

Graft Polymerization of Some Vinyl Monomers onto Acrylic Rubber. I. Chain Transfer and Grafting Reaction

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Synopsis

The grafting reactions of styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc) were investigated in the presence of *n*-butyl acrylate-acrylonitrile copolymer. Results showed that the nature of monomer and initiator were the major factors influencing the grafting activity. The grafting efficiency was 0.87 for St, 0.26 for MMA, and 0.18 for VAc under the most favorable conditions. Acrylic rubber reduced the rate of polymerization, and the retarding effect increased in the order St, MMA, VAc. The chain transfer constants for acrylic rubber were evaluated to be 4.8×10^{-4} for St, 1.27×10^{-3} for MMA, and 1.45×10^{-3} for VAc. The rate of polymerization and the grafting efficiency decreased with increasing acrylonitrile content in acrylic rubber, while the chain transfer constant of St for acrylic rubber remained practically unchanged.

INTRODUCTION

Graft polymers of rubber with vinyl monomers have been examined by various authors from different points of view. Merrett¹ and Scanlan² carried out the polymerizations of vinyl monomers in the presence of dihydro-myrcene. Graft polymers of natural rubber with styrene were investigated by Blanchett,³ Bevilacqua,⁴ and Minoura et al.⁵ Recently, radiation-induced⁶ and cationic⁷ graft polymerizations of vinyl monomers onto natural rubber have been also reported. The chain transfer constant for a backbone polymer is important to investigate the mechanism of the grafting reaction. Some reports have been published concerning the branched vinyl polymers⁸⁻¹⁰ and the chain-transfer constants for the branching reactions.^{11,12} However, very few data have been reported so far with respect to the grafting reactions of vinyl monomers onto acrylic rubber.

The present work is primarily concerned with the structural elucidation of vinyl monomer-acrylic rubber graft polymers. Polymerizations of styrene, methyl methacrylate, and vinyl acetate were carried out in the presence of acrylic rubber, with benzoyl peroxide or 2,2-azobisisobutyronitrile as a catalyst. Effects of the nature of monomer and the composition of acrylic rubber on the grafting activity are described, together with some remarks about the chain transfer constants and possible significance of the results.

EXPERIMENTAL

Materials

Benzoyl peroxide (BPO) was precipitated twice with methanol from chloroform solution and was dried in a vacuum desiccator for three days. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol solution. Potassium persulfate (KPS) was recrystallized from aqueous solution. The monomers, *n*-butyl acrylate (BA), acrylonitrile (AN), styrene (St), methyl methacrylate (MMA), and vinyl acetate (Vac), were purified and distilled. Methyl ethyl ketone (MEK) and benzene were twice distilled before use.

Preparation of Acrylic Rubber

The emulsion polymerization was carried out in a four-necked flask fitted with a stirrer, a thermometer, a nitrogen inlet tube, and a reflux condenser, to prepare various kinds of acrylic rubber. Deionized aqueous solutions of emulsifier and initiator were added into a given amount of monomers and *n*-lauryl mercaptan. The polymerization was continued at 75°C for 5 to 7 hr under nitrogen atmosphere. The standard ingredients were as follows: 500 g deionized water, 90 g *n*-butyl acrylate, 10 g acrylonitrile, 0.05 g *n*-lauryl mercaptan, 2 g sodium laurylsulfate, and 0.05 g potassium persulfate. In order to precipitate the copolymer, the emulsion was cooled and poured slowly into six times its volume of a methanol-water mixture (1:1 by volume) containing 3–5% AlCl₃, with rapid stirring.

Preparation of Graft Polymers

A measured amount of monomer was added to the acrylic rubber and allowed to swell for 48 hr in an ampoule. Then the catalyst, dissolved in the residual monomer and benzene, was added. The mixture was agitated sufficiently to provide a homogeneous phase and was degassed with nitrogen. The polymerizations were conducted with shaking at 75°C. After the required time of polymerization, the solution was poured into about eight times its volume of methanol, and the precipitate was filtered and dried.

Separation and Confirmation of Graft Polymers

The precipitated polymers were heterogeneous mixtures of homopolymers, graft polymers, and unreacted acrylic rubber. To investigate the grafting activity, fractionation methods were attempted. The homopolymers of styrene and methyl methacrylate were separated by fractional precipitation from methyl ethyl ketone solution, with methanol as the precipitant. Ten grams of each polymer was dissolved in 675 ml methyl ethyl ketone and the fractionation was carried out by adding measured amounts of methanol with stirring. The precipitate was allowed to stand for 48 hr at 30°C and then separated by decantation. Figure 1 shows typical fractionation curves of polystyrene grafted onto acrylic rubber, with benzoyl peroxide and 2,2-azobisisobutyronitrile as the catalyst. Three individual fractions were observed. The composition of each fraction was investigated

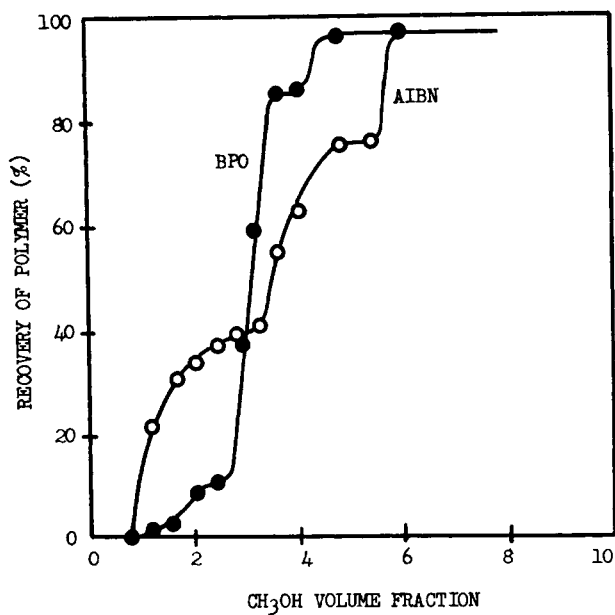


Fig. 1. Fractionation of polystyrene grafted onto 40 wt-% rubber of 90/10 *n*-butyl acrylate/acrylonitrile copolymers.

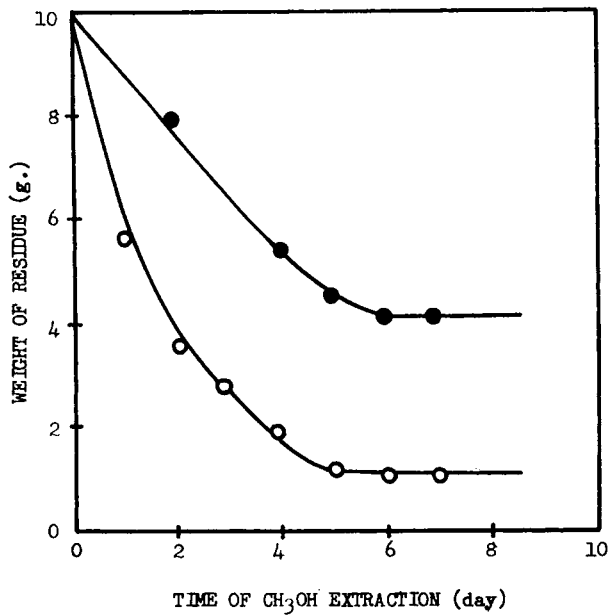


Fig. 2. Fractionation of 10 g poly(vinyl acetate) grafted onto 10 wt-% rubber of 90/10 *n*-butyl acrylate/acrylonitrile copolymers (●) and of the corresponding mixtures (○).

by carbon analysis and infrared spectroscopy. The first fraction was found to be polystyrene, based on the absence of the absorption band at 1735 cm^{-1} for the ester carbonyl group. Carbon analysis showed the second and the third fraction to be graft polymers and unreacted rubber, respectively. However, unreacted rubber did not exist where the concentration of rubber was less than 10%. This suggests that the rubber was completely grafted by polystyrene. Samples of poly(methyl methacrylate) grafted onto acrylic rubber were also fractionated by the same technique.

Solvent extraction with methanol was feasible to separate homopolymers from poly(vinyl acetate) grafted onto acrylic rubber. The soluble polymers were recovered from methanol solution with water as precipitant and were confirmed to be poly(vinyl acetate) by their infrared spectrum. As additional proof that this technique is valid, a mixture of poly(vinyl acetate) and acrylic rubber could be separated into its components by subjecting it to the same treatment. The results are shown in Figure 2.

RESULTS AND DISCUSSION

Rate of Polymerization

Styrene, methyl methacrylate, and vinyl acetate were polymerized in the presence of acrylic rubber, with various concentrations of benzoyl peroxide and 2,2-azobisisobutyronitrile. Figure 3 shows a typical set of time-conversion curves in which the monomer was methyl methacrylate. The gel

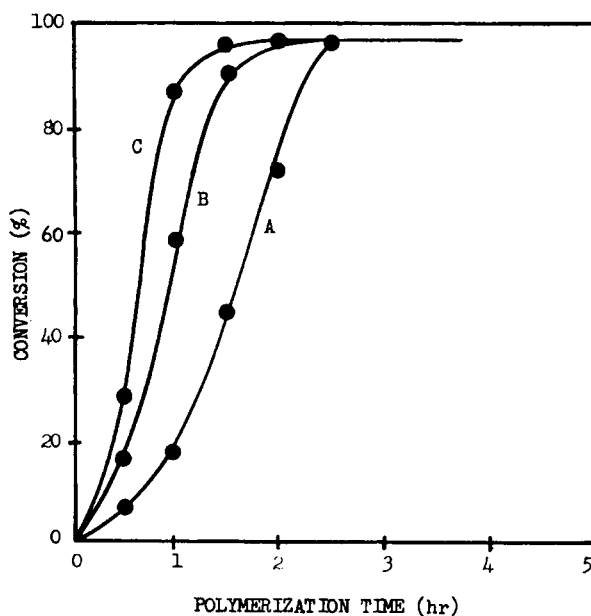


Fig. 3. Bulk polymerization of methyl methacrylate in the presence of 10 wt-% acrylic rubber at 75°C . $[\text{AIBN}]$: (A) 0.61×10^{-3} mole/liter; (B) 3.25×10^{-3} mole/liter; (C) 6.10×10^{-3} mole/liter.

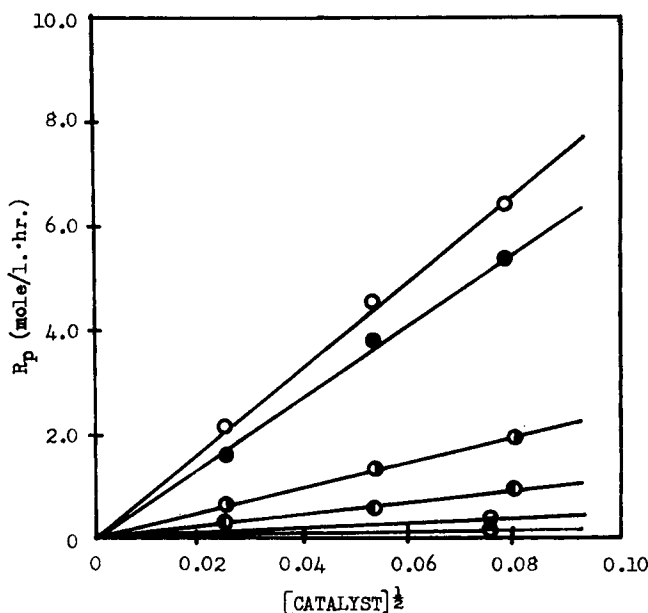


Fig. 4. Rate of polymerization vs. $[\text{catalyst}]^{1/2}$ for AIBN and BPO: (○) St-AIBN; (●) BPO; (○) MMA-AIBN; (●) BPO; (○) VAc-AIBN; (●) BPO.

effect, which was distinct in the polymerizations of styrene and methyl methacrylate, was not observed in the polymerization of vinyl acetate. Figure 4 shows the kinetic order with respect to the catalyst concentration. Each rate of polymerization, which was evaluated at about 10% conversion, was approximately proportional to the square root of the catalyst concentration. The rate of polymerization catalyzed by benzoyl peroxide was smaller than that catalyzed by 2,2-azobisisobutyronitrile, which was due to the difference of the decomposition rate of these catalysts. The rate of polymerization increased with increasing reactivity of growing homopolymer radicals in the order styrene, methyl methacrylate, vinyl acetate.

Grafting Activity

The grafting efficiency was evaluated by dividing the amount of grafted monomer by the total amount of polymerized monomer. The results are summarized in Table I.

The grafting efficiency depended upon the nature of the catalyst, and the difference of the efficiency was especially great in the polymerization of styrene, where the efficiency was 0.79 and 0.30 for benzoyl peroxide and 2,2-azobisisobutyronitrile, respectively. These are in agreement with the results reported by Merrett et al.^{1,2} They interpreted the high grafting activity of benzoyl peroxide to be the result of the combined effect of simple chain transfer and the attack of the catalyst radical on the backbone polymer. On the other hand, the low grafting activity of 2,2-azobisisobutyro-

TABLE I
Graft Polymerization of Styrene, Methyl Methacrylate, and
Vinyl Acetate onto Acrylic Rubber at 75°C.^a

Catalyst	Catalyst concn., (moles/liter) × 10 ³	Time, hr	Polymerized monomer, wt-% for initial monomer	Grafting efficiency
Styrene				
BPO	4.1	4	16.8	0.87
	17.2		35.5	0.86
	33.4		60.8	0.84
	50.0		82.0	0.79
	83.2		93.9	0.73
AIBN	6.2	4	25.9	0.36
	24.0		60.7	0.34
	49.5		94.2	0.30
	73.1		95.3	0.28
	122.6		95.7	0.24
Methyl Methacrylate				
BPO	0.6	2	54.1	0.21
		3	80.8	0.26
	3.1	2	90.5	0.18
		3	98.9	0.24
		3	99.7	0.20
AIBN	0.6	2	71.5	0.15
		3	97.8	0.18
	3.1	2	98.7	0.10
		3	98.8	0.14
	6.1	2	99.5	0.11
		3	99.8	0.12
Vinyl Acetate				
BPO	0.6	6	65.7	0.18
	3.1		88.2	0.16
	6.1		88.4	0.05
AIBN	0.6	6	85.2	0.06
	3.1		94.4	0.03
	6.1		97.5	0.01

^a The concentration of 90/10 *n*-butyl acrylate/acrylonitrile copolymers in the charge was 10 wt-%.

nitrile was connected with the inferior capacity of the relatively stable cyanoisopropyl radicals to attack the backbone polymer. The grafting efficiency increased with increasing reactivity of monomers in the order vinyl acetate, methyl methacrylate, styrene. This was adverse to the order observed in the rate of polymerization of each monomer. When backbone polymer radicals are formed by the attack of the catalyst radical, the grafting efficiency depends especially upon the efficiency of reinitiation by back-

bone polymer radicals. While styrene monomer is very reactive and the re-initiation is facilitated to result in the high grafting efficiency, the reverse is the case with vinyl acetate. It seems to be a main factor for the very low grafting efficiency of vinyl acetate that the chain transfer constant for monomer is high and the homopolymerization is facilitated.

Concentration and Composition of Acrylic Rubber

Each monomer was polymerized in benzene solution with different concentrations and various compositions of acrylic rubber. Acrylic rubber reduced the rate of polymerization. The effects are shown in Figure 5, where R_p/R_0 , the ratio of the rates in the presence and absence of rubber, is plotted against $[P]/[M]$, where $[P]$ and $[M]$ are the initial concentrations of acrylic rubber and monomer, respectively. The retarding effect increased with increasing reactivity of growing homopolymer radicals and catalyst radicals. This suggests that the retardation of the rate of polymerization is due to the

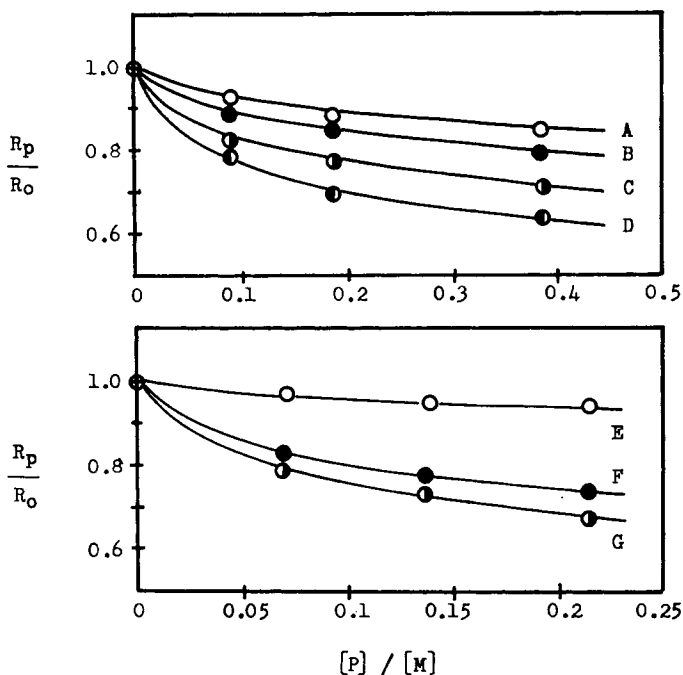


Fig. 5. Retarding effect of acrylic rubber on rates of polymerization:

	BA/AN	Monomer	Catalyst
A:	90/10	St	AIBN
B:	90/10	St	BPO
C:	90/10	MMA	BPO
D:	90/10	VAc	BPO
E:	100/0	St	AIBN
F:	80/20	St	AIBN
G:	60/40	St	AIBN

mutual combination of backbone polymer radicals and homopolymer radicals, the so-called cross termination. Vinyl acetate is relatively stable against the attack of radicals but forms very reactive radicals, which suggests the superior capacity of backbone polymer radicals to combine with homopolymer radicals. Benzoyl peroxides, as compared with 2,2-azobisisobutyronitrile, form more backbone polymer radicals by the direct attack on the backbone polymer and accelerates the cross termination.

Moreover, the retarding effect increased with increasing acrylonitrile content in acrylic rubber. This suggests that backbone polymer radicals

TABLE II
Effect of Concentration and Composition of Acrylic Rubber on
Graft Polymerization Catalyzed by BPO at 75°C

Rubber P, BA/AN wt. ratio	Monomer M	Charge [P]/[M]	Polymerized monomer, wt-% for initial monomer	Grafting efficiency
95/5	St	10/90	66.5	0.79
			95.6	0.81
80/20	St	10/90	56.8	0.76
			96.8	0.80
70/30	St	10/90	55.3	0.68
			96.2	0.73
60/40	St	10/90	54.5	0.58
			97.2	0.67
90/10	St	5/95	78.8	0.70
		10/90	72.5	0.73
		15/85	68.4	0.78
100/0	MMA	5/95	20.6	0.21
			44.5	0.27
		10/90	19.4	0.20
			40.4	0.29
		15/85	16.8	0.28
			35.3	0.33

formed on *n*-butyl acrylate units, as compared with those formed on acrylonitrile units, are higher in the efficiency of reinitiation. This is an adverse tendency to monomer reactivity ratios,¹³ according to which the reactivity of acrylonitrile radicals toward styrene monomer is higher than that of *n*-butyl acrylate radicals. The reason for this difference is not clear, but, in case of radicals formed on the backbone polymer, the reactivity may be affected by the neighboring groups. The grafting efficiency increased with increasing rubber concentration and with decreasing acrylonitrile content in acrylic rubber, as is evident in Table II. This indicates that the increase of the acrylonitrile content in acrylic rubber reduces the reinitiation by backbone polymer radicals. This is in agreement with the results observed in the retarding effect.

Chain Transfer Constant for Acrylic Rubber

The degree of polymerization is given by

$$\frac{1}{\bar{P}_n} = \frac{1}{P_{n0}} + C_p \frac{[P]}{[M]} \quad (1)$$

where \bar{P}_n and \bar{P}_{n0} are the degree of polymerization of the homopolymer formed in the presence and absence of the backbone polymer, $[P]$ and $[M]$ are initial concentrations of the backbone polymer and monomer, and C_p , the chain transfer constant, is equal to k_{tr}/k_p ; k_{tr} and k_p are the termination and propagation rate constants, respectively. Plots of $1/\bar{P}_n - 1/\bar{P}_{n0}$ versus $[P]/[M]$ for various transfer reactions are shown in Figure 6, and chain transfer constants C_p , evaluated from their slopes, are summarized in Table III. Although the retarding effect means that the simple transfer

TABLE III
Chain Transfer Constants^a

Rubber BA/AN	Monomer	$C_p \times 10^3$
100/0	VAc	1.45
100/0	MMA	1.27
100/0	St	0.48
80/20	St	0.48
60/40	St	0.48

^a Calculated from the slopes of plots of eq. (1) (Fig. 5).

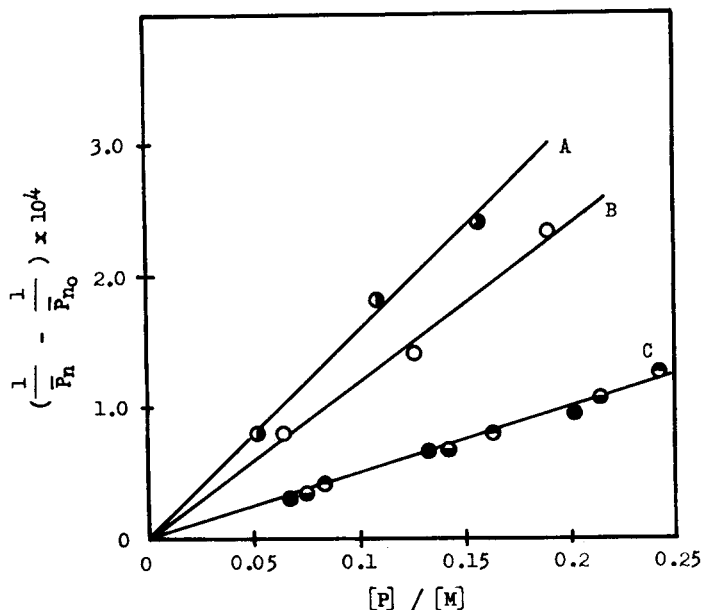


Fig. 6. Evaluation of chain transfer constants [plots of eq. (1)]: (A) VAc - BA/AN = 100/0; (B) MMA - BA/AN = 100/0; (C) St - BA/AN = 100/0 (●), - BA/AN = 80/20 (◐), - BA/AN = 60/40 (◑).

scheme cannot be strictly applicable, it is considered that the straight lines actually obtained in Figure 6 still provide a useful measure of the chain transfer constant. \bar{P}_n was calculated from the intrinsic viscosity of homopolymers recovered after removal of unreacted backbone polymers and pure graft polymers by fractionation. The respective relationships used are as follows:

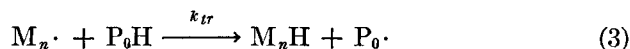
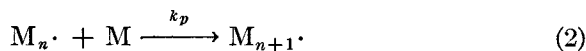
$$\text{Polystyrene}^{14}: \quad \bar{P}_n = 1.63 \times 10^3 [\eta]^{1.39}$$

$$\text{Poly(methyl methacrylate)}^{15}: \quad \bar{P}_n = 2.81 \times 10^3 [\eta]^{1.32}$$

$$\text{Poly(vinyl acetate)}^{16}: \quad \bar{P}_n = 2.91 \times 10^3 [\eta]^{1.45}$$

where $[\eta]$ is the intrinsic viscosity determined in benzene at 25°C.

In general, C_p is governed by the reactivity of radicals and the strength of C-H bonds in the backbone polymer. C_p increased with increasing reactivity of growing homopolymer radicals in the order styrene, methyl methacrylate, vinyl acetate. The high reactivity of growing homopolymer radicals means not only an increase of k_{tr} , but also an increase of k_p and does not necessarily result in a high C_p value. The normal propagation and transfer reaction is shown by eqs. (2) and (3):



where $M_n \cdot$, M, and P_0H are growing homopolymer radicals, monomer molecules, and backbone polymer molecules, respectively; k_p is affected by both the reactivities of growing homopolymer radicals ($M_n \cdot$) and monomer molecules, while k_{tr} is affected only by the reactivity of growing homopolymer radicals. The reactivities of $M_n \cdot$ and M are in the reverse order in these three vinyl monomers. Accordingly, k_{tr} seems to be affected strongly by the reactivities of $M_n \cdot$, and the C_p values are apparently in the same order as the reactivities of $M_n \cdot$. The acrylonitrile content in acrylic rubber is found to have no influence on C_p of styrene.

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