.
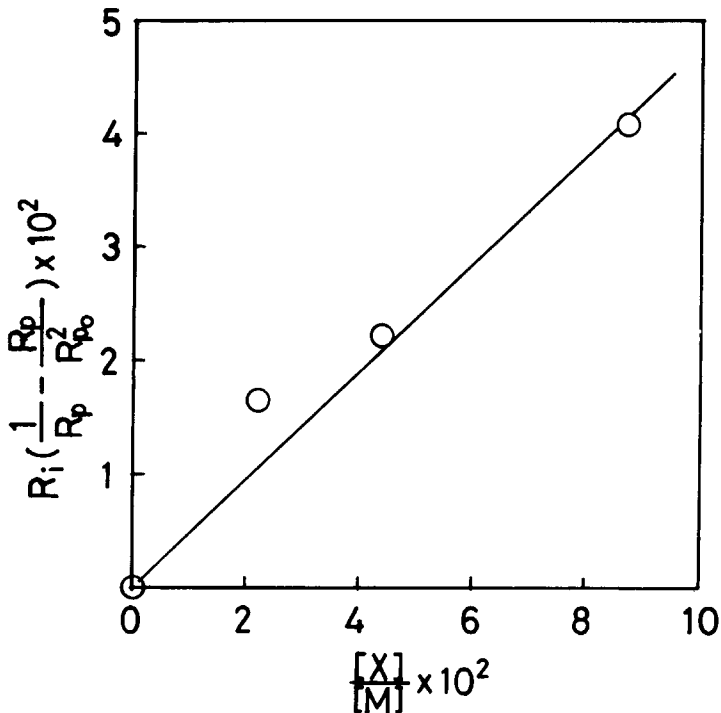
Fig. 2. Plot of $R_i(1/R_p - R_p/R_{p_o}^2)$ versus [X]/[M] for polymerization of styrene in the presence of EVNB. Reaction conditions: [M] = 7.92 × 10^{-1} mol/L; [AIBN] = 1.11 × 10^{-2} mol/L: DMF, 50 mL; 60°C; 6h.

However, Eq. (2) is not applicable for a system containing a polymeric retarder and the following equation has been derived:[2]

$$\frac{1}{R_p} - \frac{R_p}{R_{p_o}^2} = \frac{C_x[X]}{R_i[M]} \tag{3}$$

The chain transfer constant C_x of growing polymer radicals to EVNB was obtained to be 0.505 from the slope of $(1/R_p - R_p/R_{p_o}^2)$ versus [X]/[M] plot (Fig. 2).

The following relation has been obtained by Mayo et al.[8] at initial stages of polymerization:

$$\frac{1}{\overline{P}_n} = C_x\frac{[X]}{[M]} + \frac{1}{\overline{P}_{n_o}} \tag{4}$$

where $\overline{P}_n$ and $\overline{P}_{n_o}$ are the number-average degree of polymerization in the presence and absence of a chain transfer constant, respectively. The value of $1/\overline{P}_n$ of nongrafted polystyrene formed in the presence or absence of EVNB is plotted against [X]/[M] in Figure 3. From the slope, a value of 0.468 was obtained for C_x.
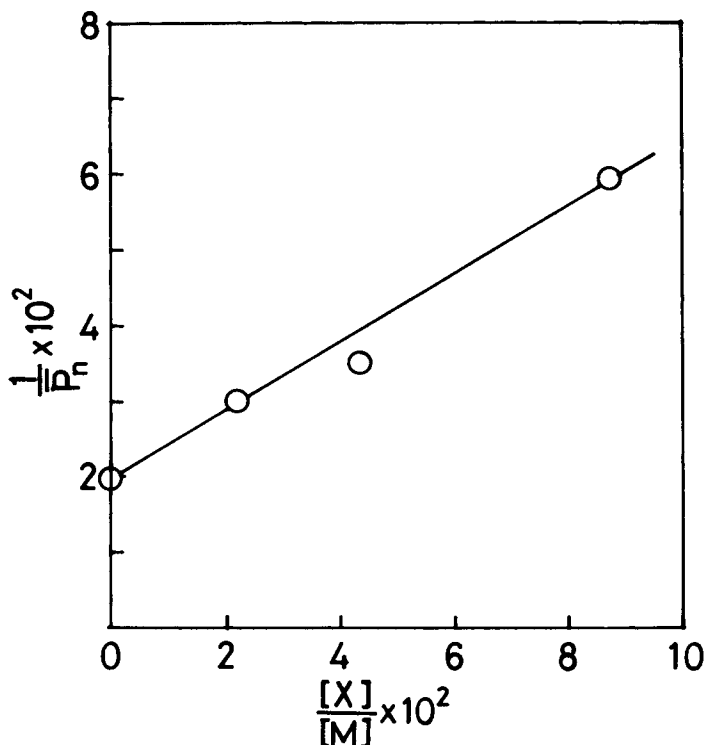
Fig. 3. Plot of $1/\overline{P}_n$ versus [X]/[M] for polymerization of styrene in the presence of EVNB. Reaction conditions: [M] = 7.92 × 10⁻¹ mol/L; [AIBN] = 1.11 × 10⁻² mol/L; DMF, 50 mL; 60°C; 6 h.

Bagdasarian' equation,[9] which relates the degree of polymerization to C_x, has been modified for the polymerization of styrene.[2]

$$\frac{1}{\overline{P}_n} = \frac{k_t R_p}{2 k_p^2 [M]^2} + \frac{k_m}{k_p} + C_x \frac{[X]}{[M]} \tag{5}$$

where k_p is the rate constant for propagation; k_m is the chain transfer constant of polymer radicals to monomer. The values of k_t/k_p^2 were calculated from $k_t/k_p^2 = R_i[M]^2/R_p^2$ for the polymerization of styrene in the presence of EVNB using the values of R_i in Table IV. The values of $1/\overline{P}_n - k_t R_p/2 k_p^2 [M]^2$ were plotted against [X]/[M] (Fig. 4). From the slope, the value of C_x was determined to be 0.430.

The values of chain transfer constants C_x of growing polystyrene radicals to EVNB obtained by these methods are summarized in Table V together with those to PVNB and IPNB as a model compound reported previously.[2] As expected, the values of C_x to EVNB are apparently higher than those to PVNB irrespective of the procedure used for the determination of C_x. However, they are much lower than those to IPNB as a model compound.[2]

It is thought that no remarkable difference exists between the electronic states of nitro groups of these compounds. Therefore, the lower values of
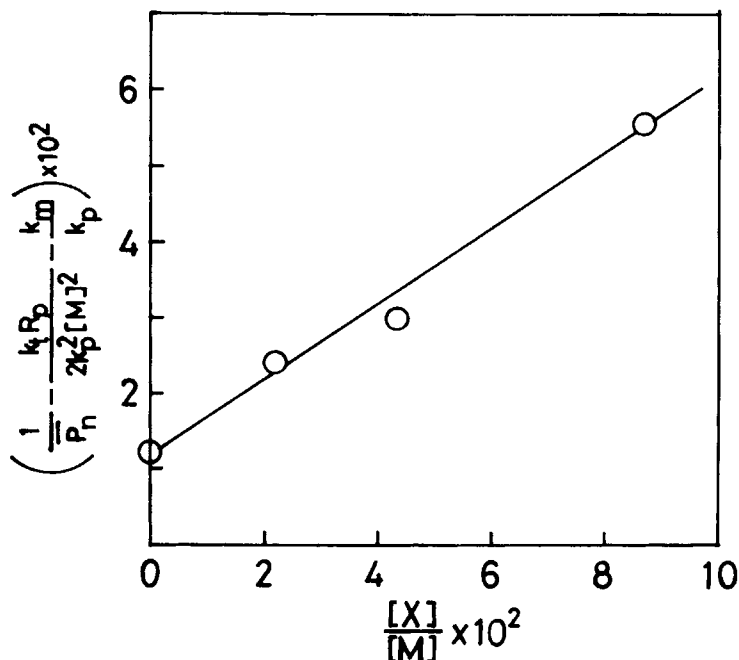
Fig. 4. Plot of $(1/\overline{P}_n - k_tR_p/2k_p^2[M]^2)$ versus $[X]/[M]$ for polymerization of styrene in the presence of EVNB. Reaction conditions: $[M] = 0.79$ mol/L, $[AIBN] = 1.11 \times 10^{-2}$ mol/L; DMF, 50 mL; 60°C; 6 h.

chain transfer constants to EVNB and PVNB are explained by the inherent property of polymers. The bulky growing polystyrene radicals are difficult to diffuse into the random coil of trunk polymer and to attack the nitro groups inside the random coil due to the steric hindrance. Furthermore, this effect is increased with the progress in grafting due to the steric hindrance of the branches already formed. The attack of growing polymer radicals to the pendant nitro groups on the trunk polymer is prevented increasingly with increasing per cent grafting as observed from the decrease in graft efficiency as shown in Table I.

Thus, steric hindrance plays an important role in this type of reaction. The nitro groups are distributed less frequently on EVNB than on PVNB. Therefore, the steric hindrance of the branches already formed is smaller for EVNB than for PVNB, and the nitro groups on EVNB are more efficiently utilized

TABLE V
Chain Transfer Constants of Polystyrene Radicals to Ethylene-Vinyl
p-Nitrobenzoate Copolymer (EVNB), Poly(vinyl p-Nitrobenzoate) (PVNB)
and Isopropyl p-Nitrobenzoate (IPNB) at 60°C

	EVNB	PVNB[2]	IPNB[2]
From Eq. (2)	—	—	0.794
From Eq. (3)	0.505	0.273	—
From Eq. (4)	0.468	0.357	0.736
From Eq. (5)	0.430	0.328	0.830

than those on PVNB for the graft copolymerization induced by the attack of growing polymer radicals to the reaction sites inside the random coil of a trunk polymer.

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