

Radiation-Induced Graft Copolymerization of Mixtures of Styrene and *n*-Butyl Acrylate onto Cellulose and Cellulose Triacetate

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Synopsis

Mixtures of styrene and *n*-butyl acrylate of various compositions were grafted onto cellulose and cellulose triacetate fibers preirradiated with γ -rays at 0°C in air. Monomer reactivity ratios of the grafted copolymers were found to be different from those of the nongrafted copolymers or those of AIBN-initiated copolymers. The active species initiating the graft copolymerization were trapped radicals for cellulose and peroxides for cellulose triacetate. Kinetic investigations of the graft copolymerization of styrene onto preirradiated cellulose triacetate fibers were also carried out, and it was found that the kinetic scheme for radical polymerization is also applicable to graft copolymerization in a heterogeneous system.

INTRODUCTION

The mechanism of radiation-induced graft copolymerization is complicated so that many problems have still been left unsolved. Especially if the reaction is carried out in a heterogeneous system, the situation becomes more intricate owing to the interactions among trunk polymer, monomer, and solvent within the matrix of the trunk polymer.

The purpose of the present investigation is to elucidate the reaction process and the active species in the graft copolymerization of mixtures of monomers onto cellulose and cellulose triacetate fibers with preirradiation technique. In the graft copolymerization, mixtures of styrene and *n*-butyl acrylate were grafted, and the monomer reactivity ratios were determined for both the grafted copolymers and the nongrafted copolymers and were compared with those of the copolymers initiated with 2,2'-azobisisobutyronitrile (AIBN). The interactions among trunk polymer, monomer, and solvent were examined by adsorption measurement, and their effects on the reaction process were discussed. The active species responsible for the initiation of graft copolymerization was determined from peroxide measurement. It was also examined whether the kinetic equations

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for ordinary radical polymerization are applicable to the graft copolymerization of styrene onto cellulose triacetate.

EXPERIMENTAL

Materials

Cellulose triacetate fibers (a product of Mitsubishi Rayon Co., continuous filament 75 den/20 fil, acetic acid content 61.1%) were extracted with water for 7 hr and then with methanol for 7 hr.

As cellulose fibers, high-tenacity rayon (a product of Toho Rayon Co.) was subjected to Soxhlet extraction with ethanol for 7 hr and then with ether for 7 hr, and dried in vacuo at room temperature.

Styrene, *n*-butyl acrylate, and methanol were purified according to the conventional methods.

Preparation of Graft Copolymers

Sample fibers, 0.3 g, were placed in glass ampoules and irradiated with γ -rays from a cobalt 60 source at 0°C in air. After the irradiation, the ampoules were kept in a Dry Ice-methanol bath, and the mixtures (in a total of 8 ml) of styrene and *n*-butyl acrylate of various compositions were added. At the same time, 8 ml methanol was also added as solvent. After degassing four times at liquid nitrogen temperature, the ampoules were sealed and heated at a given temperature to carry out graft copolymerization.

When cellulose triacetate was used as trunk polymer, the content was dissolved in methylene chloride, and the solution was precipitated with methanol in order to make the extraction of the nongrafted copolymer easier. The nongrafted copolymer was extracted with benzene for 120 hr. The residue was again dissolved in methylene chloride, and the solution was reprecipitated with methanol. The precipitate was again extracted for 72 hr, but almost none was extracted. Therefore, it seems that most of the nongrafted copolymer was extracted in the extraction for 120 hr. When high-tenacity rayon was used as the trunk polymer, nongrafted copolymer was extracted with benzene for 120 hr.

The graft copolymers of styrene and *n*-butyl acrylate onto cellulose triacetate or rayon fibers, which were isolated from the nongrafted copolymer by extraction, were refluxed for 24 hr in mixtures of 6*N* hydrochloric acid and methylene chloride or dioxane in order to hydrolyze the trunk polymer, cellulose, or cellulose triacetate and to isolate the grafted (branch) copolymer. When dioxane was used as solvent, a better yield and faster rate of hydrolysis were attained. When the hydrolysis was carried out in a homogeneous system of dioxane and 6*N* hydrochloric acid, recovery of the grafted copolymer was more than 90%, and no absorption of hydroxyl groups was observed in the infrared absorption spectra of the hydrolyzed residues, indicating that no ester group of *n*-butyl acrylate in the copolymer was hydrolyzed.

The composition of the grafted and the nongrafted copolymers (the total of that formed in solution and that within the matrix of trunk polymer) was determined from the ultraviolet absorption of styrene unit at 269 $m\mu$ using tetrahydrofuran as solvent. The degree of grafting (D.G.) and the graft efficiency (G.E.) were calculated from the following equations:

$$\text{D.G.} = \frac{\text{wt. grafted copolymer}}{\text{wt. trunk polymer}}$$

$$\text{G.E.} = \frac{\text{wt. grafted copolymer}}{\text{wt. grafted copolymer} + \text{wt. nongrafted copolymer}}$$

Viscometry

Viscosities of the grafted and the nongrafted copolymers were measured in chloroform at 30°C. The molecular weight of cellulose triacetate was calculated from the viscosities in methylene chloride-ethyl alcohol (80/20 volume ratio) at 25°C using the equation¹

$$[\eta] = 1.39 \times 10^{-4} \bar{M}_v^{0.834}$$

The molecular weight of the grafted and the nongrafted polystyrene in the kinetic experiments was determined from the viscosities in benzene solutions at 30°C using the equation²

$$\bar{M}_n = 1.67 \times 10^5 [\eta]^{1.37}$$

Adsorption of Monomers Onto Cellulose and Cellulose Triacetate Fibers

Fibers (0.15 g) were immersed in mixtures of 4 ml of monomer and 4 ml methanol, and the composition of the solution outside the fibers was determined by ultraviolet spectroscopy using an absorption of styrene at 291 $m\mu$ as the key band. About 0.1% sulfur was added to the monomer solution to inhibit the polymerization of monomer during the adsorption measurements. In a blank test in the absence of the fibers, the composition of the solutions after 18 hr at room temperature agreed with the initial composition of the solutions.

Determination of Peroxide Concentration

The determination of peroxides formed in cellulose triacetate fibers by irradiation was carried out according to Wagner's method.³ Cellulose triacetate fibers (0.3 g), irradiated, were dissolved in methylene chloride, and 5 ml isopropyl alcohol and 1 ml glacial acetic acid were added. The mixture was refluxed for 10 min, and the isolated iodine was then titrated with a *N*/100 sodium thiosulfate solution.

Polymerization of the Monomers with 2,2'-Azobisisobutyronitrile (AIBN)

AIBN-initiated copolymerization of styrene with *n*-butyl acrylate was carried out at 50°C for 70 min. Mixtures of 8 ml of monomer in 8 ml

methanol were initiated with 0.02 g AIBN. The yield was maintained to approximately 1%.

RESULTS AND DISCUSSION

Degree of Grafting and Graft Efficiency

The degree of grafting and the graft efficiency in the graft copolymerization of the mixtures of styrene and *n*-butyl acrylate are shown in Figures 1 and 2 for cellulose triacetate and cellulose fibers (rayon), respectively. The reaction was carried out at 50°C for 24 hr for either case. The nongrafted

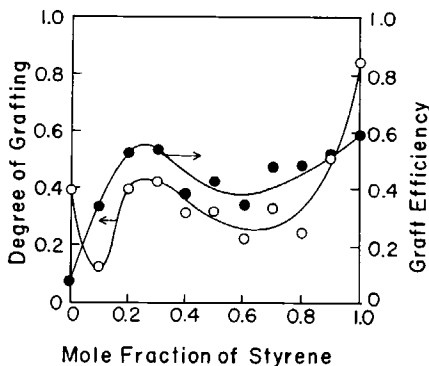


Fig. 1. Effects of composition of monomer mixtures on the degree of grafting and the graft efficiency in graft copolymerization of mixtures of styrene and *n*-butyl acrylate onto cellulose triacetate preirradiated with γ -rays in air at 0°C. Irradiation conditions: dose rate 1.67×10^6 r/hr, total dose 3.0×10^6 r. Grafting conditions: 50°C, 24 hr.

copolymer was mostly produced in solution near the fiber for cellulose triacetate as trunk polymer, whereas most of the nongrafted polymer was formed within the matrix of cellulose fibers when cellulose was used as trunk polymer.

Grafting Onto Cellulose Triacetate Fibers. When cellulose triacetate fibers were used as trunk polymer, with the addition of a small amount of styrene to *n*-butyl acrylate in the monomer mixtures, the degree of grafting decreased rather rapidly with addition of styrene, indicating a minimum at about 10% of styrene content. It is supposed that the action of styrene as a scavenger of radicals formed on the trunk polymer⁴⁻⁶ becomes more dominant than the propagation reaction in this region of smaller styrene content, so that the initiation efficiency of graft copolymerization is lowered.

With further addition of styrene to the monomer mixtures, the degree of grafting showed a maximum at about 20-30% of styrene content and then decreased with a broad minimum at about 60-70% styrene content. When a small amount of *n*-butyl acrylate (up to about 30%) was contained in the monomer mixture, the degree of grafting was remarkably affected by the reactivity of *n*-butyl acrylate in the graft copolymerization of the mixtures

of styrene and *n*-butyl acrylate. On the other hand, the rate of radical-initiated homopolymerization of *n*-butyl acrylate was faster than that of styrene. Therefore, the graft efficiency of *n*-butyl acrylate alone becomes lower than that of styrene alone. As the styrene content in the monomer mixtures increased, the graft efficiency changed rather moderately with the styrene content compared to the degree of grafting, and approached gradually that of styrene alone. It is supposed that, when the polymerization occurs within the matrix of the cellulose triacetate fibers, the reactivity of styrene increases.

Grafting Onto Cellulose Fibers. In graft copolymerization onto cellulose fibers, the degree of grafting was remarkably affected by the dose rate and became larger with higher dose rates, as seen in Figure 2. As will be shown in a later section, the active species in the graft copolymerization onto cellulose irradiated in air is the radicals which are captured in the trunk polymer cellulose. Gotoda et al.²⁰ determined the active species on the irradiated cellulose by ESR spectroscopy and the titration with ferrous ion. They observed that the rate of deactivation of the active species is temperature dependent and supposed that the active species exist with different lives, as the rate of deactivation is not uniform. Therefore, when the total dose is kept constant, at a lower dose rate the deactivation of shorter-lived radicals produced may occur during the irradiation. The decrease of the

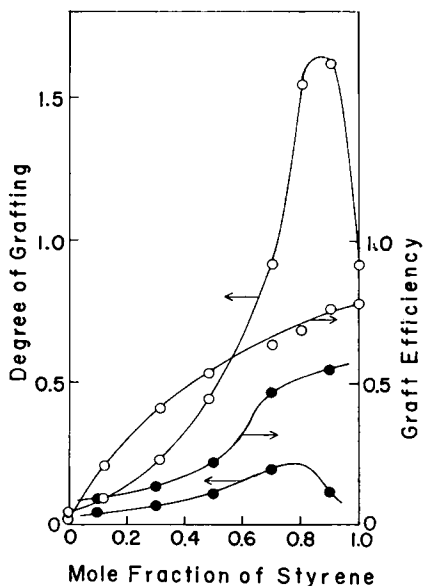


Fig. 2. Effects of composition of monomer mixtures on the degree of grafting and the graft efficiency in graft copolymerization of mixtures of styrene and *n*-butyl acrylate onto cellulose preirradiated with γ -rays in air at 0°C. Irradiation conditions: dose rate (○) 1.0×10^6 r/hr; (●) 5.0×10^4 r/hr; total dose 3.0×10^6 r. Grafting conditions: 50°C, 24 hr.

degree of grafting with decrease in the dose rate may be explained by the deactivation of a part of the radicals.

The degree of grafting increased as the fraction of styrene content in the mixtures increased, and had a maximum at 80–90% of styrene content. The graft efficiency increased also with increase in styrene content in the mixtures and approached that of styrene alone. It is not clear why a maximum degree of grafting appeared at 80–90% styrene content in the mixtures.

Intrinsic Viscosity of Copolymers

The values of the intrinsic viscosity of the grafted and nongrafted copolymers are given in Figure 3 for graft copolymerization onto cellulose triacetate. These values are fairly larger than those of the usual radical-initiated polymers. It is supposed that the rate of termination reaction is small since the polymerization system is inhomogeneous, and gel effect occurs.

Generally, the molecular weight of polymers is remarkably affected by the rate of the termination reaction, especially in copolymerization systems. The termination occurs between unlike radical chain ends as well as between like radical chain ends. The cross-termination rate constant k_{ab} is expressed by the termination rate constants k_{ia} and k_{ib} of the respective homopolymerizations:

$$k_{iab} = \phi(k_{ia} \cdot k_{ib})^{1/2}$$

where ϕ indicates the feasibility of the cross-termination compared to the termination between like radical chain ends.

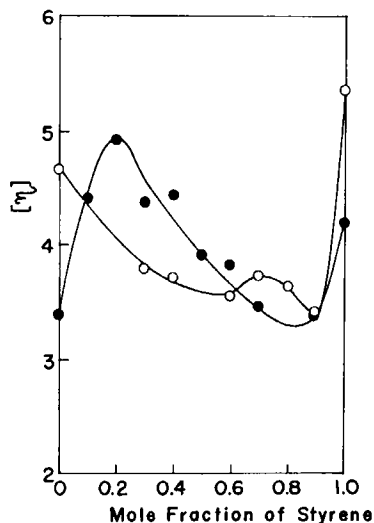
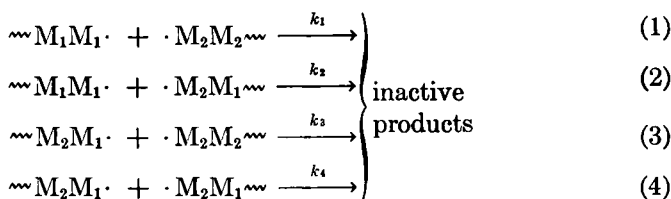


Fig. 3. Effect of composition of monomer mixtures on the intrinsic viscosity of copolymers: trunk polymer, cellulose triacetate; (○) grafted copolymer; (●) nongrafted copolymer. Experimental conditions are same as in Fig. 1.

The value of ϕ is 1 to 2 for a pair of very similar monomers, but generally it is fairly larger than 2, indicating that the cross-termination occurs more easily than the termination between like radical chain ends, and the degree of polymerization of copolymers is remarkably affected by the value of ϕ . It has been reported that the value of ϕ is also affected by the monomer composition. In the copolymerization of *n*-butyl acrylate with styrene, ϕ decreased with increasing *n*-butyl acrylate content.⁷ Barb⁸ ascribed this effect to the influence of the penultimate unit in the copolymer radicals; namely, in a mixture containing predominantly *n*-butyl acrylate, the penultimate units of the radicals ending with styrene will be mostly *n*-butyl acrylate, whereas at high styrene contents the penultimate units will be mostly styrene. Barb⁸ also assumed that the cross-termination will be hindered by the polar repulsion between the penultimate *n*-butyl acrylate unit of a copolymeric radical and the *n*-butyl acrylate end of another radical. Based on Barb's assumption, an equation was obtained which expresses the variation of ϕ as a function of the composition of the reaction mixtures and was applied to the *n*-butyl acrylate-styrene system.⁹

If the effect of the penultimate units is considered, the scheme of the cross-termination between styrene (M_1) and *n*-butyl acrylate (M_2) can be expressed as follows:



where the cross-termination rate constants, k_1 , k_2 , k_3 , and k_4 , have different values.

If $[M_2]/[M_1]$ is large, i.e., the content of *n*-butyl acrylate in the monomer mixtures is large, step (3) occurs preferentially as the termination reaction, whereas step (2) occurs if $[M_2]/[M_1]$ is small. For simplicity, if it is assumed that the reactivity of the copolymeric radicals ending with styrene is affected by the penultimate units and the effect of the penultimate units on the copolymeric radicals ending with *n*-butyl acrylate is neglected, $k_1 = k_2$, $k_3 = k_4$, and $k_1 \neq k_3$ can be obtained. It was reported that if k_3/k_1 is assumed to be $1/10$, the apparent variation of ϕ with composition of the mixtures can be explained in the styrene-*n*-butyl acrylate copolymerization system.⁹

If this assumption is thought to be applicable to the graft copolymerization, the decrease in intrinsic viscosity of grafted and nongrafted copolymers with increasing styrene content in the monomer mixtures can also be explained by the increase in the ϕ values. The intrinsic viscosities of both polystyrene- and poly(*n*-butyl acrylate)-grafted copolymers are larger than those of nongrafted polystyrene and poly(*n*-butyl acrylate) as usually reported, whereas those of nongrafted copolymers are larger than those of

grafted copolymers for less than 0.5 of the styrene fractions of monomer mixtures. This indicates the remarkable contribution of the gel effect on the formation of nongrafted copolymers within this composition range of monomer mixtures.

As will be shown later in Table II in the graft copolymerization of styrene onto cellulose triacetate, the molecular weight of the grafted polystyrene is always larger than that of nongrafted polystyrene, irrespective of the graft copolymerization conditions as usually reported for the graft copolymerization in heterogeneous systems.

Compositions of Copolymers and Monomer Reactivity Ratios

The composition curves of the grafted and the nongrafted copolymers onto cellulose triacetate fibers are shown in Figure 4, together with those of AIBN-initiated copolymers for comparison. It is observed in Figure 4 that the styrene content in the copolymers decrease in the order of the grafted, nongrafted, and AIBN-initiated copolymers. The same tendency is observed in the case of cellulose as trunk polymer, as seen in Figure 5.

The monomer reactivity ratios of copolymerization obtained from those copolymer composition curves according to Fineman-Ross' method¹¹ are tabulated in Table I. It is observed from Table I that the monomer reactivity ratios for the grafted and the nongrafted copolymers are different from those for the AIBN-initiated copolymers. In Table I, r_{St}/r_{Bu} has the same meaning as the square of geometric average of the reactivities of styrene and *n*-butyl acrylate monomer to the propagating radicals. For the AIBN-initiated copolymers and the nongrafted copolymers obtained by using cellulose triacetate as trunk polymer, this value is 2. On the other hand, this value is 2.8 for the grafted copolymer on cellulose triacetate, 6.3 for the grafted copolymer on cellulose, and 2.3 for the nongrafted copolymer produced when cellulose is used as trunk polymer, indicating a larger reactivity of styrene to polymer radicals in the formation of these copolymers than in the ordinary radical-initiated copolymerization.

TABLE I
Monomer Reactivity Ratios of Styrene with *n*-Butyl Acrylate in the Graft Copolymerization onto Cellulose and Cellulose Triacetate at 50°C

| Trunk polymer | Copolymer | r_{St} | r_{BuA} | $r_{St} \cdot r_{BuA}$ | r_{St}/r_{BuA} |
|--------------------------|------------|-------------|-------------|------------------------|------------------|
| Cellulose | grafted | 1.38 ± 0.01 | 0.22 ± 0.01 | 0.30 | 6.3 |
| | nongrafted | 0.90 ± 0.03 | 0.40 ± 0.01 | 0.36 | 2.3 |
| Cellulose triacetate | grafted | 1.16 ± 0.01 | 0.42 ± 0.01 | 0.49 | 2.8 |
| | nongrafted | 1.08 ± 0.01 | 0.54 ± 0.01 | 0.58 | 2.0 |
| AIBN-initiated copolymer | | 0.76 ± 0.01 | 0.38 ± 0.01 | 0.27 | 2.0 |

We thought that these differences could be attributed to the selective adsorption of monomer; namely, either styrene or *n*-butyl acrylate is se-

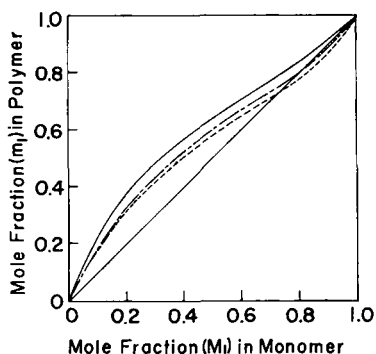


Fig. 4. Copolymer composition curves for graft copolymerization of styrene (M_1) and n -butyl acrylate (M_2) onto cellulose triacetate fibers: (—) grafted; (---) nongrafted; (- - -) AIBN-initiated.

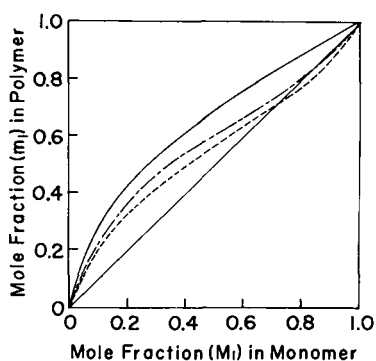


Fig. 5. Copolymer composition curves for graft copolymerization of styrene (M_1) and n -butyl acrylate (M_2) onto cellulose fibers: (—) grafted; (---) nongrafted; (- - -) AIBN-initiated.

lectively adsorbed on the trunk polymer. In order to clarify the cause of these differences, the change of the composition of monomer mixtures in the adsorption measurements on the same system of styrene- n -butyl acrylate-methanol-polymer was investigated by ultraviolet spectroscopy. From the composition of the solution outside the fibers determined by ultraviolet spectroscopy, n -butyl acrylate was found to be selectively adsorbed on the fibers in the case of cellulose triacetate; on the contrary, styrene was selectively adsorbed onto cellulose fibers, as shown in Figure 6.

In our previous report,¹¹ we obtained the gas-chromatographic retention volume as a function of temperature, using cellulose triacetate as the stationary phase and methanol, n -butyl acrylate, and styrene as the solutes. The values of enthalpy of adsorption of methanol, n -butyl acrylate, and styrene onto cellulose triacetate at 50°C, at which temperature the graft copolymerization was carried out, were -5.9, -2.5, and -0.1 kcal/mole, respectively, from Figure 1 of the previous report.¹¹ Accordingly, the adsorption onto cellulose triacetate increased in the order of styrene, n -butyl

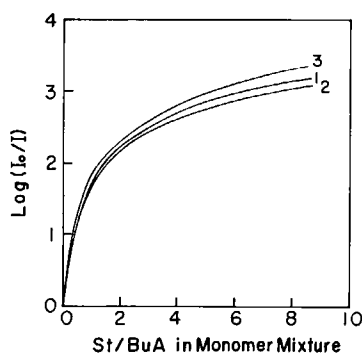


Fig. 6. Composition of the solutions outside cellulose and cellulose triacetate fibers (0.15 g) after being immersed in mixtures of 4 ml of the monomers (styrene and *n*-butyl acrylate) and 4 ml methanol for 18 hr at 25°C as determined by ultraviolet spectroscopy. Key band 291 $m\mu$; 10 mg of the solution was diluted with 10 ml tetrahydrofuran: (1) monomer solution without fibers; (2) monomer solution with cellulose fibers; (3) monomer solution with cellulose triacetate fibers.

acrylate, and methanol. This result agrees well with that of ultraviolet spectroscopy.

As will be indicated in the next section, the active species are mainly peroxides when cellulose triacetate is used as the trunk polymer. Therefore, the nongrafted copolymer may be formed in solution near the fibers mainly initiated by HO radicals produced by the decomposition of peroxides on the trunk polymer. Accordingly, when the composition of the solution outside the fibers is corrected for the selective adsorption of one of the monomers (*n*-butyl acrylate) onto the trunk polymer, the copolymer composition curve will coincide with that of the AIBN-initiated copolymers. When these results are taken into consideration and the composition of the mixtures outside the fibers are corrected (the concentration of *n*-butyl acrylate is decreased), the copolymer composition curve of the nongrafted copolymer should agree with that of the AIBN-initiated copolymer in the case of cellulose triacetate. However, the copolymer composition curve of the grafted copolymer cannot be explained solely by selective adsorption, since the styrene content in the grafted copolymer is larger. In spite of that, styrene is adsorbed with more difficulty onto cellulose triacetate than is *n*-butyl acrylate.

The grafted copolymer is thought to be produced from the radicals on the fibers. Garnett et al.⁴⁻⁶ reported that styrene adsorbed on the fibers forms a charge transfer complex with the radicals on the trunk polymer. Therefore, it is supposed that the concentration of styrene increases in the neighborhood of the radicals, or the styrene molecules adsorbed are activated. However, these assumptions have not yet been proved.

In the case of cellulose as trunk polymer, the nongrafted copolymer may be formed mostly within the matrix of trunk polymer initiated by the chain-transfer reaction of radicals to monomer or solvent. The copolymer com-

position curves of both the grafted copolymers and the nongrafted copolymers can be accounted for by the selective adsorption of styrene onto cellulose and the interaction between the trapped radicals and styrene.

Active Species in the Trunk Polymers Formed by Irradiation

In order to determine the active species initiating graft copolymerization, the determination of peroxide in the trunk polymers was carried out for both cellulose and cellulose triacetate fibers irradiated at 0°C in air, varying the dose rate and the total dose.

The results of irradiation and determination of peroxides are given in Table II for cellulose triacetate together with those of kinetic investigation of graft copolymerization of styrene onto cellulose triacetate fibers carried out simultaneously. The peroxides in cellulose triacetate formed by irradiation are proportional to the total dose irrespective of the dose rate, as seen in Figure 7. The G value of peroxide formation calculated from the slope is approximately 5. The number of peroxides per cellulose triacetate molecule after irradiation approaches an asymptote with the increase of the total dose, as seen in Figure 8. Although the formation of peroxides is proportional to the total dose, the number of peroxides per trunk polymer is almost constant, since scission of the main chain occurs at the same time. Taking the results of kinetic investigations described in the next section into consideration, it is deduced that the active species in cellulose triacetate is peroxides formed by irradiation.

On the other hand, no peroxide was detected in the irradiated cellulose (rayon). No direct experimental evidence has been reported on the active species of cellulose in the radiation-induced graft copolymerization. Now, clearly the active species in cellulose preirradiated at 0°C in air is exclusively trapped radicals. Arthur et al.¹²⁻¹⁴ found from the ESR spectra that long-lived free-radical sites in cellulose II containing regain moisture and irradiated in air at 25°C are formed by dehydrogenation at C 5 and de-

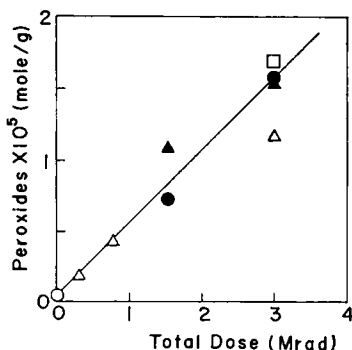


Fig. 7. Relation between total dose and concentration of peroxides in cellulose triacetate irradiated at 0°C in air. Dose rate: (O) unirradiated; (●) 6.0×10^4 r/hr; (Δ) 1.25×10^6 r/hr; (▲) 5.0×10^6 r/hr; (□) 1.0×10^6 r/hr.

TABLE II
Radiation-Induced Graft Copolymerization of Styrene onto Cellulose Triacetate Fibers by Preirradiation Technique

| Irradiation conditions | Peroxides | | Total conversion (%) | Degree of grafting | Graft efficiency | Molecular weight | |
|------------------------|------------------|--------------------------------------|----------------------|--------------------|------------------|----------------------|----------------------|
| | Total dose, Mrad | (Mole/g trunk polymer) $\times 10^6$ | | | | Number/trunk polymer | Cellulose triacetate |
| Dose rate, r/hr | | | | | | | |
| Unirradiated | | 0.03 | 0.05 | 0.095 | 0.647 | 8.40 $\times 10^4$ | 5.50 $\times 10^6$ |
| 6.0 $\times 10^4$ | 1.5 | 0.72 | 0.52 | 0.477 | 0.546 | 7.20 $\times 10^4$ | 9.87 $\times 10^6$ |
| 1.25 $\times 10^6$ | 2.9 | 1.58 | — | 0.626 | 0.569 | — | — |
| | 0.25 | 0.26 | 0.18 | 0.213 | 0.495 | 8.20 $\times 10^4$ | 2.03 $\times 10^6$ |
| | 0.75 | 0.47 | 0.34 | 0.317 | 0.505 | 7.24 $\times 10^4$ | 2.04 $\times 10^6$ |
| | 3.0 | 1.17 | 0.61 | 0.441 | 0.476 | 3.96 $\times 10^4$ | 1.50 $\times 10^6$ |
| 5.0 $\times 10^6$ | 1.5 | 1.10 | 0.48 | 0.553 | 0.611 | 4.33 $\times 10^4$ | 1.49 $\times 10^6$ |
| | 3.0 | 1.56 | 0.58 | 0.714 | 0.682 | 3.72 $\times 10^4$ | 1.01 $\times 10^6$ |
| 1.0 $\times 10^6$ | 3.0 | 1.71 | 0.70 | 0.637 | 0.820 | 4.06 $\times 10^4$ | 1.07 $\times 10^6$ |

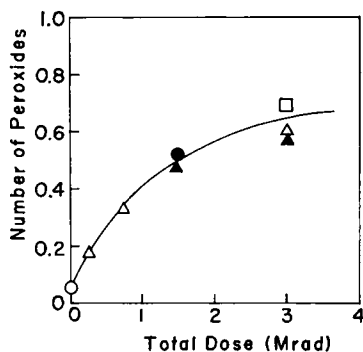


Fig. 8. Relation between total dose and number of peroxides per trunk polymer cellulose triacetate irradiated at 0°C in air. Dose rate: (O) unirradiated; (●) 6.0×10^4 r/hr; (Δ) 1.25×10^5 r/hr; (▲) 5.0×10^5 r/hr; (□) 1.0×10^6 r/hr.

hydrogenation of the OH group or dehydroxylation at C 6 of the anhydroglucose unit within the molecular lattice. The graft copolymerization onto rayon may be initiated by such trapped radicals. In a recent communication, Sakurada et al.¹⁵ considered, from the behavior of irradiated cellulose in the graft copolymerization and the measurement of ESR spectra of irradiated cellulose, that the active species in cellulose is trapped radicals.

Kinetics of Graft Copolymerization in Heterogeneous Systems

A few investigations were reported on the kinetics of graft copolymerization. For example, it was found that the rate of propagation is proportional to the square root of the initiator concentration and to the monomer concentration for the poly(methyl methacrylate)–styrene system.¹⁷

In order to examine the applicability of the kinetic scheme for the usual radical polymerization in a homogeneous system to the present systems, a kinetic investigation was carried out on graft copolymerization of styrene onto cellulose triacetate.

The kinetic investigation of graft copolymerization was carried out at 60°C in glass ampoules using 0.3 g of preirradiated cellulose triacetate fibers, 8 ml styrene, and 8 ml methanol. The reaction was continued for 20 hr, when most of the peroxides produced on the trunk polymer are consumed.

The results of the kinetic investigation are given in Table II. Both the degree of grafting and the total conversion were proportional to the square root of the peroxide concentration (Figs. 9 and 10). These results indicate that the kinetic scheme for the radical polymerization is also applicable to the graft copolymerization in a heterogeneous system. Namely, the rate of polymerization R_p can be expressed by

$$R_p = \frac{-d[M]}{dt} = k_p(f \cdot k_d/k_t)^{1/2}[\text{peroxides}]^{1/2}[M]^x \quad (x: \text{not determined})$$

Since a straight line passes through the origin in Figure 10, the graft copolymerization is not initiated by the chain transfer to the trunk polymer.

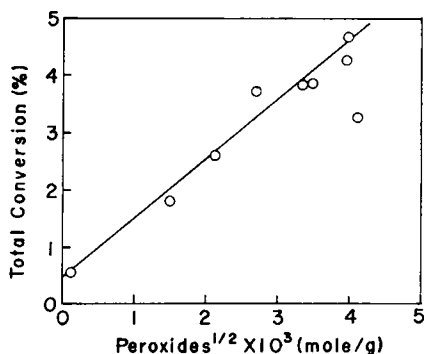


Fig. 9. Relation between total conversion and peroxide concentration in graft copolymerization of styrene onto cellulose triacetate preirradiated with γ -rays in air at 0°C . Grafting conditions: 60°C , 20 hr.

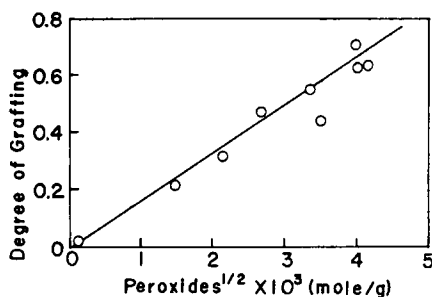
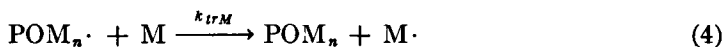
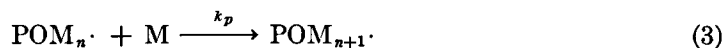
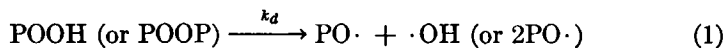


Fig. 10. Relation between degree of grafting and peroxide concentration in graft copolymerization of styrene onto cellulose triacetate. Experimental conditions are same as in Fig. 9.

When the square root of peroxide is extrapolated to zero in Figure 9, the intersection of the ordinate becomes 0.45. This is attributed to the formation of thermally initiated polystyrene homopolymer under the grafting conditions.

The relation of the number of peroxides per trunk polymer to the number of grafted polystyrene per trunk polymer is almost linear, as shown in Figure 11. From the slope of the straight line in Figure 11, the initiation efficiency of grafted polymer formation obtained, which is defined as the number of grafted polymer chains formed per number of peroxides initially present, was as low as 0.038

The elementary steps of graft copolymerization are generally as follows¹⁶:



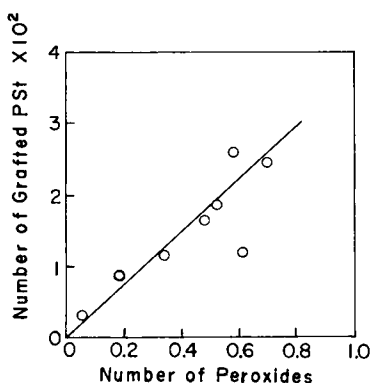
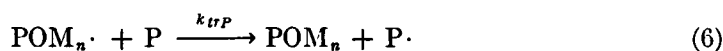
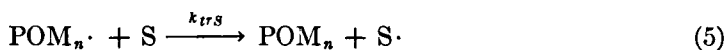


Fig. 11. Relation between number of grafted polystyrene per trunk polymer and that of peroxides per trunk polymer. Experimental conditions are same as in Fig. 9.



where P is the trunk polymer, POOH (or POOP) is the peroxide formed on the trunk polymer, k_d , k_i , k_p , and k_t are the rate constants of decomposition of peroxides, initiation, propagation, and termination, respectively, and k_{trM} , k_{trS} , and k_{trP} are the chain-transfer constants to monomer (M), solvent (S), and polymer (P), respectively.

It is reported that the termination between polystyrene radicals occurs exclusively by recombination.² If it is assumed that the value of k_t is the same for both eqs. (7) and (8), the number-average degree of polymerization of grafted polystyrene (\bar{P}_n) is expressed by

$$\frac{1}{\bar{P}_n} = \frac{fk_d[\text{POOH}] + k_{trM}[\text{POM}_n \cdot][\text{M}] + k_{trS}[\text{POM}_n \cdot][\text{S}]}{2k_p[\text{POM}_n \cdot][\text{M}]} + \frac{2k_{trP}[\text{POM}_n \cdot][\text{P}] + k_t[\text{POM}_n \cdot][\text{M}_n \cdot] + k_t[\text{POM}_n \cdot]^2}{2k_p[\text{POM}_n \cdot][\text{M}]} \quad (9)$$

Namely,

$$\frac{2}{\bar{P}_n} = C_m + \frac{C_s[\text{S}]}{[\text{M}]} + \frac{2C_p[\text{P}]}{[\text{M}]} + \frac{fk_d[\text{POOH}]}{R_p} + \frac{k_t}{k_p^2[\text{M}]^2} (R_p + R_p') \quad (10)$$

where $C_m = k_{trM}/k_p$, $C_s = k_{trS}/k_p$, $C_p = k_{trP}/k_p$, and $R_p (= k_p[\text{M}][\text{POM}_n \cdot])$ and $R_p' (= k_p[\text{M}][\text{M}_n \cdot])$ are the rate of formation of the grafted polystyrene

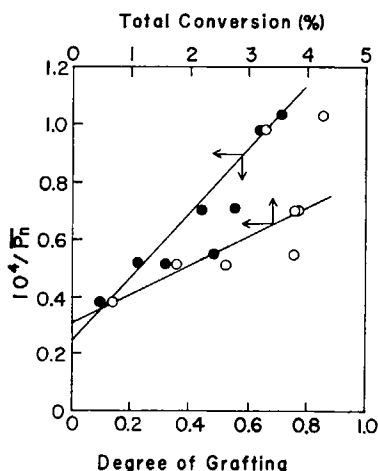


Fig. 12. Plot of $1/\bar{P}_n$ of grafted polystyrene vs. degree of grafting (O) and total conversion (●).

and the nongrafted polystyrene produced within the fiber, respectively; f is the initiation efficiency defined as

$$f = \frac{\text{number of polymer chain formed}}{1/2 \text{ number of peroxides initially present}}$$

and obtained to be 0.142 from a plot similar to Figure 11. In the right side of eq. (10), C_p is zero, as indicated above, and the second term is neglected since it is supposed to be much smaller compared to other terms. The fourth term is also neglected since $[\text{POOH}]$ is extremely small compared to $[\text{M}]$. Accordingly, the following relation is obtained:

$$\frac{1}{\bar{P}_n} = \frac{C_m}{2} + \frac{k_t}{2k_p^2[\text{M}]} (R_p + R_p'). \quad (11)$$

The overall rate of polymerization, including the nongrafted homopolymers produced outside the fibers, is plotted against $1/\bar{P}_n$ in Figure 12. The correlation is not so good. This is expected, since the polystyrene (i.e., polystyryl radicals) formed outside the trunk polymer not participating in the graft copolymerization was included. Furthermore, in eq. (11) the same value of k_t is used for both grafted and nongrafted polystyrene. For the latter, however, the value of k_t may be much larger for the homopolymers formed outside the trunk polymer. As the amount of the nongrafted polystyrene formed within the fibers was small (less than 10% of the nongrafted polymer), R_p' is negligible compared to R_p , and R_p is replotted in Figure 12 against $1/\bar{P}_n$. Although some scattering of data is observed, a fairly good correlation is obtained. The value of C_m obtained from the intercept to the ordinate was 4.8×10^{-5} , which agrees well with that of

6×10^{-5} reported in the bulk polymerization of styrene with radical initiators at 60°C .^{2,18,19}

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