

# Graft Copolymerization of Styrene onto Cellulose Acetate *p*-Nitrobenzoate by Chain Transfer Reaction

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## Synopsis

Styrene was grafted onto cellulose acetate *p*-nitrobenzoate (CANB) by chain transfer reaction of growing polymer radicals to the pendant nitro groups of CANB. A copolymer with a branch for every 17.2 nitro groups was obtained. This result indicates that the pendant aromatic nitro group is more effective in obtaining a graft copolymer by radical mechanism than pendant double bond on the trunk polymer previously reported, where graft copolymers with a branch for several hundred of double bonds are produced.

## INTRODUCTION

We have reported a novel method for preparing graft copolymers by the reaction of pendant nitro groups on trunk polymers with growing polymer radicals,<sup>1</sup> and elucidated the requirements such as reaction conditions and types of trunk polymers for obtaining highly branched graft copolymers.<sup>2-4</sup>

In the present study we intended to apply this method for cellulose acetate *p*-nitrobenzoate as a trunk polymer to prepare highly branched graft copolymers.

## EXPERIMENTAL

### Cellulose Acetate *p*-Nitrobenzoate

Cellulose acetate *p*-nitrobenzoate (CANB) was prepared by esterifying a commercial product of cellulose diacetate (Daicel Ltd.) in chloroform with *p*-nitrobenzoyl chloride in the presence of pyridine as a catalyst according to the method of Dumitriu and Simionescu.<sup>5</sup> The degree of esterification of the product was 2.38 for acetyl and 0.38 for *p*-nitrobenzoyl as determined by elemental analysis, and the number-average molecular weight ( $\bar{M}_n$ ) was  $4.67 \times 10^4$  as determined with a Hewlett-Packard 502 high-speed membrane osmometer with use of dioxane as a solvent.

### Graft Copolymerization

Predetermined amounts of CANB, styrene, and azobisisobutyronitrile (AIBN) were placed in glass ampoules containing dioxane as a solvent. After degassing several times at liquid nitrogen temperature, the ampoules were sealed and the

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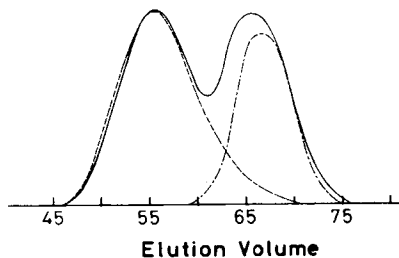


Fig. 1. GPC curves of (---) graft copolymer, (· · ·) nongrafted polystyrene, and (—) the reaction mixture consisting of graft copolymer and nongrafted polystyrene. Percent grafting 34.0%; graft efficiency 38.9%.

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 cyclohexane. The graft copolymer obtained was then hydrolyzed with 6*N* HCl at 100°C for 24 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 product consisting of the graft copolymer and nongrafted polystyrene were obtained with a Toyo Soda high-speed liquid chromatograph HLC-802UR with use of chloroform as a solvent.

## RESULTS AND DISCUSSION

Two peaks appear in a GPC curve for a reaction product consisting of graft copolymer and nongrafted polystyrene (Fig. 1). By extracting nongrafted polystyrene from the mixture with cyclohexane, the high-molecular-weight portion is assigned to graft copolymer, and the low-molecular-weight one is attributed to nongrafted polystyrene.

The results of the graft copolymerization carried out at 60°C for various periods of time are shown in Table I. The percent grafting increased from 15.8 to 44.7% by increasing the reaction time from 6 to 49 hr. The graft efficiency decreased from 57.9% for 6 hr to 31.1% for 49 hr of reaction time. The decrease of graft efficiency with reaction time is due to the steric hindrance of the branches

TABLE I  
Effect of Reaction Time on Graft Copolymerization of Styrene onto Cellulose Acetate *p*-Nitrobenzoate<sup>a</sup>

Reaction time (hr)	Total conversion (%)	Percent grafting (%)	Graft efficiency (%)	$\bar{M}_n \times 10^{-3}$		No. of nitro groups of CANB per branch	No. of PSt branches per trunk polymer
				Grafted PSt	Non-grafted PSt		
6	6.0	15.8	57.9	—	6.59	—	—
14	13.2	24.1	40.0	6.63	6.63	32.8	1.70
24	19.8	33.8	37.8	6.67	6.79	23.5	2.37
49	31.9	44.7	31.1	6.47	7.86	17.2	3.23

<sup>a</sup> CANB, 1 g; [St] =  $7.87 \times 10^{-1}$  mole/liter; [AIBN] =  $1.12 \times 10^{-2}$  mole/liter; dioxane, 50 ml; 60°C.

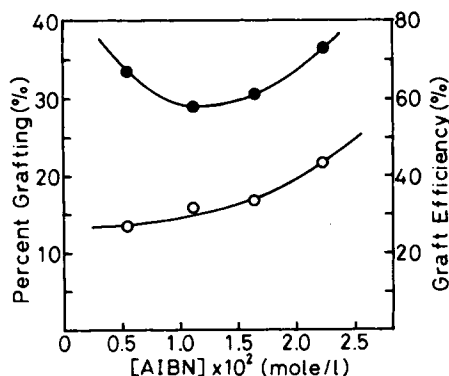


Fig. 2. Effect of AIBN concentration on (○) percent grafting and (●) graft efficiency. Reaction conditions: CANB 1 g;  $[St] = 7.87 \times 10^{-1}$  mole/liter; dioxane, 50 ml; 60°C; 6 hr.

already formed, resulting in the prevention of the attack of the growing polystyrene radicals on nitro groups on CANB.

As no induction period was observed, CANB acts as a retarder in the polymerization of styrene as previously reported for poly(vinyl *p*-nitrobenzoate)<sup>2</sup> and poly(*p*-nitrophenyl acrylate).<sup>4</sup>

The molecular weights of nongrafted polystyrene increased slightly with reaction time, whereas those of grafted polystyrene were almost constant irrespective of reaction time. The number of nitro groups of the trunk polymer CANB per polystyrene branch decreased from 32.7 to 17.2 as the reaction proceeded; namely, under these reaction conditions, a branched copolymer with a branch for every 17.2 nitro groups was obtained. The degree of polymerization of the trunk polymer CANB was 147. Therefore, the number of polystyrene branches increased from 1.70 to 3.23 with reaction time.

As the amount of AIBN increased from  $5.53 \times 10^{-3}$  to  $2.23 \times 10^{-2}$  mole/liter (Table II), both the total conversion and the percent grafting increased, but a minimum appeared in the graft efficiency (Fig. 2). The initial decrease of graft efficiency is attributed to the increase in recombination reaction between growing polymer radicals resulting in the formation of nongrafted polystyrene, as the concentration of growing polymer radicals increases with increasing AIBN concentration.

The molecular weights of both grafted and nongrafted polystyrenes decreased with increasing concentration of AIBN. The decrease in the molecular weights

TABLE II  
Effect of Initiator Concentration on Graft Copolymerization of Styrene onto Cellulose Acetate *p*-Nitrobenzoate<sup>a</sup>

[AIBN] $\times 10^3$ (mole/ liter)	Total conver- sion (%)	Percent grafting (%)	Graft effi- ciency (%)	$\bar{M}_n \times 10^{-3}$		No. of nitro groups of CANB per branch	No. of PSt branches per trunk polymer
				Grafted PSt	Non- grafted PSt		
5.53	4.5	13.4	66.8	8.09	9.57	71.7	0.78
11.2	6.0	15.8	57.9	—	6.59	—	—
16.5	6.1	16.8	61.2	6.18	5.95	43.5	1.28
22.3	7.1	21.9	66.7	5.98	4.20	33.4	1.67

<sup>a</sup> CANB, 1 g;  $[St] = 7.87 \times 10^{-1}$  mole/liter; dioxane, 50 ml; 60°C; 6 hr.

TABLE III  
Effect of Amount of Trunk Polymer on Graft Copolymerization of Styrene onto Cellulose Acetate *p*-Nitrobenzoate<sup>a</sup>

[CANB] (g)	Total conversion (%)	Percent grafting (%)	Graft efficiency (%)	Nongrafted PSt $\bar{M}_n$ $\times 10^{-3}$
0	11.2	—	—	9.57
0.25	8.8	20.1	12.7	7.75
0.50	7.3	14.2	21.7	7.33
0.75	6.6	17.9	45.5	6.88
1.00	6.0	15.8	57.9	6.59

<sup>a</sup> [St] =  $7.87 \times 10^{-1}$  mole/liter; [AIBN] =  $1.12 \times 10^{-2}$  mole/liter; dioxane, 50 ml; 60°C; 6 hr.

is due to the increase in growing polymer radicals with the increase in AIBN concentration resulting in the increase of the rate of termination reaction as compared with that of the propagation reaction. The number of branches per trunk polymer increased from 0.78 to 1.68.

With increase in the amount of the trunk polymer CANB in the reaction mixture (Table III), the total conversion decreased because of the retardation of CANB. The percent grafting decreased initially and then became almost constant irrespective of the amount of trunk polymer, and the graft efficiency increased linearly with the increase in CANB as observed from Figure 3. The graft efficiency increases, since the reaction of growing polystyrene radicals with the nitro groups on CANB leading to the grafted polystyrene occurs more frequently than the recombination of two growing polystyrene radicals with increase in concentration of CANB.

Previously, we had carried out graft copolymerization of styrene and methyl methacrylate onto cellulose acetate acrylate and cellulose acetate vinylacetate as trunk polymers with pendant double bonds, and obtained graft copolymers with a branch for several hundred double bonds.<sup>6,7</sup> Compared to the pendant double bond on the trunk polymers, the pendant aromatic nitro group is by far more effective in obtaining graft copolymers by radical mechanism, since graft copolymers with a branch for tens of nitro groups are formed.

In the present study, a graft copolymer was prepared with a branch for every 17 nitro groups for the longest reaction time of 49 hr, whereas a branch was obtained for every 23 nitro groups for a reaction time of 48 hr under similar reaction conditions when poly(vinyl *p*-nitrobenzoate) was used as a trunk polymer. This

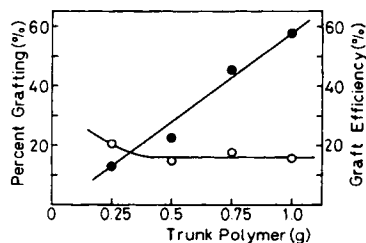


Fig. 3. Effect of amount of trunk polymer cellulose acetate *p*-nitrobenzoate (CANB) on (○) percent grafting and (●) graft efficiency. Reaction conditions: [St] =  $7.87 \times 10^{-1}$  mole/liter; [AIBN] =  $1.12 \times 10^{-2}$  mole/liter; dioxane, 50 ml; 60°C; 6 hr.

is attributed to the difference in the extent of steric hindrance, since the nitro groups on CANB exist less frequently than those on poly(vinyl *p*-nitrobenzoate).

Since the degree of polymerization of the trunk polymer CANB used in this study was rather low, that is to say 147, the number of branches was not high. However, it is expected that graft copolymers with a large number of branches can be prepared if the molecular weight of trunk polymer is high.

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