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RADIATION-INDUCED GRAFTING OF STYRENE TO POLYETHYLENE AND HEXATRIACONTANE

by

Ihab Labib Kamel

Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

1971

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APPROVAL SHEET

Title of Thesis: Radiation-Induced Grafting of Styrene to Polyethylene and Hexatriacontane

Name of Candidate: Ihab Labib Kamel

Doctor of Philosophy, 1971

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ABSTRACT

Title of Thesis: Radiation-Induced Grafting of Styrene to Polyethylene and Hexatriacontane

Author, degree sought, date: Ihab Labib Kamel, Ph.D., 1971

Thesis directed by: Professor Joseph Silverman
Department of Chemical Engineering

The radiation induced graft polymerization of styrene to low density polyethylene film was studied at room temperature as a function of the sorbed styrene and compared with the grafting to hexatriacontane (HTC). Two methods were used for varying the concentration of styrene in the polyethylene: (1) exposing the film to monomer vapor for various time intervals; (2) immersing the film in various solutions of styrene and methanol. In both methods, similar grafting rates were obtained as a function of monomer concentration; vapor phase grafting gave lower yield values due to the effect of diffusion. Methanol diffusion into polyethylene was found to be negligible and did not influence the kinetics of the grafting reaction. The grafting rate of styrene to polyethylene film exhibited a maximum at 4% styrene concentration when grafting in the vapor phase and at 6.2% when grafting with a methanol solution.

The results are explained in terms of the concentration of sorbed monomer and its effect on the viscosity of the amorphous region of polyethylene when partially swollen by the monomer.

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The proposed model conflicts with those of earlier publications which explain the accelerating effect of methanol on the grafting rate in terms of radiation protection effects and chain conformation. Supporting evidence for the mechanism is presented by kinetic data and molecular weight measurements when grafting styrene vapor to HTC crystals over a dose rate range of 3×10^3 to 3×10^5 rad/hr.

Grafting styrene liquid to HTC crystals was performed with different HTC-styrene suspensions and compared with calculations based on several models. The results fit a model which postulates 100% efficiency of radical migration to the surface of the crystals and conversion to graft chains.

An important practical consequence is the demonstration of how monomer vapor and dilute monomer solutions can yield much higher grafting rates than pure monomer liquid, and how the gain in grafting yield can be accompanied by a better product and reduced monomer losses.

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Chapter I

INTRODUCTION

Radiation induced grafting of a monomer to a formed polymer is potentially one of the most important applications of ionizing radiation to industrial processes. A description of the method is given in Appendix A. Because the grafted molecule is composed of a main chain composed of one monomer and side chains composed of another monomer, the characteristics of the copolymer combine those of the two constituents. The technique is a rather powerful means of obtaining a polymeric material with properties to fit a highly specified application at hand. Grafting of styrene to polyethylene by ionizing radiation has long been used as the model system for these studies which aim at understanding the problems associated with this technique.

After twenty years of research there are still some unknown features in this system. The principal problem to which this work has addressed itself is the effect of crystallinity and the effect of monomer concentration in polyethylene on the outcome of the grafting reaction.

In this chapter a summary of the principal kinetic features of the system and a survey of the pertinent literature is presented.

Kinetics of Grafting

The kinetics of grafting by the free radical process is frequent-

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ly described in the manner of Chapiro [10]. Symbols are defined in the text and listed in Appendix E.

If one considers a formed polymer P which contains a monomer M as a consequence of exposure to that monomer, the initiation processes induced by radiation are:

$$M \xrightarrow{\sim} M^{\bullet} \qquad (1)$$

$$P \xrightarrow{\sim} P^{\bullet} \qquad (2)$$

Where M = monomer molecule,

$M^{\bullet}$ = monomer radical,

P = polymer molecule,

and $P^{\bullet}$ = polymer radical.

The rates of free radical production (initiation rates) are given by

$$R_i^m = I \, \phi_m \, C_m \qquad \text{and} \qquad (3)$$

$$R_i^p = I \, \phi_p \, C_p \quad , \qquad (4)$$

where R_i^m and R_i^p = the rates of chain radical initiation in the monomer and polymer respectively (mol $l.^{-1}$ sec^{-1}),

C_m and C_p = concentrations of monomer and polymer respectively in the swelled polymer (mol/l.),

ϕ_m and ϕ_p = yields of free radicals per unit concentration and per unit radiation in the monomer and in the polymer respectively (sec^{-1}),

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I = radiation dose rate (rad/sec),

and t = reaction time (sec).

In the styrene-polyethylene system, the radiation yield of radicals in the monomer is a tenth of the radiation yield in the polymer. To a first approximation, therefore, one usually neglects chain initiation in the styrene. It will be demonstrated in Chapter III, however, that homopolymerization of the monomer may not be neglected in some grafting systems.

The propagation rate of the growing chains of the grafted polymer is

$$-dC_m/dt = k_p C_m C_{p\cdot} \quad , \tag{5}$$

where k_p = specific rate constant for propagation (l. mol^{-1} sec^{-1})

and $C_{p\cdot}$ = concentration of free radical initiated on the polymer (mol/l.).

Two growing polymer chains will terminate each other either by recombination or disproportionation to produce neutral polymer chains. The general form of the termination rate is

$$R_t = k_t C_{p\cdot}^2 \quad , \tag{6}$$

where k_t = specific rate constant for termination (l. mol^{-1} sec^{-1}).

Chain transfer reactions may also occur. Since chain transfer is a minor effect in the styrene-polyethylene system, we will ignore it in this treatment.

Under steady state conditions the rate of radical chain formation

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equals the rate of radical chain destruction. This leads to the steady state radical concentration

$$C_{p\cdot} = (\phi_p I/k_t)^{\frac{1}{2}} C_p^{\frac{1}{2}} \tag{7}$$

Substituting equation (7) into (5) one obtains the grafting rate

$$R_{p,g} = -dC_m/dt = (k_p/k_t^{\frac{1}{2}}) (I \phi_p C_p)^{\frac{1}{2}} C_m \tag{8}$$

where $R_{p,g}$ = rate of conversion of monomer to graft.

These are the characteristic results of the well established theory of steady state free radical polymerization in a homogeneous system and its application to a grafting system where all the radicals are produced only on the backbone polymer.

When the system under consideration is diffusion controlled, Chandler et al.[19] found that equation (8) should be modified as follows:

$$R_{p,g} = (k_p/k_t^{\frac{1}{2}}) (I \phi_p C_p)^{\frac{1}{2}} C_m F, \tag{9}$$

where $F \leq 1$ and is defined by

F = diffusion factor =

$$\frac{8}{\pi^2}\left[\sum_{n=1,3,\ldots}^{\infty} \frac{1}{n^2} \frac{a}{a+K} - \frac{1}{t} \sum_{n=1,3,\ldots}^{\infty} \frac{K}{(a+K)^2} \left(e^{-(a+K)t} - 1\right)\right] \tag{10}$$

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where $a = \pi^2 n^2 D/L^2$,

D = diffusion coefficient,

L = film thickness,

and $K = k_p (I \phi_p C_p/k_t)^{\frac{1}{2}}$.

Equations (8) and (9) describe the rate of weight gain by a formed polymer as a consequence of the radiation induced formation of radical sites and the addition of a monomer to the polymer.

Grafting of Styrene to Polyethylene

The radiation induced graft polymerization of styrene to polyethylene films has been studied over the past twenty years in various laboratories around the world. The majority of the investigations were concerned with the study of the kinetics of the simultaneous irradiation and grafting of polyethylene film in equilibrium with an excess of styrene monomer. A few papers studied other methods of grafting in this system such as post-irradiation grafting or grafting with monomer in solution. In general, it has been shown that the rate and the extent of grafting of the monomer to the polyethylene backbone are dependent upon such variables as dose, dose rate, temperature, degree of crystallinity, film thickness and the presence of oxygen.

The morphology of polyethylene structure added a great deal of difficulty to the interpretation of the kinetic data. Since polyethylene is composed of crystalline regions surrounded by amorphous regions, the question of the effect of crystallinity on the grafting

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yield was an important one to answer. It was found by the ESR and other methods for radical measurements that crystallinity has little effect on the G-value for radical production by radiation [10,35]; but because the monomer diffuses only into the amorphous regions, as was observed from the absorption data [13,15] and the morphological studies [17], some research workers [16,19] theorized that the radicals formed inside the orderly and compact crystalline regions quickly terminate each other leaving only the relatively few surface radicals to react with the monomer units. They concluded that the graft yield is mainly due to the radicals formed in the amorphous region.

If this is the case, why is there grafting on polyethylene crystals at all? Radicals formed on the surface of the crystals are almost negligible and there is no contact between the radicals inside the crystals and the monomer. Machi and Silverman [14] suggested migration of the radicals inside the crystalline region to the surface where they react with the monomer. This last theory agrees with the work of Kawai, Keller and Charlesby [35] who used such a mechanism to explain the lack of change of molecular weight when irradiating single crystals of polyethylene while the yield of unsaturation and hydrogen was unchanged. One of the objectives of the present investigation is to determine if this radical diffusion does in fact take place. Grafting styrene on hexatriacontane (HTC) crystals was used as the experimental method accompanied by calcula-

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tions to show the possible reaction schemes that could take place. HTC is a 36-carbon normal alkane which is insoluble in styrene. It is a good model for crystalline polyethylene. Because of the simplicity and the small size of the HTC crystals, grafting with HTC-styrene suspensions approaches that of a homogeneous system. This makes it possible to study the relationship between the number of primary alkyl radicals produced by gammas in HTC and the number of grafted chains.

Gas-phase grafting on HTC is not complicated by the simultaneous polymerization of appreciable amounts of styrene. It provides the added advantage that the graft copolymer can be easily separated and its molecular weight can be measured. Since the HTC chain is very small (36 units) in comparison with the grafted polystyrene chain (~1000 units), the grafted polymer has the characteristics of polystyrene, and its molecular weight is approximately that of polystyrene chains.

Several contradictory theories have appeared concerning the grafting of styrene to polyethylene; they do not provide a unified explanation that relates the roles of crystallinity, diffusion and the reaction-zone condition to the rate of grafting of the monomer to the polyethylene film. Weight increase of a grafted film was found to be proportional to reaction time and some workers reported a decrease in reaction rate with film thickness [11,19] while the rate of weight gain was independent of the radiation dose. They explained their findings on the basis of a diffusion controlled

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reaction. However, several other workers [1,11,12,13,20] have found experimentally that thick films of polyethylene graft faster than thin ones, an evidence which rules out a diffusion controlled reaction.

Conditions in the amorphous region of polyethylene played a significant role in the outcome of the grafting reaction. Some workers have reported that grafting of styrene to high density polyethylene films is greater than to low density films under the same conditions, despite the fact that the former is more crystalline. These results were obtained when grafting styrene liquid [11,13,14] or styrene vapor [18] to the two types of polyethylene. There is an apparent contradiction in this observation because, assuming that grafting takes place at a certain rate in the amorphous region, we would expect an increase in yield with the increase in the amorphous content of the film. This contradiction was explained by Machi and Silverman [14] as due to an increase in the viscosity of the amorphous region with the increase in the density of the film. This theory, however, lacks the direct measurements of various concentrations on the grafting rate. It was one of the objectives of this research to find the experimental means for changing the concentration of the monomer inside the polyethylene film and to determine experimentally the role of concentration in the outcome of the grafting reaction.

Machi and Silverman summarized the apparent and covalent grafting rates of liquid styrene to high and low density polyethylene films, to polyethylene single crystals and to the completely amorphous

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ethylene-propylene copolymer [14]. These results, shown in Figure 1, are included here for comparison with the present experimental data which were obtained by grafting at lower monomer concentrations (Chapter III). In their work the gain in polyethylene film weight determined after soaking the grafted film in benzene was termed the apparent graft to distinguish it from the covalent or the true graft. The true graft was separated by dissolving the grafted film in xylene at 100°C followed by precipitation in methanol.

Stability of Polyethylene Films Grafted in Liquid Styrene

From the discussion and data presented in this chapter, it is evident that styrene homopolymer will form when irradiating a mixture of polyethylene film in an excess of liquid styrene. The presence of the ungrafted homopolymer not only complicates the kinetic picture of the grafting reaction, but also reduces the quality of the final product. After irradiation and before the usual benzene extraction, the film often has a milky appearance and is less transparent than the untreated film [24].

In general, the presence of free polystyrene chains inside the polyethylene matrix presents the possibility of an unstable final product. The copolymer deterioration has indeed been observed when the grafted polyethylene film comes in contact with a polystyrene solvent such as benzene [11,12,22,23,24]. In contrast with this result, it was found that the grafted film obtained by post-irradiation immersion in styrene is apparently homogeneous and no

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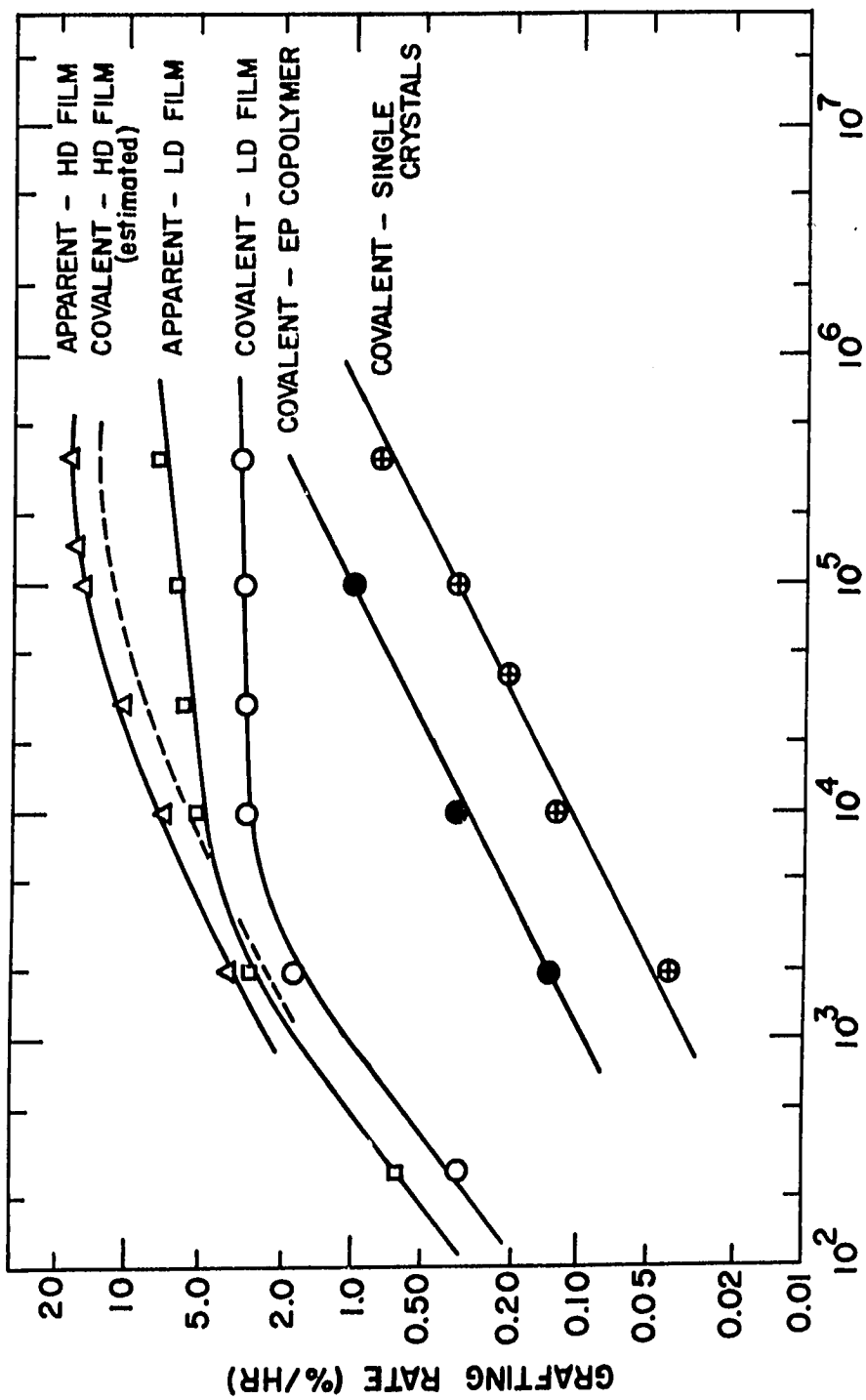

Figure 1. Grafting rate of styrene to polyethylene as a function of dose rate.[14] Polymer irradiated in liquid monomer at room temperature.

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bubbles formed in it when soaked in benzene [22]. The formation of bubbles was also observed after irradiation and before extraction when the film was left in contact with the monomer for several hours [11]; this is apparently due to the solubility of the occluded polystyrene in the styrene monomer.

The formation and growth of bubbles in the grafted polyethylene has been carefully studied in this laboratory [24]. The authors observed no bubble formation before the extraction of the film with benzene when the grafted film was examined under an optical microscope. However, the transparency of the film decreased with dose rate, a fact they related to an increase in the number of microcells of occluded homopolymer. A rapid growth of bubbles was also observed by the same authors at higher dose rates, which they explained as due to the rapid migration of the relatively shorter chains of homopolymer formed at the high dose rates. Thus, the extent of deterioration of the grafted polyethylene is dependent only upon the quantity and the molecular weight of the occluded ungrafted polystyrene in the film and upon the length of time this film has been in contact with the solvent.

The deterioration of the appearance and physical properties of the grafted film caused a lack of industrial interest in this grafting system. This result was one of the reasons for initiating this investigation, especially when the modification of the mechanical properties of the grafted polyethylene film was found to be quite

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significant, if contact of a polystyrene solvent with the film was avoided. Machi and Silverman [14] noted a linear increase in the yield strength and the initial modulus of elasticity with polystyrene content; also a slower increase in tensile strength at break (Figure 2). When the grafted polystyrene, however, was rigorously extracted with benzene, Ballantine et al. [2] found a decrease in the tensile strength and a sharp reduction in the elongation at break.

The practical significane of the above findings is clear. The results showed that radiation-induced grafting can produce useful, uniform polymer blends with improved mechanical properties if extraction of the homopolymer is avoided. The uncertainty of the long range behavior of the occluded homopolymer combined with the limitations of the copolymer's contact with organic solvents will no doubt hinder its use. The advantages of the grafted polymer can be fully utilized only if the occluded homopolymer is eliminated or minimized to a great extent.

The present investigation took upon itself the minimization of the homopolymer problem, because of the industrial potential of such a system. From the study of the kinetics of homopolymerization versus graft polymerization, we can see the dependence of the former on the monomer concentration inside the film. A low monomer concentration will reduce the initiation of the homopolymer chains, while the initiation of the grafted chain is unaffected. All these indications focused the present study of grafting styrene to

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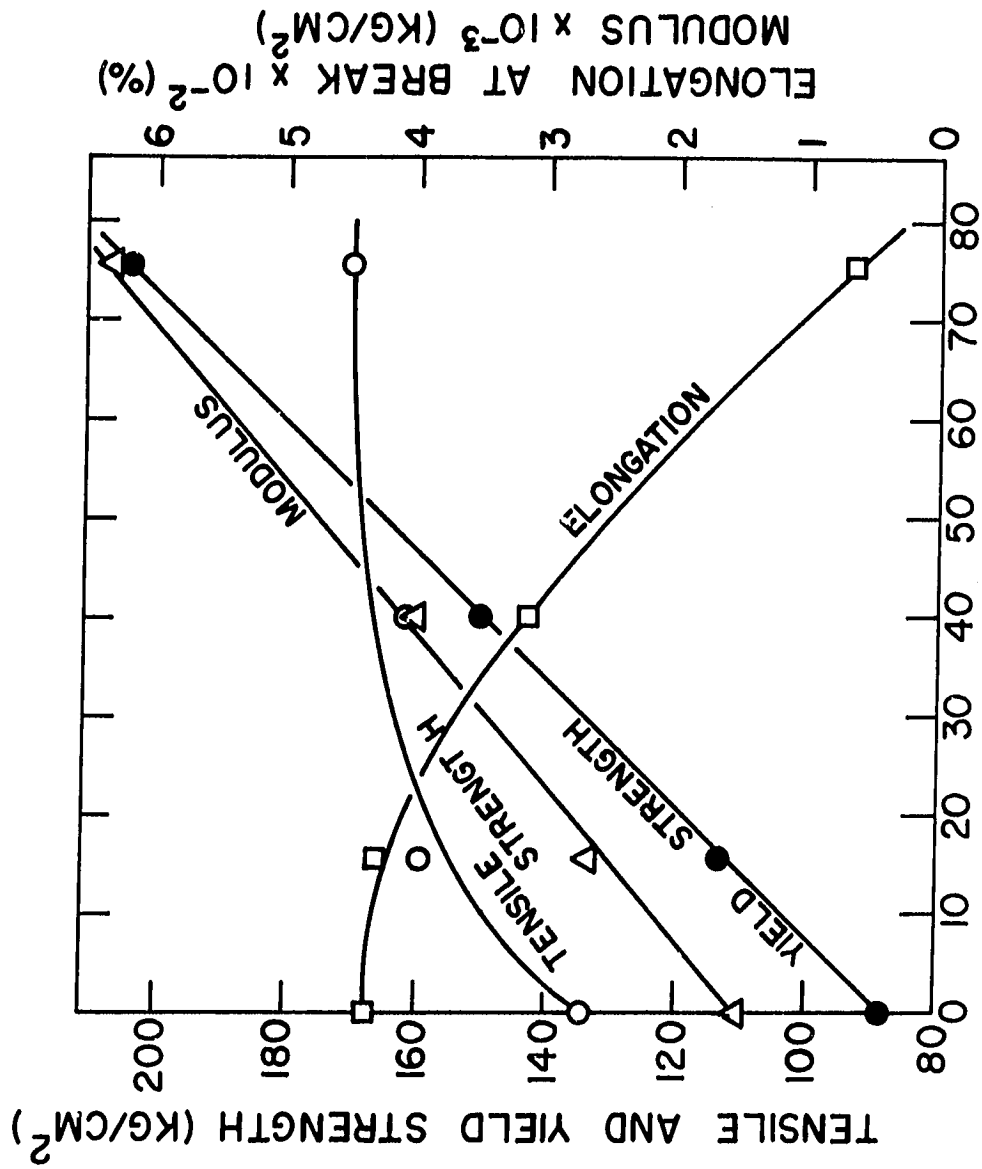

Figure 2. Polystyrene content versus tensile properties of grafted polyethylene. (14) (Reprinted with permission of the authors.)

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polyethylene at reduced monomer concentrations in order to improve both the yield and the product.

Grafting at Various Monomer Concentrations

Two methods were used to vary the monomer concentration in the polyethylene film during grafting.

1. Dilution of the styrene monomer with a suitable solvent.
2. Exposure of the film to styrene vapor for various time intervals prior to irradiation.

The effect of the styrene concentration change on the reaction kinetics was measured and a self-consistent model was devised for its explanation. The model describes how accelerated rates of grafting and a generally improved copolymer are obtained with the added benefit of reduced consumption of monomer. It also provides information on the rapid movement of alkyl radicals in crystalline alkanes.

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Chapter II

EXPERIMENTAL

Materials

Strips (1x6 cm) of additive free 0.063-mm DuPont low density polyethylene film were used in all the polyethylene grafting experiments. The strips used in the grafting experiments with gaseous styrene were washed in benzene. They were dried at 50°C for 1 hour before further drying at 0.1 Torr for 15 hours and stored in a vacuum dessicator.

Polyethylene samples used in the liquid phase grafting were usually not subjected to further purification. It was determined earlier that there was no detected difference between washed and unwashed films as far as the liquid phase grafting reaction was concerned.

Low density polyethylene sheet 0.85 mm thick was used for the experiments on the diffusion of liquid styrene. It was used without further purification.

Commercial grade styrene, a product of Eastman Organic Chemical Company, stabilized with tert-butylpyrocatechol was first washed three times with a 10% aqueous solution of sodium hydroxide and then three times with distilled water. It was dried over calcium chloride and then over calcium hydride. The styrene was then vacuum distilled over calcium hydride at a pressure of 20 Torr corresponding to 35°C overhead temperature and stored in the dark at 5°C. Distilla-

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tion rate was about 20 cm^3/hr with a reflux to distillate ratio of 3:1. Distilled styrene was only used for a maximum period of two weeks; any amount left after this period was usually redistilled. Before use, a styrene sample was added to methanol to test for any polymerization.

Hexatriacontane (HTC) crystals (a C_{36} n-alkane), obtained from Eastman Organic Chemical Company, were first recrystallized from a 1% solution in hexane. Spectrograde hexane, a product of Phillips Petroleum Company, was heated to 70°C to dissolve all HTC crystals. The solution was slowly cooled to room temperature. The precipitated crystals were then separated from the solvent by filtering through a fine grade fritted glass filter. The crystals were subsequently dried under 0.1 Torr for four days. The dried crystals were dissolved in Spectrograde heptane at 70°C to make a 1% solution. The solution was again slowly cooled to room temperature to recrystallize the HTC. The crystals were filtered and dried as before. A test for dryness was made by evacuating a weighed sample of the dried HTC crystals at a pressure less than 1.0×10^{-5} Torr for 24 hours; no loss in weight was detected.

Spectrograde methanol and Baker grade n-octane were used without further purification. Reagent grade benzene was redistilled before use in the irradiation experiments.

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Experimental Procedure

Monomer Diffusion

The diffusion rate of styrene vapor into polyethylene film was measured by a desorption technique similar to the one used by McCall [15]. The strips were strung together on a small copper wire. The average weight of the sample was about 0.22 g. The sample was placed in the upper compartment of an ampule containing liquid styrene at the lower portion. The ampule was connected to a vacuum line and the monomer degassed by repeated freezing and thawing and then the ampule was sealed at a pressure below 2×10^{-5} Torr. The sample was then transferred to a constant temperature bath at 25°C and left in contact with the vapor for a predetermined period of time. The ampule was then removed from the bath and opened; at that moment a stopwatch was started and the sample was quickly hung on the hook of an analytical balance, and its weight was recorded with time. These weight values were plotted versus time and then extrapolated back to zero time to determine the monomer concentration. (See Appendix B.)

Swelling measurements in the case of styrene solutions were performed in a similar fashion. Strips of polyethylene sheet, 0.85 mm thick, were immersed in various styrene-methanol mixtures and styrene-octane mixtures at 25°C. Enough solution (~1000 ml) was used so that the concentration changes in the liquid phase arising from sorption of solution by the polyethylene were negligible. After

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selected intervals, the strips were removed from the solution and rapidly wiped dry. The samples were then hung vertically on the hook of an analytical balance and the weight change as a function of time was recorded by a method similar to the vapor-phase desorption experiment. Extrapolation of these values to zero time gave the degree of swelling.

The composition of the liquid absorbed in the polyethylene samples was determined in the following manner. Several strips of 0.85 mm thick polyethylene totaling 3-7 g in weight were equilibrated in various methanol styrene mixtures at 25°C for 45 hours. Soon after being wiped dry, the samples were placed in a tube fitted with a stopcock connected to a liquid nitrogen cooled trap. The tube was then evacuated by a rotary vacuum pump for 18 hours. By this process the liquid absorbed in the polyethylene was transferred to the cold trap. The trapped liquid was examined for methanol content by a F&M 720 gas chromatograph fitted with an 8 ft column packed with 10% Carbowax 20 M on Chromsorb G(AW).

Vapor-Phase Grafting to Polyethylene

For vapor-phase irradiations, styrene-polyethylene samples were mounted and degassed by the same procedure described for the vapor-phase diffusion experiment above. The degassed samples were then transferred to a 25°C constant temperature bath and were left to equilibrate with the vapor for a period of time chosen to give the desired monomer concentration in the film before the start of

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the irradiation; the samples were then irradiated. At the end of the irradiation period, each sample was removed from the radiation cell and opened, within 3 minutes from removal from the radiation field. The moment the ampule was opened, a stopwatch was started and the sample was quickly hung on the hook of an analytical balance and its weight as a function of time was recorded. These weight values were extrapolated back to zero time to measure the total weight of the grafted film plus the monomer at the end of the irradiation time (W_1). This was usually done for a period of thirty minutes after which the sample was transferred to a vacuum dessicator and left at 0.1 Torr for 15 hours and again weighed (W_2). Following evacuation, the grafted samples were soaked in benzene for 5 days to remove the extractable homopolymer. It was then dried for 15 hours at 0.1 Torr and weighed (W_3). From the original weight of the polyethylene sample before exposure to styrene vapor (W_o), the following information could be calculated:

Concentration of monomer in the film at the end of irradiation (weight %) $= \frac{W_1 - W_2}{W_o} \times 100$; (11)

Total gain in weight (weight %) $= \frac{W_2 - W_o}{W_o} \times 100$; (12)

Extractable homopolymer (weight %) $= \frac{W_2 - W_3}{W_o} \times 100$; (13)

Apparent graft yield (weight %) $= \frac{W_3 - W_o}{W_o} \times 100$. (14)

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The concentration of monomer in the film at the start of each irradiation was determined from the monomer diffusion experiment and the known exposure time of the film to vapor. The net weight gain is termed the apparent graft since it contains not only the covalently bonded graft copolymer but also an unextracted occluded portion of the homopolymerized styrene.

Grafting to Polyethylene With Liquid Monomer Solutions

For the solution grafting experiment, strips of film were immersed in styrene-methanol mixtures in a glass tube. Each mixture was degassed by four cycles of freezing and thawing under vacuum and then sealed off at 10^{-4} Torr. The sample was kept at room temperature overnight and then irradiated. Each tube was opened within 5 minutes after its removal from the radiation field. Post-irradiation grafting in this time interval was found to be negligible by an earlier experiment. The grafted film was subsequently removed from the styrene-methanol mixture and soaked in benzene for 3 days to remove the extractable homopolymer. It was then dried at 0.1 Torr for 15 hours. The weight difference before and after grafting gave the apparent graft.

HTC Grafting

In the grafting of HTC crystals with styrene vapor, a sample of HTC (200-300 mg) was put into an 8 mm O.D. glass tube containing styrene monomer in the lower portion. The monomer was then degassed by repeated freezing and thawing under vacuum and then the sample tube

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was sealed at a pressure below 2 x 10^{-5} Torr. Following its irradiation, the small tube containing the grafted HTC was removed from the larger tube and evacuated for 15 hours at 0.1 Torr to remove traces of monomer and then weighed. The difference in weight before and after evacuation was taken as the grafted polymer, since the homopolymer formation is negligible in this system (16).

For the purpose of molecular weight measurements described below, the polystyrene graft was separated from the unreacted HTC by dissolving the mixture in n-hexane at 50°C followed by filtration. The solubility of polystyrene in n-hexane was found to be negligible up to 60°C.

The grafting of liquid styrene to HTC results in the production of homopolymerized styrene as well as the HTC-polystyrene graft copolymer, the latter two are not easily separated since the long polystyrene side chain dominates the properties of the graft molecule. In this work they are carried along together as the total polymer is separated from the monomer and the ungrafted HTC. This was accomplished by first precipitating the sample in an excess of methanol and filtering it to separate the styrene monomer. The unreacted HTC was then separated from the precipitate by dissolving the total polymer in n-hexane followed by filtration. In order to eliminate the traces of monomer occluded in polystyrene, the polymer was re-dissolved in benzene. The solution was first frozen in a methanol-dry-ice bath then transferred to an ice-water bath and evacuated for 15 hours (34).

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Radiation Dosimetry and Viscosity Determinations

All irradiations were performed at room temperature with the 5000 curie ^{60}Co source of the University of Maryland Gamma Laboratory [28]. No provisions were made for temperature control; temperature fluctuations during irradiation did not exceed $2^{\circ}C$. Dose rates were determined with a Fricke dosimeter [29,30] at several selected positions in the irradiation cell.

The viscosity average molecular weight of the styrene-grafted HTC samples was calculated from intrinsic viscosity measurements in benzene at $30^{\circ}C$ and the relationship, [32]

$$[\eta] = 1.54 \times 10^{-4} (\bar{M}_v)^{0.73} , \qquad (15)$$

where $\bar{M}_v$ = viscosity average molecular weight,
and $[\eta]$ = intrinsic viscosity [33].

Viscosity measurements were made with an Ubbelohde suspended-level dilution viscometer in a water bath maintained at $30.00 \pm 0.02^{\circ}C$. In each case at least three different concentrations were used to obtain the extrapolated value of the intrinsic viscosity. (See Appendix D.)

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Chapter III

RESULTS

Diffusion of Styrene Vapor in Polyethylene Film

The styrene concentration in polyethylene film can be varied by changing the exposure time of the film to the monomer vapor. This method can be employed in a practical way to study the grafting kinetics versus styrene content because of the relatively low rate of diffusion of the vapor into the film. The equilibrium concentration of 15% is reached in 3-5 minutes when 0.063 mm film is soaked in liquid styrene as compared to 30 hours when the same film is exposed to styrene vapor.

The measurement of the concentration of monomer in the film was performed by a desorption technique illustrated in Figure 3 for a film which has been exposed to monomer vapor for 30 hours. The logarithm of the styrene weight versus time always showed an initial linearity which justified a linear extrapolation to zero time. The initial linearity of the desorption curve could be explained by the almost flat velocity profile inside the film at the start of the desorption, which causes a constant diffusivity across the film and hence a linear dependence of the logarithm of concentration on time.

Data similar to that in Figure 3 was obtained for exposure times ranging up to 40 hours. The ordinate intercept in each plot defines the monomer concentration in the film after a particular exposure

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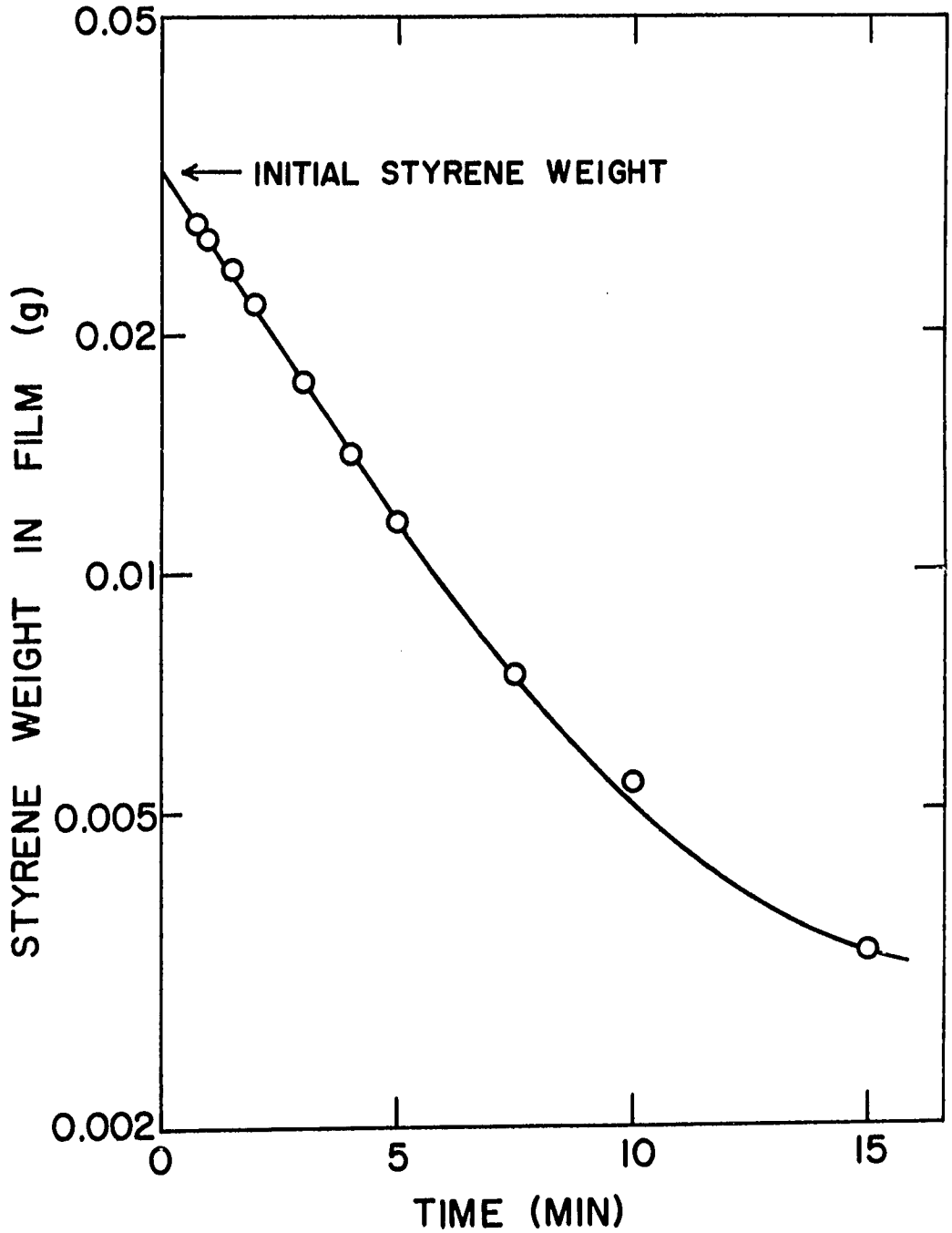

Figure 3. Desorption of styrene from polyethylene film previously exposed to styrene vapor for 30 hr at 25°C.

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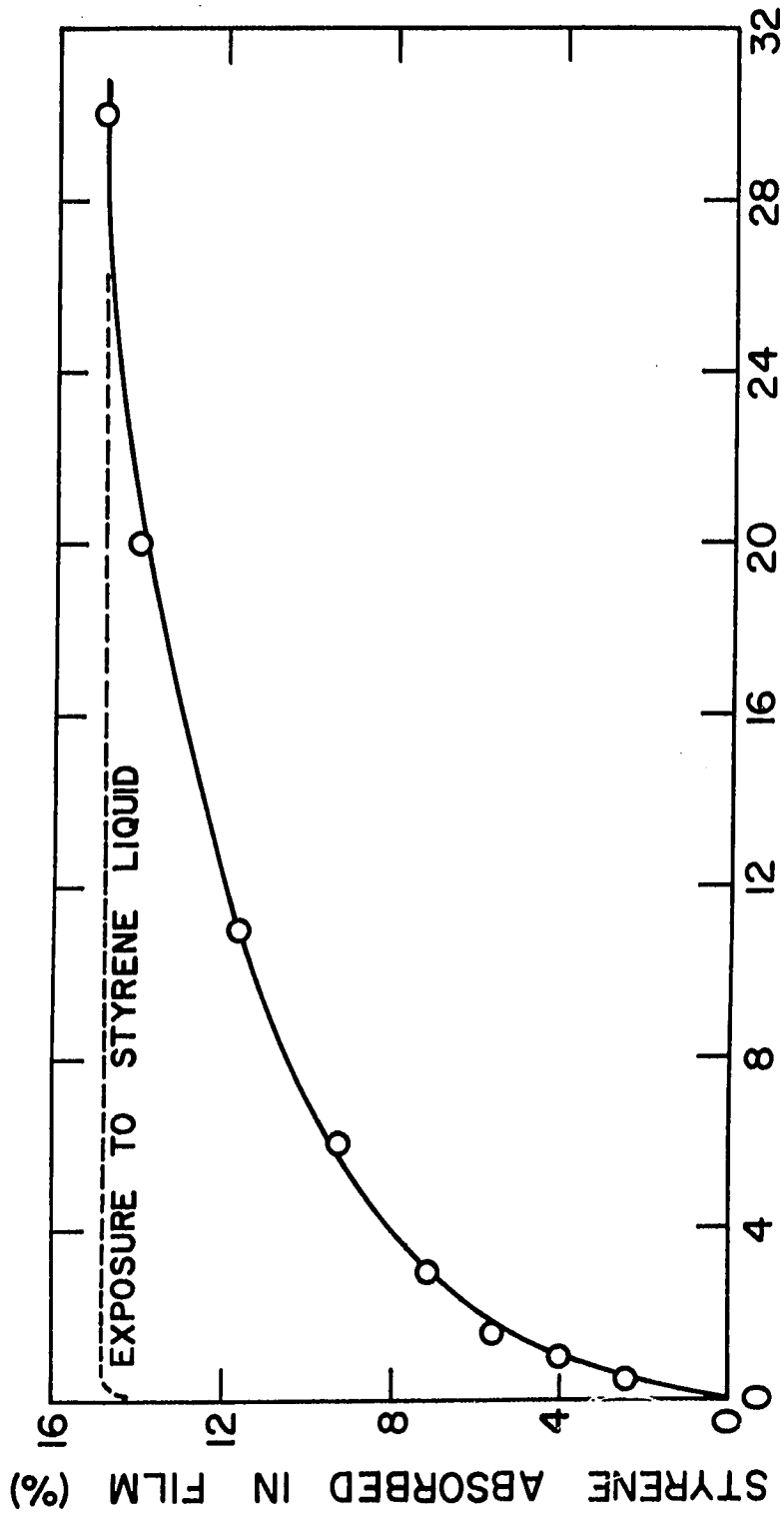

Figure 4. Swelling of polyethylene by exposure to styrene vapor at 25°C.

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time. The concentrations are plotted in Figure 4 and compared with those in which the film is exposed to liquid styrene[31]. This plot clearly shows the boundary resistance in the case of vapor diffusion.

Assuming a diffusivity of the form $D = D_o \exp(aC/C_o)$ and a linear boundary resistance coefficient similar to the one usually used with convective heat transfer, one obtains the numerical solution of the diffusion equation in one dimension (Appendix C). The equation has the form,

$$\partial C/\partial t = \partial/\partial x \, (D \, \partial C/\partial x), \tag{16}$$

with the following initial and boundary conditions:

$$C = 0 \quad \text{at } t = 0 \; ; \tag{17}$$

$$D \, \partial C/\partial x = h \, (C_o - C) \quad \text{at } x = l \; ; \tag{18}$$

$$\partial C/\partial x = 0 \quad \text{at } x = 0 \, , \tag{19}$$

$$\text{where } D = D_o \exp(aC/C_o) \; ; \tag{20}$$

C_o = the solubility of styrene in ungrafted polyethylene (mol/cm^3) ;

D = the concentration dependent diffusion coefficient of styrene liquid in polyethylene (cm^2/sec) ;

D_o = the diffusion coefficient at zero concentration ;

a = constant ;

h = boundary resistance coefficient (cm/sec) ; and

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l = half the film thickness (cm).

The calculated solution was made to fit the absorption data, shown in Figure 4, by choosing a suitable value for the boundary resistance coefficient h. Values of $h = 2.0 \times 10^{-7}$ cm/sec and $D = 4.9 \times 10^{-9} \exp(2.0\ C/C_o)$ cm^2/sec gave the best fit to the experimental results. The numerical solution also showed that the monomer concentrations reached a relatively flat profile after a period of two and a half hours, which indicates that the boundary resistance, except for this initial period, is the predominant resistance to the diffusion of monomer in the film.

To further test this finding, it was assumed that the velocity of the monomer in the film D/l, is much greater than, h, the velocity of the monomer as it penetrates the boundary. This gives rise to a flat velocity profile and a rate of weight gain by the film of the form

$$dC/dt = (h/l)\ (C_o - C)\ . \qquad (21)$$

The solution to this equation is

$$(1 - C/C_o) = \exp(-ht/l)\ . \qquad (22)$$

A plot of $\ln(1 - C/C_o)$ versus t should yield a straight line with a slope of -h/l. Such a plot of the absorption data is shown in Figure 5. The expected straight line relationship is observed.

Significant departure of the experimental data from equation (22)

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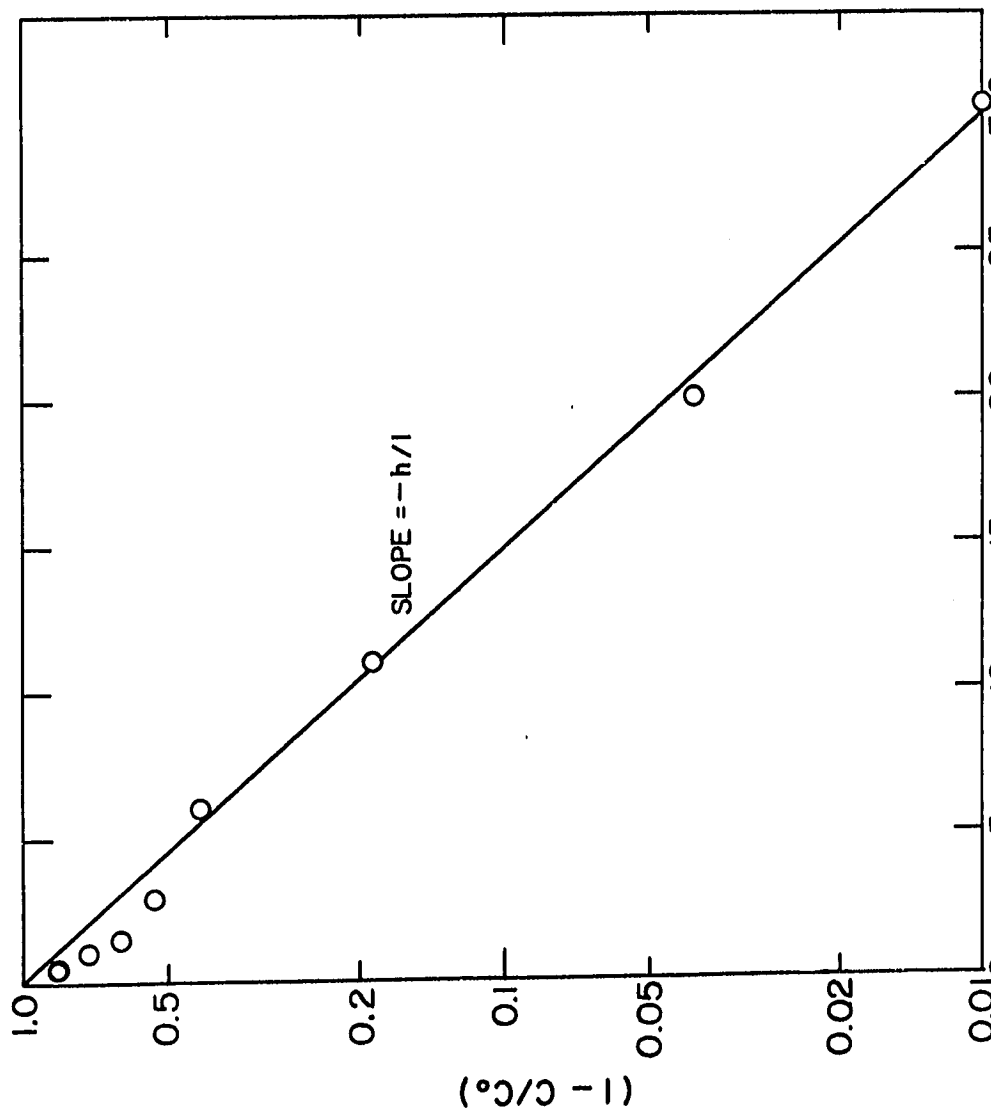

Figure 5. Correlation of the swelling data of Figure 4 using equation 21.

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occurred in the first two hours because of a low value of the diffusivity at the low concentration of monomer according to equation (20). This result confirms that the resistance at the boundary is controlling to the extent that we can ignore the diffusion through the film except at low concentrations when the resistance inside the film is significa t. This calculation gives a value of $h = 1.4 \times 10^{-7}$ cm/sec, which is in reasonable agreement with the value computed numerically. It is probably a typical value for all low density polyethylene films although this hypothesis is yet to be tested. The boundary resistance makes it possible to use the vapor method as a means of varying the monomer concentration in the film before the start of irradiation.

Grafting of Styrene Vapor to Polyethylene Film

Figure 6 shows the result of the grafting yield versus the initial concentration of monomer which was obtained by varying the film exposure to vapor. This is the result of 4 hours of irradiation at a dose rate of 2×10^4 rad/hr at room temperature (20°C). The homopolymer yield is obtained by soaking the film in benzene for five days. Similarly, Figure 7 shows the same yield as a function of an average monomer concentration in the film. This was taken as the arithmetic mean of the concentrations at the beginning and at the end of the grafting; the latter were determined by the desorption experiments described in Chapter II. It is recognized that, in general, the concentration does not vary linearly with time and that the true time average concentration is lower. Nevertheless, the

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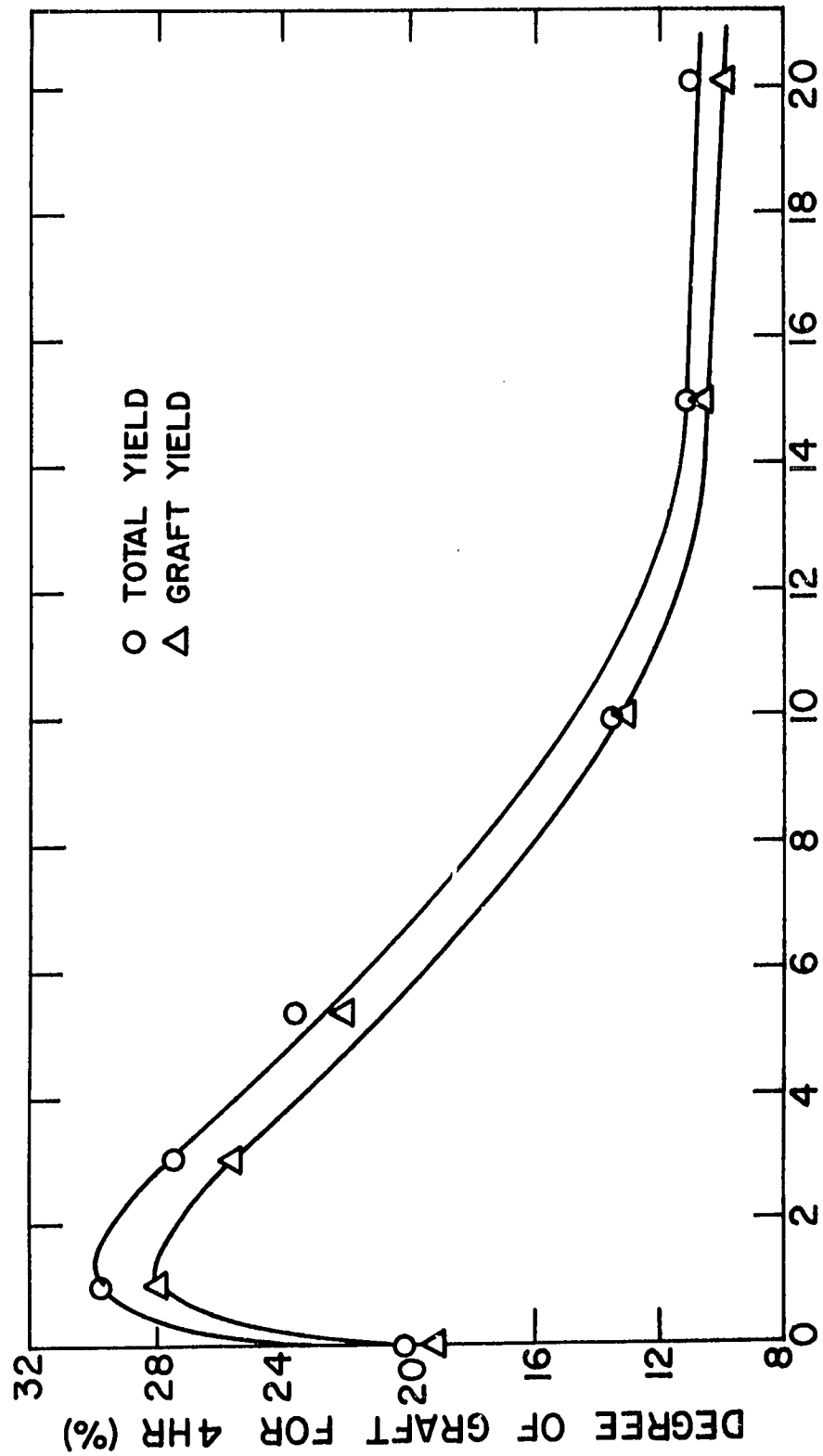

Figure 6. Average graft rate versus pre-irradiation exposure to styrene vapor. Grafting at 20°C and 1.98 x 10^4 rad/hr; swelling at 25°C.

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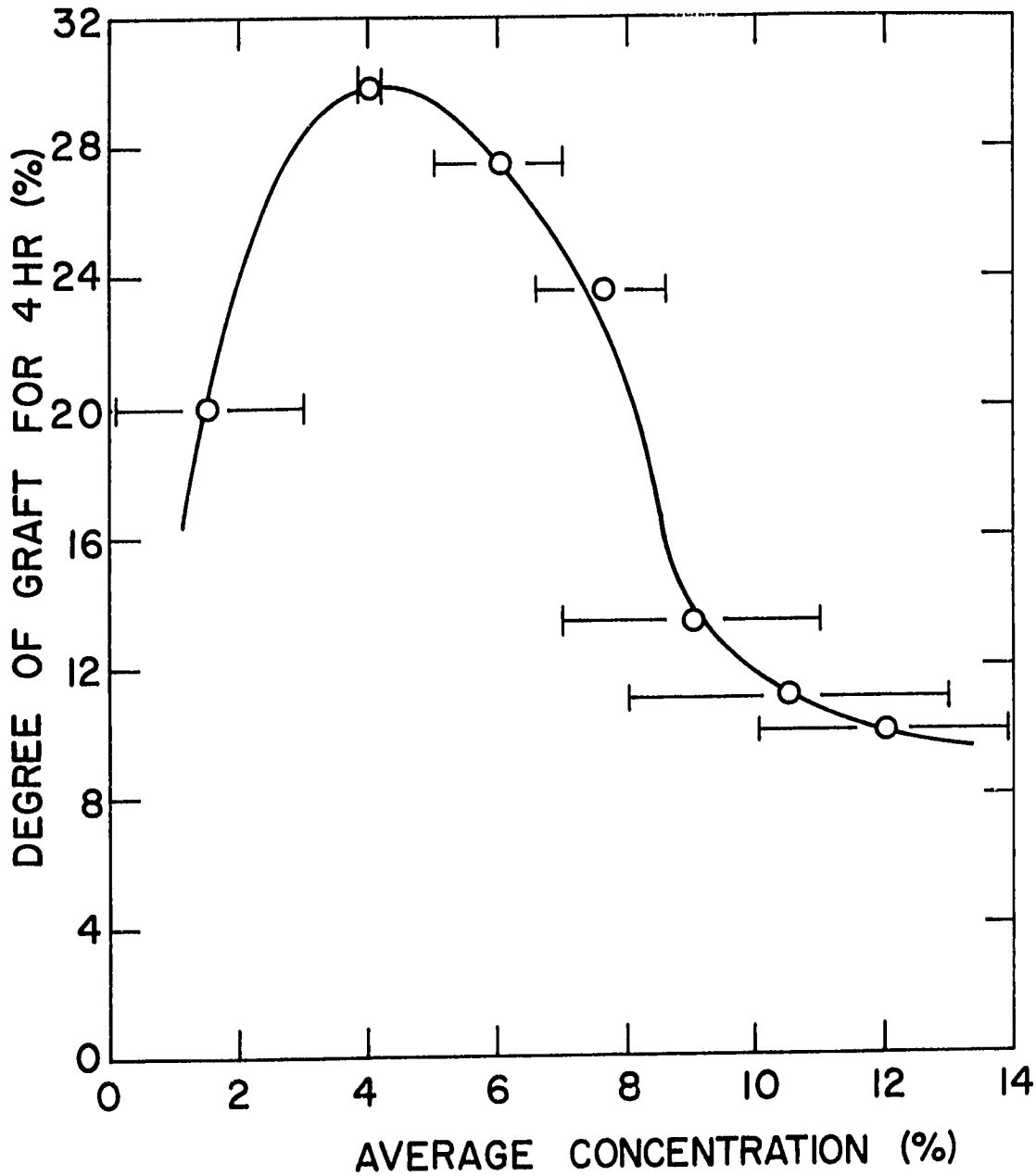

Figure 7. Effect of swelling of polyethylene by exposure to styrene vapor on graft rate. Polymer irradiated in monomer vapor at 20°C and 1.98×10^4 rad/hr.

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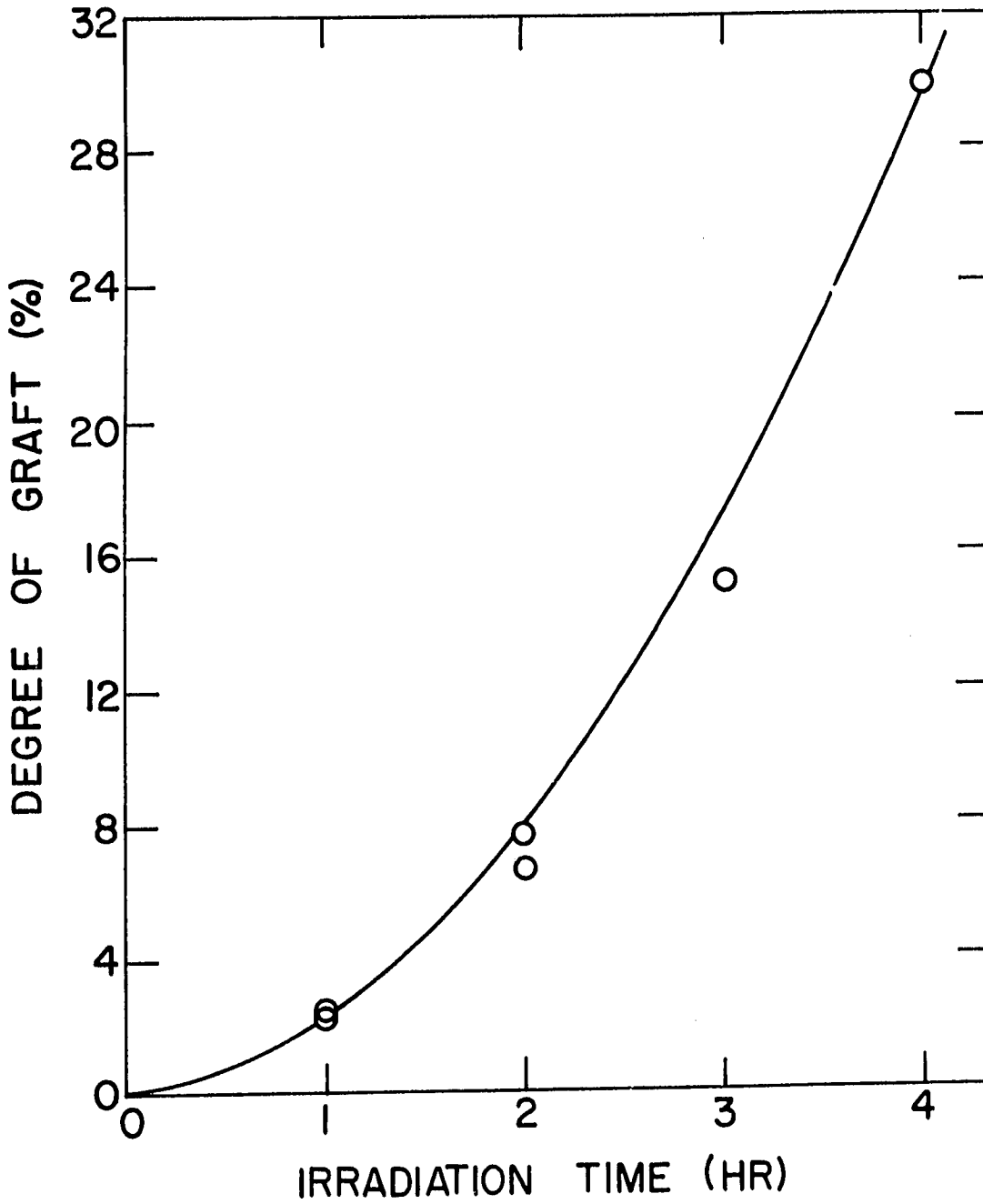

Figure 8. Degree of grafting polyethylene versus irradiation time. Polymer irradiated in monomer vapor at 20°, 1.98×10^4 rad/hr and 1 hr pre-irradiation exposure to styrene vapor.

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figure is useful in the discussion presented below.

Figures 6 and 7 show that the weight gain of the film has a maximum value at one hour exposure to vapor, which corresponds to a starting monomer concentration and an average monomer concentration of 4%. It is noteworthy that the maximum yield with a gaseous monomer is almost twice that obtained with a liquid monomer.

Examination of the grafted film with an optical microscope showed a very homogeneous product. The grafted film kept its clear appearance in all the cases and could not be distinguished from untreated film except by the slight stiffness of the films with a high degree of grafting. After soaking for 4-5 days in benzene, the grafted films were free of bubbles at all monomer concentrations except at values near the saturation concentration. When the exposure of the film to vapor exceeds 20 hours, bubbles start to appear after benzene soaking, although they are still few in number. This film, nevertheless, kept its clear appearance on direct examination.

Figure 8 shows the yield as a function of time for the case of one hour exposure of the film to styrene vapor. This result clearly shows the unsteady state nature of the vapor phase reaction. This run was made at a dose rate of 2×10^4 rad/hr at room temperature.

Grafting of Styrene in Solution to Polyethylene Film

The rate of swelling of 0.85 mm thick polyethylene strips in pure styrene and mixtures of styrene and methanol is shown in Figure 9. The styrene concentrations were measured by the desorp-

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tion technique described previously. Equilibrium was attained in ten hours in all cases. This indicates that equilibrium was attained in a few minutes for the 0.065 mm thick samples actually used for grafting, in contrast to the thirty hours required for the same film thickness in vapor phase (Figure 4).

The equilibrium swelling of polyethylene, shown in Figure 10, decreases with increasing methanol fraction. No swelling is observed in pure methanol. The composition of the sorbed solution in the polymer, as determined by gas-chromatography, is shown in Table I for various compositions of the outside solution. From these data we can see that the swelling is almost entirely due to styrene. The methanol content in the sorbed solution is very low regardless of the concentration of the outside solution. Also included in Table I are the data of Odian et al. [27] for comparison. The very low equilibrium solubility of methanol in the polyethylene film made this method a convenient one for varying the styrene concentration in the film without the interference of methanol with the grafting reaction. The obvious advantage of this method is the fast equilibration of the film with the monomer.

Figure 10 and Table II show the grafting rate of styrene to polyethylene in 3 hr at 9.5×10^4 rad/hr and 20°C. The rate was shown to increase steadily as the styrene was diluted and reached a maximum at 70 vol % methanol. The same results were plotted against the degree of swelling in Figure 11, which shows that the weight

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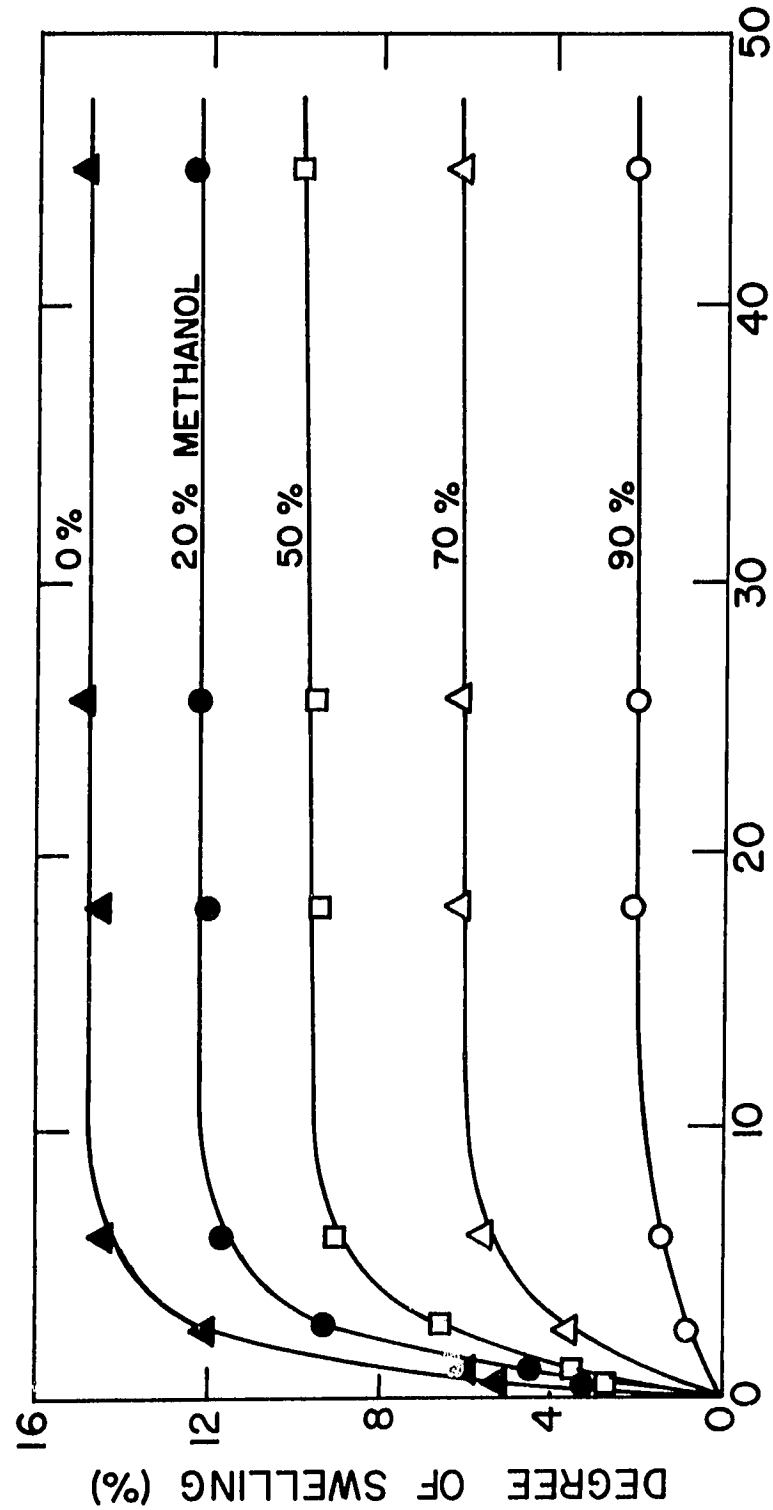

Figure 9. Effect of methanol on swelling of polyethylene in liquid styrene-methanol solutions at 25°.

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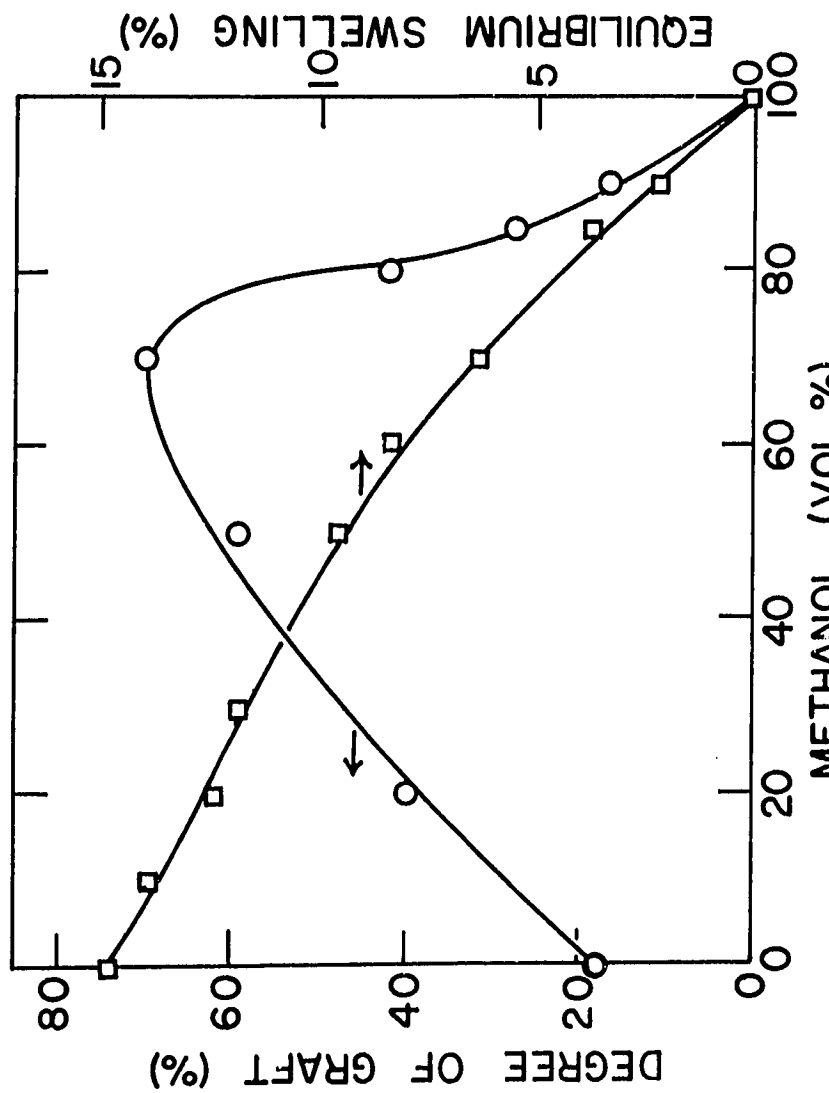

Figure 10. Plots of (O) amounts of graft for 3 hr and (□) equilibrium swelling of polyethylene versus methanol concentration in outside stirred methanol solution. Grafting at 20° and 9.5 x 10^4 rad; swelling at 25°.

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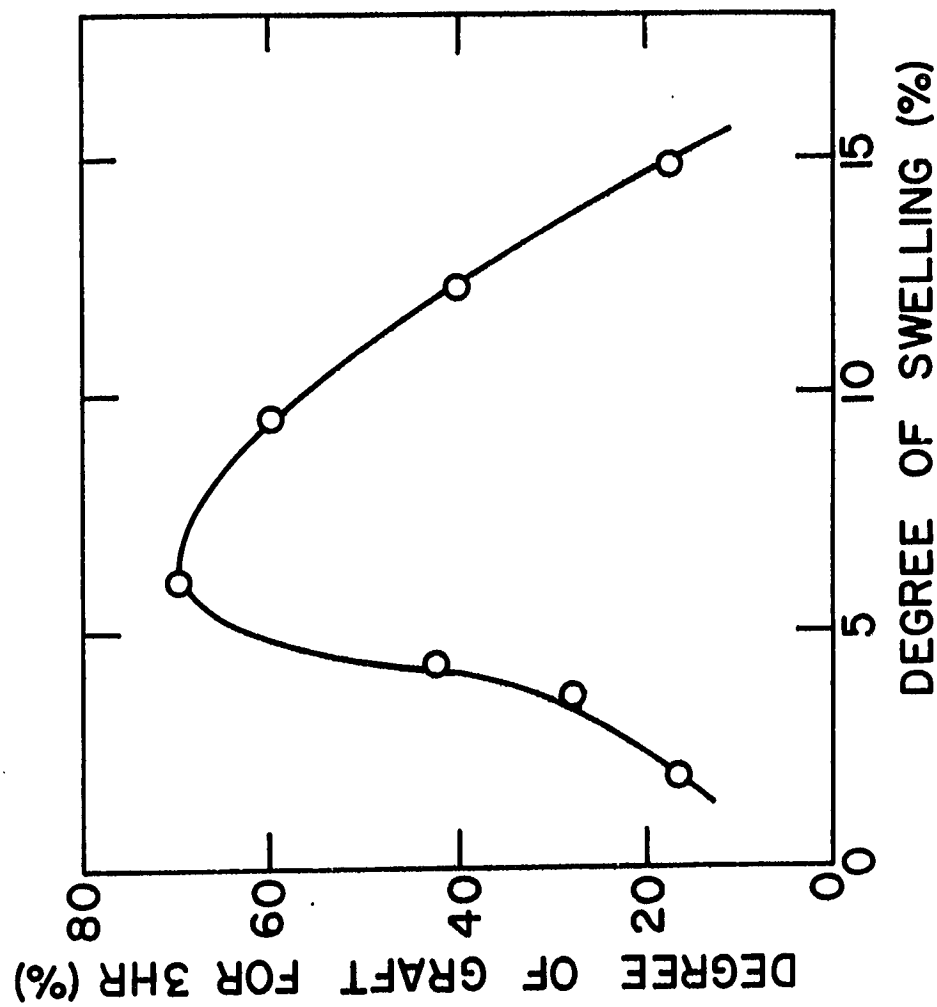

Figure 11. Effect of swelling of polyethylene on rate of grafting. Polymer irradiated in styrene-methanol solution at 20°C and 9.5 x 10^4 rad/hr.

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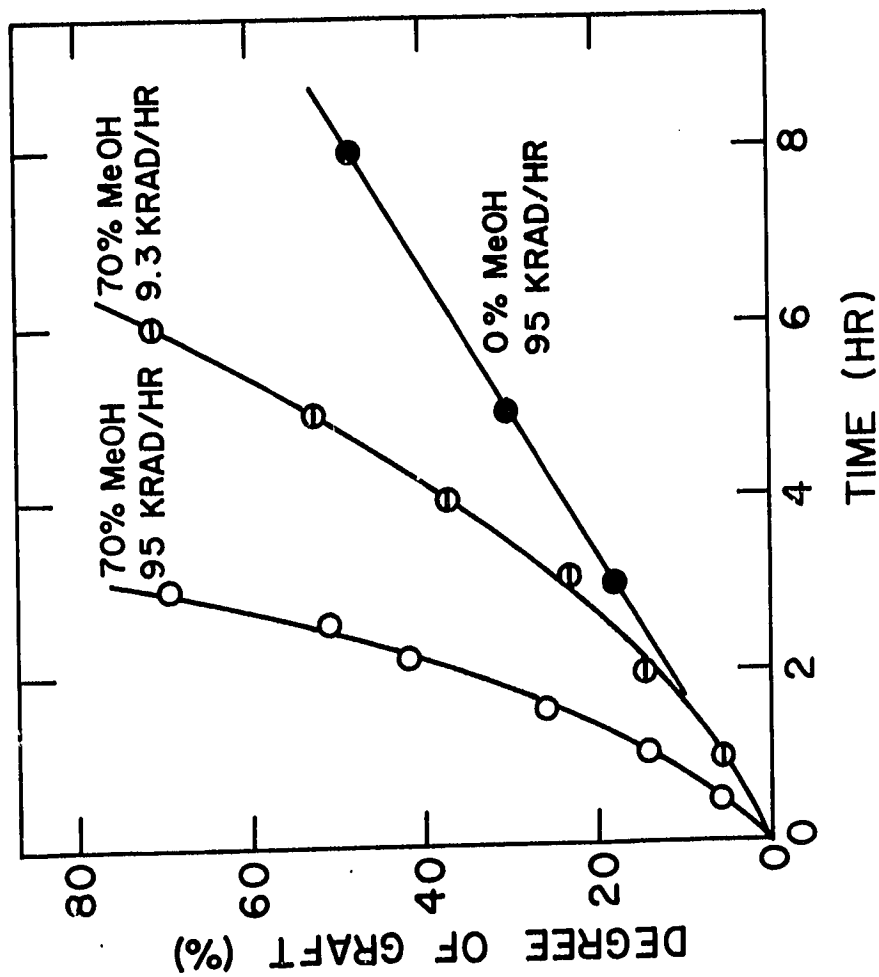

Figure 12. Degree of grafting liquid styrene to polyethylene versus irradiation time. Polymer irradiated in styrene-methanol solutions at 20°C.

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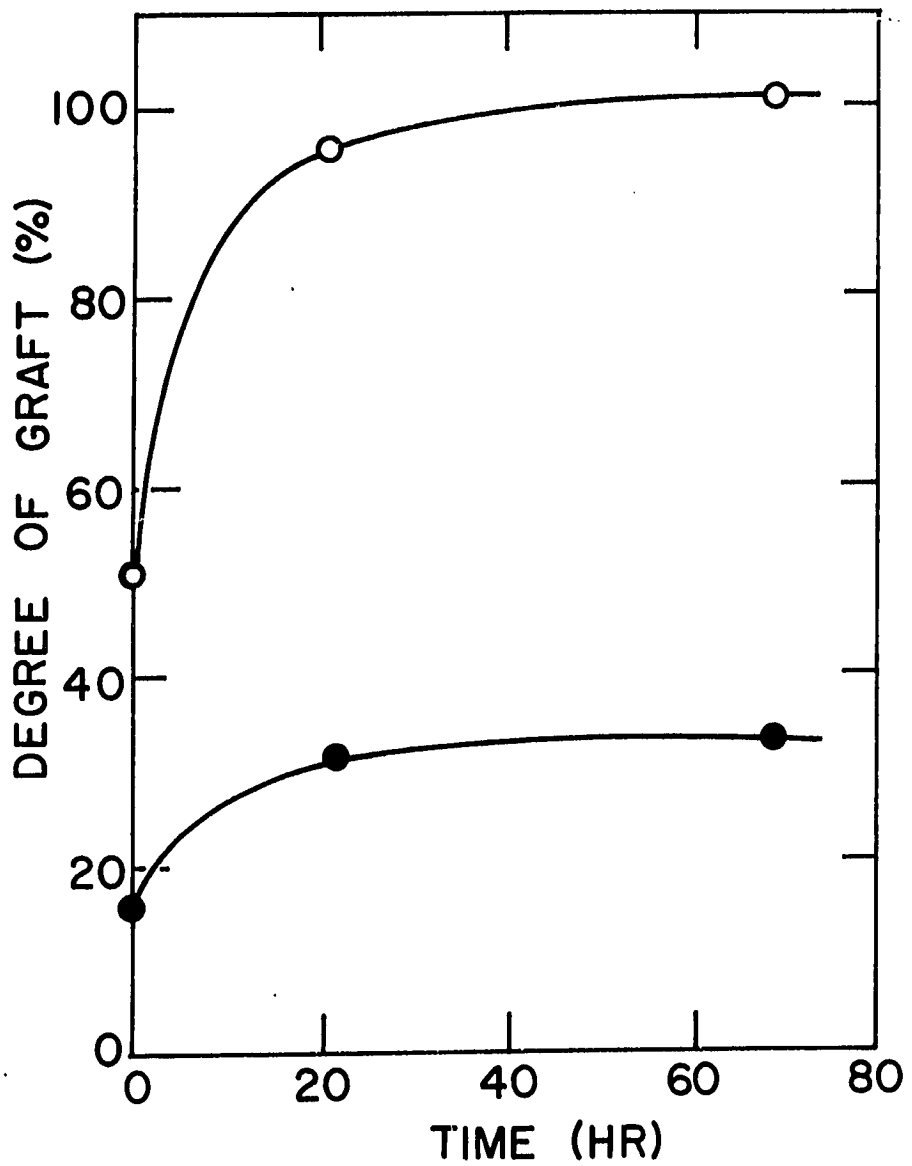

Figure 13. Post-effect of styrene graft in (O) liquid styrene-methanol-polyethylene system and (●) liquid styrene-polyethylene system. Irradiation dose: 9.5×10^4 rad/hr for 2.5 hr; irradiation at 20°C, post grafting at 27°C.

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TABLE I

Swelling of Polyethylene by Methanol-Styrene Solution at 25°C

Methanol content of outside solution vol %	Swelling at Equilibrium wt %	Methanol content of sorbed solution vol %	
		This work	Odian et al.[5]
0	14.8		
10	13.9		1.9
20	12.3	0.9	
30	11.8	0.9	1.6
50	9.5	1.9	2.2
60	8.2		
70	6.2	2.5	4.0
85	3.7	3.4	
90	2.2	3.8	7.5

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TABLE II

Effect of Methanol on the Grafting of Styrene to Polyethylene[a]

Methanol in outside solution vol %	Degree of graft for 3 hr %
0	17.5
20	39.7
50	59.3
70	69.7
80	42.0
85	27.6
90	16.3

[a] Dose rate, 9.5×10^4 rad/hr; temperature, 20°C; irradiation time, 3 hr.

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TABLE III

Swelling of Polyethylene by n-Octane-Styrene Solution at 25°C

n-Octane content of outside solution vol %	Swelling at equilibrium wt %
0	14.8
20	16.5
50	16.9
80	14.7
100	12.7

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gain reaches a maximum of 70% at a styrene content of 6.2%.

The degree of grafting versus time is shown in Figure 12 when grafting pure styrene and 30 vol % styrene in styrene-methanol solution at 20°C and 9.5×10^4 and 9.3×10^3 rad/hr; unsteady state kinetics seem to prevail.

Table III shows the swelling of polyethylene by solutions of n-octane and styrene at 25°C. The equilibrium swelling changes very little with the concentration of the outside solution indicating that both styrene and n-octane diffuse effectively into the film.

Figure 13 shows the post effect. The irradiated sample was kept sealed after removal from the radiation field in order to measure the continued grafting to long lived radicals. The plot indicated that the post effect is more pronounced in styrene-methanol solution grafting than in the grafting of styrene monomer.

Grafting of Styrene to Hexatriacontane (HTC)

The vapor-phase grafting yield versus time for the styrene-HTC system is shown in Figures 14 & 15; the straight line behavior indicates a steady state mechanism. The rate of conversion as a function of dose rate is shown in Figure 16 and the corresponding molecular weight versus dose rate is shown in the same plot. The yield was found to change very little with increasing dose rate for dose rates higher than 4×10^4 rad/hr. At lower dose rates, the dependence of graft rate on dose rate is 0.55. The molecular weight was found to be proportional to $I^{-0.65}$ for the dose rate

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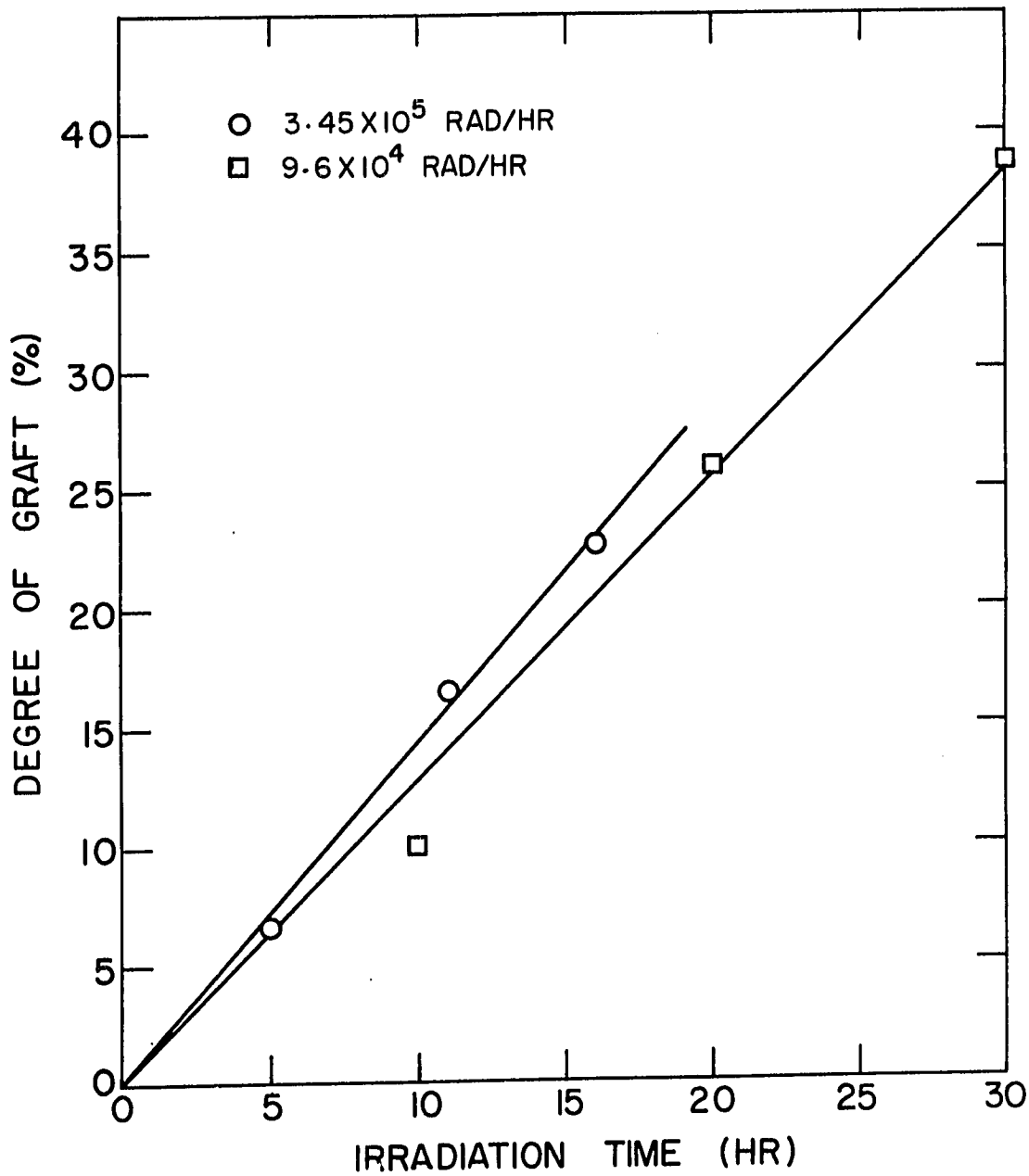

Figure 14. Degree of grafting styrene vapor to HTC versus irradiation time at 20°C.

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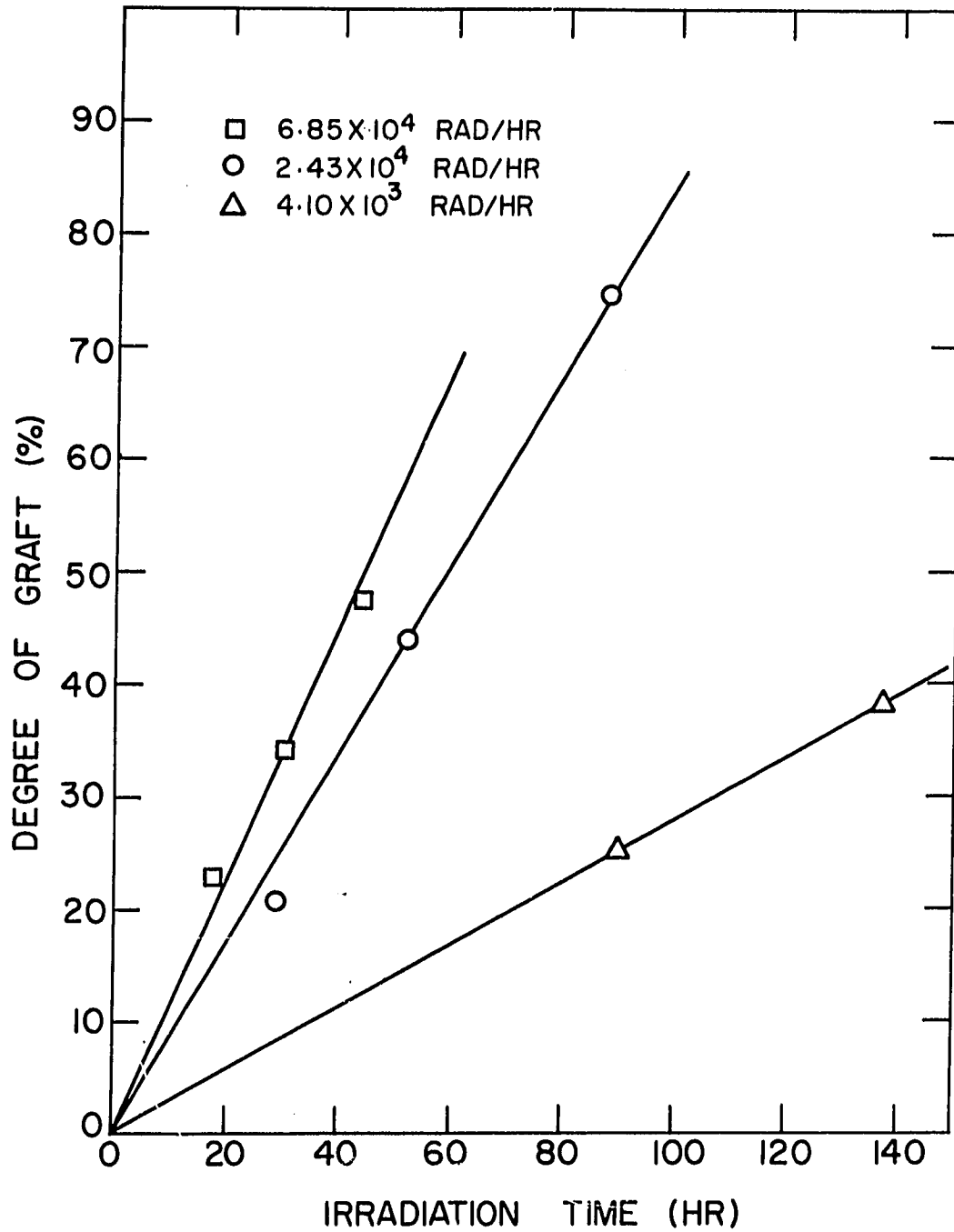

Figure 15. Degree of grafting styrene vapor to HTC versus irradiation time at 20°C.

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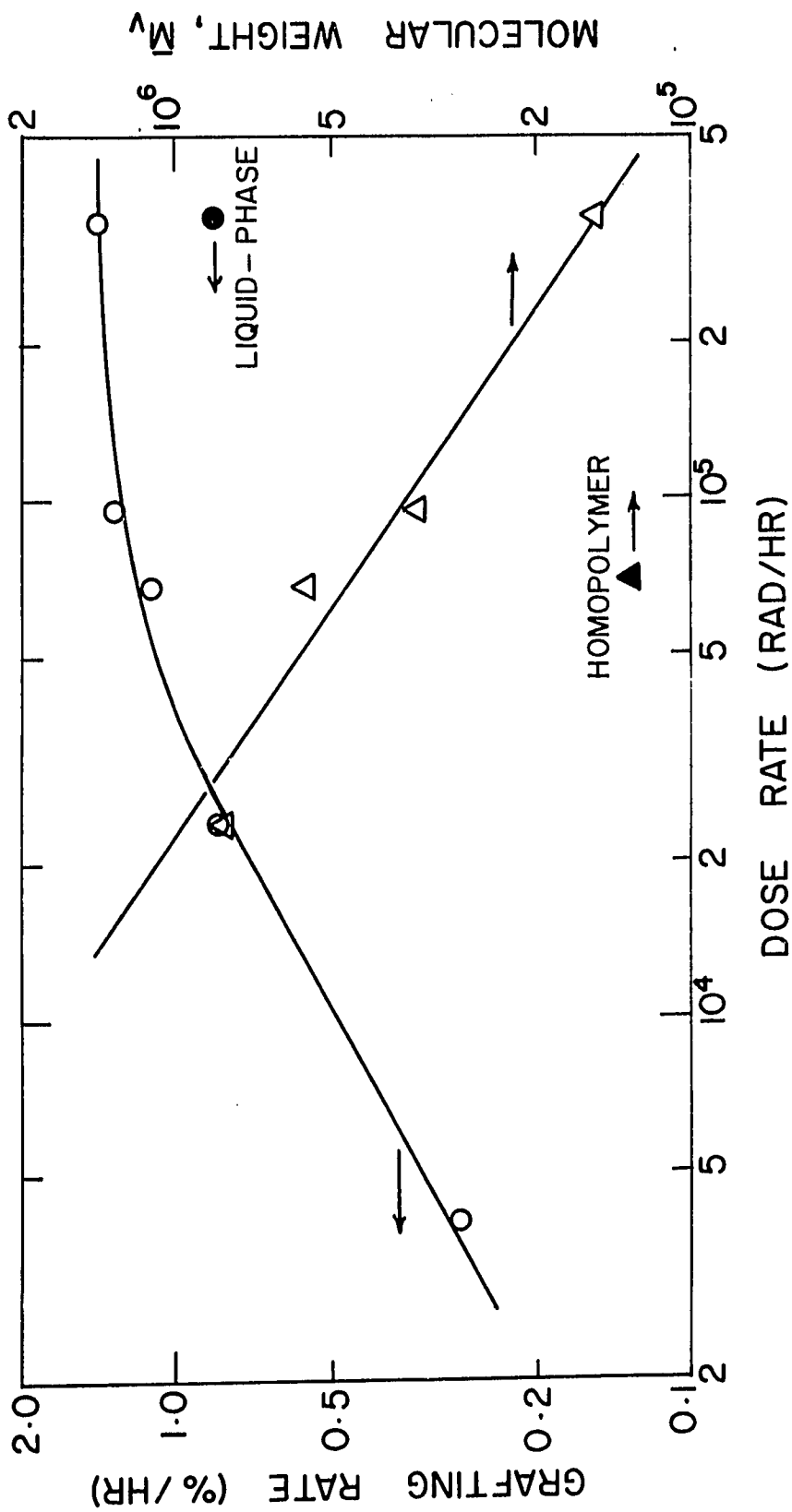

Figure 16. Dose rate dependence of the grafting rate of styrene vapor to HTC and the viscosity average molecular weight of the graft at 20 C.

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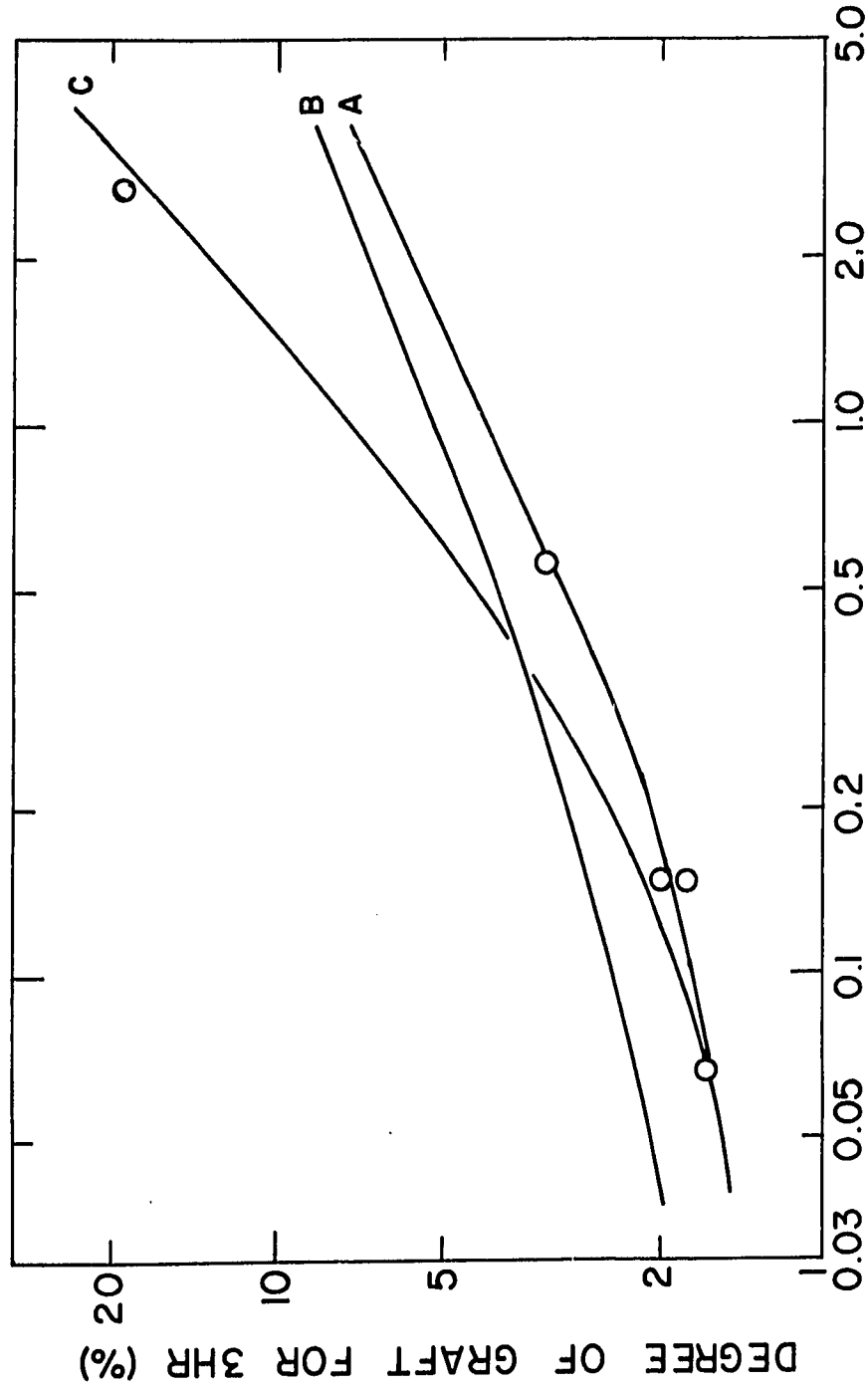

Figure 17. The effect of HTC/styrene ratio on the degree of grafting styrene liquid for 3 hr to HTC at 20°C and 3.5 x 10^5 rad/hr. Solid lines represent calculations: A is equation 23; B is equation 26; and C is equation 27.

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range of 2×10^4 to 3×10^5 rad/hr.

Grafting data for liquid styrene to HTC crystals at different ratios of HTC/styrene are shown in Figure 17. These experimental results were compared with several kinetic models, also shown in the same figure, in order to qualitatively show the possible mechanism by which the radicals that form in the alkane interact with styrene. These mechanisms are as follows:

1. The homogeneous model: This model assumes that the HTC is homogeneously distributed in the styrene liquid as if in solution. The contribution of HTC in this case is an increase in the radical population due to its interaction with radiation. The steady state kinetics of this system are expected to follow those of styrene homopolymerization and the conversion rate of the monomer will be

$$R_p^t = k_p \, C_m \, C_r.$$

$$r_p^t = 3.6 \times 10^5 \, (k_p/k_t^{\frac{1}{2}}) \, (R_i^m)^{\frac{1}{2}} \, (1 + b)^{\frac{1}{2}} \qquad (23)$$

where $b = R_i^p/R_i^m$;

$C_r.$ = total concentration of radicals (mol/l.) = $C_p. + C_m.$;

$C_p.$ and $C_m.$ = the concentration of radicals initiated in the polymer and monomer, respectively (mol/l.), and

r_p^t = total polymerization rate (%/hr).

2. The independent processes model: This model assumes that monomer

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radicals and polymer radicals are completely independent from one another. In this case the monomer radicals will terminate each other only, and similarly, the polymer radicals will terminate each other only. The termination rates of monomer radicals, R_t^m, and polymer radicals, R_t^p, are

$$R_t^m = k_t\, C_m^2. \tag{24}$$

$$R_t^p = k_t\, C_p^2. \tag{25}$$

At steady state, the total polymerization rate, r_p^t, will be

$$r_p^t = 3.6 \times 10^5\, (k_p/k_t^{\frac{1}{2}})\, (R_i^m)^{\frac{1}{2}}\, (1 + b^{\frac{1}{2}}) \tag{26}$$

3. The heterogeneous model: This model assumes that the reaction takes place only in the liquid phase and that the volume occupied by the alkane crystal has no reaction. This model is the closest to the actual experiment since styrene does not diffuse into the alkane crystals. Assuming that steady state conditions prevail and that any radical can interact with any other, the total conversion rate of the monomer is

$$r_p^t = 3.6 \times 10^5\, (k_p/k_t^{\frac{1}{2}})\, (R_i^m)^{\frac{1}{2}}\, (1 + b)^{\frac{1}{2}}\, (V_t/V_m) \tag{27}$$

where V_t and V_m = total volume and monomer volume respectively.

It should be noted that in calculating the conversion rate from the above models, it was assumed that every radical formed in the alkane would react with the monomer. Parameter values used in

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the calculations are as follows:

G_p = 6 radicals/100 eV = radical yield in HTC (43)

G_m = 0.6 radicals/100 eV = radical yield in styrene (37)

$k_p/k_t^{\frac{1}{2}}$ = 5.15 x 10^{-3} $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $sec^{-\frac{1}{2}}$ (37)

R_i^m = 4.98 x 10^{-8} mol l^{-1} sec^{-1} at a dose rate of 3.5 x 10^5 rad/hr

The heterogeneous model shows the best agreement with the data over the entire concentration range. At low HTC concentrations, the mixture has the appearance of a stable suspension of low viscosity. At the highest HTC concentrations, it has the appearance and consistency of a solid wax.

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Chapter IV

DISCUSSION

In Chapter I the results of liquid phase grafting of styrene to polyethylene were reviewed. Factors affecting the yield and the mechanism of the reaction were pointed out and an explanation of the behavior of this system was proposed in terms of the viscosity of the amorphous region of the polymer and its relation to the concentration of the sorbed monomer. This chapter provides strong experimental evidence for the proposed explanation on the basis of measured effects of monomer concentration in polyethylene film on the kinetics of the grafting reaction.

The experimental results in the grafting of styrene to HTC crystals provides further support for the proposed mechanism. This reaction occurs on the surface of the crystals without the complication of the high viscosity conditions that prevail in polyethylene film. In addition, the HTC-styrene data demonstrate the migration of alkyl radicals to the surface of HTC crystals where they are converted to graft chains with high efficiency by liquid styrene.

An important practical consequence of the study is that grafting at low monomer concentration is shown to increase the yield and improve the quality of the grafted film by reducing the homopolymer content.

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Variation of Styrene Concentration in Polyethylene Film

In order to study the effect of monomer concentration on the rate of grafting, one requires a practical method for varying the monomer concentration in the film. In this investigation, two methods were used: (1) exposure of the film to styrene vapor for various time periods; (2) equilibration of the film with various styrene-methanol solutions.

The first method, the vapor-phase system, is based on the slow diffusion of monomer vapor into the film. The film was found to reach its equilibrium styrene concentration after about 30 hr of exposure to the monomer vapor (Figure 4). With this method, however, the styrene concentration in the film varies during the irradiation period depending upon the relative speeds of the monomer consumption by the grafting reaction and its diffusion into the film.

When equilibration with monomer solution is used, the film attains its equilibrium concentration in a very short period. Figure 9 shows that the equilibrium concentrations in all dilutions were reached in less than 10 hr with a 0.85mm polyethylene film. Since the diffusion coefficient is probably independent of film thickness, (C/C_o) is a unique function of (Dt/l^2) independent of the thickness (21). Thus the corresponding time for a 2.5 mil film to reach equilibrium is less than 100 sec. For a film soaked in a 70% methanol solution, the average diffusion rate of the monomer in going from zero to the saturation concentration is 200%/hr. A more

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extended calculation shows that the diffusion rate that brings the monomer concentration in the film from 90% of the equilibrium value to the saturation value is 100%/hr, which is about five times the expected reaction rate. We can, therefore, safely state that grafting in a styrene-methanol solution takes place at the monomer concentration close to equilibrium with the outside solution.

The very low, almost negligible, swelling of polyethylene with methanol by the second method can be seen in Table I. This finding is important in the explanation of the grafting data in that system. The fact that the sorbed solution is composed mainly of styrene makes the comparison between the liquid system and the vapor-phase system very useful since the kinetics of the grafting reaction in both systems is affected only by the variation in the monomer concentration in the film.

Grafting of Styrene Vapor to Polyethylene Film

The mechanism of reaction: The vapor-phase grafting results (Figures 6-8) show that the graft yield can be increased by reducing the monomer concentration in the film below the equilibrium value. At a 4% concentration, the yield reaches its maximum and further reduction causes it to decrease. This behavior suggests that two opposing effects occur as the monomer concentration inside the film is changed. The results can be explained by assuming that (1) the monomer dissolves only in the amorphous region of the film, (2) the grafting reaction occurs only in the amorphous region and on the

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surface of the crystals, and (3) the increasing monomer concentration causes a decrease in the viscosity of the amorphous region.

If we assume that decreasing the monomer concentration inside the film will have no effect on other variables, we should anticipate a lower grafting yield. The overall grafting rate ($R_p = k_p C_m C_{r\cdot}$) is directly proportional to the monomer concentration in the absence of concomitant changes. However, a decrease in monomer concentration can cause a pronounced increase in the viscosity of the amorphous region; the effect of this reasonable assumption is to decrease the termination rate constant relative to the propagation rate constant. The substantial decrease in the termination rate is due to the reduction in the mobility of the chain radicals that are necessary for the termination process. When termination of the chains is completely prevented, $dC_{r\cdot}/dt = R_i$ and the grafting yield is $\frac{1}{2} k_p C_m R_i t^2$, provided $k_p C_m R_i$ is constant. Figure 18 shows that the grafting yield with the monomer concentration at 4% throughout the experiment fits the square dependence on time expected on the basis of this model.

It is instructive to consider similar analyses at the other monomer concentrations in the film. Figure 7 shows the yield at the seven concentrations studied. Note that in each case, the points are for an average concentration. The bars represent the measured range through which the concentration varies from the beginning to the end of the irradiation; only at the maximum is

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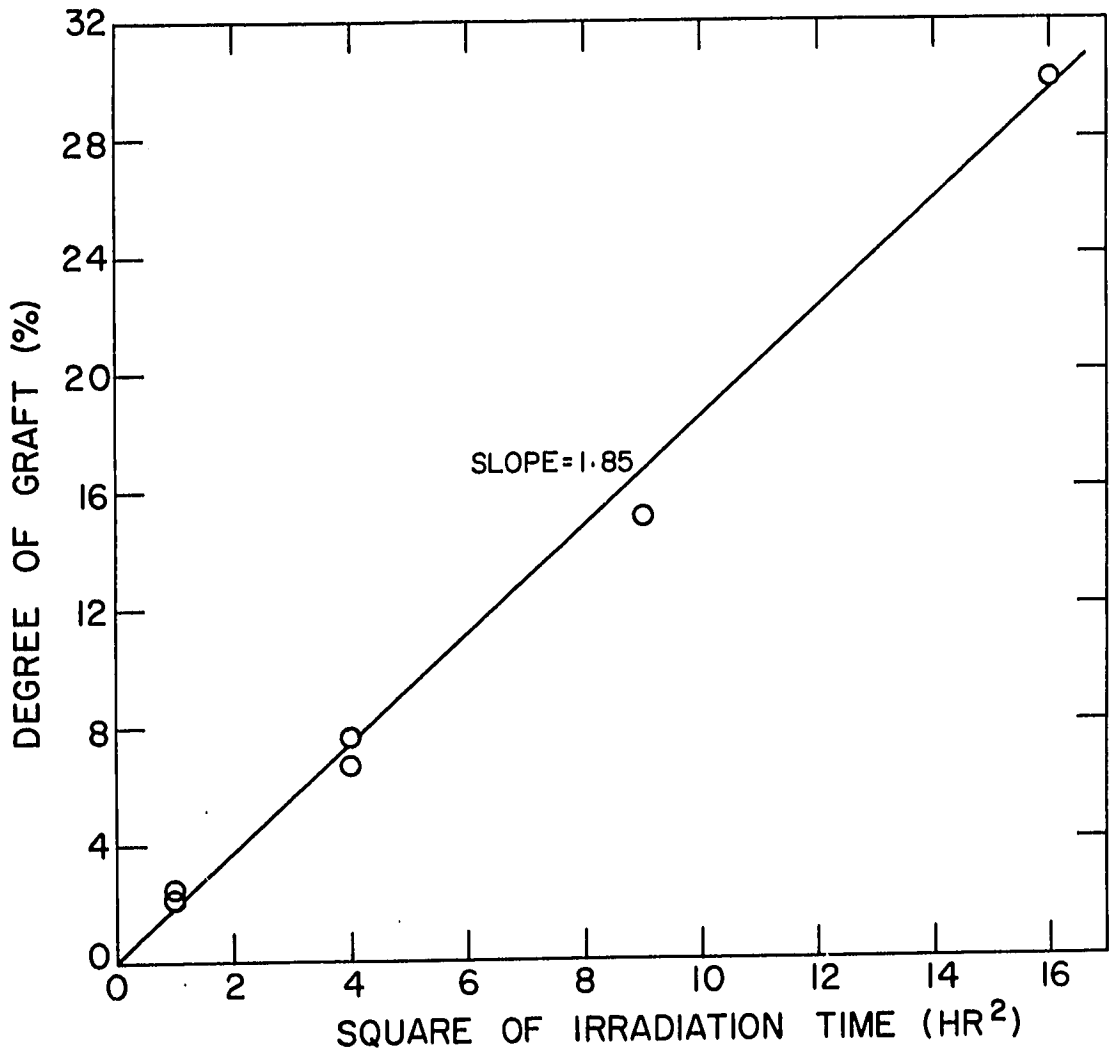

Figure 18. Degree of grafting styrene to polyethylene versus square of irradiation time. Polymer irradiated in monomer vapor at 20 C, 1.98×10^4 rad/hr and 1 hr pre-irradiation exposure to styrene vapor.

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the concentration range small. This variation during a run is not only dependent upon the relative speeds of monomer consumption by the reaction and monomer diffusion into the film, but it is also affected by the accumulation of polystyrene in the film. Chandler et al.[38] reported an increase of styrene solubility in low density polyethylene film from 15% to 30% caused by a 24% polystyrene graft. This increase in solubility will cause the driving force for diffusion to increase with the grafting yield. The increased diffusion rate is confirmed by the results shown in Figure 19 where the monomer concentration was measured during grafting as a function of time. The average monomer concentration in the film first decreases due to a faster consumption of monomer by the reaction and then increases sharply to reach the original value as the diffusion rate begins to dominate the reaction rate.

After prolonged pre-irradiation exposure to vapor, the monomer concentration in the film is close to the equilibrium value which prevails during grafting with liquid styrene. When the graft begins, the monomer concentration is depleted and a steady state concentration is reached which is lower than the equilibrium value. Under the conditions used to obtain the data for Figure 6, the time average monomer concentration in the film during the grafting with vapor is 0.73 C_0. The graft rate in this experiment is 0.73 times that of the graft with liquid styrene under comparable circumstances. Since the liquid graft involves steady state radical concentrations, one may conclude that the graft with more than 10% sorbed styrene

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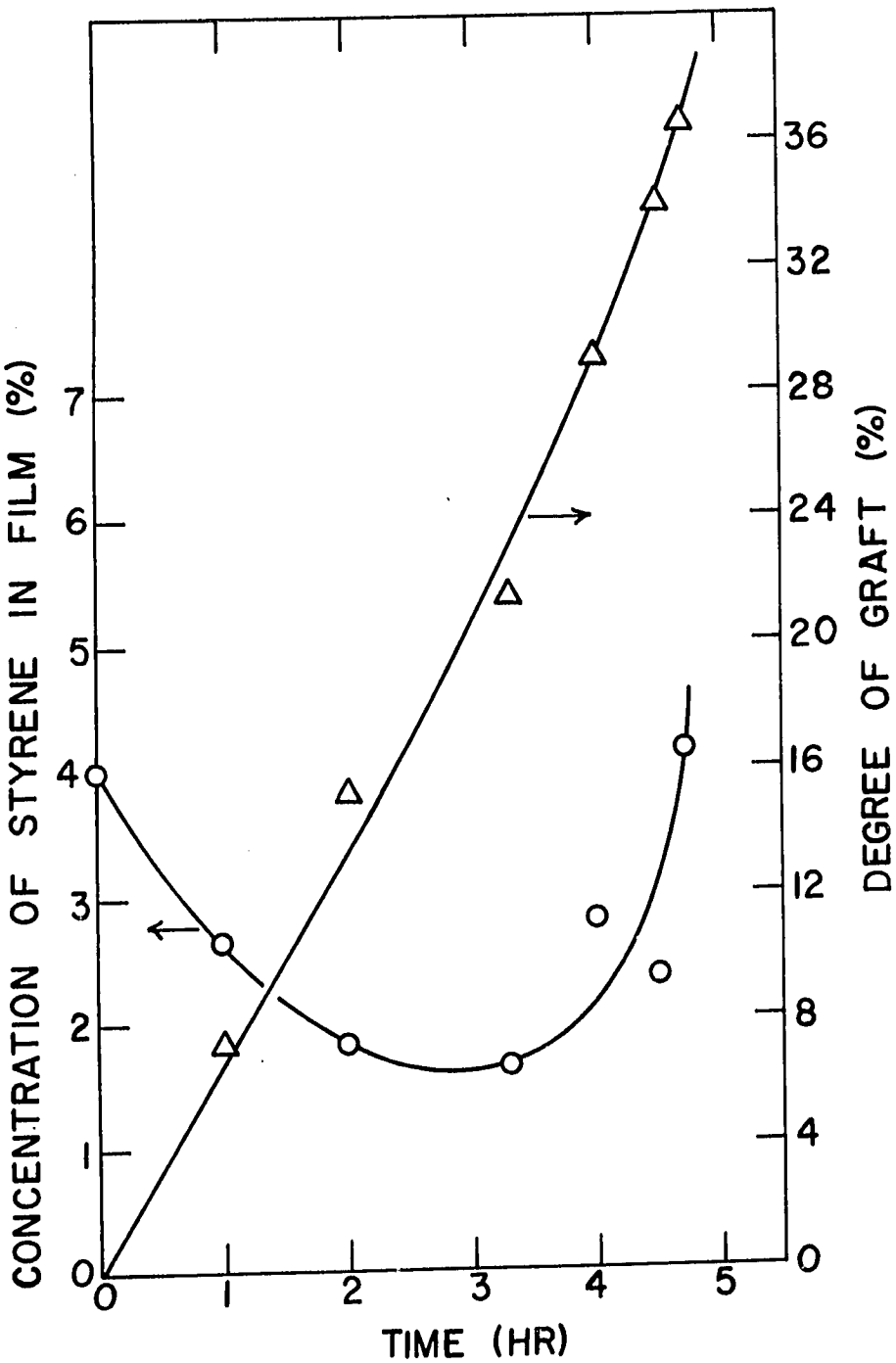

Figure 19. Degree of grafting styrene to polyethylene and the concentration of monomer inside the polymer film versus irradiation time. Polymer irradiated in monomer vapor at 20°C, 9.6×10^4 rad/hr after 1 hr exposure to monomer vapor at 25°C.

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takes place by a similar mechanism with similar values for k_p and k_t.

G-value for chain production: An attempt was made to analyze the slope of the data in Figure 8 to obtain the G-value for chain production. From the figure,

$$\tfrac{1}{2} k_p C_m R_i = 1.85\ \%/hr^2 \cdot (6.75 \times 10^{-9})$$

Also, from standard conversion constants,

$$G = R_i / 2.6 \times 10^{-13}\ I\ .$$

The k_p value for pure styrene at 20°C is 31 l. mol^{-1} sec^{-1} (18); for styrene in amorphous polyethylene, k_p is unknown but it is certainly lower. The liquid value leads to a minimum G of 0.44. A typical G for primary radical production in polyethylene is about ten times this value. The fact that the actual k_p is lower accounts for at least part of the discrepancy. Also the reduced k_p suggests that the conversion of primary radicals to chain radicals may not compete as effectively with the bimolecular recombination reaction of the primaries.

The generally lower grafting yields of the vapor-phase system compared with those obtained in the methanol-solution system (discussed below), can be explained by the effect of the diffusion resistance in the vapor-phase on the average G-value for chain-radical production in the film. The increased boundary resistance to

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diffusion in the vapor phase causes the grafting reaction to occur close to the surface of the film. This has also been observed when grafting thick polyethylene films with liquid styrene [21] and was termed surface grafting in comparison with bulk grafting in the case of thin films. Since the diffusion of the monomer to the inner region of the film is very low due to the rapid reaction at the surface, the bimolecular termination of primary radicals takes place in this region. The loss of primary radicals lowers the average G-value for chain production in the film and hence lowers its grafting yield.

The location of the grafted chains at the surface of the film in the vapor-phase further restricts the mobility of the chains to the extent of preventing their termination, and the yield follows a square of time dependence. In the methanol-solution system, where the distribution of the grafted chains is homogeneous, the yield is proportional to $t^{1.43}$.

Other experimental observations also point to the occurrence of surface grafting in this system. One observation which has significant practical application is the small amount of the occluded homopolymer in the grafted film. Grafting at a low monomer concentration, or at a high viscosity, should cause an increase in the yields of both the grafted polymer and the occluded homopolymer. However, the film grafted in the vapor-phase shows no change in its transparency, up to 40% graft, and no bubble formation

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was observed when the grafted film was soaked for five days in benzene. This indicates that the homopolymer occluded inside the film is negligible. This is consistent with the view that the grafting occurs close to the outer surface of the film where the homopolymer can be easily washed out without any significant deterioration to the quality of the film.

Problems associated with a detailed analysis: The attempt to obtain the G-value for radicals is only one facet of the problem of developing a detailed analytical description of the grafting system, particularly when the concentration of monomer varies with time. Since D and k_t are both functions of concentrations, the complete description of the system can be summarized by the following equations:

$$\partial C_m/\partial t = \partial/\partial x \, (D \, \partial C_m/\partial x) - R_p \; ; \tag{28}$$

$$C_m \, (0,x) = C_1 \; ; \tag{29}$$

$$\partial C_m/\partial x = - h/l \, (C - C_o) \quad \text{at } x = 0 \; ; \tag{30}$$

$$\partial C_m/\partial x = 0 \quad \text{at } x = l \; ; \tag{31}$$

$$D = D_o \exp (aC/C_o) \times (\text{an unknown function of } \int_o^t R_p \, dt) \; ; \tag{32}$$

$$C_{oo} = C_o + n \int_o^t R_p \, dt \; ; \tag{33}$$

n = slope of the linear relationship between the styrene solubility and the polystyrene graft [38] ;

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$$R_p = k_p C_m C_{r\cdot} \; ; \tag{34}$$

$$C_{r\cdot} = (R_i/k_t)^{\frac{1}{2}} \quad \tanh \left[t \, (R_i \, k_t)^{\frac{1}{2}} \right] \; ; \tag{35}$$

k_t = an unknown function of viscosity ;

and k_p = an unknown (but not very sensitive) function of viscosity.

The solution of the above system of simultaneous equations should give a complete description of the vapor-phase grafting system. The model involves so many unknowns that it is not particularly useful for fitting the experimental data.

Further complications in the kinetics arise as a consequence of the formation of polystyrene homopolymer inside the film. Simplified theories have been proposed for limiting ideal grafting systems [21,38]. Some of the simplifications include constant values for D, k_p, k_t, $C_{r\cdot}$ and C_{oo}. In the present system these simplifications are inapplicable and will lead to erroneous conclusions. Thus, only the preceding qualitative picture is included in this discussion concerning the mechanism of the grafting reaction. These are further substantiated by the grafting data obtained with the methanol-solution system.

Grafting of Styrene to Polyethylene Films in Styrene-Methanol Solutions

The explanation given for the kinetics of grafting in this system is based on the negligible swelling of polyethylene with

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methanol which was found in this work and in other work cited in the literature [27]. When polyethylene films were equilibrated with various mixtures of styrene and methanol, the maximum concentration of methanol in the sorbed solution was found to be less than 4% in all cases (Table I). This finding fits the explanation for the increase in the rate of grafting with increasing methanol concentration in the monomer solution as due only to the low monomer concentrations inside the film; the dilution merely controls the concentration of styrene in the film. This explanation differs from previously reported findings.

Earlier proposed mechanisms: Both Dobo et al. [25] and Odian et al. [27] found an accelerating effect when grafting polyethylene with styrene in an alcohol solution. Dobo related this effect to a decrease in the radiation protection of polyethylene by styrene due to the use of a solvent. This, however, cannot be valid if the solvent does not diffuse in the film to an appreciable extent as is the case in the present system. Also, when the alcohol was replaced by a solvent that diffused equally in polyethylene, namely n-octane, the opposite effect was observed; i.e. a steady decrease in the yield with the decrease in styrene concentration [27]. The mechanism of the radiation protection proposed by Dobo cannot be valid in this case.

Odian et al. [27] were aware of the low methanol content in the films. Nevertheless they proposed that the increase in the

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grafting rate was due to the coiling of the non-polar grafted chains by the polar alcohol in the film so that the termination was sharply reduced. Such an effect has been reported by Chapiro[39,40] for the polymerization of styrene in methanol-styrene solutions; however he observed no accelerating effect when the alcohol content was less than 70 vol %. Since the methanol content inside the film is trivial, a mechanism based on chain conformation cannot be valid.

Comparison of vapor and liquid data: The equilibrium swelling of polyethylene, shown in Figure 9 and Table I, decreases with increasing methanol solution. The data demonstrate how control of the concentration of styrene in the outside solution provides a convenient method for changing its concentration inside the film.

If the styrene concentration inside the film is the only important variable when grafting with various liquid methanol-styrene solutions, the grafting rates versus sorbed monomer content should be similar to those obtained by grafting with pure styrene vapor. This similarity can be observed by a comparison of Figures 10-12 with Figures 6-8. The rate of grafting in the liquid system was found to have a maximum at a styrene concentration in the film of 6.2% (Figure 11). The unsteady state behavior of liquid grafting versus time (Figure 12) is attributed, as in the vapor system, to the long period of time required for the radical population to reach steady state under conditions of high viscosity.

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Thus, the mechanism developed for vapor-phase grafting fits this system as well.

One ostensible discrepancy is the higher optimum grafting concentration in the liquid system, 6.2%, compared to 4% in the vapor-phase system. This is due to the fact that the reaction with styrene vapor is limited to the regions near the film surface; the measured average optimum concentration for the film is necessarily lower than the concentration in the reaction region. Since grafting with a styrene-methanol solution occurs uniformly throughout the entire bulk of the film, the measured optimum concentration is slightly higher than in the vapor-phase system.

The post irradiation grafting effect was also investigated in the methanol solution system to confirm the existence of long lived radicals. It can be seen in Figure 13 that the after-effect is much greater in this system than when grafting with pure monomer at the same dose. This indicates that a larger population of radicals accumulates in the methanol solution system because of a lower termination rate in the highly viscous polyethylene-styrene matrix.

Grafting of Styrene to HTC

The grafting of styrene vapor to HTC crystals occurs only on the surface of the crystals as styrene vapor does not diffuse inside the crystalline structure[17]. Figures 14 and 15 show the percent graft versus time at various dose rates.

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The straight line plots show a steady state process where the radical population reaches a constant value in a short period of time. This fast radical buildup can be verified by a simple calculation. The experiment which would lead to the largest non-steady state contribution is the one performed at 4.1×10^3 rad/hr. The radical lifetime at the steady state is $(R_i\ k_t)^{-\frac{1}{2}}$; twice this value is the time required for the radical population to build up to 95% of its steady state value [42]. Since $R_i = 7.1 \times 10^{-9}$ mol l.$^{-1}$ sec^{-1} at 4.1×10^3 rad/hr, then an approximate value for the unsteady state period can be obtained from the following reasonable assumptions: the G-value for radicals is 6 [43]; $k_p = 31$ l. mol^{-1} sec^{-1} [18]; $k_p\ k_t^{-\frac{1}{2}} = 0.5$ l.$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ sec$^{-\frac{1}{2}}$ [19] and the system can be treated as a homogeneous solution for this purpose. On the basis of these assumptions, the time required for the system to reach the steady state is about 5 min which is a negligible period for this run.

It is of interest to determine the efficiency of conversion of the primary HTC radicals to growing chains by the monomer vapor. The G-values for chain-radical initiations can be calculated from the rates of grafting (r_p), the viscosity average molecular weights ($\overline{M}_v$) and the dose rates (I) by means of the equation

$$G = 3.8 \times 10^{10}\ \ r_p / I\ \overline{M}_v\ . \qquad (36)$$

The constant 3.8×10^{10} is a collection of the appropriate conversion factors; it is calculated from the reasonable assumptions that the

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termination involves combination of two radical chains and that the number average molecular weight is $\frac{1}{2}\overline{M}_v$. The G-values obtained in this manner are shown in Table IV. The yield for chain production in the HTC-styrene system (G = 1.3) is seen to be much lower than that for primary radical production (G = 6) [43]. This inefficiency can arise from the recombination of some primary radicals which are then unable to form growing chains. The conglomeration of the HTC single crystals to form clusters of larger but looser structures creates a resistance to the diffusion of monomer to the surface of these crystals. Although there is evidence that migration of radicals to the surface of a single crystal is rapid [35], the inhibited movement of gaseous monomer molecules in an agglomerate tends to favor bimolecular recombination of the radicals relative to monomer reaction.

The plot of the graft rate versus dose rate (Figure 16) indicates that the reaction with monomer vapor is diffusion controlled. At dose rates below 2×10^4 rad/hr, the rate of grafting has a half order dependence on the dose rate. Thus, at these low dose rates, the supply of monomer by diffusion equals the rate of its consumption throughout the reaction. At higher dose rates, the monomer grafting rate exceeds its diffusion rate and the rate of grafting becomes almost independent of dose rate.

A comparison between grafting with monomer vapor and monomer liquid is also shown in Figure 16. Despite the lower G-value (as

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TABLE IV

Effect of Dose Rate on G for Chain-Radicals

When Grafting Styrene to HTC

$I \times 10^{-4}$ rad/hr	r_p, %/hr	$\overline{M}_v \times 10^{-5}$	G, radicals/100eV
2.4	0.82	9.5	1.38
6.8	1.1	4.6	1.35
9.5	1.3	3.7	1.38
35	1.4	1.5	1.02

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shown below), gas phase grafting gave higher yields and produced longer grafted chains. This result suggests that the mobility of the chain radicals at the crystal surface is somewhat inhibited in the gaseous system leading to generally lower termination rates.

The results of post-irradiation grafting of styrene to HTC are shown in Figure 20. The initial graft rate with liquid styrene was found to be twice as fast as with styrene vapor. In the absence of other effects, the slope would be proportional to the monomer concentration at the surface. This result indicates that the effect of the much lower monomer concentration in the gas phase is compensated in part by the decrease in k_t.

Grafting styrene liquid to HTC crystals was performed at HTC/styrene ratios that varied from 0.07 to 2.7 (Figure 17), the maximum ratio being the same as the polymer/monomer ratio in low density polyethylene film in equilibrium with styrene. The experimental results were compared with calculations based on three different models (page 48). The heterogeneous model (equation 27) gave the closest fit to the experimental data. Two important results are apparent from this experiment:

1. No viscosity effect was observed in the system. Even at an HTC/styrene ratio of 2.7, where the suspension appears to be a solid wax, the graft rate fits the heterogeneous model with the same $k_p/k_t^{\frac{1}{2}}$ value as for the radical polymerization of pure liquid styrene. When the rate of conversion at the HTC/styrene ratio of

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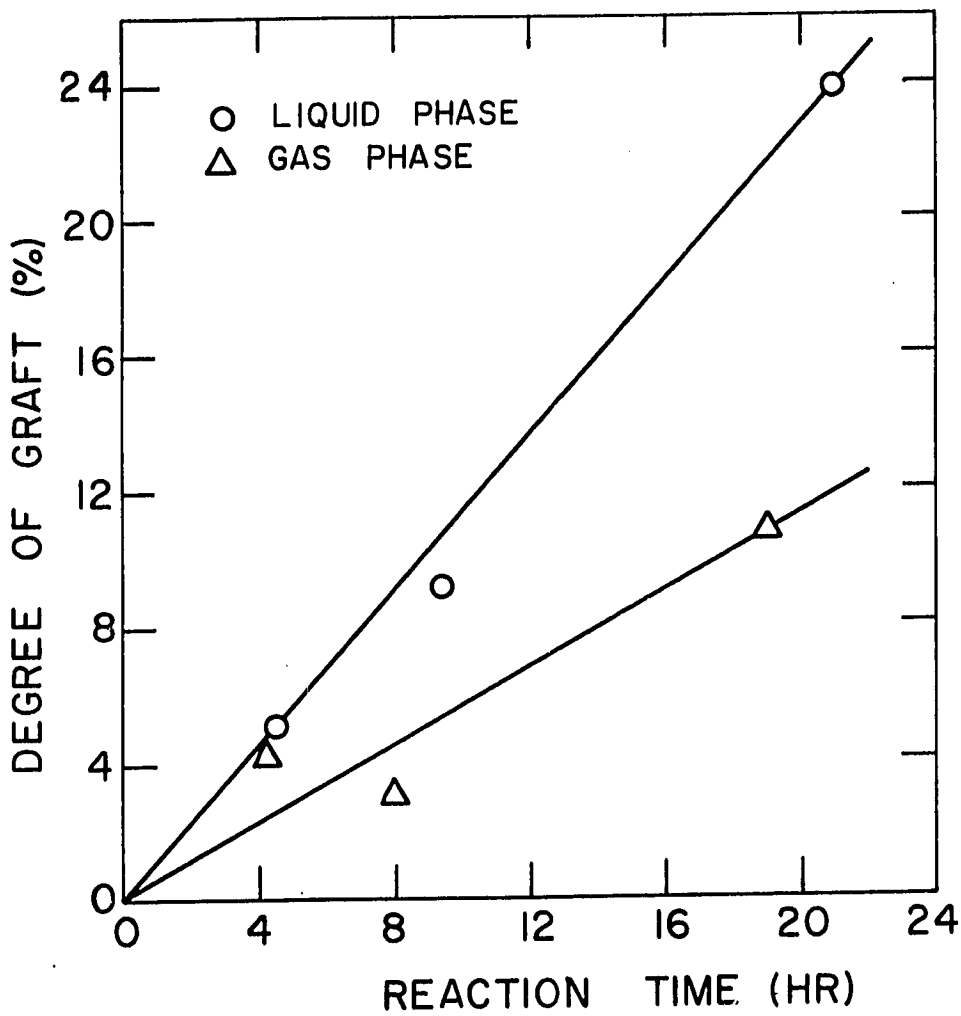

Figure 20. Degree of post-irradiation grafting of styrene vapor and styrene liquid to HTC versus reaction time at 25°C. HTC irradiated at 20°C and 9.6 x 10^4 rad/hr for 120 hr.

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2.7 was compared to that in polyethylene film, the result in the film was found to be almost twice that in the crystals, although the ratio of polymer to monomer was identical. The high conversion rate in the film can be attributed, therefore, to a viscosity effect which does not exist in the highly crystalline HTC. The absence of a viscosity effect suggests that HTC is highly crystalline, even when quenched rapidly. The accelerating effects in polyethylene films, therefore, require not only a certain polymer/monomer ratio, but also the existence of the alkane polymer in the form of disordered chains which increase the viscosity of the medium.

A similar trend was also reported by Shinohara et al.(41) These authors found an increase in the vapor phase grafting of styrene to polyethylene single crystal aggregates when these aggregates were fast filtered and pressed. The reason for the increased grafting efficiency of the pressed aggregates, they explained, is that the applied pressure partially injured and destroyed the single crystal aggregates, increasing the amorphous content of the sample.

2. The experimental results agree with the calculations based on the assumption that every radical produced in the HTC crystals migrates to the surface and forms a chain. The efficiency of chain-radical formation, therefore, is substantially higher than in the gas phase because of the ease of dispersion of the alkane crystals in the liquid that makes possible the wetting of every crystalline surface by a high concentration of the monomer.

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Chapter V

CONCLUSIONS

1. Exposure of polyethylene film to styrene vapor, or equilibration of the film with styrene-methanol solutions are two practical methods that enable one to control the monomer concentration inside the film at some desired level. The former method is diffusion controlled.

2. Grafting of styrene to polyethylene film shows accelerated rates when the concentration of the monomer in the film is below the equilibrium value. The graft rate has a maximum value at 4% average styrene concentration when grafting with monomer vapor, and at 6.2% when grafting with styrene in methanol solution.

3. When a polyethylene film is partially swollen with styrene, the amorphous region has a high viscosity which reduces the termination reaction of chain radicals relative to the propagation reaction. Accumulation of radicals occurs in the amorphous matrix causing the degree of graft to vary non-linearly with time. Accelerated rates of grafting occur due to an increase in $k_p/k_t^{\frac{1}{2}}$.

4. Grafting of polyethylene film with styrene vapor was found to yield a significant improvement in the appearance and stability

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of the copolymer. No loss in the transparency of the film was observed and no bubble formation occurred when the copolymer was soaked in benzene. The improvement is due to a low homopolymer content which is a result of the high resistance to diffusion of the vapor in the film. This diffusion resistance causes the graft to occur close to the surface of the film. The surface resistance coefficient for the diffusion of vapor into the film was determined to be 2×10^{-7} cm/sec.

5. Grafting of polyethylene film with styrene-methanol solution occurs at styrene concentrations in equilibrium with the outside solution because of the rapid diffusion of monomer in the liquid phase. The content of methanol in polyethylene is less than 4% of the sorbed solution, regardless of the composition of the outside solution. At this level, methanol has no effect on the kinetics of the graft.

6. Grafting of styrene vapor to HTC crystals show a low G-value for chain radicals of 1.4, which is a fourth of the yield of primary radicals. The inefficiency of converting primary radicals to chain-radicals appears to be caused by the slow penetration of monomer into the crystal aggregates. Calculations based on a G = 6 for chain-radicals agree with the grafting of styrene liquid to HTC.

7. No viscosity effect was found when grafting styrene liquid to

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HTC, even at the HTC/styrene ratio comparable to the polymer/monomer ratio of the amorphous regions of polyethylene film in equilibrium with styrene. The graft yield at this ratio was about one half the graft yield of polyethylene film.

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APPENDIX A

Graft Copolymers Prepared by Ionizing Radiation

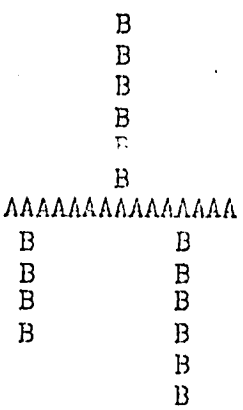
Nonrandom Copolymers

Nonrandom copolymers has attracted great scientific interest as an attractive method for the modification of polymer characteristics which could lead to unlimited industrial applications. Two known types of these copolymers exist, which as their name implies, are composed of two or more monomer units which are not randomly arranged.

The first type is the block copolymer in which the polymer chains are composed of blocks of the individual monomer units.

AAAAAAAAAAAAABBBBBBBBBBBAAAAAA

The second and the most common type of nonrandom copolymers are the graft copolymers. In this type the macromolecule is composed of a main chain of a homopolymer, usually called the backbone, while the second polymer comprises the side chains which grow out of the homopolymer backbone.



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There are many methods for producing nonrandom copolymers, for example the use of peroxides, mastication and ultraviolet radiation, in addition to the use of high energy radiation. These methods, in general, induce active sites in one or both polymer units to be joined. These active sites on a polymer unit may either react with another site on a different polymer unit or add surrounding monomer units.

Typical industrial examples of graft modifications are the improvement of the adhesive properties of polytetrafluoroethylene by grafting its surface with styrene [1,2], and the preparation of ion exchange membranes using sulfonated polyethylene-styrene grafts which combine the mechanical properties of polyethylene and the ion-exchange properties of sulfonated polystyrene [3].

The introduction of grafted chains can be limited only to the surface of the backbone or can be extended to the bulk of the polymer depending on where the effect of the grafted polymer is best utilized.

Radiation Induced Reactions

The use of radiation in polymerization and grafting has many advantages over chemical methods. For example, the initiation step is almost independent of temperature and radicals are uniformly produced throughout the material at a rate that is only a function of the radiation intensity. This simplifies control over the reaction rate and the molecular weight of the product. This technique can be applied to many monomer-polymer pairs and

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sometimes to reactions that are not possible or convenient with other methods. The radiation induced reaction could also occur at very low temperatures or in the solid state.

The application of high energy radiation to processes on the industrial scale is strongly connected to the convenience, the acceptability and the economics of such processes. This explains why most of the reactions studied are self propagating or where a relatively small dose can produce a large effect. Examples of this type of reaction are the polymerization of vinyl monomers, the grafting of vinyl monomers to different polymers, the cross-linking of polymers, the radiation sterilization and the application of radiation in the medical and biological fields. Because only small doses of radiation are considered in the above reactions, the radiation damage to the bulk material is negligible and the cost of the process is greatly reduced.

The present industrial usage of radiation is still very limited due to problems in source technology and the relatively expensive use of isotopes. But despite all the problems connected with field, radiation processing is slowly gaining ground in industry and is competing with chemical and other methods of processing several specialty products where the pronounced effects of radiation can be fully utilized (8,9).

Methods of Radiation Induced Graft Polymerization

In general, methods for the radiation production of graft

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copolymers fall into three different categories:

1. The simultaneous irradiation of a polymer-monomer mixture, usually in an inert atmosphere or in vacuum.

2. Pre-irradiation of the polymer only; this can be accomplished either in vacuum or in air followed by removal of the polymer from the radiation field and addition of the monomer. When the polymer has been irradiated in vacuum, trapped long-lived radicals are produced which are later attacked by the monomer units and produce the grafted polymer. In the case of polymer irradiation in air, peroxide and hydroperoxide groups are formed; when the polymer is subsequently heated in the presence of the monomer, these groups decompose with the production of free radicals which initiate the grafted polymer chains.

3. Irradition of two polymers; this method is rarely used because of its low efficiency.

The first method is by far the most widely used. The grafted polymer yield is relatively high in this method because of a higher radical yield, however, homopolymer is always obtained by the direct effect of radiation on the monomer. The advantage of the second method is the prevention of the homopolymer formation by preventing the exposure of the monomer to the radiation field. This result, however, is accomplished at the expense of a rather low radical yield, since most of the radicals will terminate each other once the polymer is removed from the radiation

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field. The pre-irradiation method, in general, gives a more stable product due to the absence of the contamination with the homopolymer, but the yield of grafting is generally very low.

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APPENDIX B

Summary of Desorption Experiments

in Vapor Phase

Time of exposure to monomer vapor, hr	Polyethylene film weight, g	Desorption time, min	Styrene weight in film, mg
0.5	0.2171	0.75	4.5
		1.0	4.3
		1.5	3.9
		2.0	3.6
		3.0	2.9
		4.0	2.4
		5.0	2.1
		7.5	1.6
		10	1.2
		15	0.9
1.0	0.2248	1.0	6.5
		1.5	5.5
		2.0	4.8
		2.5	4.2
		3.0	3.7
		4.0	3.1
		5.0	2.6
		7.5	1.7
		10	1.2

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Time of exposure to monomer vapor, hr	Polyethylene film weight, g	Desorption time, min	Styrene weight in film, mg
1.0	0.2248	15	0.7
1.5	0.2196	0.75	9.5
		1.0	8.7
		1.5	7.3
		2.0	6.4
		3.0	5.0
		4.0	4.0
		5.0	3.4
		7.5	2.2
		10	1.5
		15	0.8
3.0	0.2196	0.75	13.1
		1.5	12.1
		2.0	9.9
		3.0	8.0
		4.0	6.6
		5.0	5.4
		7.5	3.6
		10	2.6
		15	1.6
6.0	0.2168	0.75	14.7

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Time of exposure to monomer vapor, hr	Polyethylene film weight, g	Desorption time, min	Styrene weight in film, mg
6.0	0.2168	1.0	13.7
		1.5	11.6
		2.0	10.0
		3.0	7.8
		4.0	6.4
		5.0	5.5
		8.0	3.2
		10	2.5
		15	1.5
11.0	0.2248	0.75	22.8
		1.0	21.7
		1.5	19.7
		2.0	17.8
		3.0	14.6
		4.0	11.4
		5.0	8.9
		7.5	5.1
		10	3.5
		15	2.0
20.0	0.2196	0.75	27.4
		1.0	26.2

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Time of exposure to monomer vapor, hr	Polyethylene film weight, g	Desorption time, min	Styrene weight in film, mg
20.0	0.2196	1.5	24.1
		2.0	22.2
		3.0	18.0
		4.0	14.7
		5.0	12.5
		7.5	7.8
		10	5.5
		15	2.9
30.0	0.2171	0.75	27.5
		1.0	26.3
		1.5	24.0
		2.0	21.7
		3.0	17.3
		4.0	14.1
		5.0	11.6
		7.5	7.4
		10	5.4
		15	3.3
39.2	0.2168	0.75	25.2
		1.0	24.3
		1.5	22.6

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Time of exposure to monomer vapor, hr	Polyethylene film weight, g	Desorption time, min	Styrene weight in film, mg
39.2	0.2168	2.0	21.0
		3.0	18.4
		4.0	15.9
		5.0	13.4
		7.5	7.7
		10.5	5.4
		15	3.7

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APPENDIX C

Numerical Solution of the Diffusion Equation in the Vapor Phase

Equations 16 and 20, page 26, were transformed into five simultaneous ordinary differential equations by writing the x - variable in the finite difference form. The thickness of the film slab was divided into ten compartments, and solution was only obtained for half the thickness.

The accuracy of the computation was checked by using $\frac{1}{2}\Delta X$ as the size of the division; this gave negligible differences. ΔT was chosen so that

$$D\Delta T/(\Delta X)^2 = 0.3$$

The actual program print is shown on the next page.

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```
                    ***MIMIC SOURCE-LANGUAGE PROGRAM***

DIFFUSION OF STYRENE VAPOR INTO POLYETHYLENE FILM
CONSTANTS
                    CON(L,DTMIN,DTMAX)
PARAMETERS
                    PAR(H,D0,CT,MAXT)
MAIN PART
          C6        C4+(.4*H*L/D0)*(1.-C5)*EXP(-2.*C5)
          DC5DT     12.5*(EXP(2.*C6)-2.*EXP(2.*C5)+EXP(2.*C4))
          DC4DT     12.5*(EXP(2.*C5)-2.*EXP(2.*C4)+EXP(2.*C3))
          DC3DT     12.5*(EXP(2.*C4)-2.*EXP(2.*C3)+EXP(2.*C2))
          DC2DT     12.5*(EXP(2.*C3)-2.*EXP(2.*C2)+EXP(2.*C1))
          DC1DT     12.5*(EXP(2.*C2)-2.*EXP(2.*C1)+EXP(2.*C0))
          DC0DT     25.0*(EXP(2.*C1)-EXP(2.*C0))
          C5        INT(DC5DT,0.0)
          C4        INT(DC4DT,0.0)
          C3        INT(DC3DT,0.0)
          C2        INT(DC2DT,0.0)
          C1        INT(DC1DT,0.0)
          C0        INT(DC0DT,0.0)
          CAVE      (.5*C0+C1+C2+C3+C4+.5*C5)*.2
FINISH STATEMENT
                    FIN(CAVE,1.)
                    FIN(T,MAXT)
HEADER STATEMENT
                    HDR(TIME,C5,C4,C3,C2,C1)
                    HDR(TIME,C0,CAVE)
                    HDR
READOUT STATEMENT
                    OUT(T,C5,C4,C3,C2,C1)
                    OUT(T,C0,CAVE)
                    OUT
END STATEMENT
                    END

                        ***SORT DIAGNOSTICS FOLLOW***
```

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APPENDIX D

Molecular Weight Calculations and Data

An Abbelohde viscometer was used to measure the viscosities of dilute solutions of polystyrene in benzene at 30°C. The average flow time for the pure solvent ($\bar{t}_b$) and each polymer solution ($\bar{t}_s$) was obtained using three or four measurements per average. From these values the specific viscosity, η_{sp}, was calculated as follows:

$$\eta_{sp} = (\bar{t}_s - \bar{t}_b)/\bar{t}_b$$

The values of η_{sp}/C, where C is the polymer concentration in grams per deciliter, were plotted versus C and the plot extrapolated to infinite dilution to obtain the intrinsic viscosity,

$$[\eta] = (\eta_{sp}/C)_{C \to 0}$$

The viscosity average molecular weight was then calculated from the intrinsic viscosity by the use of equation 15.

Viscosity Data

Dose Rate rad/hr	$\bar{t}_b$ min	C g/dcl	$\bar{t}_s$ min
3.45×10^5	2.436	0.261	3.024
		0.174	2.823
		0.131	2.723

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Dose Rate rad/hr	$\overline{t}_b$ min	C g/dcl	$\overline{t}_s$ min
9.6×10^4	2.435	0.355	4.273
		0.284	3.873
		0.237	3.593
		0.178	3.260
6.85×10^4	2.437	0.402	5.506
		0.268	4.323
		0.201	3.766
		0.089	2.985
2.43×10^4	2.44	0.247	4.840
		0.165	3.768
		0.124	3.505
		0.062	2.933

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APPENDIX E

Definition of Symbols

a = constant.

$b = R_i^p / R_i^m$.

C = concentration, mol/l.

C_o = solubility of styrene in pure polyethylene, mol/cm^3.

C_{oo} = solubility of styrene in polystyrene-grafted polyethylene, mol/cm^3.

D = diffusion coefficient, cm^2/sec.

D_o = diffusion coefficient at zero concentration, cm^2/sec.

F = diffusion factor defined by equation 10.

G = number of radicals produced/100 eV of radiation absorbed.

h = boundary resistance coefficient, cm/sec.

I = radiation dose rate, rad/sec.

$K = k_p (I \phi_p C_p / k_t)^{\frac{1}{2}}$.

k_p = specific rate constant for propagation, l. $mol^{-1} sec^{-1}$.

k_t = specific rate constant for termination, l. $mol^{-1} sec^{-1}$.

L = film thickness, cm.

l = half the film thickness, cm.

$\overline{M}_v$ = viscosity average molecular weight.

n = constant.

R_i = rate of chain radical initiation, mol $l.^{-1}$ sec^{-1}.

R_p = rate of chain propagation, mol $l.^{-1}$ sec^{-1}.

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$R_{p,g}$ = rate of conversion of monomer to graft, mol $l.^{-1}$ sec^{-1}.

R_t = rate of chain radical termination, mol $l.^{-1}$ sec^{-1}.

t = reaction time, sec.

$\bar{t}_b, \bar{t}_s$ = average flow time through the viscometer for pure benzene and polymer solution respectively, min.

V_m, V_t = monomer volume and total volume respectively, cm^3.

Greek Letters

$[\eta]$ = intrinsic viscosity.

η_{sp} = specific viscosity.

ϕ = yield of free radicals per unit concentration and per unit radiation in the monomer, sec^{-1}.

Subscripts

m = monomer.

p = polymer.

$m^\cdot$ = monomer radical.

$p^\cdot$ = polymer radical.

$r^\cdot$ = radical.

Superscripts

m = monomer.

p = polymer.

t = total.

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