

Graft Copolymerization of Styrene onto Poly(vinyl *p*-Nitrobenzoate) by Chain Transfer Reaction

SHIGEO NAKAMURA, HIDEAKI SATO,* and KEI MATSUZAKI,
*Department of Industrial Chemistry, Faculty of Engineering, University of
Tokyo, Bunkyo-ku, Tokyo, Japan*

Synopsis

To obtain highly branched graft copolymers, styrene (St) was grafted onto poly(vinyl *p*-nitrobenzoate) (PVNB) as a trunk polymer through the chain transfer reaction of growing polystyrene (PSt) radicals to the pendent aromatic nitro groups on the trunk polymer. The number of PSt branches increased with St concentration at constant concentrations of PVNB and azobisisobutyronitrile (AIBN) as an initiator, and decreased with AIBN concentration at constant PVNB and St concentrations. The maximum number of branches attained was 43 (\bar{P}_n of PVNB was 970), which corresponds to 23 monomer units of PVNB per PSt branch. It is confirmed from the results of infrared spectroscopy that the addition of the growing polystyrene radicals occurs not at the benzene rings but at the nitro groups on the benzene rings. Polymerization of St was also carried out in the presence of isopropyl *p*-nitrobenzoate (IPNB) as a model compound of PVNB. IPNB was found to retard the polymerization of styrene more strongly than PVNB. The chain transfer constant of the polystyrene radicals to IPNB was more than twice as large as that to PVNB.

INTRODUCTION

Aromatic nitro compounds act as inhibitors or retarders in the free-radical polymerization of vinyl monomers depending on the type of monomer used. It is reported that they inhibit the polymerization of vinyl acetate, retard that of styrene, and have weakly retarding effects on the polymerization of methyl methacrylate and methyl acrylate.¹ Although the proposed mechanisms for the reaction of the aromatic nitro compounds with growing polymer radicals are still conflicting, it is established that addition of growing polymer radicals to the oxygen atoms of the nitro groups occurs.²⁻⁴

Accordingly, it is expected that a highly branched graft copolymer can be obtained as a result of the reaction of the growing polymer radicals with the aromatic nitro groups on a polymer if the free-radical polymerization of a vinyl monomer, whose radical has appropriate reactivity to the aromatic nitro groups, is carried out in the presence of the polymer containing aromatic nitro groups. In a previous report,⁵ we have confirmed this expectation by use of poly(vinyl *p*-nitrobenzoate) as a trunk polymer and styrene as a monomer.

Now, we wish to report the effect of various reaction conditions on the for-

* Present address: Fuji Photo Film Co., Ltd., Nakanuma, Minamiashigara, Kanagawa, Japan.

mation of highly branched graft copolymers, and also the mechanism of the graft copolymerization and the chain transfer reaction of growing polystyrene radicals to the aromatic nitro groups. Polymerization of styrene was also carried out in the presence of isopropyl *p*-nitrobenzoate as a model compound of poly(vinyl *p*-nitrobenzoate), and the chain transfer constant of growing polystyrene radicals to the nitro groups of isopropyl *p*-nitrobenzoate was determined and compared with that to the nitro groups of poly(vinyl *p*-nitrobenzoate).

EXPERIMENTAL

Poly(vinyl *p*-Nitrobenzoate)

Poly(vinyl *p*-nitrobenzoate) (PVNB) was prepared by the esterification of poly(vinyl alcohol) with *p*-nitrobenzoyl chloride according to the method of Magagnini et al.⁶ The poly(vinyl alcohol) used was a commercial product of Kuraray Ltd. To obtain a fully esterified product, the esterification was repeated again. The degree of esterification of the product was 99.6% as determined by elemental analysis, and the molecular weight was 1.87×10^5 as determined with a Hewlett-Packard 502 high-speed membrane osmometer using dimethylformamide (DMF) as a solvent. This molecular weight corresponds to a number-average degree of polymerization (\overline{P}_n) of 970.

Isopropyl *p*-Nitrobenzoate

Isopropyl *p*-nitrobenzoate (IPNB) was prepared by the esterification of isopropyl alcohol with *p*-nitrobenzoyl chloride according to the method of Buchener and Meisenheimer,⁷ mp 109°C from ethanol (reported⁷ mp 111°C); IR (KBr) 1710 (C=O), 1347 (ν_s NO₂), 1521 (ν_a NO₂), 1095, 1279 cm⁻¹ (C—O).

ANAL. Calcd for C₁₀H₁₁O₄N₁ (209.21): C, 57.39; H, 5.30; N, 6.70. Found: C, 58.09; H, 5.36; N, 6.70.

Graft Polymerization

Predetermined amounts of PVNB, styrene, and azobisisobutyronitrile (AIBN) were placed in glass ampoules containing 50 ml DMF. 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 period of reaction, the contents were poured into methanol-water (7:3 by volume), and the precipitate was filtered and dried. Nongrafted polystyrene was removed by extraction with methyl acetate for 72–144 hr until no polystyrene was detected in the extract. The graft copolymer obtained was then hydrolyzed with an aqueous hydrogen iodide solution (57%) at 130°C for 3–12 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.

Polymerization of Styrene in the Presence of Isopropyl *p*-Nitrobenzoate

Styrene was polymerized by use of AIBN as catalyst and DMF as solvent in the presence of IPNB for 6 hr at 60°C in glass ampoules. After a predeter-

mined period of reaction, the contents were poured into a mixture of methanol and water (7:3 by volume), and the precipitate was filtered and dried.

Determination of Rate of Initiation

In a four-necked flask equipped with a reflux condenser, a thermometer, and a dropping funnel, predetermined amounts of PVNB, styrene, and AIBN were dissolved in 50 ml DMF. Then, 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 measured spectrophotometrically from the optical density at 520 $m\mu$ with a Hiram Rika photoelectric spectrometer Model 6B.

RESULTS AND DISCUSSION

Graft Copolymerization

The results of the graft copolymerization carried out at 60°C for various periods of time are shown in Table I. The per cent grafting increased from 8.1% to 41.1% by increasing the reaction time from 6 to 48 hr. The graft efficiency hardly depended on the reaction time, but a slightly larger value was observed at the shortest reaction time of 6 hr. The molecular weights of both grafted and nongrafted polystyrenes slightly increased with reaction time, and the latter was approximately twice as large as the former. Therefore, it is supposed that in the reaction conditions studied, the nongrafted polystyrene is mostly formed by the recombination of the growing polystyrene radicals.

The number of monomer units of the trunk polymer PVNB per polystyrene branch decreased from 43 to 23 as the reaction proceeded. This indicates that the growing polystyrene radicals add to the nitro groups on the trunk polymer PVNB continually with reaction time. The number of polystyrene branches per PVNB molecule calculated by use of the degree of polymerization of PVNB of 970 increased from 22 to 43 as the reaction time increased, indicating the formation of highly branched graft copolymers.

The concentration of styrene in the polymerization mixtures was then ap-

TABLE I
Effect of Reaction Time on Graft Copolymerization
of Styrene onto Poly(vinyl *p*-Nitrobenzoate)^a

Reaction time, hr	Total conversion, %	Per cent grafting, %	Graft efficiency, %	$\bar{M}_n \times 10^{-3}$		No. of monomer units of PVNB per PSt branch	No. of PSt branches per PVNB molecule ^b
				Grafted Pst	Nongrafted Pst		
6	4.5	8.1	38.1	—	—	—	—
14	9.9	15.1	32.4	1.25	2.62	43	22
24	16.2	24.2	31.9	1.40	2.86	30	32
48	26.1	41.1	33.7	1.79	3.07	23	43

^a [PVNB] = 9.01×10^{-2} mole/l. (concentration of repeating unit of PVNB); [St] = 7.81×10^{-1} mole/l.; [AIBN] = 1.06×10^{-2} mole/l.; DMF, 50 ml; 60°C.

^b Pn of PVNB, 970.

TABLE II
Effect of Reaction Time on Graft Copolymerization
of Styrene onto Poly(vinyl *p*-Nitrobenzoate)^a

Reaction time, hr	Total conversion, %	Per cent grafting, %	Graft efficiency, %	$\bar{M}_n \times 10^{-3}$		No. of monomer units of PVNB per PSt branch	No. of PSt branches per PVNB molecule ^b
				Grafted PSt	Nongrafted PSt		
3	3.1	27.7	95.4	—	—	—	—
6	6.8	31.3	48.5	2.70	3.51	47	21
15	15.4	47.6	33.2	3.45	—	39	25
24	22.3	73.8	35.6	3.77	4.42	27	36

^a [PVNB] = 8.22×10^{-2} mole/l. (concentration of repeating unit of PVNB); [St] = 1.43 mole/l.; [AIBN] = 9.69×10^{-3} mole/l.; DMF, 50 ml; 60°C.

^b Pn of PVNB, 970.

proximately doubled while the other reaction conditions were kept almost the same, and the graft polymerization was carried out varying the reaction time. As shown in Table II, compared to the results in Table I, both the total conversion and the per cent grafting were increased by doubling the concentration of styrene. The molecular weights of the grafted and nongrafted polystyrenes were also higher. Although the molecular weight of the nongrafted polystyrene was larger than that of the grafted one, in this case the former is less than twice the latter. The graft efficiency was as high as 95.4% for a reaction time of 3 hr, and then decreased with reaction time. The decrease in graft efficiency is explained by the steric hindrance of branches already formed; that is to say, the attack of the growing polystyrene radicals on the nitro groups of PVNB was prevented increasingly with the progress in grafting. As indicated above, this tendency was also observable in Table I, even though it is less remarkable.

The number of monomer units of PVNB per polystyrene branch decreased from 47 to 27 by increasing the reaction time from 6 to 24 hr. Accordingly, the number of polystyrene branches per PVNB molecule increased from 21 to 36 with increased reaction time. When the results of Table II are compared with those of Table I for the same duration of reaction, it is evident that more highly branched graft copolymers can be obtained by doubling the concentration of styrene.

In the infrared spectra of the grafted polystyrene separated from the trunk polymer PVNB by hydrolysis of ester groups, an absorption due to C=O of carboxyl groups was observed at 1684 cm^{-1} , which was produced by the hydrolysis of ester groups. No absorption due to nitro groups at 1520 cm^{-1} was detected. Therefore, it is assumed that the growing polymer chains add to either the nitro groups⁴ or the nitroso groups² produced in the elimination of an oxygen of the nitro groups by the growing polymer chains. The addition of the growing polymer chains to the benzene rings suggested by Price et al.⁸ does not occur.

As the amount of AIBN increased from 4.85×10^{-3} mole/l. to 1.45×10^{-2} mole/l. (Table III), the total conversion increased, but the percent grafting and the graft efficiency decreased. The number of monomer units of PVNB per polystyrene branch decreased from 104 to 42. Accordingly, polystyrene branches per PVNB molecule increased with increased AIBN concentration.

TABLE III
Effect of Azobisisobutyronitrile Concentration
on Graft Copolymerization of Styrene onto Poly(vinyl *p*-Nitrobenzoate)^a

[AIBN] × 10 ³ , mole/l.	Total conversion, %	Per cent grafting, %	Graft efficiency, %	$\overline{M}_n \times 10^{-3}$		No. of monomer units of PVNB per PSt branch	No. of PSt branches per PVNB molecule ^b
				Grafted PSt	Nongrafted PSt		
4.85	4.7	40.7	92.0	7.85	—	104	9
6.79	5.6	37.8	71.2	5.83	2.70	84	12
9.69	6.8	31.3	48.5	2.70	3.51	47	21
14.5	7.5	16.8	23.8	1.96	3.65	42	23

^a [PVNB] = 8.22×10^{-2} mole/l. (concentration of repeating unit of PVNB); [St] = 1.43 mole/l.; DMF, 50 ml; 60°C; 6 hr.

^b \overline{P}_n of PVNB, 970.

With the increase in AIBN concentration, the molecular weight of the grafted polystyrene decreased from 7.85×10^3 to 1.96×10^3 , whereas that of the nongrafted one increased.

Polymerization Scheme

The following elementary reactions may be considered in this graft polymerization system:

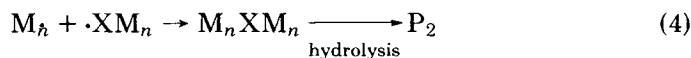
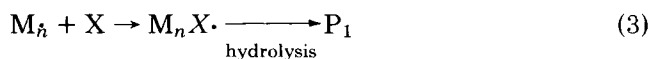
Initiation



Propagation



Formation of grafted polystyrene



Formation of nongrafted polystyrene



where M is the monomer styrene, X is the nitro group on PVNB, S is the solvent DMF, R· is the initiator (AIBN) radical, M_n· is the polystyrene radical with *n* monomer units, P₁ and P₂ represent the grafted polystyrene obtained by hydrolysis, and P₃, P₄, and P₅ denote the nongrafted polystyrenes.

In eq. (3), a growing polystyrene chain adds to a nitro group; and in eq. (4), two growing polystyrene radicals add to a nitro group. Equations (6) and (7) represent the chain transfer reaction to the solvent DMF and the termination

TABLE IV
Effect of Amount Poly(vinyl *p*-Nitrobenzoate) on Graft Copolymerization of
Styrene onto Poly(vinyl *p*-Nitrobenzoate)^a

[PVNB] × 10 ² , mole/l. ^b	Total conversion %	Percent Grafting %	Graft efficiency %	Nongrafted PSt \bar{M}_n × 10 ⁻³
0	10.2	—	—	4.19
2.25	8.3	15.3	9.9	2.71
4.51	6.5	11.5	18.8	2.24
6.67	4.9	9.2	30.0	1.83
9.01	4.5	8.1	38.1	—

^a [St] = 7.81×10^{-1} mole/l.; [AIBN] = 1.06×10^{-2} mole/l.; DMF, 50 ml; 60°C; 6 hr.

^b Concentration of repeating unit of PVNB.

reaction with the primary radicals, respectively. In the above reaction scheme, the molecular weights of P₂ and P₃ will be twice as large as those of P₁, P₄, and P₅.

When the concentration of initiator AIBN is low, the concentration of initiator radicals and growing polystyrene radicals are also low, and reactions (5) and (7) hardly occur. Accordingly, the nongrafted polystyrene is mostly formed by reaction (6). The chain transfer constant of growing polystyrene radicals to DMF⁹ is reported to be 4.0×10^{-4} , whereas the chain transfer constant to PVNB was determined to be approximately 0.3, as will be described in detail later. When the concentrations of PVNB (8.22×10^{-2} mole/l.) and DMF (11.4 mole/l.) in the polymerization mixtures are taken into account, the rate of chain transfer reaction to DMF becomes approximately one tenth of that to PVNB. If it is assumed that the nongrafted polystyrene is formed exclusively by the chain transfer to DMF, a very high graft efficiency amounting to 92% can be explained. As the graft efficiency is high, it is supposed that not only reaction (3) but also reaction (4) occurs. Therefore, the molecular weight of grafted polystyrene becomes higher than that of the nongrafted polystyrene. When the concentration of growing polystyrene radicals becomes larger, reaction (5) occurs more frequently. Accordingly, most of the nongrafted polystyrene is formed by reaction (5). As the graft efficiency

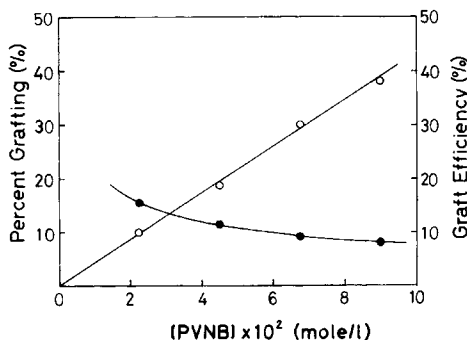


Fig. 1. Effect of PVNB concentration on per cent grafting and graft efficiency in the graft copolymerization of styrene onto poly(vinyl *p*-nitrobenzoate) (PVNB): (O) per cent grafting; (●) graft efficiency; [PVNB], concentration of repeating unit of PVNB. Reaction conditions: [M] = 7.81×10^{-1} mole/l.; [AIBN] = 1.06×10^{-2} mole/l.; DMF, 50 ml; 60°C; 6 hr.

is small, the grafted polystyrene is supposed to be formed by reaction (3). Therefore, the molecular weight of the nongrafted polystyrene becomes larger than that of the grafted polystyrene. Thus, it is concluded that the concentration of initiator has a remarkable effect on the molecular weight of both grafted and nongrafted polystyrenes.

With increase in the amount of PVNB in the reaction mixtures, the total conversion decreased (Table IV). As no induction period was observed in this graft copolymerization system, PVNB acts as a retarder in the polymerization of styrene. The per cent grafting decreased from 15.3% to 8.1%, but the graft efficiency increased linearly with the increase in PVNB as observed from Figure 1, since the reaction of growing polystyrene radicals with the nitro groups on PVNB leading to the grafted polystyrene becomes more frequent than the recombination of two growing polystyrene radicals with increase in concentration of PVNB. As the total conversion decreased due to the retardation by PVNB, the per cent grafting decreased even though the graft efficiency increased.

It is supposed that the chain transfer constant to the solvent DMF is fairly large, as the molecular weight of polystyrene obtained is as low as 4.19×10^3 in the absence of PVNB.

Determination of Rate of Initiation

In order to determine the rate of initiation, a predetermined amount of DPPH was added to the reaction mixtures containing PVNB in the concentrations from 0 to 9.01×10^{-2} mole/l., and the change of the absorbance at $520 \text{ m}\mu$ was measured at predetermined intervals. An example of a plot of the absorbance versus reaction time is shown in Figure 2.

The rate of initiation (R_i) was determined from the following equation:

$$R_i = -\frac{d[\text{DPPH}]}{dt} = \frac{[\text{DPPH}]}{\text{inhibition period}} \quad (8)$$

As shown in Figure 2, an abrupt change of the absorbance is observed when the DPPH added was completely consumed by the radicals produced. Therefore, the inhibition period was determined from the intersection of two straight lines. The values of the rate of initiation obtained for the systems containing various amounts of PVNB are given in Table V. The initiation

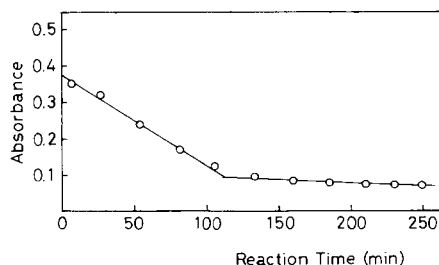


Fig. 2. Decrease of absorbance at $520 \text{ m}\mu$ during the course of polymerization in the presence of poly(vinyl *p*-nitrobenzoate) (PVNB) and 1,1-diphenyl-2-picrylhydrazyl (DPPH). Reaction conditions: $[\text{M}] = 7.81 \times 10^{-1}$ mole/l.; $[\text{AIBN}] = 1.06 \times 10^{-2}$ mole/l.; $[\text{PVNB}] = 2.25 \times 10^{-2}$ mole/l.; $[\text{DPPH}] = 4.45 \times 10^{-4}$ mole/l.; DMF, 50 ml; 60°C .

TABLE V
Rate of Propagation, Rate of Initiation, and Initiator Efficiency in Polymerization of Styrene in the Presence of Poly(vinyl *p*-Nitrobenzoate)^a

$[X] \times 10^2$, mole/l.	$\frac{[X]}{[M]} \times 10^2$	$R_p \times 10^6$, mole/ l.-sec	$R_i \times 10^6$, mole/ l.-sec	Nongrafted PSt \bar{P}_n	Initiator efficiency f
0.00	0	3.69	8.95	40.3	0.59
2.25	2.88	3.00	6.74	26.1	0.45
4.51	5.77	2.35	6.45	21.6	0.43
6.76	8.66	1.77	5.98	17.6	0.40
9.01	11.5	1.63	5.84	—	0.39

^a $[X]$: Concentration of repeating unit of PVNB; $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

efficiency f given in Table V was 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, was assumed to be 7.10×10^{-6} sec⁻¹.¹⁰ As expected, the value of f decreased from 0.59 to 0.39 with the increase in the amount of PVNB. This is attributed to the increase in viscosity of the system and in the direct attack of the initiator radicals on the nitro groups of PVNB.

Using the relation $R_i = 2k_t R_p^2 / (k_p^2 [M]^2)$, the value of k_t/k_p^2 was found to be 2.01×10^3 mole-sec/l. in the absence of PVNB. This value agrees well with that of 2.3×10^3 mole-sec/l. calculated from k_t of 7.2×10^7 l./mole-sec and k_p of 176 l./mole-sec reported by Matheson et al.¹¹

Polymerization of Styrene in the Presence of IPNB

In the polymerization of styrene in the presence of IPNB as a model compound of PVNB, the rate of polymerization decreased with increase in the amount of IPNB (Table VI), and the molecular weight of polystyrene decreased with increase in the amount of IPNB. When the effect of the amount of IPNB on the R_p is compared with that of PVNB, it is observed that IPNB is a more effective retarder than PVNB (Fig. 3).

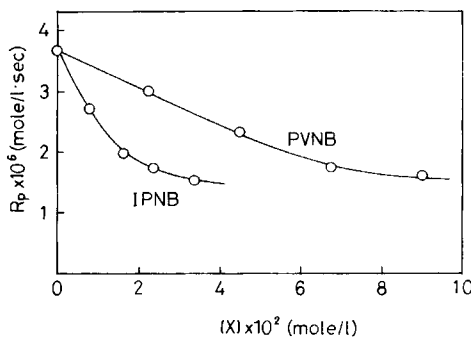


Fig. 3. Comparison of the rate of polymerization of styrene in the presence of poly(vinyl *p*-nitrobenzoate) with that in the presence of isopropyl *p*-nitrobenzoate (IPNB); $[X]$, concentration of repeating unit of PVNB or IPNB. Reaction conditions: $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

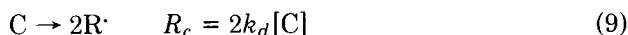
TABLE VI
Results of Polymerization of Styrene in the Presence
of Isopropyl *p*-Nitrobenzoate^a

$[X] \times 10^2$, mole/l.	$\frac{[X]}{[M]} \times 10^2$	$R_p \times 10^6$, mole/ l.-sec	$R_i \times 10^8$, mole/ l.-sec	Poly- styrene \bar{P}_n
0	0	3.69	8.95	40.3
0.776	0.994	2.71	8.95	34.9
1.64	2.10	1.98	8.95	26.2
2.39	3.06	1.75	8.95	23.1
3.40	4.35	1.55	8.95	16.7

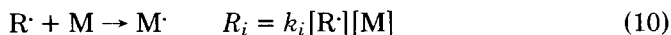
^a $[X]$: Concentration of IPNB; $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

Determination of Chain Transfer Constants to PVNB and IPNB

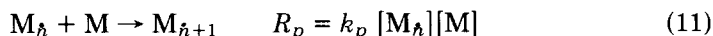
Kice^{12,13} has carried out the polymerization of methyl acrylate and methyl methacrylate in the presence of inhibitors such as benzoquinone, chloranil, and trinitrotoluene and proposed a rate equation including a term related to inhibitors. Furthermore, Kar et al.¹⁴ derived a simpler rate equation by assuming that the cross-termination constant is a geometric mean of the respective termination constants. In a way similar to that of Kar et al., we assume the following reaction scheme in order to determine the chain transfer constants of growing polystyrene radicals to PVNB and IPNB:



Initiation:



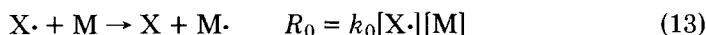
Propagation:



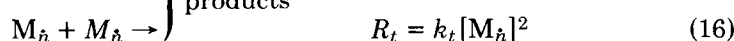
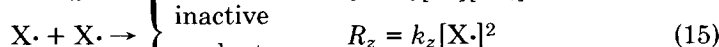
Chain transfer:



Reinitiation:



Termination:



where C is the initiator, M the monomer, X the nitro compound or the nitro group of the trunk polymer, R· the initiator radical, M_n the growing polymer radical containing n monomer units, and X· the polymer radical having an X radical at its chain end.

If it is assumed that the reinitiation is negligible ($R_0 = 0$) and the cross-ter-

mination constant is a geometric mean of the respective termination constants ($k_c^2 = k_t k_z$) the following equation can be derived from the steady-state assumption of $[M_n]$ and $[X\cdot]$:

$$\frac{1}{R_p} = \frac{k_x [X]}{R_i k_p [M]} + \frac{k_t^{1/2}}{R_i^{1/2} k_p [M]} \quad (17)$$

The second term on the right side of eq. (17) is the inverse of the rate of polymerization in the absence of inhibitor and may be written as $1/R_{p0}$. Thus, eq. (17) reduces to

$$\frac{1}{R_p} = \frac{k_x [X]}{R_i k_p [M]} + \frac{1}{R_{p0}} \quad (18)$$

Equation (18) can be applied to a low molecular weight nitro compound such as IPNB.

However, for a system containing polymer with nitro groups such as PVNB, reaction (14) can be neglected when the initiator concentration is high, since the molecular weight of the nongrafted polystyrene is twice as large as that of the grafted one, as in the case given in Table I, namely, addition of the second polymer radical to nitro groups hardly occurs. Reaction (15) can also be neglected when steric hindrance due to the bulkiness of the polymer radicals is taken into account. Therefore, by neglecting the eqs. (14) and (15), and also the reinitiation eq. (13), and assuming the steady-state condition of $[M_n]$, eq. (19) is obtained:

$$\frac{1}{R_p} - \frac{R_p}{R_{p0}^2} = \frac{k_x [X]}{R_i k_p [M]} \quad (19)$$

The chain transfer constant k_x/k_p of growing polymer radicals to IPNB was found to be 0.794 from the data given in Table VI by plotting $1/R_p$ versus $[X]/[M]$ according to eq. (18) (Fig. 4). The chain transfer constant (k_x/k_p) of growing polymer radicals to PVNB was found to be 0.273 from the plot of $R_i(1/R_p - R_p/R_{p0}^2)$ versus $[X]/[M]$ according to eq. (19) by use of the data given in Table V (Fig. 5).

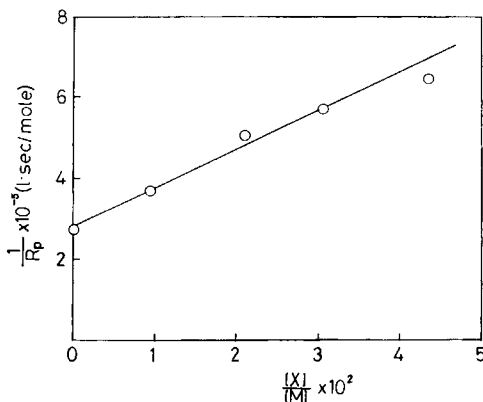


Fig. 4. Plot of $1/R_p$ vs. $[X]/[M]$ for polymerization of styrene in the presence of isopropyl *p*-nitrobenzoate (IPNB); $[X]$, concentration of IPNB. Reaction conditions: $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

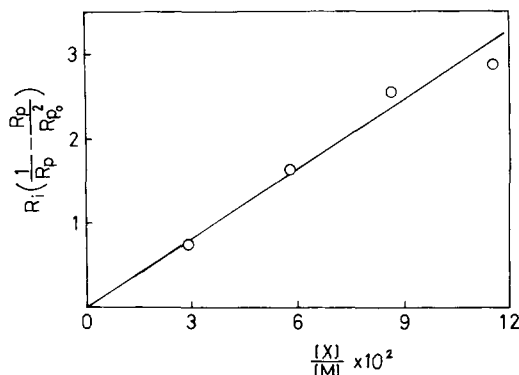


Fig. 5. Plot of $R_i(1/R_p - R_p/R_{p0}^2)$ vs. $[X]/[M]$ for polymerization of styrene in the presence of poly(vinyl *p*-nitrobenzoate) (PVNB); $[X]$, concentration of repeating unit of PVNB. Reaction conditions: $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

The following relation has been obtained by Mayo et al.¹⁵ between the inverse of the degree of polymerization ($1/\bar{P}_n$) and $[X]/[M]$:

$$\frac{1}{\bar{P}_n} = C_s \frac{[X]}{[M]} + \frac{1}{\bar{P}_{n0}} \quad (20)$$

where \bar{P}_n and \bar{P}_{n0} are the degree of polymerization in the presence and absence of a chain transfer agent, respectively, and $C_s (= k_x/k_p)$ is the chain transfer constant. In Figure 6, $1/\bar{P}_n$ of nongrafted polystyrene formed in the presence or absence of PVNB is plotted versus $[X]/[M]$. From the slope, a value of 0.357 was obtained for k_x/k_p . The value of k_x/k_p for polystyrene radicals growing onto IPNB was also found to be 0.736 by plotting $1/\bar{P}_n$ of the polystyrene produced in the presence and absence of IPNB versus $[X]/[M]$ (Fig. 6).

Bagdasarian¹⁶ has indicated that in the polymerization of vinyl monomer

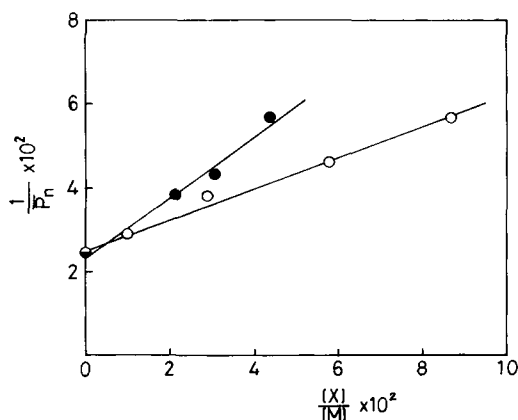


Fig. 6. Plot of $1/\bar{P}_n$ vs. $[X]/[M]$ for polymerization of styrene in the presence of poly(vinyl *p*-nitrobenzoate) (PVNB) and isopropyl *p*-nitrobenzoate (IPNB). $[X]$, concentration of repeating unit of PVNB (O) and IPNB (●). Reaction conditions: $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

TABLE VII
Comparison of Chain Transfer Constants of
Polystyrene Radicals to Poly(vinyl *p*-Nitrobenzoate)
and Isopropyl *p*-Nitrobenzoate Determined by Various Methods

	PVNB	IPNB
From eq. (18)	—	0.794
From eq. (19)	0.273	—
From Mayo's equation	0.357	0.736
From Bagdasarian's equation	0.328	0.830

in the presence of an inhibitor, the chain transfer constant k_x/k_p of polymer radicals to an inhibitor can be expressed by eq. (21):

$$\frac{1}{\bar{P}_n} = \frac{1}{2} (1 + \lambda) \frac{k_t R_p}{k_p^2 [M]^2} + \frac{k_m}{k_p} + \beta \frac{k_x [X]}{k_p [M]} \quad (21)$$

where k_m is the chain transfer constant of polymer radicals to monomer; λ is k_{td}/k_t , where k_{td} is the rate constant for termination by disproportionation; and β is a constant representing the number of polymer molecules formed as a result of a chain transfer reaction.

If the value of R_i is known, k_t/k_p^2 can be calculated from the following relation:

$$R_i = \frac{2k_t/k_p^2 R_p^2}{1 + x [M]^2} \quad (22)$$

where x is k_{td}/k_t , and $x = 0$ for styrene.

Using the values of R_i given in Tables V and VI, k_t/k_p^2 was calculated for the polymerization of styrene in the presence of PVNB or IPNB. From a value of 6.2×10^{-5} for k_m/k_p in the polymerization of styrene,¹⁷ the values of

$$\frac{1}{\bar{P}_n} - \frac{k_t R_p}{2k_p^2 [M]^2} - \frac{k_m}{k_p}$$

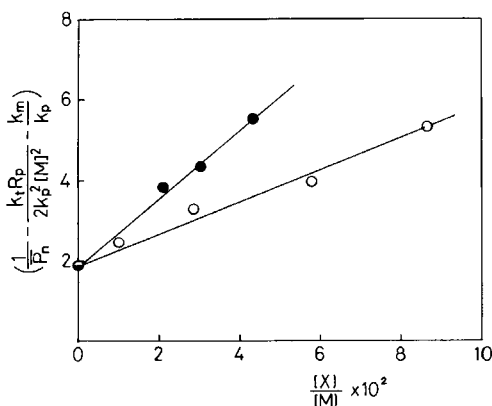


Fig. 7. Plot of $(1/\bar{P}_n - k_t R_p / 2k_p^2 [M]^2)$ vs. $[X]/[M]$ for polymerization of styrene in the presence of poly(vinyl *p*-nitrobenzoate) (PVNB) (O) and isopropyl *p*-nitrobenzoate (IPNB) (●); $[X]$, concentration of repeating unit of PVNB and IPNB. Reaction conditions: $[M] = 7.81 \times 10^{-1}$ mole/l.; $[AIBN] = 1.06 \times 10^{-2}$ mole/l.; DMF, 50 ml; 60°C; 6 hr.

were calculated and plotted versus $[X]/[M]$ according to eq. (21) (Fig. 7). From this plot, the chain transfer constants of polystyrene radicals to PVNB and IPNB were found to be 0.328 and 0.830, respectively. The values of chain transfer constants of polystyrene radicals to PVNB and IPNB obtained by various methods are summarized in Table VII.

As both PVNB and IPNB behave as retarders in the polymerization of styrene, the values of chain transfer constants calculated from eq. (21) derived by Bagdasarian for an inhibitor are thought to be more reasonable than those calculated from eq. (20) derived by Mayo et al. Equation (19) was obtained by assuming that the addition of the second polymer radical to the nitro groups which already have a grafted polymer chain rarely occur if the initiator concentration is high. However, this requirement is not always fulfilled in the reaction conditions studied as observed in Tables II and III. Accordingly, the most reliable value for the chain transfer constant of polystyrene radicals to PVNB is thought to be obtained from Bagdasarian's equation, while a reliable chain transfer constant of polystyrene radicals to IPNB can be determined from eq. (20) and Bagdasarian's equation.

The chain transfer constant of polystyrene radicals to IPNB as a model compound of PVNB is more than twice as large as that to PVNB. This lower value of chain transfer constant to PVNB may be attributed partly to the higher reactivity of the nitro groups of IPNB to polystyrene radicals. Moreover, it is thought that the bulky polystyrene radicals are difficult to diffuse into the random coil of PVNB molecules and to attack the nitro groups inside the random coil due to the steric hindrance. The steric hindrance of the branches already formed also disturbs the chain transfer reaction; namely, the attack of the growing polystyrene chains on the nitro groups on PVNB was prevented increasingly with progressive grafting, since the graft efficiency decreased with reaction time.

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