Radiation-Induced Graft Copolymerization of Styrene to Cellulose*

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Synopsis

The radiation-induced graft copolymerization of styrene to cellulose has been studied in vacuo at 30°C and at dose rates from (0.37 to 8.73) $\times$ 10^{-2} W/kg. Dioxan was used as solvent for monomer and polystyrene homopolymer, and water (2% total volume) was incorporated as swelling agent for cellulose. The concentration of styrene in the bulk medium was varied from 0.432 to 3.46 moles/l., and the rates of both grafting and homopolymerization were shown to be proportional to [monomer] $\cdot$ [intensity]$^{1/2}$. The value of 3.3 $\times$ 10^{-4} l. mole^{-1} sec^{-1} derived for k_p^2/k_t in homopolymerization is similar to that for normal free-radical polymerization of styrene. However, reduced termination during grafting yielded a much higher value (58 l. moles^{-1} sec^{-1}). Degradation of cellulose in the absence of monomer was followed viscometrically, and values of 13.5 and 24.6 were derived for G (scission) in vacuo and in air, respectively.

INTRODUCTION

Much information concerning the characterization of cellulose graft copolymers has accumulated in recent years, an emphasis being placed on improving the parent polymer through grafting with selected monomers. Hence, the bulk of research into graft polymers has been aimed at studies of their physical and structural properties, with less interest being shown in the factors governing their formation. Few attempts have been made to elucidate the mechanisms involved in mutual radiation-induced graft polymerizations. This is particularly so in systems involving cellulose as the polymer substrate owing to their complexity.

Odian and co-workers made the broadest and earliest investigations of the mutual grafting of styrene to polyethylene[1,2] and to nylon[3] under a variety of experimental conditions. From these, values for k_p^2/k_t in the grafting reaction were obtained. In grafting to polyethylene, k_p^2/k_t was found to increase with increasing concentration of methanol in the outside solution, due to insolubilization of the graft polymer chains. For the latter case, values for k_p^2/k_t were found to be independent of the methanol content of the monomer solvent, thus suggesting that insolubilization of graft polymer chains is not a feature of the copolymerization.

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Chandler et al.[4] used the mutual grafting technique to graft polyethylene films with mixtures of styrene and acrylonitrile. Equilibrium and diffusion data on styrene and polyethylene from a previous paper were used to deduce monomer concentrations during grafting. Values of k_p^2/k_t were calculated to be approximately 10^8 times as great as in bulk styrene polymerization. Reduced termination and propagation rate constants for the grafting reaction relative to the corresponding homopolymerization are used to explain this, with the decrease being greater for termination than propagation. Kesting et al.[5] undertook a kinetic analysis of the results obtained in the preirradiation grafting of styrene to cotton, and an equation for polymerization with time was derived which showed compatibility with the experimental data.

Vanderkooi et al.[6,7] measured the concentration-dependent diffusion coefficient of styrene into ethyl cellulose films and used the results to analyze their mutual grafting in the vapor phase. A value of 0.3 l. mole^{-1} sec^{-1} for k_p^2/k_t was obtained, which was stated to be indicative of restricted radical termination.

Stannett et al.[8,9] investigated the mutual radiation grafting of styrene and acrylonitrile to wool using water and methanol as swelling agents. In both cases, water was found to be the more efficient swelling agent, and the grafting reactions were observed to be diffusion controlled. A kinetic treatment was developed by Araki et al.[10] to explain the results. An equation was derived which satisfied the experimental data.

In a study of the grafting of styrene to poly(vinyl chloride), Takamatsu et al.[11] obtained values of approximately 0.2 l. mole^{-1} sec^{-1} for k_p^2/k_t at the lowest monomer concentrations. On increasing the monomer concentration, the values of k_p^2/k_t fell to 7×10^{-4} l. mole^{-1} sec^{-1}, which is close to the value for bulk polymerization. This change is explained in terms of plasticization of PVC by the monomer giving increased segmental motion and thus increasing k_t by facilitating radical combination.

In a comprehensive series of publications, Dilli and Garnett[12–20] have attempted a mechanistic approach to the grafting of vinyl monomers to cellulose under a variety of conditions. Detailed studies of the radiation-induced grafting of monomer to cellulose have been reported, with particular interest being shown in the effect of both wetting and nonwetting solvents on the grafting reaction. An increase in the viscosity of the grafting solution at the grafting site was attributed to an increase in the magnitude of k_p^2/k_t.

Through work undertaken in this laboratory, it is now possible to obtain the concentration of monomer at the grafting sites. A further complication to an understanding of the kinetics of grafting to cellulose involves the lack of knowledge concerning the role of the swelling agent and the monomer solvent. This point has also been clarified.

In this paper the kinetics of grafting in the cellulose–styrene–dioxan–water system is investigated, and a treatment of experimental data, similar to that of Odian, is applied to enable k_p^2/k_t to be calculated for both copolymerization and homopolymerization.

EXPERIMENTAL

Materials

Styrene was purified by standard methods and vacuum distilled. Pure dioxan was obtained using the method of Baxendale and Rodgers.[21] Peroxidation of the purified product was minimized by storage over sodium in the dark at low temperature. Deionized water was used throughout, apart from dosimetry for which triply distilled water was required. Strips of regenerated cellulose film (5 cm $\times$ 2 cm $\times$ 0.005 cm) were Soxhlet extracted with methanol to remove plasticizer and dried to constant weight in vacuo at 40°C. Cadoxen, used for viscosity measurements, was prepared according to Segal and Timpa.[22]

Preirradiation Procedure

Selection of Solvent Medium. The majority of grafting and homopolymerization experiments in this work were carried out using solutions of styrene in dioxan–water. The water concentration was maintained at 2% (v/v) throughout, the other components being varied as required. A maximum of 2% water was found to be consistent with producing homogeneous solutions for monomer concentrations in the range 5–40% of the bulk solution, while still allowing solubility of the polystyrene homopolymer produced during irradiation.

Preparation of Samples for Irradiation. Dry, tared films were placed in rimless test tubes (16 $\times$ 125 mm). Ampoules were made from these tubes through connection to a 20-cm length of 4-mm-internal-diameter glass tubing incorporating a P.T.F.E. sleeve supplied by J. Young Ltd. Acton (Fig. 1). During glass blowing, moisture condensed in the vicinity of the film which required drying in a vacuum oven for two days to ensure its complete removal. When the films were dry, 10 cc of monomer solution were added as quickly as possible, and the ampoules were transferred to a vacuum line. Degassing by means of freeze-thaw cycles was carried out prior to sealing the ampoules at $1.33 \times 10^{-3}\,\mathrm{Nm^{-2}}$. Degassing was taken to be complete, when the solid monomer solution melted without the formation of bubbles and also when no bubbles remained on the film surface.

Irradiation

All samples were irradiated at 30°C in the 9000-curie radiation facility located at the University of Salford. Variation in dose rate was achieved by adjusting the distance between the sources and the samples. The total absorbed dose was regulated by controlling the overall exposure time for a given dose rate. In order to minimize cellulose main-chain degradation, dose rates and total doses were kept as low as possible, consistent with a study of the monomer and intensity dependence of grafting and homopolymerization. Dose rates were limited to a range of $(0.373–8.73) \times 10^{-2}$ W/kg as measured by the ferrous sulfate dosimeter, assuming $G_{Fe^{3+}} = 15.6$. In all cases, the total dose was below 1.5×10^3 J/kg.
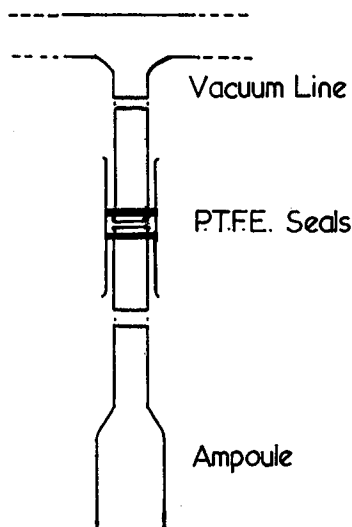
Fig. 1. P.T.F.E. sleeve joint for attaching ampoule to vacuum line.

Postirradiation Procedure

Cellulose–Styrene Copolymer. After removal of the grafted films from the ampoules, the extent of swelling and concentration of available monomer were determined. The films were then soaked in benzene to remove loosely bound homopolymer, Soxhlet extracted with benzene for 48 hr, and subsequently washed in methanol. The extracted films were then vacuum dried before weighing. This process was repeated to constant weight.

The degree of grafting is given by

$$\% \text{ grafting} = \frac{100 \ (\text{weight of grafted product} - \text{weight of original cellulose})}{\text{weight of original cellulose}}$$

Polystyrene Homopolymer. Polystyrene homopolymer was isolated by precipitation of the irradiated solution in an excess of cold methanol. The polymer was filtered, washed thoroughly with methanol, and dried at 40°C under vacuum to constant weight. The concentration of homopolymer is expressed as moles of styrene converted to polymer per liter of original monomer solution.

Swelling of Grafted and Ungrafted Cellulose. Weighed, dry films were placed in the monomer solution which was maintained at constant temperature (30°C). Swollen samples were withdrawn, quickly surface dried between filter papers, transferred to a tared weighing bottle, and the whole reweighed. The degree of swelling is given by

$$\% \text{ swelling} = \frac{100 \ (W_1 - W_0)}{W_0}$$

where W_1 = weight of swollen film and W_0 = weight of original film.   For nongrafted films, the degree of swelling was measured at different times until the equilibrium value was obtained.   In the case of grafted films, the total swelling was determined immediately after removal of an irradiated film from its ampoule.   In both cases, the styrene content of a swollen film was estimated afterward, as described by us in a previous communication.[23]

RESULTS AND DISCUSSION

Factors Affecting Grafting and Homopolymerization

Certain factors concerned in both the grafting and homopolymerization reactions require clarification prior to any kinetic study being undertaken, for example: (i) the role of water in swelling, grafting, and homopolymerization; (ii) the effect of vacuum; (iii) the effect of radiation on cellulose; (iv) changes in film accessibility during grafting; (v) the influence of free-radical inhibitors on the grafting and homopolymerization reactions; (vi) postirradiation grafting.   These will now be considered in turn.

The Role of Water in Swelling, Grafting and Homopolymerizaton

Usmanov[24] recognized in early work that polar wetting agents for cellulose, including alcohols, were conducive to successful grafting with acrylonitrile.   Huang and Rapson[25] found that in the absence of water as swelling agent, no grafting was obtained in the styrene–cellulose fiber system, whereas small quantities of water sufficed to yield substantial grafting. Chapiro and Stannett[26] studied the cellulose–styrene–dioxan–water system, noting that considerable increases in grafting yields were obtained on increasing the water content of the monomer solution from zero to 1.5%.

Dilli and Garnett have investigated the effects of a wide range of monomer solvents, both nonwetting[16] and wetting,[17] on the grafting reaction.   It was concluded that in order to achieve appreciable grafting, the cellulose must first be swollen, thus permitting access of the monomer to the active sites.

The results obtained in this study demonstrate fully the importance of water as a swelling agent for cellulose.   In the absence of water, swelling reaches a rapid equilibrium considerably below that obtained in the presence of water.   This corresponds to adsorption of the monomer solution onto the film surface but no penetration of the substrate.   The role of water in the grafting process is mainly one of increased accessibility.   In the presence of water, the plots of per cent grafting against irradiation time are approximately linear for a range of monomer concentration.   In the absence of water, a similar grafting rate is observed up to 2% conversion.   At this point a decrease in the rate is observed corresponding to grafting being restricted to the cellulose surface owing to lack of access of monomer to the interior active sites.

Close agreement was obtained for styrene homopolymerization up to a concentration of 1.5×10^{-2} mole/l. of polymer in the bulk solution, both in

the presence of water and without water. At this point a decrease in the homopolymerization rate is observed in the absence of water, suggesting that water serves to enhance the rate of homopolymerization.

The Effect of Vacuum on the Equilibrium Swelling of Cellulose Film

Figures 2 and 3 show clearly the effect of degassing on the equilibrium swelling of cellulose film for a range of monomer concentrations. Through-
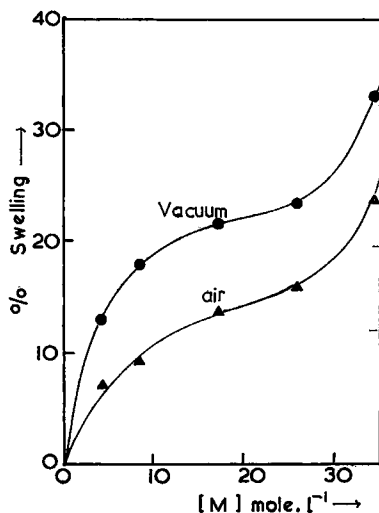
Fig. 2. Comparison of the swelling of cellulose in various monomer solutions, in air (▲) and under vacuum (●).
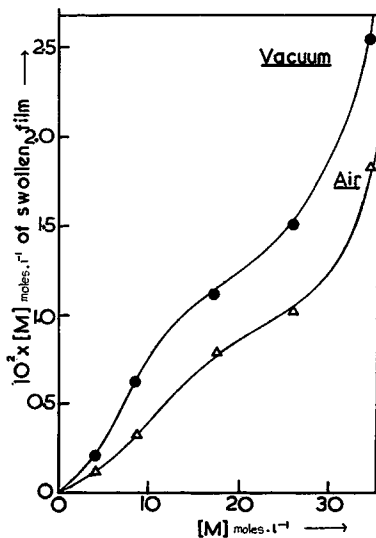
Fig. 3. Effect of degassing on the monomer content of swollen films, in solutions of various monomer concentrations.

out this range, increases in swelling of substrate are matched by increases in the monomer concentration of the film. Both series of results produce S-shaped plots for the extent of equilibrium swelling for various monomer concentrations. Such curves are characteristic of those obtained in moisture sorption studies involving cellulose.

The effect of vacuum on the grafting and homopolymerization reactions supports the above observations. In both cases the presence of air causes a decrease in the polymerization rate in the initial stages. It would appear that this effect decreases with increasing exposure to radiation. In the absence of a degassing cycle, air is available to quench cellulose radicals before grafting can occur. However, a more important factor is thought to be the reduced concentration of monomer at the active sites. Thus degassing causes an increase in accessibility through removal of air, the resultant void being filled by the monomer solution.

The Effect of Radiation on Regenerated Cellulose Film

Simultaneous. In order to determine the effect of radiation on cellulose, samples were irradiated for known times under conditions typical of those used in a grafting study, in the absence of monomer. Viscosity measurements were carried out at 25°C using Cadoxen as a solvent for both the irradiated celluloses and the unirradiated standard. The Mark-Houwink values[27] for cellulose in this solvent at 25°C are

$$K = 1.8 \times 10^{-2} \text{ dl/g}$$

and

$$\nu = 0.77$$

as obtained from light scattering studies such that

$$[\eta] = K \, \bar{Z}_v^\nu$$

where $\bar{Z}_v$ is the viscosity-average degree of polymerization.

The effect of air in the cellulose degradation was shown by irradiating two series of samples, one in air, the other under vacuum. The intrinsic viscosity $[\eta]$ for different cellulose samples was determined in the normal manner in a suspended-level dilution viscometer. Using the Mark-Houwink values quoted, the viscosity-average molecular weights were obtained. These viscosity-average molecular weights were converted to number-averages using the equation appropriate for a random distribution,[28,29] viz.,

$$\bar{M}_v = \bar{M}_n \, [(\nu + 1) \cdot \Gamma \, (\nu + 1)]^{1/\nu}$$

where Γ denotes the gamma function. For cellulose in Cadoxen, $\nu = 0.77$, which gives the relationship

$$\bar{M}_v = \bar{M}_n \, (1.894)$$

whereby the number-average molecular weights are derived.

From the variation of the number-average molecular weight with total dose for cellulose, it is possible to acquire information regarding the depolymerization process, through the determination of G values for scission of the cellulose backbone.
Thus,

$$\frac{N_A}{\bar{M}_n} = \frac{N_A}{(\bar{M}_n)_0} + (6.242 \times 10^{17} \times G)r$$

where N_A = the Avogadro number, $(\bar{M}_n)_0$ = the number average molecular weight of unirradiated cellulose, $\bar{M}_n$ = the number-average molecular weight of the irradiated cellulose, r = the total dose in J/kg $\times$ 10^4, and G = the number of scissions produced in the cellulose backbone per 100 eV of absorbed radiation energy.   Thus,

$$\frac{1}{\bar{M}_n} = \frac{1}{(\bar{M}_n)_0} + \left(\frac{6.242 \times 10^{17} \times G}{6.023 \times 10^{23}}\right)r.$$

Thus $1/\bar{M}_n$, when plotted against the absorbed dose expressed in J/kg $\times$ 10^4, gives a linear plot (Fig. 4).   From the slope, a value for G(scission) is obtained since

$$\text{slope} = 1.036 \times 10^{-6} \times G\text{(scission)}.$$

For celluloses irradiated under vacuum, the value of G(scission) was found to be 13.5, whereas that in air was 24.6.   This shows conclusively that oxygen enhances the radiation-induced degradation of the cellulose backbone.

In order to determine the minimal dosage required to cause measurable change in the intrinsic viscosity of irradiated celluloses, the percentage change in $[\eta]$ was plotted against log total dose expressed in J/kg $\times$ 10^2,

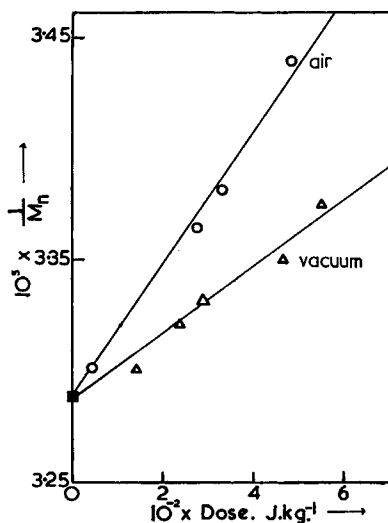Fig. 4. Determination of G(scission) for cellulose, on irradiation in air and under vacuum.

which produces a linear plot. Figure 5 shows the extrapolation to zero percent, giving a threshold value of 89 J/kg for cellulose irradiated under vacuum. For celluloses irradiated in air, a more complex picture emerges. This plot is not linear but shows a divergence at 200 J/kg. Continuation of C to D gives a value corresponding to the threshold dosage of the vacuum-irradiated sample. At point D, a change in slope occurs suggesting the threshold dosage for air-irradiated samples to be much lower than those irradiated under vacuum. These threshold dosages observed for regenerated cellulose film are much lower than those observed by other workers dealing with natural celluloses. Glegg and Kertesz[30] observed a threshold falling in the narrow range of 341 to 640 J/kg. Saeman et al.[31] obtained values of 284 J/kg in the X-ray degradation of soft wood pulp and 812 J/kg for the degradation of cotton linters. This large difference in threshold dosage reflects the susceptibility of regenerated cellulose film to radiation damage relative to that obtained with natural cellulose.

Aftereffect Degradation. This phenomenon is characterized by a progressive decrease in the intrinsic viscosity beyond that measured as soon as possible after irradiation, i.e.,

$$\text{aftereffect} = [\eta]_i - [\eta]_f$$

where $[\eta]_i$ = the intrinsic viscosity immediately after irradiation, and $[\eta]_f$ = the intrinsic viscosity when no measurable change is observed.

Figure 6 shows the significance of aftereffect degradation for a series of celluloses irradiated to different total doses. In every case the major part of the total breakdown was caused by the aftereffect. The percentage aftereffect in samples irradiated in air is marginally less than for vacuum-irradiated samples. This suggests that primary degradation is greater
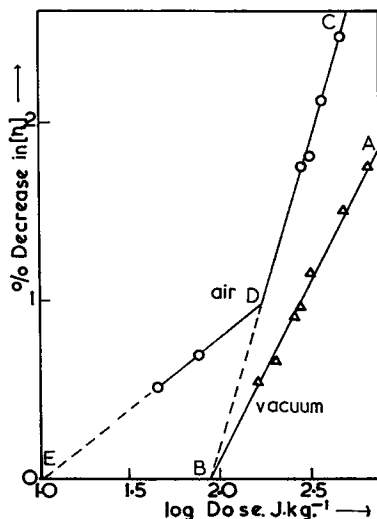

Fig. 5. Determination of the threshhold doseage (in J kg⁻¹) on irradiation of cellulose.

in air than under vacuum.   The gradual decrease in the percentage after-effect with increasing dose corresponds with a gradual interaction between the active sites in cellulose and atmospheric oxygen as it slowly diffuses through to the less accessible regions of the substrate.   This results in a reduction of the radical concentration and a corresponding decrease in after-effect.

The role of the solvent in cellulose degradation is not clear.   However, the radiolysis products of both components of the mixture (dioxane–water) are potentially good radical-propagating species and would tend to enhance the already appreciable degradation of the substrate.

In view of the observed effects of radiation on cellulose, for all future irradiations of cellulose steps were taken to minimize postirradiation degradation.

Changes in Film Accessibility during Grafting

The effect of grafting on the swelling of the substrate was studied for a range of monomer concentrations.   In all cases, at low degrees of conversion, the extent of swelling increased linearly with grafting.   This increased swelling is accompanied by an increase in the monomer concentration within the film.   At higher degrees of conversion, a slight acceleration in the extent of swelling is observed.   However, the increased swelling due to grafting is small relative to the equilibrium swelling of degassed ungrafted films.   Thus, an increase in grafting results in increased accessibility of the monomer to the grafting sites and enhances the efficiency of the grafting process.

The Influence of Free-Radical Inhibitors on the Grafting and Homopolymerization Reactions

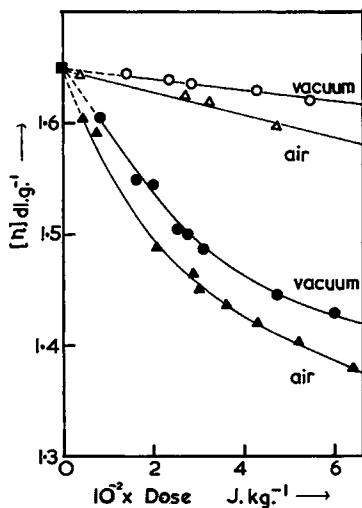Grafting vinyl monomers to cellulosic materials initiated by high-energy

Fig. 6. After effect degradation of irradiated cellulose: (O),(△) $[\eta]$ measured immediately after irradiation; (●),(▲) $[\eta]$ measured after 21 days.

gamma radiation could involve either an ionic or a free-radical mechanism. In radiation-induced polymerizations, both mechanisms are thought to occur simultaneously, with either predominating depending on the reaction conditions. In general, polymerizations involving ionic intermediates are favored by low temperatures, solid phase, high-purity reagents, and the utilization of ultrahigh vacuum. It was anticipated that the conditions prevailing in this study, i.e., 30°C, solution phase, and moderately efficient vacuum degassing (1.33×10^{-3} Nm^{-2}) would negate any appreciable participation of an ionic mechanism.

The results obtained in experiments carried out using 0.05% w/v p-benzoquinone in the monomer solution as a free-radical inhibitor support this view (Fig. 7). In the presence of the inhibitor, little or no grafting or homopolymerization is observed. This is contrary to the formation of ionic intermediates which would have been unaffected by p-benzoquinone. Chapiro and Stannett,[32] using conditions conducive to ionic intermediate formation, observed that the presence of p-benzoquinone resulted in a marked acceleration of the homopolymerization of styrene. This acceleration is stated to be a result of the high electron affinity of the styrene molecule. Hence, if the electrons are trapped by the quinone to form stable negative ions, the lifetimes of all the ionic species necessarily increase, resulting in the occurrence of ionic processes.

Postirradiation Grafting

It is a feature of the irradiation facility utilized in this study that irregular interruptions in exposure occur. Quoted irradiation times allow for such interruptions. This approach assumes that grafting and homopolymerization cease on discontinuation of exposure. In addition, a finite time interval exists between cessation of irradiation and the postirradiation procedure being carried out. The significance of such postirradiation effects is demonstrated in Figures 8 and 9. It is obvious that postirradiation effects are phenomena of the adopted procedure. However, the level of increased grafting and homopolymerization is negligible relative to that occurring during simultaneous irradiation.

Postirradiation effects in grafting arise out of the presence of reactive trapped radicals within the cellulose substrate. These radicals are known to be long-lived and capable of reacting with suitable species over an extended period. The occurrence of small postirradiation effects in homopolymerization is possibly the result of energy transfer to the monomer from the other components of the monomer–substrate system.

In view of the above observations, interruptions during exposure and delays in sample processing after irradiation were minimized. In general, interruptions accounted for approximately 6–8% of the time between initial exposure and the processing of the grafted films and homopolymer.

The Monomer Dependence of Grafting and Homopolymerization

The monomer dependence of both the grafting and homopolymerization reactions was found for a range of monomer concentrations (5–40% v/v) of
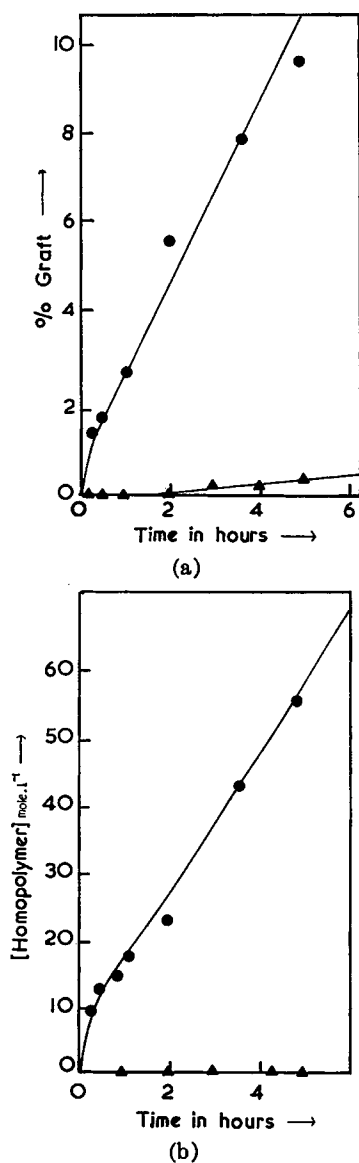
Fig. 7. Effect of p-benzoquinone (0.05% w/v) on (a) grafting and (b) homopolymeriza-
tion: (●) without inhibitor; (▲) with inhibitor.

the grafting medium (Figs. 10 and 11).   A graphical representation is given
verifying the dependence of R_p (grafting and homopolymerization) on the
first power of the monomer concentration (see Fig. 12). R_p for grafting
is defined as the number of moles of styrene grafted in unit time per liter
of swollen cellulose film.   Monomer concentrations are expressed as moles
of styrene per liter of swollen film (measured prior to commencement of
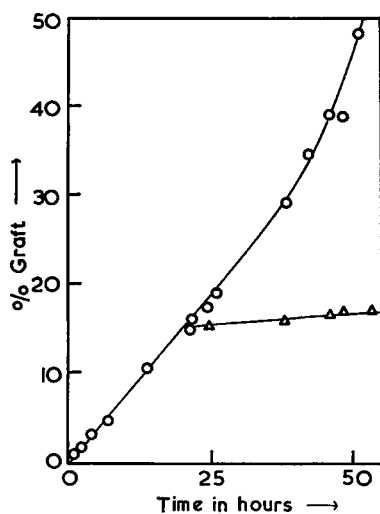irradiation).

Fig. 8. Postirradiation effects on grafting: (O) normal grafting; (△) postirradiation grafting.
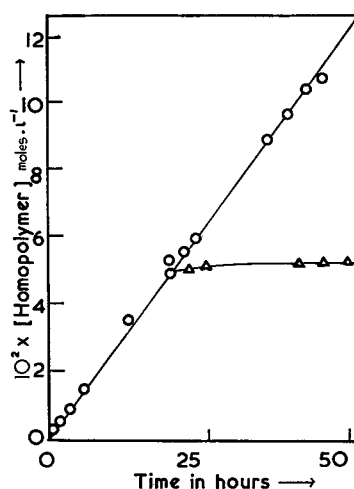
Fig. 9. Postirradiation effects on homopolymerization: (O) normal polymerization (△) postirradiation polymerization.

For homopolymerization R_p is given as the number of moles of styrene converted to homopolymer in unit time per liter of monomer solution. This approach is thought to give a more realistic representation of reaction conditions at the grafting site. It is important to note that the monomer concentration within a film is not necessarily the same as that in the bulk monomer solution, but that it bears a close relationship to the swelling characteristics of the cellulose substrate.
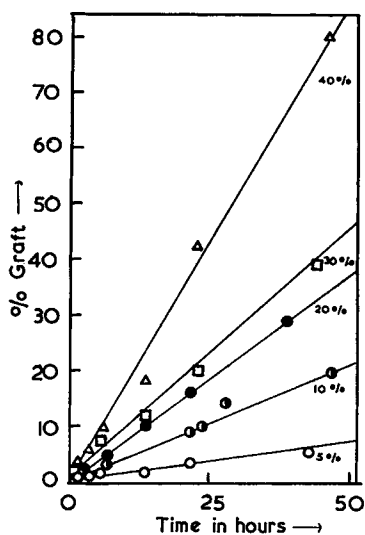
Fig. 10. Dependence of grafting on monomer concentration of the bulk solution [M]:
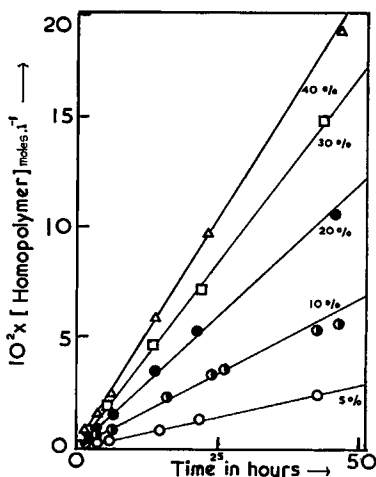(O) [M] = 0.432 mole/l.; (◑) 0.864; (●) 1.728; (□) 2.595; (△) 3.460.

Fig. 11. Dependence of homopolymerization on monomer concentration of the bulk
solution [M]: (O) [M] = 0.432 mole/l.; (◑) 0.864; (●) 1.728; (□) 2.595; (△) 3.460.

The Intensity Dependence of Grafting and Homopolymerization

The intensity dependence was investigated for a range of absorbed dose
rates, (0.37 to 8.73) × 10^{-2} W/kg. The results of the individual plots have
been combined in Figure 13, which demonstrate an intensity dependence for
both grafting and homopolymerization of approximately 0.5, thus indicating
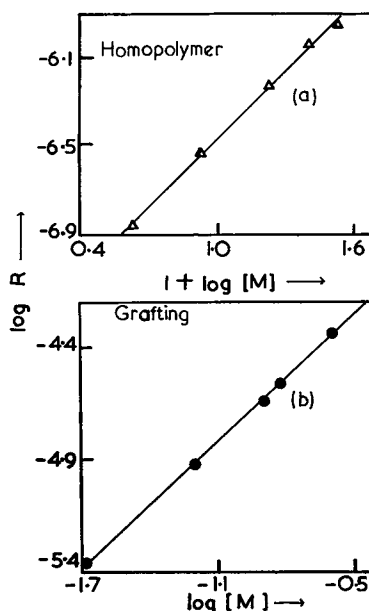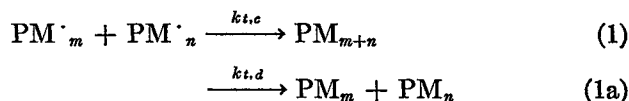that bimolecular termination is operational in both cases.

Fig. 12. Log reaction rate vs. log [M] for (a) homopolymerization and (b) grafting R expressed in moles/l. of bulk per sec (a) and in moles/l. of swollen film per sec (b); [M] expressed in moles/l. of bulk (a) and in moles/l. of swollen film (b).
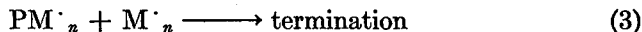
Such termination can occur in a variety of ways:

(a) Between grafted polymer radicals, or homopolymer radicals:

$$\text{PM}^{\cdot}_{m} + \text{PM}^{\cdot}_{n} \xrightarrow{k_{t,c}} \text{PM}_{m+n} \tag{1}$$

$$\xrightarrow{k_{t,d}} \text{PM}_{m} + \text{PM}_{n} \tag{1a}$$

(b) Between copolymer and solvent radicals, or homopolymer and solvent radicals:
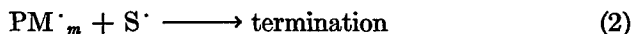
$$\text{PM}^{\cdot}_{m} + \text{S}^{\cdot} \longrightarrow \text{termination} \tag{2}$$

(c) Between graft copolymer and homopolymer radicals:

$$\text{PM}^{\cdot}_{n} + \text{M}^{\cdot}_{n} \longrightarrow \text{termination} \tag{3}$$

Termination via eq. (2) is unlikely in this system since the concentration of cellulose in a swollen film in g./l. of cellulose–styrene–dioxan–water is considerably greater than the concentration of styrene, dioxan, or water. Table I shows the concentration of each of the components of a swollen film for a particular grafting medium.

Termination via eq. (3), although present to some extent, was thought unimportant since it does not alter the values of the various calculated terms (see Analysis). Odian et al.[3] have investigated this point, producing an equation relating to the internal polymerization process, i.e., that occurring inside the backbone polymer.
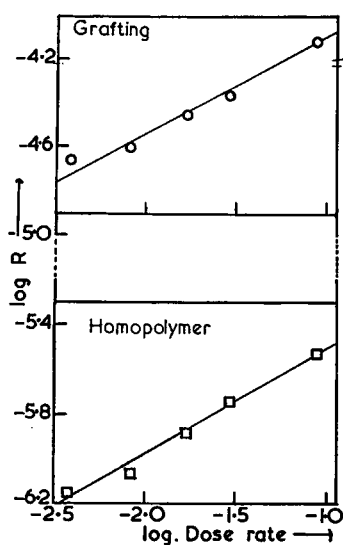
Fig. 13. Dependence of (a) grafting and (b) homopolymerization rates on radiation intensity. R expressed in moles/l. of swollen film per sec (a) and in moles/l. of bulk per sec (b). Dose rate expressed in W/kg.

TABLE I

Liquid Composition of the Bulk Medium and Concentration of Monomer in Film for Varying Concentrations of Monomer in the Bulk Medium

Concentration of cellulose–dioxan–styrene–water system, g/l.				Monomer concn. in film, mole/l. of swollen film $\times 10^2$	Styrene concn. in bulk medium, mole/l.
Styrene	Dioxan	Cellulose	Water		
2.16	160	1252	3.53	2.08	0.432
6.51	202	1187	4.10	6.26	0.896
12.8	242	1125	6.50	12.3	1.73
15.7	230	1124	6.90	15.1	2.59
26.5	310	1028	11.1	25.5	3.43

Hence, for simplicity, termination is considered to occur in the present system by eqs. (1) and (1a). In copolymerization, one usually assumes termination of the grafting reaction to be bimolecular. However, if considerable radical burial is evident in the grafting, one could propose that the mode of termination be monomolecular. The above results clearly demonstrate the absence of monomolecular termination either in grafting or homopolymerization.

KINETIC ANALYSIS

In this discussion of the kinetics of grafting and homopolymerization in the dioxan–styrene–water–cellulose system, certain assumptions are made:
(i) The monomer solution is available at all the grafting sites.

(ii) Grafting takes place in the accessible regions of the backbone polymer. For simplicity, the cellulose film is considered to be 100% accessible. (In fact, D_2O infrared absorption experiments show it to be $\sim$80% accessible.[33]) In view of the small film thickness (0.005 cm) and the swelling efficiency of the grafting medium, such an assumption is reasonable.

(iii) In the expression of grafting rates and monomer concentrations, the individual volumes of cellulose, styrene, dioxan, and water are additive without contraction or expansion of volume. Though a considerable over-simplification, this assumption is thought unlikely to affect the relative validity of the various calculated terms.

(iv) The grafting reaction is not diffusion controlled. This assumption is justified, since equilibirum swelling is attained in all cases prior to the commencement of irradiation.

Since consistency of technique was maintained throughout and factors thought likely to influence grafting were investigated successfully, the mechanism of the grafting and homopolymerization processes can be considered. It is of interest to determine the specific rates of graft copolymerization and homopolymerization together with the k_p^2/k_t values for the various cellulose–styrene–dioxan–water systems. Data used in determination of reaction rates were restricted to the initial stages of grafting and homopolymerization.

The rate of graft polymerization and homopolymerization is given by

$$R_p = k_p \left(\frac{R_t}{2k_t}\right)^{1/2} [M] \qquad (4)$$

where k_p and k_t = propagation and bimolecular termination rate constants, respectively; $R_P \equiv R_G$ = moles of styrene grafted per liter of cellulose–styrene–dioxan–water per second, in the grafting reaction; $R_P \equiv R_H$ = moles of styrene converted to homopolymer per liter of bulk monomer solution per second, in the homopolymerization reaction; [M] = the monomer concentration (in grafting this is expressed as moles of styrene per liter of cellulose–styrene–dioxan–water, whereas in homopolymerization it is expressed as moles of styrene per liter of bulk solution); and R_t = moles of free radicals produced on the cellulose polymer per liter of swollen film per second (in homopolymerization R_t is expressed as the concentration of homopolymer radicals per liter of bulk solution per second).

The rate of initiation for both grafting and homopolymerization is obtained by

$$R_t = \frac{G \phi \rho_p}{N_A \times 100} \qquad (5)$$

where G = the number of free radicals produced in the system per 100 eV of absorbed radiation energy, N_A = the Avogadro number, ϕ = the radiation intensity in eV per gram of cellulose per second ($= 2.26 \times 10^{13}$ eV/g sec), and ρ_p = the concentration of accessible cellulose in grams per liter of swollen film in grafting, or the number of grams of monomer solution per liter of swollen film in homopolymerization.

The results of the monomer and intensity dependence of both grafting and homopolymerization are consistent with eq. (4), and hence this approach appears valid.

Rearrangement and squaring of eq. (4) gives

$$k_p{}^2/k_t = 2R_p{}^2/R_t \; [\text{M}]^2. \tag{6}$$

Calculated values for R_t and $k_p{}^2/k_t$ for the grafting of styrene to cellulose in a dioxan–water medium are given in Table II. Since only qualitative importance is attached to values of $k_p{}^2/k_t$, the use of eq. (6), ignoring termination between graft copolymer and homopolymer radicals, is justified. The rates of initiation, R_t, were calculated from eq. (5) using a G(radical) value for cellulose radical production of 2.88. Values of ρ_p were calculated from the known weight fractions of each of the components of a swollen film and their respective densities, measured at 30°C. The density of regenerated cellulose film, measured by the flotation technique using benzene and carbon tetrachloride, was found to be 1.47 g/cc.

TABLE II

$K_p{}^2/K_t$ in Grafting for the Bulk Monomer Concentrations in Table I; Values Obtained from R_p and R_i Employing Literature Values[34] for G(radical) of Cellulose

Monomer concn. in bulk grafting medium, moles/l.	Monomer concn. in film, moles/l. of swollen film $\times 10^2$	R_p (moles grafted. 1^{-1} of swollen film. sec^{-1})	R_i, mole $1.^{-1}$ sec^{-1} $\times 10^9$	ρ_p, g/l. of swollen film	$k_p{}^2/k_t$, l. mole^{-1} sec^{-1}	Monomer concn. in bulk, % (v/v)	Swelling at equilibrium based on initial film weight, %
0.432	2.08	4.24	1.34	1252	62.2	5	13.2
0.863	6.26	11.9	1.27	1187	57.1	10	18.0
1.73	12.3	22.4	1.20	1125	54.2	20	21.5
2.59	15.1	27.4	1.20	1124	54.8	30	23.3
3.46	25.5	46.4	1.10	1028	60.5	40	32.8

Accepted values for $k_p{}^2/k_t$ in the free-radical polymerization of pure styrene at 25°C are of the order of 1×10^{-4} l. mole^{-1} sec^{-1},[38] which is smaller by 6×10^5 than the values obtained in this study for the copolymerization of styrene and cellulose. These values compare favorably with those of Odian et al.[3] obtained for the grafting of styrene to nylon, of 20 l. mole^{-1} sec^{-1}. In a study of the grafting of styrene to polyethylene,[1,2] Odian et al. obtained values for $k_p{}^2/k_t$ ranging from 0.12 to 8.3 l. mole^{-1} sec^{-1} depending on the volume of methanol in the outside solution. In this case, the change in $k_p{}^2/k_t$ with increasing methanol concentration is attributed to the insolubilization of the graft polymer chains. The high values of $k_p{}^2/k_t$ obtained in this study suggest that in the monomer solution very high molecular weight branches are obtained giving rise to an increased viscosity in the region of the grafting sites relative to that of the bulk solution. This, in

turn, will cause a decrease in the termination rate due to decreased mobilization of the branches. Thus, a Trommsdorff effect is operational at the grafting sites.

Values for the rate of initiation, R_i, for the homopolymerization reaction were obtained through use of a composite G(radical) value. This assumes that each of the components of the monomer solution contributes to the initiation of homopolymerization to an extent dependent on its G(radical) value and its weight fraction in the mixture. The individual G values used were cellulose,[34] 2.88; water,[35] 4.8; styrene,[36] 0.69; and dioxan,[37] 2.0.

Thus denoting weight fraction by W,

$$G_{composite} = (G_{styrene} \times W_{styrene})$$

$$+ (G_{water} \times W_{water}) + (G_{dioxan} \times W_{dioxan}).$$

This calculated composite G(radical) value enables a realistic approach to the mechanism of homopolymerization to be made. Since composite G values are used, composite values for ρ(monomer and solvent) were calculated. Thus ρ(composite) = (weight of styrene + weight of dioxan + weight of water) in g/l. of the monomer solution. Calculated values of G(radical) composite, ρ(composite), R_i, and k_p^2/k_t are given in Table III.

TABLE III

K_p^2/K_t in Homopolymerization (h) for the same Bulk Monomer Concentrations as in Tables I and II; Values Obtained from Rates of Homopolymerization R_p (h) Together with Values of R_i Calculated from the Composite G(radical) of each Bulk Medium

Monomer concn. in bulk, mole/l.	G(radical) composite	ρ(composite) g/l. $\times 10^{-3}$	R_i(h), mole l.$^{-1}$ sec^{-1} $\times 10^{10}$	R_p(h), mole l.$^{-1}$ sec^{-1} $\times 10^7$	k_p^2/k_t, l. mole^{-1} sec^{-1} $\times 10^4$
0.432	2.10	1.017	8.01	1.39	2.58
0.864	2.0	1.011	7.57	2.97	3.13
1.73	1.8	0.999	6.74	5.97	3.54
2.59	1.7	0.986	6.29	9.05	3.86
3.46	1.6	0.973	5.84	11.2	3.58

The values of k_p^2/k_t obtained in this study of styrene homopolymerization are in good agreement with those of other workers and with the accepted value for the free-radical polymerization of the pure styrene. An increase in k_p^2/k_t is observed with increasing concentration of monomer due to changes in the viscosity of the monomer solution and consequent restriction of movement of the growing polymer chains.

Utilization of known values of k_p^2/k_t and k_p for the free-radical polymerization of styrene, 1×10^{-4} l. mole^{-1} sec^{-1} and 55 l. mole^{-1} sec^{-1}, respectively, enables values for k_t to be calculated.

Rearrangement of eqs. (5) and (6) yields

$$G = \frac{N_A \times 100 \times R_i}{\rho \phi}$$

and

$$R_t = \frac{2R_p{}^2 k_t}{[M]^2 (k_p)^2}$$

Hence values for G(composite) may be derived. Table IV shows values of composite G(radical) obtained for various monomer concentrations. It is seen that these values compare favorably with those used in the determination of experimental $k_p{}^2/k_t$ values for homopolymerization.

TABLE IV

Calculated G(radical) Values of the same Bulk Homopolymerization Media as in Tables I, II, and III; Obtained from R_p(h) Together with Values of R_t Calculated on the Basis of Literature Values for $k_p{}^2/k_t$

Monomer concn. in bulk, moles/l.	ρ (composite), g/l. of bulk solution $\times 10^{-3}$	R_t(h) calculated, moles l.$^{-1}$ sec^{-1} $\times 10^{10}$	R_p(h), moles l.$^{-1}$ sec^{-1} $\times 10^7$	$k_p{}^2/k_t$, l. mole^{-1} sec^{-1} $\times 10^{-4}$ (from literature values)	G(radical), composite, calculated
0.432	1.017	7.17	1.39	2.88	1.9
0.864	1.011	8.23	2.97	2.88	2.1
1.73	0.999	8.29	5.97	2.88	2.2
2.59	0.986	8.44	9.05	2.88	2.3
3.46	0.973	7.25	11.18	2.88	2.0

Experimentally determined $k_p{}^2/k_t$ values are in close agreement with those obtained using a literature value for k_p and a value of k_t calculated from quoted values of $k_p{}^2/k_t$ and k_p. This indicates that the individual experimental values of k_p and k_t for the radiation-induced homopolymerization of styrene, as described, are probably of similar order to the literature values of k_p and k_t.

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