

Graft Copolymerization of Styrene onto Poly(*p*-Nitrophenyl Acrylate) by Chain Transfer Reaction

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Synopsis

Styrene (St) was polymerized in the presence of poly(*p*-nitrophenyl acrylate) (PNPA) with azobisisobutyronitrile as an initiator to prepare graft copolymers through the chain transfer reaction of growing polystyrene (PSt) radicals to the aromatic nitro groups on PNPA. The maximum number of branches attained was 16.4 (\bar{P}_n of PNPA was 1780), which corresponds to 108 monomer units per PSt branch. This is far less than the value of 43, previously obtained for poly(vinyl *p*-nitrobenzoate) as a trunk polymer. Therefore, several model compounds for trunk polymers were prepared, and the chain transfer constants of PSt radicals to these model compounds were determined. As a result of the Hammett plot, it is concluded that higher electron attracting property of the substituents increases the reactivity of nitro groups to the growing PSt radicals, resulting in more highly branched graft copolymers.

INTRODUCTION

When a vinyl monomer is polymerized with a radical initiator in the presence of a polymer with pendant aromatic nitro groups, a graft copolymer is obtained through the chain transfer reaction of growing polymer radicals to the aromatic nitro groups.¹ We could obtain a highly branched graft copolymer with the number of branches of 43 (\bar{P}_n of the trunk polymer 970) corresponding to 23 monomer units of trunk polymer per branch, when poly(vinyl *p*-nitrobenzoate) was used as a trunk polymer and styrene as a monomer.²

The graft frequency, namely, the number of branches per trunk polymer depends on the trunk polymer-monomer combinations. We have derived the relationship among the chain transfer constant of growing polymer radicals to the pendant aromatic nitro groups, the extent of monomer conversion and the number of branches, and compared the relation with experimental results.³

In the present study, we carried out graft copolymerization by use of poly(*p*-nitrophenyl acrylate) as a trunk polymer and styrene as a monomer. Polymerization of styrene was also carried out in the presence of model compounds for trunk polymers with pendant *p*-nitrophenyl groups, and the chain transfer constants obtained were discussed from the viewpoint of their chemical structures.

EXPERIMENTAL

Materials

p-Nitrophenyl acrylate was prepared by adding dropwise acryloyl chloride to an aqueous solution of *p*-nitrophenol and KOH according to the procedure of Gaetjen and Morawetz,⁴ melting point 65.5°C from ethanol (literature,⁴ 65–65.5°C).

Poly(*p*-nitrophenyl acrylate) (PNPA) was obtained by bulk-polymerization of *p*-nitrophenyl acrylate at 70°C with azobisisobutyronitrile (AIBN) as an initiator in a sealed glass ampoule. The product was extracted with chloroform, and the insoluble residue was used for further experiments. The number-average degree of polymerization was 1780 as determined with a Hewlett-Packard 502 high-speed membrane osmometer on poly(methyl acrylate) obtained by the hydrolysis of PNPA and subsequent methylation of poly(acrylic acid) with diazomethane.

p-Nitrophenyl isobutyrate (NPIB) was synthesized by adding isobutyryl chloride to a solution of *p*-nitrophenol in anhydrous pyridine at 0°C. After the addition was completed, the mixture was warmed for 10 min, and then poured into ice water with vigorous stirring. The precipitate was washed with a 5% aqueous solution of Na₂CO₃, melting point 39°C from ethanol (literature,⁵ 39–40°C).

p-Nitrophenyl isopropyl ether was prepared from isopropyl bromide and *p*-nitrophenol by the method of Bamkole et al.,⁶ boiling point 135°C/7 Torr (literature,⁶ 154°C/13 Torr).

p-Nitrocumene was synthesized by the nitration of cumene with a mixture of concentrated sulfuric acid and concentrated nitric acid after the procedure of Hansch and Helmkamp.⁷ The crude product was repeatedly rectified to remove *o*-nitrocumene, boiling point 120°C/12 Torr (literature,⁷ 120°C/7 Torr).

Graft Polymerization

Predetermined amounts of PNPA, styrene and AIBN were placed in a glass ampoule containing 30 ml of dimethyl formamide (DMF). After degassing several times at liquid-nitrogen temperature, the ampoules were sealed and grafting reaction was carried out at 60°C. After a predetermined 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. Nongrafted polystyrene was removed by extraction with cyclohexane for 24 hr. 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 number-average molecular weights of the grafted and nongrafted polystyrenes were determined with a Hewlett-Packard Model 302B vapor pressure osmometer or calculated from the GPC curves obtained with a Toyo Soda high-speed liquid chromatograph HLC-802UR.

Determination of Rate of Initiation

Predetermined amounts of PNPA, styrene, and AIBN were introduced into a four-necked flask equipped with a stirrer, a reflux condenser, and a thermometer containing 60 ml of DMF. Then 10 mg of 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 the concentration of remaining DPPH was determined from the absorbance at 520 nm of the diluted solution.

Polymerization of Styrene in the Presence of Model Compounds

Styrene was polymerized with AIBN as a catalyst and DMF as a solvent in the presence of model compounds for 6 hr at predetermined temperatures in glass ampoules. After the reaction was stopped, the polystyrene precipitated was filtered and dried.

RESULTS AND DISCUSSION

Graft Copolymerization

The results of graft copolymerization of styrene onto PNPA carried out at 60°C for various periods of time are shown in Table I. The percent grafting increased from 7.2% to 50.3% as the reaction time was increased from 4 to 24 hr. The graft efficiency slightly increased with reaction time, but is by far lower than the efficiency (approximately 30%) that was observed for poly(vinyl *p*-nitrobenzoate) (PVNB) as a trunk polymer under similar conditions.² The molecular weight of nongrafted polystyrenes was approximately twice as large as that of grafted polystyrenes. The number average monomer units of the trunk polymer PNPA per polystyrene branch was 258 for 15 hr and 108 for 24 hr of reaction time, which was quite larger than 43 and 23 observed for PVNB.² PNPA acts as a retarder in the polymerization of styrene because no induction period was observed.

As the amount of AIBN increased from 8.73×10^{-3} mole/liter to 2.3×10^{-2} mole/liter, the total conversion increased and the percent grafting slightly decreased, but the graft efficiency decreased from 4.7% to 2.7% (Table II). The molecular weight of nongrafted polystyrene decreased from 1.14×10^4 to 7.90

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

Reaction time, hr	Total conversion, %	Percent grafting, %	Graft efficiency, %	$\bar{M}_n \times 10^{-4}$		No. of monomer units of PNPA per PSt branch	No. of PSt branches per PNPA molecule ^b
				Grafted PSt	Nongrafted PSt		
4	7.5	7.2	5.0	—	2.14	—	—
8	14.3	12.0	4.6	—	1.99	—	—
15	24.1	26.7	6.1	1.19	1.92	258	6.9
24	32.0	50.3	7.2	1.05	2.15	108	16.4

^a [PNPA] = 6.47×10^{-2} mole/liter (concentration of repeating unit of PNPA); [St] = 2.18 mole/liter; [AIBN] = 1.06×10^{-2} mole/liter; DMF, 30 ml; 60°C.

^b \bar{P}_n of PNPA, 1780.

TABLE II
Effect of Azobisisobutyronitrile Concentration on Graft Copolymerization of Styrene onto Poly(*p*-Nitrophenyl Acrylate)^a

[AIBN] × 10 ³ , mole/liter	Total conversion, %	Percent grafting, %	Graft efficiency, %	$\bar{M}_n \times 10^{-3}$ nongrafted PSt
8.73	9.3	4.0	4.7	11.4
15.5	11.9	3.9	3.6	9.0
23.0	14.4	3.6	2.7	7.9

^a [PNPA] = 7.40×10^{-2} mole/liter (concentration of repeating unit of PNPA); [St] = 1.25 mole/liter; DMF, 30 ml; 60°C; 6 hr.

× 10³. The decrease of the graft efficiency is due to the increase of termination by recombination between growing polymer radicals.

As the amount of PNPA was increased from 0 to 12.94×10^{-2} mole/liter, the graft efficiency increased almost linearly, but the total conversion and percent grafting decreased, and the molecular weight of grafted and nongrafted polystyrenes decreased (Table III). The number of monomer units of PNPA per polystyrene branch was almost independent of the amount of PNPA, and the number of polystyrene branches per PNPA molecule was from 6 to 7. The graft efficiency increased with increasing amount of PNPA, because the frequency of the reaction between growing polystyrene radicals and the nitro groups on PNPA increases. However, the total conversion and percent grafting were reduced with the increase in the concentration of PNPA due to the retardation by PNPA.

Determination of Rate of Initiation

The rate of initiation (R_i) was determined by adding a predetermined amount of DPPH to the reaction mixtures containing PNPA or NPIB and measuring the change of the absorbance at 520 nm at predetermined intervals. The rate of initiation (R_i) is related to the inhibition period by the following equation:

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

TABLE III
Effect of Amount of Poly(*p*-Nitrophenyl Acrylate) on Graft Copolymerization of Styrene onto Poly(*p*-Nitrophenyl Acrylate)^a

[PNPA] × 10 ² , mole/liter ^b	Total conver- sion, %	Percent grafting, %	Graft efficiency, %	$\bar{M}_n \times 10^{-4}$		No. of monomer units of PNPA per branch	No. of PSt branches per PNPA molecule ^c
				Grafted PSt	Nongrafted PSt		
0	27.5	—	—	—	2.24	—	—
3.24	25.2	27.4	3.0	1.49	2.13	282	6.3
6.47	24.1	26.7	6.1	1.33	1.92	258	6.9
12.94	22.5	20.1	9.8	1.02	1.88	263	6.8

^a [St] = 2.18 mole/liter; [AIBN] = 9.14×10^{-3} mole/liter; DMF, 30 ml; 60°C; 15 hr.

^b Concentration of repeating unit of PNPA.

^c \bar{P}_n of PNPA, 1780.

As an example, it is shown in Figure 1, that at the early stage the absorbance decreased linearly with time until the DPPH was completely used up by the radicals produced, and then the absorbance changed very slowly. The induction 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 PNPA or NPIB are given in Table IV. The initiation efficiency f given in Table IV was calculated from $R_i = 2k_d f(\dot{C})$, in which k_d , the rate of decomposition of AIBN in the polymerization of styrene in DMF at 60°C, was assumed to be $7.10 \times 10^{-6} \text{ sec}^{-1}$.⁸ The values of f decreased from 0.70 to 0.50 with increasing amount of PNPA. However, when NPIB was added to the reaction mixture, the value of f was almost the same as that in the absence of NPIB. The decrease of the value of f in the presence of PNPA is attributed not to the direct attack of the initiator radicals on the nitro group of PNPA, but to the increase in viscosity as the value of f is not affected by the addition of NPIB.

Determination of Chain Transfer Constants to PNPA and Model Compounds

For the polymerization of vinyl monomers in the presence of inhibitors, Kar et al.⁹ derived a rate equation by assuming that the cross-termination constant is a geometric mean of the respective termination constants:

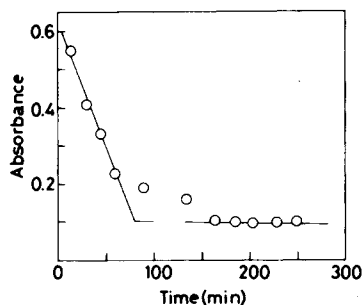


Fig. 1. Dependence of absorbance at 520 nm during the polymerization of styrene in the presence of poly(*p*-nitrophenyl acrylate) (PNPA) and 1,1-diphenyl-2-picryl hydrazyl (DPPH). Reaction conditions: $[M] = 1.25$ mole/liter; $[AIBN] = 8.73 \times 10^{-3}$ mole/liter; $[PNPA] = 7.39 \times 10^{-2}$ mole/liter; $[DPPH] = 3.51 \times 10^{-4}$ mole/liter; DMF, 60 ml; 60°C.

TABLE IV

Rate of Propagation, Rate of Initiation, and Initiator Efficiency in Polymerization of Styrene in the Presence of Poly(*p*-Nitrophenyl Acrylate) (PNPA)^a and *p*-Nitrophenyl Isobutyrate (NPIB)^b

	$[X] \times 10^2$, mole/liter	$\frac{[X]}{[M]} \times 10^2$	$R_p \times 10^6$, mole/liter sec	$R_i \times 10^6$, mole/liter sec	Nongrafted PSt \bar{P}_n	Initiator efficiency f
PNPA	0.00	0.00	6.18	8.74	101	0.70
	3.73	2.98	5.83	7.73	88	0.63
	7.39	5.91	5.37	7.31	75	0.59
	14.80	11.84	4.62	6.22	63	0.50
NPIB	6.83	5.46	4.42	8.62	52	0.69
	13.65	10.92	3.67	8.70	47	0.69

^a $[X]$: Concentration of repeating unit of PNPA; $[M] = 1.25$ mole/liter; $[AIBN] = 8.73 \times 10^{-3}$ mole/liter; DMF, 60 ml; 60°C; 6 hr.

^b $[X]$: Concentration of IPNB; $[M] = 1.25$ mole/liter; $[AIBN] = 8.73 \times 10^{-3}$ mole/liter; DMF, 60 ml; 60°C, 6 hr.

$$1/R_p = C_x[X]/R_i[M] + 1/R_{p0} \quad (2)$$

where $[M]$ and $[X]$ are the concentration of monomer and retarder, R_p and R_{p0} the rates of polymerization in the presence and absence of retarder, respectively, and C_x is the chain transfer constant to retarders.

However, for a system containing a polymeric retarder such as PNPA, eq. (2) is not applicable because of the steric hindrance due to bulkiness of polymer radicals, and the following equation has been obtained²:

$$1/R_p - R_p/R_{p0}^2 = C_x[X]/R_i[M] \quad (3)$$

The chain transfer constant C_x of growing polymer radicals to PNPA was obtained to be $(5.0 \pm 0.5) \times 10^{-2}$ from the value of R_i obtained above and the slope of the $(1/R_p - R_p/R_{p0}^2)$ versus $[X]/[M]$ plot according to eq. (3). The value of C_x to NPIB, which is the low molecular model compound of PNPA, was found to be $(9.7 \pm 1.0) \times 10^{-2}$ by plotting $1/R_p$ versus $[X]/[M]$ according to eq. (2).

The following relation has been obtained by Mayo et al.¹⁰ between the degree of polymerization (\bar{P}_n) and $[X]/[M]$:

$$1/\bar{P}_n = C_x[X]/[M] + 1/\bar{P}_{n0} \quad (4)$$

where \bar{P}_n and \bar{P}_{n0} are the number-average degree of polymerization in the presence and absence of a chain transfer agent, respectively. From the slope of the relation of $1/\bar{P}_n$ of nongrafted polystyrenes formed in the presence and absence of PNPA and $[X]/[M]$, a value of (4.8 ± 0.5) was obtained for C_x . The value of C_x for polystyrene radicals to NPIB was found to be $(9.7 \pm 1.0) \times 10^{-2}$ from the plot of $1/\bar{P}_n$ of polystyrenes produced in the presence and absence of NPIB versus $[X]/[M]$.

Bagdasarian¹¹ has indicated that in the polymerization of vinyl monomers in the presence of an inhibitor, the chain transfer constant C_x of polymer radicals to an inhibitor can be expressed by eq. (5).

$$\frac{1}{\bar{P}_n} = \frac{1}{2} (1 + \lambda) \frac{k_t R_p}{k_p^2 [M]^2} + \frac{k_m}{k_p} + \beta C_x \frac{[X]}{[M]} \quad (5)$$

where k_p is the rate constant for propagation; k_t is the rate constant for termination; k_m is the rate constant for chain transfer to monomer; $\lambda = k_{td}/k_t$, where k_{td} is the rate constant for termination by disproportionation (in the polymerization of styrene, $k_{td} = 0$; therefore, $\lambda = 0$); and β is a constant representing the number of molecules formed as a result of a chain transfer reaction. The values of k_t/k_p^2 were calculated for the polymerization of styrene in the presence of PNPA and NPIB with use of the value of R_i given in Table IV and by

$$R_i = \frac{2k_t/k_p^2 R_p^2}{1 + \lambda [M]^2} \quad (6)$$

From a value of 6.2×10^{-5} for k_m/k_p in the polymerization of styrene,¹² the values

$$1/\bar{P}_n - k_t R_p / 2k_p^2 [M]^2 - k_m/k_p \quad (7)$$

were calculated and plotted against $[X]/[M]$. The chain transfer constants of polystyrene radicals to PNPA and NPIB were found to be $(5.7 \pm 0.5) \times 10^{-2}$ and $(1.09 \pm 0.10) \times 10^{-1}$, respectively.

The values of chain transfer constants of polystyrene radicals to PNPA and

NPIB obtained by various methods are summarized in Table V. The chain transfer constant to PNPA is about half of that to NPIB as the model compound. In the previous report,² the chain transfer constant of polystyrene radicals to poly(vinyl *p*-nitrobenzoate) (PVNB) was less than half of that to isopropyl *p*-nitrobenzoate (IPNB) as a model compound. The difference between the chain transfer constant to PVNB and that to IPNB was attributed to the difficulty of the bulky polystyrene radicals to diffuse into the random coil of trunk polymer and to attack the nitro groups inside the random coil due to the steric hindrance. The values of chain transfer constants obtained for PNPA and NPIB also support this explanation.

As mentioned above, we could obtain a highly branched graft copolymer (23 monomer units of trunk polymer per branch), when PVNB was used as a trunk polymer.² On the other hand, when PNPA was used as a trunk polymer, we obtained less branched graft copolymers under similar reaction conditions (at most 108 monomer units of trunk polymer per branch). The difference is thought to be due to the polar effect of the ester bond connecting the polymer backbone and pendant *p*-nitrophenyl groups as mentioned in the following.

Several investigations have been reported for the effect of substituents on the chain transfer constants of the inhibitors and retarders. Sinit'sina and Bagdasarian¹³ found that the chain transfer constants to *m*- and *p*-substituted nitro compounds obey the Hammett rule in the inhibited polymerization of methyl methacrylate, and the constant ρ is +0.8. Tüdös and co-workers¹⁴ made a kinetic investigation on the inhibition effect of *sym*-trinitrobenzene and its substituted derivatives on the polymerization of styrene, and found that the rate of inhibition obeys the Hammett rule and the constant ρ is +1.6. Ota and co-workers¹⁵ investigated polymerization of styrene in the presence of *p*- and *m*-substituted nitrobenzenes, and found that the chain transfer constants obey the Hammett rule and the constant ρ is +1.52.

In order to examine the effect of substituents on the chain transfer constants, styrene was polymerized in the presence of *p*-nitrocumene and *p*-nitrophenyl isopropyl ether as model compounds of trunk polymers with pendant nitrophenyl groups such as poly(*p*-nitrostyrene) and poly(*p*-nitrophenyl vinyl ether) under the same reaction conditions as for *p*-nitrophenyl isobutyrate. The values of C_x of polystyrene radicals to these model compounds were determined by use of eq. (2) (Table VI). In Figure 2 the values of $\log C_x$ are plotted versus Hammett σ constant.¹⁶ The chain transfer constants increased as the electron attracting property of the substituents increased. Although the experimental data are very limited, almost linear relationship was obtained between logarithmic chain transfer constants and Hammett σ constants, and the ρ value of +1.4 was obtained from the slope.

TABLE V
Comparison of Chain Transfer Constants of Polystyrene Radicals to Poly(*p*-Nitrophenyl Acrylate) and *p*-Nitrophenyl Isobutyrate Determined by Various Methods

	PNPA	NPIB
From eq. (2)	—	0.097
From eq. (3)	0.050	—
From Mayo's equation	0.048	0.097
From Bagdasarian's equation	0.057	0.109

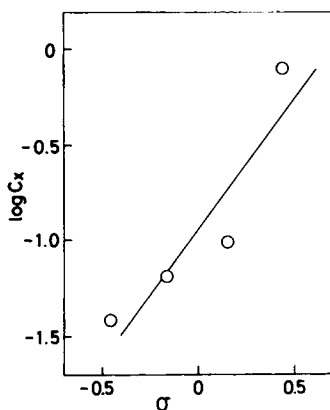
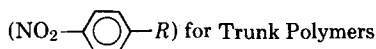


Fig. 2. Plot of $\log C_x$ vs Hammett's σ constant for the substituents R of model compounds.

TABLE VI
Chain Transfer Constants of Polystyrene Radicals to Several Model Compounds



	R	$C_x \times 10^2$	Hammett σ constant (ref. 16)
p -Nitrophenyl isopropyl ether	$-\text{O}-\text{C}_3\text{H}_7$	3.8	-0.45
p -Nitrocumene	$-\text{C}_3\text{H}_7$	6.4	-0.15
p -Nitrophenyl isobutyrate	$-\text{O}-\text{C}(=\text{O})-\text{C}_3\text{H}_7$	9.7	0.16
Isopropyl p -nitrobenzoate	$-\text{C}(=\text{O})-\text{O}-\text{C}_3\text{H}_7$	79.4 ^a	0.45 ^b

^a Reference 2.

^b Value for $-\text{COOC}_2\text{H}_5$.

Therefore, in these reaction systems, higher electron attracting property of the substituent on benzene ring existing in p -position to the nitro groups increases the reactivity of nitro groups to the growing polystyrene radicals resulting in higher chain transfer constant.

When PVNB was used as a trunk polymer, graft copolymer with a large number of branches of low molecular weight were obtained, and the graft efficiency was also high. However, when PNPA was used as a trunk polymer, graft copolymers with a small number of branches of high molecular weight were obtained, and the graft efficiency was low. This difference is due to the difference between chain transfer constants to these two trunk polymers. A trunk polymer with high chain transfer constant is more suitable for getting more highly branched graft copolymers.³ The chain transfer constant to isopropyl p -nitrobenzoate is the highest of the four model compounds of trunk polymers. Accordingly, as the trunk polymer PVNB is the most suitable for obtaining highly branched graft copolymer of the four trunk polymers. This high reactivity of nitro group on PVNB is due to the high electron attracting property of the ester group of this trunk polymer.

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