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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
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To cite this Article Wilson, J. E.(1971) 'Radiolytic Grafting of Styrene on Polymethylpentene Film', Journal of Macromolecular Science, Part A, 5: 4, 777 — 792

To link to this Article: DOI: 10.1080/00222337108061058

URL: http://dx.doi.org/10.1080/00222337108061058

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J. MACROMOL. SCI.–CHEM., A5(4), pp. 777-792, July, 1971

Radiolytic Grafting of Styrene on Polymethylpentene Film

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SUMMARY

Gamma ray initiated grafting of styrene on three polymers gave rates in the order polyethylene > polypropylene > polymethylpentene, with saturation absorption of styrene in the order polymethylpentene > polypropylene > polyethylene, indicating that the plasticizing action of absorbed styrene possibly causes increased termination rate and reduced over-all grafting rate. The rate of styrene grafting on polymethylpentene was unaffected by temperature change in the range from 23 to 85°C. Above a certain critical film thickness, styrene grafting rate is proportional to film surface area rather than film weight.

I. INTRODUCTION

Polymethylpentene film was selected as the polymer substrate to be used in this investigation for two reasons. First, little or no work on the radiolytic grafting of monomers on polymethylpentene has been published. Second, comparison of the grafting behavior of poly(4-methylpentene-1) with that of other hydrocarbon polymers such as polyethylene and polypropylene should be of interest.

II. EXPERIMENTAL PROCEDURE

The 0.5 Ci ^{60}Co source was designed in the form of a hollow cylinder very similar in size and shape to the one described by Daniels [1]. Along the central axis of such a source the radiation intensity reaches a maximum at the center and falls off toward both ends of the cylinder [1]. Each film sample measured 0.5 by 2.0 cm, and was placed in a section of a glass reaction tube measuring 2.5 cm in length and 0.7 cm in inside diameter. Spacing and centering techniques were employed such that the reaction tube was always positioned at the same point in the center of the ^{60}Co source during each irradiation run. This method provided constancy of dosage rate, and resulted in good reproducibility of grafting rate from run to run.

Ferrous sulfate dosimetry [2] was used to determine the radiation dose rate in the center of the source at the location where the film grafting reactions were run. The concentration of ferric ion formed was computed from the absorbance of the solution at 305 nm measured with a Beckman DB-G spectrophotometer. The average of two determinations gave a dose rate of 840 R/hr.

Each monomer was distilled and stored over anhydrous calcium sulfate at refrigerator temperature before use. Just prior to making a grafting run, oxygen was removed from the monomer in a suitable high vacuum system. The procedure involved several successive cycles of freezing the monomer in a Dry Ice trap, pumping down, and melting the monomer again. In the last step, the monomer was transferred to the reaction tube surrounded by a Dry Ice bath. The reaction tube containing polymer film and monomer was hermetically sealed off with a hand torch while pumping on the system. The reaction tube was then centered inside the ^{60}Co cylinder in a fixed position.

The styrene provided by the above method may be referred to as "moderately dry." Metz and others have resorted to extensive baking of the glass apparatus and rigorous drying treatments to produce "extremely dry" styrene [3, 4], and have found that the radiolytic bulk polymerization of such styrene takes place by predominantly ionic rather than free radical mechanisms. However, a search of the literature discloses that virtually all of the radiolytic grafting work on polyethylene and polypropylene has been done with "moderately dry" monomers prepared by drying over anhydrous calcium sulfate or by some similar technique. To permit comparisons with such work, the present investigation has been carried out with "moderately dry" styrene and other monomers.

After completion of the irradiation of the reaction tube containing polymeric film and monomer, the film was extracted by stirring in warm benzene for 48 hr, then dried in air and weighed. The purpose of this technique was to remove any homopolymer in or on the film. The procedure used has been found reasonably successful in this regard by several investigators [5-7]. A correction for film weight loss during extraction was made by running a blank (ungrafted) film through the extraction and drying procedure. Unless otherwise noted, all grafting runs were carried out at the temperature of the irradiation room, 23 ± 1°C.

Per cent grafting was computed from corrected film weight (P_0) prior to grafting and weight after grafting (P_g) as follows:

$$\text{Per cent grafting} = \left[\frac{P_g - P_0}{P_0}\right] \times 100 \tag{1}$$

In several cases the weight of the swollen film (P_S) at the end of the run was determined by quickly drying the film between filter papers and weighing it in a weighing bottle. The per cent swelling uncorrected for grafting was calculated as follows:

$$\text{Per cent swelling} = \left[\frac{P_S - P_0}{P_0}\right] \times 100 \tag{2}$$

In the high temperature runs, temperature was controlled by means of a glass constant temperature jacket located within the hollow source. The constant temperature jacket was shaped like a hollow cylinder, and the reaction tube containing film and monomer was inserted into the center of the constant temperature jacket. Distilled water was pumped to and from the jacket by a Haake Model FE circulator, rated at a temperature control capability of ±0.005°C by the manufacturer. Estimated temperature control within the reaction tube was better than ±0.1°C, based on measurements made in the center of the constant temperature jacket.

III. RESULTS AND DISCUSSION

A. Comparison with Other Polymers

Figure 1 compares the grafting rates of styrene on polymethylpentene, polypropylene, and polyethylene at room temperature and at the same dosage rate. The per cent grafting vs. time curve is linear for all three polymers, at least in the initial portion of the curve.

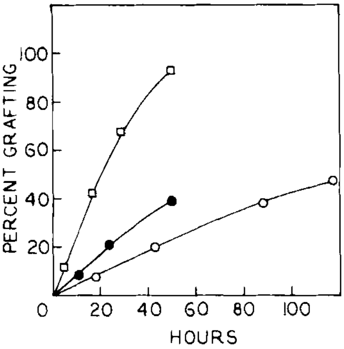


Fig. 1. Room temperature grafting of styrene on three polymeric films: (○) 0.0055 in. polymethylpentene; (●) 0.00075 in. polypropylene; and (□) 0.0085 in. polyethylene (0.960 density).

The polymeric films indicated in Fig. 1 are of different thicknesses, and it is known that very thick films can slow down the penetration of monomer to the grafting site causing a reduction in the observed grafting rate. Such is not believed to be the case for the films used in Fig. 1, based on the pertinent data to be summarized below.

The differences in rate shown in Fig. 1 must depend upon the mechanism of the grafting reaction. In attempting to explain these differences, it will be assumed that a free radical polymerization mechanism is involved, since Metz and others have shown that "moderately dry" styrene probably polymerizes by a free radical mechanism [3, 4]. The expression for the rate of radiation-induced polymerization by a free radical mechanism can be written [8]:

$$\text{rate} = k_p k_t^{-1/2} R_i^{1/2} [M] \tag{3}$$

where k_p and k_t are rate constants for propagation and termination, respectively, and [M] equals monomer concentration. The R_i term indicates the total rate of initiation by several possible free radical types, and includes for each radical an efficiency factor representing the fraction of radicals of that type which are successful in initiating chains by reaction with a monomer molecule. Dosage rate will affect R_i, because an increase in dosage rate will increase the rate of formation of all types of free radicals. While Eq. (3) was derived for use in a homogeneous liquid system, it can provide a basis for discussing a free radical polymerization mechanism in a highly viscous polymeric medium if the properties of the medium are taken into account.

Qualitative information on the types of free radicals formed in these polymers by gamma irradiation is available from ESR spectroscopy studies. The ESR spectra of irradiated polyethylene vary greatly with the irradiation conditions, and have been interpreted as caused by a variety of radical types including the following [9-11]:

$\sim\!\sim CH_2-\dot{C}H-CH=CH-CH_2\sim\!\sim$

I

$\sim\!\sim CH_2-\dot{C}H-CH_2\sim\!\sim$

II

$\sim\!\sim CH_2-\dot{C}H-CH_3$

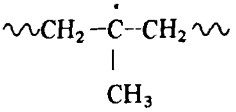
III

Such radicals, when formed in polyethylene film, are presumably capable of initiating styrene grafting. Details of the initiation step for each radical type are lacking, including knowledge of the efficiency factor and effective radical lifetime under grafting conditions.

The ESR spectra of irradiated polypropylene have been attributed to a large number of possible free radicals, including [12-14]:

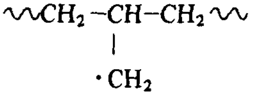
$\sim\!\sim CH_2-\dot{C}H-CH_2\sim\!\sim$

IV



$\sim\!\sim CH_2-\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}-CH_2\sim\!\sim$

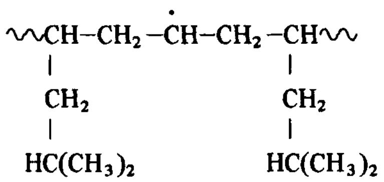
V



$\sim\!\sim CH_2-\underset{\displaystyle \cdot CH_2}{\underset{|}{CH}}-CH_2\sim\!\sim$

VI

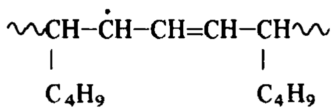
Gamma irradiation of poly(4-methylpentene-1) has also been studied by ESR spectroscopy. At liquid nitrogen temperature the ESR spectrum was attributed to the following structure [15]:



$$\begin{array}{ccccccccc} \sim\!\sim CH & - & CH_2 & - & \dot{C}H & - & CH_2 & - & CH\sim\!\sim \\ | & & & & & & & & | \\ CH_2 & & & & & & & & CH_2 \\ | & & & & & & & & | \\ HC(CH_3)_2 & & & & & & & & HC(CH_3)_2 \end{array}$$

VII

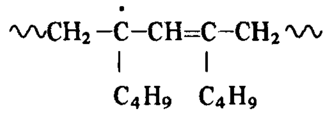
On warming to -30°C, a new spectrum was obtained which was interpreted as arising from allylic radicals:



$$\begin{array}{ccccccccc} \sim\!\sim CH & - & \dot{C}H & - & CH & = & CH & - & CH\sim\!\sim \\ | & & & & & & & & | \\ C_4H_9 & & & & & & & & C_4H_9 \end{array}$$

VIII

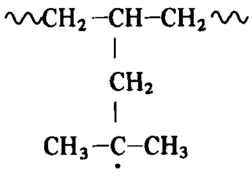
Other work [16] along similar lines revealed the presence of at least one more radical at liquid nitrogen temperature, believed to have the structure



$$\begin{array}{ccccccccc} \sim\!\sim CH_2 & - & \dot{C} & - & CH & = & C & - & CH_2\sim\!\sim \\ & & | & & & & | & & \\ & & C_4H_9 & & & & C_4H_9 & & \end{array}$$

IX

or possibly



$$\begin{array}{ccccc} \sim\!\sim CH_2 & - & CH & - & CH_2\sim\!\sim \\ & & | & & \\ & & CH_2 & & \\ & & | & & \\ CH_3 & - & \underset{\bullet}{C} & - & CH_3 \end{array}$$

X

When the sample was warmed the spectrum changed, indicating transformations to other radicals which were not identified.

Although the role of each radical type in the initiation of polymer film grafting is unknown, there is no reason to assume that the radicals from polyethylene are more efficient initiators than those from polymethylpentene, or vice versa. For each polymer the value of R_i can be estimated from the radiochemical yield of free radicals, G_R. However, the G_R values available are not accurate enough to permit a meaningful comparison of the three polymers. It is concluded that the present knowledge of the R_i factor in Eq. (3) cannot provide a specific explanation for the grafting rate differences shown in Fig. 1.

Noting that many of the postulated free radicals are formed by the abstraction of a tertiary hydrogen atom, it might be thought that the rate differences in Fig. 1 could be explained on the basis of differing degrees of branching in the polymer main chain and side chains. Polypropylene contains one branch (and one tertiary hydrogen) for every three carbon atoms, and the same ratio exists for polymethylpentene if both main and side chains are included. Polyethylene contains very minor amounts of chain branching as revealed by IR studies. Examination of Fig. 1, however, shows a high grafting rate for polyethylene and low grafting rates for polypropylene and polymethylpentene. Hence, while branching may play some part in determining the rate of grafting, it must not be the dominant factor.

Equation (3) shows polymerization rate dependent on the first power of monomer concentration, and such is the case for homogeneous free radical polymerization in the liquid phase. When the reaction takes place within a polymer film, an increase in monomer concentration may also cause an increase in k_t as shown by Takamatsu [17] for the styrene/polyvinylchloride grafting system. Since k_t is a measure of the recombination rate of active centers at the end of growing chains, its value will be affected by the molecular motion of the grafted branches, which in turn is facilitated through the absorption of monomer by the polymer. Takamatsu estimated that an increase in absorbed styrene concentration from 2.0 to 5.2 mole/liter caused k_t to increase by a factor of about 300. He demonstrated the plasticizing action of the styrene by recording successive changes in the polymeric stress/strain curves as the concentration of monomer in the polymer increased. In the present work, the saturation styrene absorption at room temperature for each polymer was measured and compared with the grafting rate taken from Fig. 1. The data are presented in Table 1.

The rate is roughly inversely proportional to the styrene saturation concentration, a relation somewhat superficial because it fails to take account of the other factors in Eq. (3). It does suggest that styrene may have a plasticizing action, increasing the value of k_t and decreasing the over-all rate of grafting as expected from Eq. (3).

Table 1

Polymer	Grafting rate (%/hr)	Styrene[a] absorption (% wt gain)	Estimated styrene concentration (mole/liter)
Polymethylpentene	0.47	19.6	1.33
Polypropylene	0.89	8.8	0.70
Polyethylene	2.40	4.5	0.40

[a] Using samples that had not been irradiated.

One of the other factors in Eq. (3) is the propagation rate constant, k_p, and it is useful to inquire what effect the monomer plasticizing action would have on the value of k_p. It would appear that monomer plasticizing action would have some effect on k_p, which involves the diffusion of a polymeric radical and a small monomer molecule, but not as much effect as it does on k_t which involves the diffusion toward each other of two large polymeric radicals.

B. Comparison of Monomers

Rates of grafting of styrene and methyl methacrylate on polymethylpentene film are compared in Fig. 2. The autocatalytic character of the methyl methacrylate curve has also been observed in the grafting of methyl methacrylate on polyethylene [18], and has been attributed to the gel effect often noted in methyl methacrylate polymerization.

Attempts were made to graft acrylonitrile on polymethylpentene under the same irradiation conditions, but any grafting that resulted was too small to measure. Independent experiments in the absence of radiation indicated that polymethylpentene films immersed in acrylonitrile showed no weight increase, demonstrating that the monomer did not penetrate into the films. Under such conditions the monomer could not reach the free radical sites in the film that initiate grafting.

Figure 3 presents per cent grafting vs. uncorrected per cent swelling for 0.0055 in. thick polymethylpentene and 0.0085 in. polyethylene in styrene. The curve obtained in both cases is linear, indicating that grafting is proportional to swelling and vice versa. At all values of per cent grafting, the per cent swelling is greater for polymethylpentene than for polyethylene,

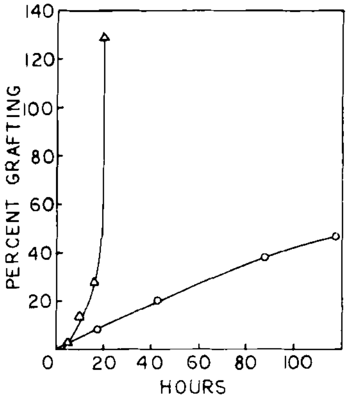


Fig. 2. Grafting of liquid styrene (○) and methyl methacrylate (△) on 0.0055 in. film of polymethylpentene.

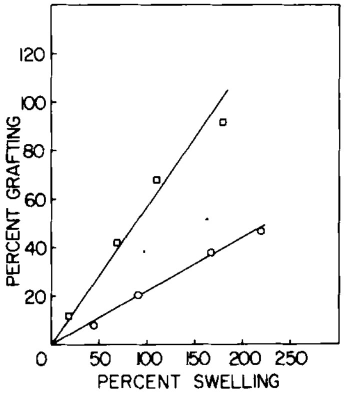


Fig. 3. Grafting vs. swelling in liquid styrene at room temperature for 0.0055 in. polymethylpentene (○) and 0.0085 in. polyethylene (□) of 0.960 density.

as expected in view of the greater styrene absorption for polymethylpentene than for polyethylene (Table 1).

Figure 3 shows large uncorrected swelling values in the range of 100 to 200%. This is not surprising in view of the changed character of the grafted polymer. The increased percentage of grafted styrene branches in a polymer makes it capable of absorbing a much higher percentage of liquid styrene. A similar effect was observed by Kawase [19], who studied the saturation absorption of several alkyl methacrylates by polypropylene. It was noted that polypropylene absorbed several times as much of a particular alkyl methacrylate after radiolytic grafting of the alkyl methacrylate on the polypropylene as it did in the ungrafted state.

Comparison of Figs. 1 and 3 is of interest. Referring to Fig. 1, per cent grafting on polyethylene is about 70% and that on polymethylpentene is about 14% in the first 30 hr, both curves being approximately linear during that time period. The linearity of the curves indicates essentially unchanged grafting polymerization rate in the same period. Yet Fig. 2 shows uncorrected swelling in 30 hr of about 120% for polyethylene and 70% for polymethylpentene, corresponding to large increases in [M] in Eq. (3) for both types of film. In order to account for the constancy in rate, some other factor in Eq. (3) must also be changing to balance the effect of the increase in [M]. It is reasonable to postulate that the plasticizing action of increased monomer concentration produces an increase in the rate of polymeric radical recombination, k_t, thus balancing the effect of increased [M] and preserving rate constancy. For methyl methacrylate such a balancing of these two effects is evidently not perfect (Fig. 2), possibly because of this monomer's well known gel effect which causes k_t to decrease and the over-all rate to increase as polymerization progresses.

C. Effect of Temperature

The initial portion of the per cent grafting vs. time curve for styrene/polymethylpentene at several temperatures is shown in Fig. 4. The computed initial grafting rates are plotted against temperature in Fig. 5, and there is evidently little change in grafting rate over the 23 to 85°C range.

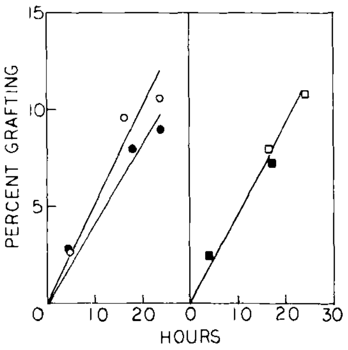


Fig. 4. Grafting of styrene monomer on 0.0090 in. film of polymethylpentene at 40°C (○); 55°C (●); 70°C (□); and 85°C (■).

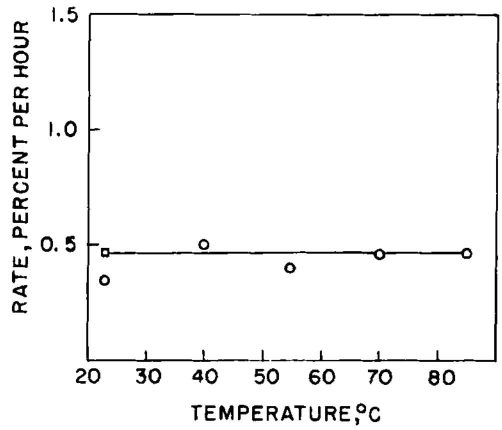


Fig. 5. Styrene grafting rate vs. temperature for polymethylpentene film; (○) 0.0090 in. and (□) 0.0055 in. thickness.

The lack of rate variation indicates a zero energy of activation for the grafting of styrene on polymethylpentene in this temperature range. Ballantine [6] studied the grafting of styrene (dried over calcium sulfate) on polyethylene in the range from 0 to 53°C, using polyethylene films that had been irradiated at 30°C in vacuo. The initial grafting rate in that range was essentially independent of temperature, but the lengthier runs showed greater amounts of styrene grafted as the temperature increased. Ballantine noted that a change in temperature influences grafting rate by its effect on three parameters: 1) rate of styrene diffusion into the film, 2) propagation rate, and 3) termination rate involving radical recombination, which is a diffusion-controlled process. A major factor preventing higher grafting rates as temperature increases may be the greater free radical mobility and the resulting increase in termination rate.

The possibility of some cationic polymerization in the styrene/polymethylpentene system cannot be ruled out. The monomer may have been dried more thoroughly than expected, and Ueno [4] has shown that radiolytic styrene polymerization is predominantly cationic under very dry conditions. Bulk polymerization of styrene dried with calcium hydride was studied from -20 to 70°C and the rate showed a maximum at about 30°C, the height of the maximum varying with the batch of styrene used. Earlier results [20] on styrene dried with sodium alloy showed a negligible activation energy in the range from -20 to 80°C.

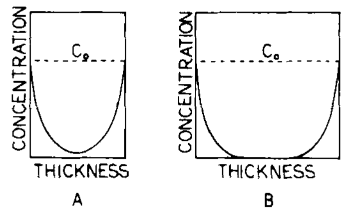


Fig. 6. Hypothetical monomer concentration function vs. film thickness compared for a thin film (A) and a thick film (B).

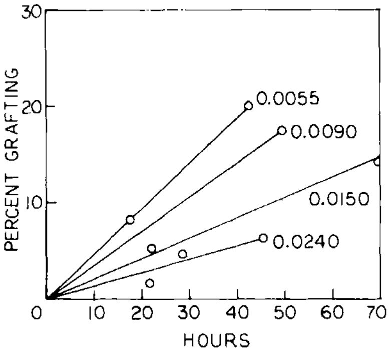


Fig. 7. Grafting of styrene on polymethylpentene film of several thicknesses; film thicknesses indicated in inches. Rate for 0.0090 in. film was substantiated by other runs of 88.7 and 116.9 hr duration.

D. Effect of Film Thickness

Several investigators have observed that the monomer may take longer to diffuse into thicker films, causing an apparent decrease in grafting rate. For example, Chapiro [21] found that the rate of grafting of styrene on polyvinyl chloride film at 20°C was entirely controlled by the rate of diffusion of monomer into the interior of the film. When the reaction temperature was increased to 60°C, the monomer diffused into the film more rapidly and the reaction rate was no longer limited by the monomer diffusion rate.

The situation that probably exists inside the polymer film can be illustrated by reference to Fig. 6, which compares a thin film (A) with a much thicker film (B). Considering film (A) first, the solid curve shows monomer concentration as a function of film thickness some time after the start of the grafting reaction. The shape of the curve is completely arbitrary, and is only intended to show that the monomer concentration is considerably reduced in the center of the film as a result of the grafting reaction. The dotted line indicates the concentration, C_0, that would be obtained in the absence of the grafting reaction.

In the thicker film, (B), the monomer reacts and is consumed before it can diffuse to the center of the film. The supply of monomer in a considerable portion of the center of the film is completely exhausted. Under these circumstances the monomer penetrates to a limited depth, d, and all of the grafting takes place within a distance d from the surface of the film. Hence, if the film were thick enough, the weight of monomer grafted per unit time should be proportional to film surface area rather than film weight. It follows that the rate of film grafting per unit surface area should become constant above a certain critical film thickness.

This hypothesis has been tested for the radiolytic grafting of styrene on polymethylpentene. Figure 7 presents the initial portion of the grafting vs. time curve for several thicknesses of polymethylpentene film. Figure 8 presents the computed grafting rate per unit surface area as a function of film thickness. As an example of the computation, the 0.0055-in. film grafts styrene at a rate of 0.473%/hr. Assuming a density of 0.83 g/cc, each square centimeter of film weighs 11.6 mg and gains (11.6 X 0.00473) mg/hr, or 0.0548 mg/hr. Since the film has two surfaces, this corresponds to 0.027 mg/hr per square centimeter of film surface as shown in Fig. 8.

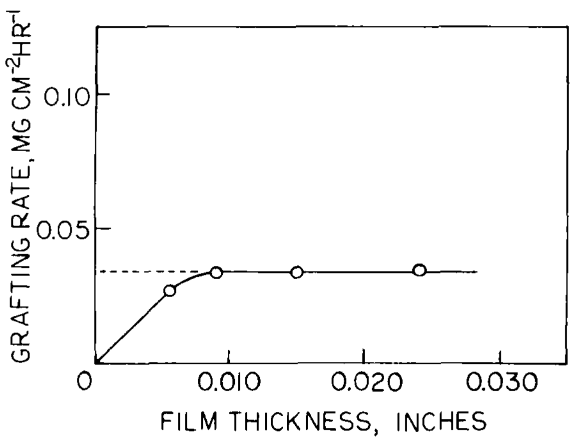


Fig. 8. Grafting rate per square centimeter of surface vs. film thickness for styrene on polymethylpentene.

Figure 8 indicates that grafting rate per unit surface area becomes constant at 0.034 mg/sq cm/hr above a film thickness of about 0.008 in. This would correspond to a monomer penetration depth of about 0.004 in., reckoned on the basis of original film dimensions before the start of swelling due to monomer absorption. The monomer concentration must increase constantly in the affected portion of the film during grafting as shown by the large monomer absorption recorded in Fig. 3.

For the purpose of simplicity, the curve in Fig. 8 is drawn arbitrarily as a straight line from the origin to the dotted horizontal portion. The section mentioned may not be linear, but must depend in a complex way upon the monomer concentration across the thickness of the film.

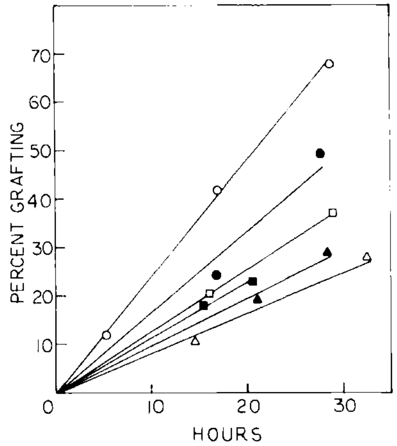


Fig. 9. Grafting of styrene on polyethylene film (0.960 density) of various thicknesses; (○) 0.0085, (□) 0.0180, (△) 0.0275, (●) 0.0150, (■) 0.0055, and (▲) 0.0235 in. thick.

The proposed hypothesis was also checked for the case of styrene grafting on polyethylene film. Figure 9 presents grafting curves for several film thicknesses, and Fig. 10 shows grafting rate per unit surface area as a function of film thickness. In this case the rate becomes constant at 0.29 mg/sq cm/hr above a film thickness of about 0.010 in. This corresponds to a monomer penetration depth of about 0.005 in.

The slightly greater penetration depth might be unexpected in view of the faster grafting reaction for polyethylene. However, it can be explained by considering the per cent styrene absorbed by the two polymers after

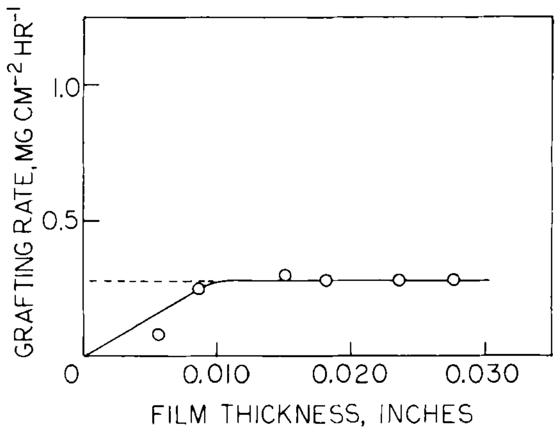


Fig. 10. Grafting rate per square centimeter of surface vs. film thickness for styrene on polyethylene (0.960 density).

grafting has taken place for a certain length of time. For example, after 30 hr of grafting, Fig. 1 shows 70 and 14% grafting for polyethylene and polymethylpentene, respectively. These figures correspond to 120 and 70% swelling, respectively, for polyethylene and polymethylpentene (Fig. 3). Thus, for any grafting time selected, monomer absorption will be greater for polyethylene and will probably involve a thicker surface layer. Hence, the greater penetration depth for polyethylene shown in Fig. 10 is reasonable.

In view of the simple assumptions underlying the relation shown in Figs. 8 and 10, it may be found to apply to other monomer/polymer systems. Supporting evidence for the postulated shape of the concentration curves in Fig. 6 is provided by the work of Matsuo [22], who analyzed styrene concentration across polypropylene film thickness during radiolytic grafting and obtained concentration curves similar to a catenary in shape.

ACKNOWLEDGMENTS

This work was supported by a research grant from the National Aeronautics and Space Administration. Polymeric films were supplied by Imperial Chemical Industries and Allied Chemical Corporation. Appreciation is also due to Mr. Donnie Shaw and Mr. Melford Henderson, who assisted in the experimental work and in preparing the drawings.

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Accepted by editor November 5, 1970
Received for publication January 13, 1971