

Graft Frequency of Graft Copolymers by Chain Transfer of Growing Polymer Radicals to Trunk Polymers Containing Nitro Groups

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Synopsis

The relationship between the chain transfer constant, extent of monomer conversion, and number of branches was derived for the graft copolymerization through chain transfer of growing polymer radicals to the pendent aromatic nitro groups on the trunk polymer. The equation derived enables us to predict the number of branches for a given monomer trunk polymer. The relationship obtained is compared with the experimental data previously reported for the graft copolymerization of styrene onto poly(vinyl *p*-nitrobenzoate). The value of a' , the ratio of nitro groups with branches to those which are attacked by polystyrene radicals, is less than unity except for the graft copolymers obtained with high initiator concentrations and at early stages of the reaction. This lowering of a' is attributed to the steric hindrance of branches already formed on the trunk polymer which prevents the attack of polystyrene radicals on the nitro groups and side reactions, such as reaction of the nitroso groups formed as an intermediate with styrene.

INTRODUCTION

When free-radical polymerization of a vinyl monomer is carried out in the presence of a polymer containing pendent aromatic nitro groups, a highly branched graft copolymer is obtained by chain transfer of growing polymer radicals to the aromatic nitro groups on the trunk polymer.¹ The number of branches is dependent on the monomer-trunk polymer system, and also on reaction conditions.^{1,2} We obtained a graft copolymer with 43 branches (\bar{P}_n of the trunk polymer 970) corresponding to 23 monomer units of trunk polymer per branch when poly(vinyl *p*-nitrobenzoate) (PVNB) was used as a trunk polymer and styrene as a monomer.²

In the present work we derived the relationship between the chain transfer constant, extent of monomer conversion, and the number of branches in the graft copolymerization. This relationship, which may be used to predict the number of branches for a given monomer-trunk polymer system, was compared with the experimental data previously reported for the graft copolymerization of styrene onto PVNB.²

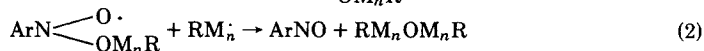
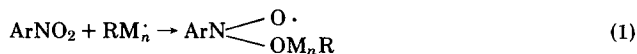
THEORY

Several mechanisms have been proposed for the reaction of aromatic nitro compounds with growing polymer radicals. Price and Durham³ concluded that growing polymer radicals attack the aromatic nuclei of the nitro compounds and,

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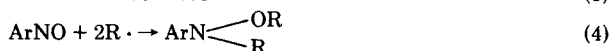
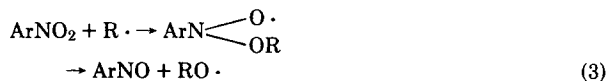
consequently, a substitution reaction takes place on the aromatic nucleus. However, it has been established that addition products of growing polymer radicals with the oxygen atoms of the nitro groups are formed.⁴⁻⁷ We confirmed this from the infrared spectra of the grafted polystyrene separated from the trunk polymer PVNB by hydrolysis of ester groups² and the ¹H NMR spectra of the reaction products of isopropenyl *p*-nitrobenzoate with methyl methacrylate.⁸

On the basis of benzoyl peroxide-initiated polymerization of allyl acetate, Hammond and Bartlett⁴ suggested the following mechanism for the attack of a radical on the oxygen atom of aromatic nitro group:



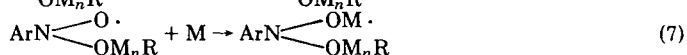
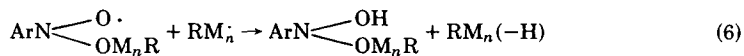
where Ar is the aromatic nucleus, M is the monomer, R is the fragment of initiator, and $\text{RM}_n \cdot$ is the growing polymer radical containing *n* monomer units.

Using 2-cyano-1-methylethyl radicals from the thermal decomposition of azobisisobutyronitrile as a model for polymer radicals, Inamoto and Simamura⁵ examined reactions of the radicals with nitrobenzenes and interpreted their results by the following mechanism:

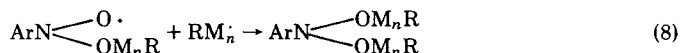


where $\text{R} \cdot$ is the initiator radical.

Bevington and Ghanem⁶ carried out the polymerization of styrene in the presence of ¹⁴C-labeled nitro compounds and an initiator and supported the mechanism proposed by Inamoto and Simamura.⁵ In addition, they indicated that reaction (6) also occurs and that the intermediate in eq. (3) occasionally reacts with the monomer to reinitiate polymerization as shown in eq. (7):



Tüdos and co-workers⁷ suggested that the following addition reaction should also be considered:



Therefore, the scheme for the reaction of aromatic nitro groups on the trunk polymer with growing polymer radicals is expected to be as given in Figure 1, even though the exact reaction mechanism of retardors has not been completely clarified.⁹ In this reaction scheme the growing polymer radicals add to the oxygen atom of the nitro group to give intermediate radicals (I). Most of the radicals decompose through monomolecular reaction to form nitroso groups. The nitroso groups then combine with two growing polymer radicals resulting in two branches on a nitro group (reaction A). Some of the intermediate radicals (I) terminate through disproportionation (reaction B) or recombination (reaction C) with growing polymer radicals yielding one or two branches on a nitro group. Under favorable conditions the polymerization is initiated from the intermediate radicals, and two branches are produced on the nitro groups (reaction D).

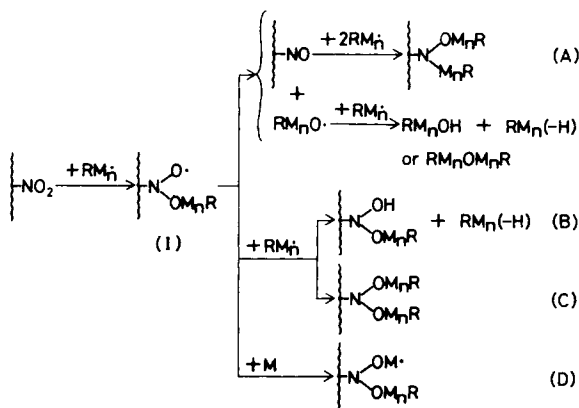
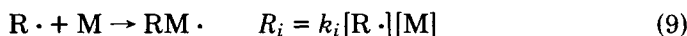


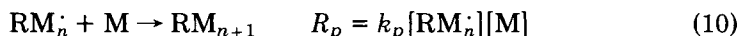
Fig. 1. Reaction scheme of aromatic nitro groups of trunk polymer with growing polymer radicals.

For the derivation of the relationship between the chain transfer constant, extent of monomer conversion, and number of branches in the graft copolymerization, the following elementary reactions are taken into consideration:

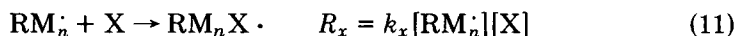
Initiation:



Propagation:



Chain transfer:



Reinitiation:



where X is the nitro group on the trunk polymer, and $RM_n X \cdot$ the intermediate radical (I) in Figure 1.

If it is assumed that $R_p \gg R_i + R_i'$, the rate of disappearance of the monomer may be represented as

$$-\frac{d[M]}{dt} = k_p [RM_n \cdot] [M] \quad (13)$$

Similarly, the rate of consumption of the nitro group may be expressed as

$$-\frac{d[X]}{dt} = k_x [RM_n \cdot] [X] \quad (14)$$

Equations (13) and (14) are combined to give

$$\frac{d[X]}{[X]} = C_x \frac{d[M]}{[M]} \quad (15)$$

where C_x is the chain transfer constant of growing polymer radicals to the nitro groups on the trunk polymer. The integration of eq. (15) leads to

$$\ln \frac{[X]}{[X]_0} = C_x \ln \frac{[M]}{[M]_0} \quad (16)$$

where $[M]_0$ and $[X]_0$ are the initial concentrations of monomer and nitro groups on the trunk polymer, respectively.

If the volume contraction of the reaction systems due to polymerization is neglected, the fraction of nitro groups consumed (p) and the extent of monomer conversion (α) may be written as follows:

$$1 - p = \frac{[X]}{[X]_0} \quad (17)$$

$$1 - \alpha = \frac{[M]}{[M]_0} \quad (18)$$

By substituting eqs. (17) and (18) in eq. (16), we have

$$\ln(1 - p) = C_x \ln(1 - \alpha) \quad (19)$$

Then, the fraction of nitro groups consumed by the reaction with growing polymer radicals is expressed as

$$p = 1 - (1 - \alpha)^{C_x} \quad (20)$$

If $\alpha \ll 0.2$, $(1 - \alpha)^{C_x}$ may be approximated to $1 - C_x \alpha$. Therefore, eq. (20) leads to

$$p = C_x \alpha \quad (21)$$

The number of branches per nitro group, P_G , is expressed as

$$P_G = ap = a[1 - (1 - \alpha)^{C_x}] \quad (22)$$

where a is the number of branches per nitro group reacted with growing polymer radicals, and $1 \leq a \leq 2$ for the reaction scheme given in Figure 1. In eq. (22), $a = 2$ means that all the nitro groups reacted have two branches, and when $a = 1$, reaction (B) occurs predominantly.

The reciprocal of P_G equals the number of nitro groups on the trunk polymer per branch and is expressed as

$$n = \frac{1}{P_G} = \frac{1}{a[1 - (1 - \alpha)^{C_x}]} \quad (23)$$

Assuming the value of a to be constant, for example, 2 in eqs. (22) and (23), the values of P_G and n may be predicted from the chain transfer constant C_x and the extent of the monomer conversion α for a given monomer-nitro group-containing trunk polymer system. A higher value of P_G , that is, a smaller value of n , indicates the possibility that a highly branched graft copolymer may be obtained.

From eqs. (22) and (23) it is concluded that a system with a smaller value of C_x is not suitable for the preparation of highly branched graft copolymers. However, a system with a higher value of C_x does not necessarily result in highly branched copolymers, as P_G and n depend not only on C_x but also on a , the number of branches per nitro group reacted with growing polymer radicals.

Assuming the value of a to be 1 and 2, the relationship between α and n is obtained from eq. (23) for varying values of C_x (Fig. 2).

It is difficult, however, to determine exactly the number of branches per nitro group reacted with growing polymer radicals from experimental data. Even if two branches are formed on a nitro group of trunk polymer, hydrolysis of the ester group yields one grafted polymer (Fig. 3) for PVNB as a trunk polymer.

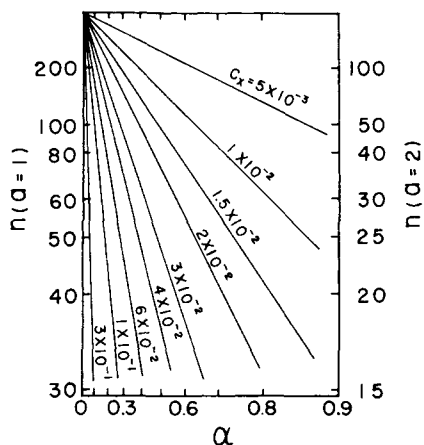


Fig. 2. Relationship between extent of monomer conversion (α) and number of nitro groups in the trunk polymer per branch (n) for varying values of the chain transfer constant of growing polymer radicals to the nitro groups of the trunk polymer C_x for $\alpha = 1$ and 2.

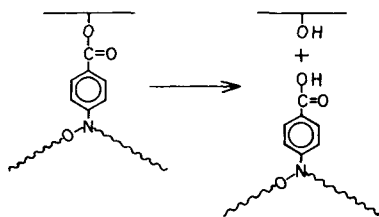


Fig. 3. Hydrolysis of polystyrene-grafted poly(vinyl *p*-nitrobenzoate).

The number of grafted polymers separated by hydrolysis equals the number of nitro group-containing branches irrespective of the number of branches. P_G' is defined as the number of nitro group-containing branches divided by the initial number of nitro groups. If each nitro group reacted with growing polymer radicals has a branch, P_G' equals P_G . When the second branch is formed on some of the nitro groups already having a branch, P_G' becomes smaller than P_G .

The ratio of the nitro groups having branches to those reacted with growing polymer radicals, a' , is defined as

$$a' = \frac{P_G'}{p} = \frac{P_G'}{1 - (1 - \alpha)C_x} \quad (24)$$

The value of a' can be determined experimentally by separating branches from the trunk polymer, for example, by hydrolyzing ester groups in the case of PVNB as a trunk polymer. Therefore, the value of a' calculated from eq. (24) can be compared with that obtained experimentally.

The above treatment will be applied not only to the aromatic nitro group-containing polymers as a trunk polymer but also to those containing any type of side groups to which growing polymer radicals adds easily.

TABLE I
 Values of P_G and α' Obtained for the Graft Copolymerization of Styrene onto Poly(vinyl *p*-Nitrobenzoate)

No.	Reaction conditions			Results				$P_G \times 10^3$	$[1 - (1 - \alpha)C_x] \times 10^3$	α'
	$[PVNB]^a \times 10^2$ mole/l.	$[ST], \times 10$ mole/l.	$[AIBN] \times 10^2$ mole/l.	Time, hr	$\alpha \times 10^2$	Percent Grafting, %	Graft Efficiency, %			
1	9.01	7.81	1.06	14	9.9	15.1	32.4	23.3	33.3	0.700
2				24	15.2	24.2	31.9	33.3	56.4	0.594
3				48	26.1	41.1	33.7	43.5	94.2	0.462
4	8.22	14.3	0.969	6	6.8	31.3	48.5	21.3	22.7	0.938
5				15	15.4	47.6	33.2	25.6	53.2	0.481
6				24	22.3	73.8	35.6	37.0	79.0	0.468
7	8.22	14.3	0.485	6	4.7	40.7	92.0	9.61	15.6	0.616
8				6	5.6	37.8	71.2	11.9	18.4	0.647
9				6	6.8	31.3	48.5	21.3	22.7	0.938
10				6	7.5	16.8	23.8	23.8	25.2	0.944

^a Concentration of repeating unit of PVNB.

Comparison with Experimental Data

The values of P_G' and a' calculated for the previously reported results² on the graft copolymerization of styrene onto PVNB are given in Table I. The values of a' decrease with reaction time and become even less than 0.5 for long reaction times (Table I). Moreover, a' depends on the concentration of initiator AIBN. At higher concentrations of the initiator a' is very close to unity, whereas at low concentrations a' becomes considerably less.

The following three cases help explain this phenomenon: (1) the assumption $R_p \gg R_i + R_i'$ is not fulfilled; (2) attack of the growing polymer radicals on the nitro groups is prevented by the steric hindrance of branches already formed on the trunk polymer, so that the apparent chain transfer constant of growing polymer radicals to the nitro groups on the trunk polymer, C_x , is decreased; and/or (3) side reactions occur by which the intermediate (I) and/or nitroso groups formed through reaction (A) are consumed without formation of branches.

The rate of initiation R_i is $1/27$ of that of propagation R_p even at the highest PVNB concentration employed.² The rate of reinitiation should be very low, therefore the assumption $R_p \gg R_i + R_i'$ is valid. The values of a' decrease with reaction time, namely, with increase in percent grafting. Accordingly, the steric hindrance of branches already formed is responsible for the lowering of a' as a result of decrease in the apparent chain transfer constant of growing polymer radicals to nitro groups. However, even when the percent grafting is not as high, the value of a' is less than unity. Therefore, further explanation is required.

It has been reported that both nitrosobenzene¹⁰ and substituted aromatic nitroso compounds¹¹ react directly with styrene in addition to their reactions with radicals. This type of reaction is also thought to occur for the aromatic nitroso groups on the trunk polymer. As the percent grafting increases, the attack of the growing polymer radicals on the nitroso groups on the trunk polymer will be difficult due to the steric hindrance of branches already formed, and the reaction of nitroso groups with styrene will be more favorable. In conclusion, not only the steric hindrance of branches already formed but also side reactions, such as the nitroso groups formed as an intermediate with styrene, are responsible for the lowering of the value of a' to less than unity.

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