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# RADIATION-INDUCED GRAFT POLYMERIZATION OF 4-VINYLPYRIDINE TO POLYETHYLENE

by

ARIF AHMET DERMAN

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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## Abstract

RADIATION-INDUCED GRAFT POLYMERIZATION OF 4-VINYLPYRIDINE TO POLYETHYLENE

by

Arif Ahmet Derman

Adviser: Professor George Odian

The radiation-induced graft polymerization of 4-vinylpyridine to high density polyethylene films has been studied under a wide range of reaction conditions of initiation rate, monomer concentration and polymer film thickness. The reaction conditions were chosen to include both diffusion-free and diffusion-controlled graft polymerization.

The grafting rate was found to be independent of polymer film thickness at low thicknesses. At high thicknesses, the rate was inversely dependent on the first-power of thickness. The dependence of the grafting rate on the initiation rate was 1/2-order for low polymer film thicknesses and low radiation intensities but changed to 1/4-order at high thicknesses and high intensities. The grafting rate was first-order in monomer at low radiation intensities and low thicknesses but 1/2-order at high intensities and high thicknesses. The results are discussed in terms of the occurrence of diffusional-control in the graft polymerization process and the applicability of the quantitative predictions of our theoretical work.

# ACKNOWLEDGEMENTS

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## INTRODUCTION

During the last two decades, radiation induced graft polymerization of monomers to a solid polymer backbone has received considerable attention from a large number of investigators. Commercial availability of high energy radiation sources coupled with the ability to produce desirable chemical and physical modifications in the properties of polymers brought forward extensive research in this area of polymer chemistry(1-4).

Although it is possible to chemically graft a polymer(4, 5), high energy radiation has the following advantages:

(a) unselective absorption of radiation in matter enables one to graft any monomer to any polymer under appropriate conditions,

(b) the produced graft polymer is free of contaminants, such as, initiator and chain transfer agent fragments

and (c) the grafting reaction can either be performed homogeneously throughout thick layers of polymer or can be limited to a surface zone of any desired thickness.

The radiation induced graft polymerization mechanism, although well studied, is far from being completely understood. The kinetics of monomer addition, which was long assumed to be similar to ordinary free radical polymerization kinetics, has been shown to be subject to certain peculiar effects depending on the conditions of grafting. These effects are thought to arise due to the inability of the monomer to diffuse in the polymer matrix, into the reaction sites, to keep pace with the rate of reaction(6, 7). On the

other hand, recent work in our laboratories on the well-studied styrene-polyethylene system has shown that the grafting kinetics are far different and complex than the ordinary free radical polymerization kinetics(8, 9). The rate dependence on monomer was observed not to be of first order, as is in the case of free radical polymerization(10), but 3/2 order at a dose rate of 0.00076 Mrad/hr. The dependence increased to 5/2 order with increasing dose rate. Also, the usual square-root dependence of the rate of grafting on the initiation rate dropped to zero order at high dose rates. Furthermore, using extremely dry monomers, the radiation induced graft polymerization of styrene, acrylonitrile, 4-vinylpyridine and vinyl-n-butyl ether on polyethylene, polytetrafloroethylene and on polyvinyl chloride has been shown to proceed through an ionic mechanism(11).

It is surprising that the kinetic order in monomer, even for the styrene-polyethylene system has not been established. Most of the studies in literature assumed first order dependence without experimental verification. Clearly, further work is desired for the elusidation of the mechanism and kinetics of graft polymerization.

This thesis puts forward our efforts on the study of the graft polymerization kinetics of 4-vinylpyridine-polyethylene system.

The main reasons behind the choice of this particular grafting system can be outlined as follows:

(a) the monomer, 4-vinylpyridine, can be polymerized easily by radical and/or ionic means(15),

(b) it was hoped that the polar nature of the monomer coupled with the high reaction rates observed as compared to styrene could easily shift the grafting kinetics to the diffusion-controlled state within the dose rate and thickness range of our $Cs^{137}$ gamma source and polyethylene film, respectively,

and (c) using the same polymer that was used in the recent work with styrene(8, 9) is thought to bring forward interesting kinetical comparisons.

In this study, we have centered our efforts on the speed and nature of the grafting reaction. We have not entered into the molecular aspects and parameters of the grafted chain. Our aim was:

(a) to investigate the main kinetic parameters, namely M and $R_i$ and their effect on the grafting rate,

(b) to establish the nature of the grafting reaction,

(c) to study the diffusional effects on the grafting kinetics

and (d) to experimentally verify the proposed theoretical analysis on the graft polymerization mechanism(12-14).

## GRAFTING TECHNIQUES

There are several grafting techniques one can employ to carry out graft polymerization.

(a) Mutual Grafting of Monomer and Polymer

In this technique, a polymer film is totally immersed in monomer or in a monomer solution and then subjected to irradiation. Usually, the irradiation step is carried out after the system has reached swelling equilibrium. During irradiation, radicals are produced on the polymer backbone and initiate the grafting reaction. The efficiency of grafting depends on the relative sensitivity of the monomer and polymer to irradiation. If the $G_R$ value(for definition, see Appendix 1) of polymer is greater than the $G_R$ value of the monomer, the grafing reaction will predominate over homopolymerization. If, however, the monomer is more radiation sensitive, homopolymerization will predominate.

(b) Pre-irradiation of Polymer

The formation of undesirable homopolymer in the preceeding technique can be avoided if the initiation and polymerization steps are separated. In this technique, the polymer is irradiated alone, in vacuo or in an inert atmosphere and then brought in contact with monomer in liquid or vapor state. Irradiation produces trapped radicals in the polymer matrix that subsequently react with the monomer. The mechanism of graft polymerization is the same as in the latter technique except that the initiation step is separated from the propagation and termination steps.

A variation of this technique is the irradiation of the polymer in air or oxygen instead of an inert atmosphere. This results in the formation of peroxides and/or hydroperoxides which decompose and react with the monomer when the system is subsequently heated.

## THE MECHANISM OF GRAFT POLYMERIZATION

The interaction of high energy radiation, such as gamma-rays, with organic molecules in general and polymers in particular, involves the interaction with their orbital electrons, resulting in their ejection or exitation. The ejected electrons carry enough kinetic energy to further react with molecular species (atoms, ions, radicals, etc.) along their paths. The over-all picture is quite complex(1) but the net result is the formation of radicals and ions along the tracks of radiation. These active species are responsible for the initiation of graft polymerization.

Radiation-induced graft polymerization has been shown to proceed through a radical mechanism(16). Electron spin resonance studies with polyethylene has shown that the produced radicals are mainly alkyl and allyl type(17, 18)and that these radicals initiate the grafting reaction(19, 20).

Radical chain processes are characterized in three main steps, namely, initiation, propagation and termination. The following series of equations are generally accepted for the various steps of the grafting reaction;

Initiation

$$P \xrightarrow{k_o} P\cdot \quad , R_i = k_o I \qquad (1)$$

$$P\cdot + M \xrightarrow{k_{ii}} PM\cdot \quad , R_{ii} = k_{ii}[P\cdot][M] \qquad (2)$$

Propagation

$$PM_n^{\cdot} + M \xrightarrow{k_p} PM_{n+1}^{\cdot} \quad , R_p = k_p[PM_n^{\cdot}][M] \qquad (3)$$

Termination

$$PM_n^{\cdot} + PM_m^{\cdot} \xrightarrow{k_t} PM_{n+m}^{\cdot} \quad , R_t = 2k_t[PM_n^{\cdot}]^2 \qquad (4)$$

If one makes the general assumption that the kinetic chain is long, then equation (2) can be neglected as compared to equation (3), the rate of grafting is then expressed by equation (3).

Under the conventional steady-state assumption that the radical concentration remains constant during the course of the reaction, for the rate of graft polymerization one can obtain,

$$R_p = (k_p/k_t^{1/2})MR_i^{1/2} \qquad (5)$$

an expression exactly analogous to the ordinary free-radical homopolymerization kinetics. This rate equation has also been derived without using the steady-state assumption(12, 16).

According to equation (5), the rate of graft polymerization should be dependent on the square-root of initiation rate and consequently to the radiation intensity. Such a dependence has been observed for several systems like methyl methacrylate-polyethylene(21), acrylonitrile-polyethylene(21), vinyl acetate-Teflon(16) and styrene-Teflon(22). Takamatsu and Shinohara(23) investigated the styrene-polyvinyl chloride system with the pre-irradiation method. A square-root dependence was observed for both the monomer vapor and liquid within the dose-rate range of 0.005-0.1 Mr/hr(for definition of terms, see Appendix 1). At higher dose-rates, although the same dependency existed for the liquid monomer, the dependency dropped to zero-order for the monomer vapor. In all cases, the rate of graft polymerization for the monomer vapor was found to be higher than that of the monomer liquid although the concentration of the former is lower in the polymer matrix. This behaviour has been attributed to the plastisizing effect of styrene. With the increase of styrene concentration absorbed in the polyvinyl chloride film, the termination rate constant($k_t$) has been shown to increase, decreasing the rate of graft polymerization. Studies on polyethylene terephthalate fibers with styrene(24) also brought forward the square-root dependence on the dose-rate. Styrene in this work was diluted with dimethyl sulfoxide to aid swelling.

Deviations from this expected dependence have been observed for several other systems and attributed to the diffusional control in the grafting reaction.

For the styrene-polyethylene system, the graft polymerization rate has been found to be independent on the dose-rate between 0.018-0.26 Mr/hr(6). A similar result was also observed by Ballantine(21).

The dependence of the rate of graft polymerization on the monomer concentration is predicted to be first-order with respect to equation (5). Although experimental work is quite scarce on this line, available data in literature show some deviations from the expected behaviour. As described earlier, for the styrene-polyethylene system this dependence has been found to be 3/2-order but increased to 5/2-order with the increase in the dose-rate. The 3/2-order with respect to monomer concentration has been explained by the dependency of the initiation rate on the monomer concentration. If reaction (2) on page 5 is slower than reaction (1), equation (2) then becomes the rate determining step. Also, assuming that the termination step occurs, as usual, by bimolecular coupling and/or disproportionation then the rate will be 3/2-order with respect to monomer concentration. The higher 5/2 order was not explainable but high viscosity of the reaction medium, energy-transfer processes and primary radical termination have been considered as probable phenomena that can produce such an order(9). Ballantine(21) also observed 5/2-order dependence.

Unfortunately, a common practice in published monomer-polymer grafting studies has been to plot the grafting rate versus added solvent concentration, generally producing a complex bell-shaped curve. Such curves result when an unsuitable diluent is used to vary the monomer concentration. The net effect is the simultaneous variation of the monomer concentration

and the termination rate constant($k_t$) which makes a quantitative interpretation of the monomer order impossible.

Silverman(24) varying the styrene concentration by diluting it with methanol, a non-solvent for grafted polystyrene chains and a compound that does not swell polyethylene to any extent(30), observed such a curve. The rate of grafting increased initially with monomer concentration, reached a maximum and decreased with further increases in the styrene concentration. The decrease in the grafting rate has been attributed to the decrease in the viscosity of the reaction medium, resulting in an increase in the termination rate relative to propagation. Odian(26), also observed the same behaviour. The same bell-shaped curves were also observed in the studies of grafting styrene vapor on polyethylene(25).

Wilson et al., realizing the difficulty in the variation of the monomer concentration without effecting $k_t$, attempted to keep the internal viscosity constant by using appropriate styrene-alcohol-benzene mixtures that yield the same value of Hildebrand solubility parameter($\delta$)(see Appendix 1). Using such mixtures he observed a linear dependence of the rate of grafting on the monomer concentration for styrene-polyethylene(27), styrene-Nylon(28), pentaflorostyrene-Nylon(28) and styrene-polyvinyl chloride(29) systems.

Although the above results are in line with the theoretical expectations(eq. 5), they are based on two assumptions that may not be true. It was assumed that:

(a) the composition of the monomer-alcohol-benzene mixtures absorbed in the polymer matrix is the same as the composition of the solution in the surrounding medium and

(b) the amount of solution absorbed by the polymer, i.e. percent swelling, is independent on the composition of the mixture.

Both assumptions need experimental verification.

In graft polymerization, the reaction medium is the swollen polymer matrix and high viscosity of this medium severely effects the propagation and termination steps. Studying the styrene-polyethylene system Chandler(31) determined the reaction rate constants. The $k_p^2/k_t$ value for the grafting reaction was found to be 0.28 liter/mole-sec. On the other hand, Tobolsky and Baysal(32) obtained a value of 0.000114 liter/mole-sec for the homopolymerization of styrene.

It is immediately evident that the value of $k_p^2/k_t$ for the grafting reaction is far larger than the corresponding value for the homopolymerization. Such a difference is not surprising in view of the highly viscous nature of the reaction medium. Increase in the viscosity as discussed earlier brings forward a decrease in the termination rate due to the difficulty experienced by the polymeric radicals to diffuse and react with each other(23, 33). The propagation rate constant($k_p$) is assumed not to be much effected by the viscosity of the medium since it involves the reaction of a polymeric radical with a highly mobile monomer molecule. Similar high $k_p^2/k_t$ values has been observed for the styrene-polyvinyl chloride system(23).

A further indication of a decrease in the termination rate would be an increase in the molecular weight of the grafted chain. Under similar irradiation conditions, the molecular weight of the grafted chain has been observed to be at least three times greater than that of the homopolymer formed. This behaviour was observed for styrene-polyethylene and styrene-rubber systems(13, 34).

Apart from the kinetical parameters, radiation induced graft polymerization mechanism is under the influence of diffusional parameters like polymer film thickness(L) and monomer diffusion coefficient(D). Several workers have investigated the effect of film thickness on the grafting rate.

Hoffman(6) studying styrene-polyethylene system observed that the grafting rate for 1.5 and 2 mil films are higher than the 5 mil film for both high and low density polyethylene. However, the rates of grafting for 5, 10 and 20 mil films were essentially the same. Chen(35), observed a different behaviour, for 1.5, 4 and 10 mil films the rate increased with increasing film thickness. Ballantine(36), using 4 and 10 mil films observed the same effect. On the other hand, Odian(37) found the grafting rate for 3 and 5 mil films to be the same. Wilson(38) investigating the styrene-poly(4-methyl pentene-1) system observed a gradual decrease in the grafting rate with increasing film thickness.

From the above results it is observable that the literature work along this line is scattered with conflicting results and therefore no firm conclusions can be made on the effect of film thickness on the grafting rate. Recently, a more systematic work on the styrene-polyethylene system has been reported. Odian and his workers(13) successfully demonstrated that the effect of film thickness on the grafting rate is dependent on other parameters like the rate of initiation($R_i$), monomer diffusion coefficient(D), etc. At a dose-rate of 0.11 Mr/hr, the rate was independent on film thickness upto 3 mils and decreased linearly with increasing thickness in line with the proposed theoretical analysis.

There are several theoretical analyses that have been put forward to account for the effect of monomer diffusion on the graft polymerization kinetics(13, 39). Here, a brief summary of Odian's theoretical analysis will be presented.

## THEORETICAL ANALYSIS

As described previously, in the mutual graft polymerization method, a polymer film of thickness(L) is immersed in the monomer and after maintaining swelling equilibrium the system is exposed to radiation. Radiation forms radical sites on the polymer backbone and graft polymerization is initiated at these sites. As the grafting reaction progresses more monomer diffuses into the reaction medium to replace that which reacted. The grafting reaction consists of a diffusional process followed by a polymerization process and may become diffusion controlled depending on the rates of the two processes.

Applying Fick's second law of diffusion(40) to graft polymerization, one can obtain,

$$(R_p)_{dx} = (dc/dt) + d/dx(D\ dc/dx) \qquad (6)$$

where $(R_p)_{dx}$ is the rate of graft polymerization at a differential thickness dx,

$dc/dt$ is the change in the concentration at dx with time, t,

$d/dx(D\ dc/dx)$ is the rate of monomer diffusion in and out of that thickness dx and

x is any distance measured from the center of the film.

Under steady-state conditions, in which the monomer concentration and the grafting rate has reached constant values throughout the film thickness, the term dc/dt will be zero and equation (6) becomes,

$$(R_p)_{dx} = d/dx(D\ dc/dx) \qquad (7)$$

The steady-state condition does not necessarily mean that the monomer concentration and the grafting rate are constant and uniform throughout the film thickness. It simply refers to the fact that both quantities have reached constant values at all differential thicknesses yielding a constant profile and that there are no further changes.

CASE 1 D is not dependent on concentration(c)

When the monomer diffusion coefficient D is not a function of concentration then equation (7) simplifies to,

$$(R_p)_{dx} = D\, d/dx(dc/dx) = D\, d^2c/dx^2 \qquad (8)$$

The rate of grafting at any differential thickness dx can be expressed as,

$$(R_p)_{dx} = aC^v \qquad (9)$$

where

$$a = (k_p/k_t^z)R_i^w \qquad (10)$$

Substitution of eq. (9) into eq. (8) yields a second order differential equation that can be solved for c.

The rate equation(eq. 9) shown above is a general expression and accounts for all the possibilities of different modes of initiation and termination. For ordinary free-radical polymerization kinetics where the initiation step is not dependent on the monomer concentration and termination is by bimolecular coupling(eq. 5), the values of the exponential parameters v, z and w are 1, 1/2 and 1/2, respectively. For different modes of initiation and termination these parameters take different values and the use of this general rate expression makes the solution of equation (8) applicable to any kinetic mode.

It should be pointed out at this time that, the experimentally determined grafting rate is the average grafting rate, $\overline{R}_p$, averaged over the entire thickness,

$$\overline{R}_p = (2/L)\int_0^{L/2} (R_p)_{dx} = (2a/L)\int_0^{L/2} (C)_{dx}\, dx \qquad (11)$$

Substituting the solution of equation (8) into equation (11) and further integrating, one can obtain an expression for $\overline{R}_p$(due to the complexity of the rate expression it will not be shown here, the reader is referred to reference 14.)

Two important limiting cases arise from the rate expression:

(a) Diffusion-free reaction

In this case, at any differential thickness, dx, the monomer concentration(c) is equal to the equilibrium monomer concentration(M) and the diffusion-free grafting rate is determined to be,

$$(\bar{R}_p)_{df} = aM^v = (k_p/k_t^z)R_i^w M^v \qquad (12)$$

an equivalent expression to equation (9) when C=M. It should be observable that the rate of grafting is not a function of diffusional parameters L and D. This case arises under the following conditions;

(i) high monomer diffusion coefficient and/or

(ii) low radiation intensity and/or

(iii) slow propagation(low $k_p$) and/or

(iv) fast termination(high $k_t$).

(b) Diffusion-controlled reaction

Under the conditions of exacly opposite behaviour to that presented above, the grafting system follows a different pattern and the rate of graft polymerization is expressed as,

$$(\bar{R}_p)_{dc} = (2/L)\left[ (2aDM^{v+1})/(v+1) \right]^{1/2} \qquad (13)$$

In this case, the monomer concentration drops sharply as one proceeds from the film surface towards the center and at the center the monomer concentration approaches to the value of zero.

Comparing equations (12) and (13), the following differences can be observed as one moves from the diffusion-free to the diffusion-controlled kinetics, (i) the dependence of the rate of graft polymerization on film thickness(L) changes from 0 to -1 order,

(ii) the initiation rate exponent, w, decreases from w to w/2 order and

(iii) the monomer exponent changes from v to (v+1)/2 order.

Assuming that ordinary graft polymerization conditions prevail, i.e. v=1, w=1/2 and z=1/2, the general rate expression simplifies to(13),

$$\bar{R}_p = \left[ (k_p/k_t^{1/2})R_i^{1/2}M \right](\tanh A)/A \qquad (14)$$

where A is a characteristic parameter and is expressed as,

$$A = \left[ (k_p/k_t^{1/2})(R_i^{1/2}/D) \right]^{1/2} L/2 \qquad (15)$$

Under the condition that $A \leq 0.1$, then tanh A=A and the rate expression (eq.14) simplifies to,

$$\bar{R}_p = (k_p/k_t^{1/2})R_i^{1/2}M \qquad (16)$$

and therefore for A values lower than 0.1 the grafting kinetics are diffusion-free. It is notable that this expression is exactly analogous to that of ordinary free radical homopolymerization kinetics(10).

When $A \geq 6$, tanh A=1.0 and equation (14) reduces to,

$$\bar{R}_p = \left[(k_p/k_t^{1/2})R_i^{1/2}M\right]^{1/2}/A$$

$$= 2(k_p/k_t^{1/2})R_i^{1/4}MD^{1/2}/L \qquad (17)$$

Under these conditions(v=1, w=1/2 and z=1/2) as one goes from the diffusion-free to diffusion-controlled state the grafting rate becomes inversely dependent on L as in the general case and the initiation rate exponent drops from 1/2 to 1/4 order. The monomer exponent does not change.

CASE 2 D is dependent on concentration(c)

The grafting kinetics become more complex if the monomer diffusion coefficient is a function of concentration. When the diffusion of a liquid into a solid is concerned, generally this is the case and the diffusion coefficient is usually expressed as(45, 46),

$$D = D_o e^{d(c/c_o)} \qquad (18)$$

where $D_o$ and d are constants for a particular polymer-liquid system, c is

the liquid concentration at a particular time and $c_o$ is the saturation concentration.

Substitution of equation (18) into equation (6) yields an expression that can only be approximated by numerical integration. The results(41) of such mathematical treatment indicate that:

(a) the dependence of the grafting rate on L and $R_i$ is exactly the same as presented in Case 1 and

(b) the rate of grafting depends on the monomer concentration to the order of,

$$v_{dc} = (v_{df} + 1)/2 - 1/2\left[(d-0.135d^{1/2})/(d+v_{df}+1-0.27d^{1/2})\right] \quad (19)$$

where $v_{df}$ and $v_{dc}$ are the monomer orders in the diffusion-controlled and diffusion-free states, respectively.

Using the above equation, for the usual case of $v_{df}=1$, one can easily calculate the monomer order($v_{dc}$) for different values of d. When d=0, as in Case 1, the right hand side of the equation will be zero and $v_{dc}=v_{df}=1$. With increasing d values, $v_{dc}$ approaches close to a value of 0.5 and at very high d values $v_{dc}=0.5$.

The equations presented in this summary are universal in nature, they are applicable to any monomer-polymer graft polymerization system operating under any mode of initiation, propagation and termination. The analysis is also applicable to ionic as well as radical polymerization mechanisms.

# EXPERIMENTAL TECHNIQUES

## A - CHEMICALS

(a) 4-vinylpyridine - The crude monomer(commercial grade) was supplied by Eastman & Kodak Co. as a dark brown liquid containing t-butylcatechol as inhibitor. Attempts to remove the inhibitor by shaking with caustic soda was ineffective. Therefore the monomer was distilled without any preliminary purification. The distillation was carried out under vacuum through an 18-inch column packed with Fenske helices. Oxygen and water free nitrogen was purged through the system continuously throughout the distillation. The distillation apparatus is shown in Figure 1.

Nitrogen gas entered the system at inlet (i), bubbled through an alkaline pyrogallol solution(42) at (a) which was used to absorb any traces of oxygen. Then, the gas passed through a column of calcium chloride (b) to aid drying. A positive pressure of nitrogen gas was always maintained at apparatus (a) to avoid leakage of air through the greased joints and connection tubes due to vacuum build-up. This was achieved by maintaining a higher rate of flow of nitrogen to apparatus (a) than that enters the system. The rate of flow of nitrogen into the distillation system was controlled by valve (j). The excess nitrogen escaped from the system through a loosely fitted plug at (h). During the distillation, tightning of this plug is an indication of variation from the set rate of flow and therefore vacuum build-up. For this reason, the looseness of this plug should be checked periodically and maintained throughout the operation.

The distillation system consisted of a boiling pot(c), a hand-made 18-inch column(d) and a distillation head(g). In order to maintain a high rate of distillation without excessive bumping the tip of the column was designed in such a way that the surface area of contact of entering vapor with the Fenske

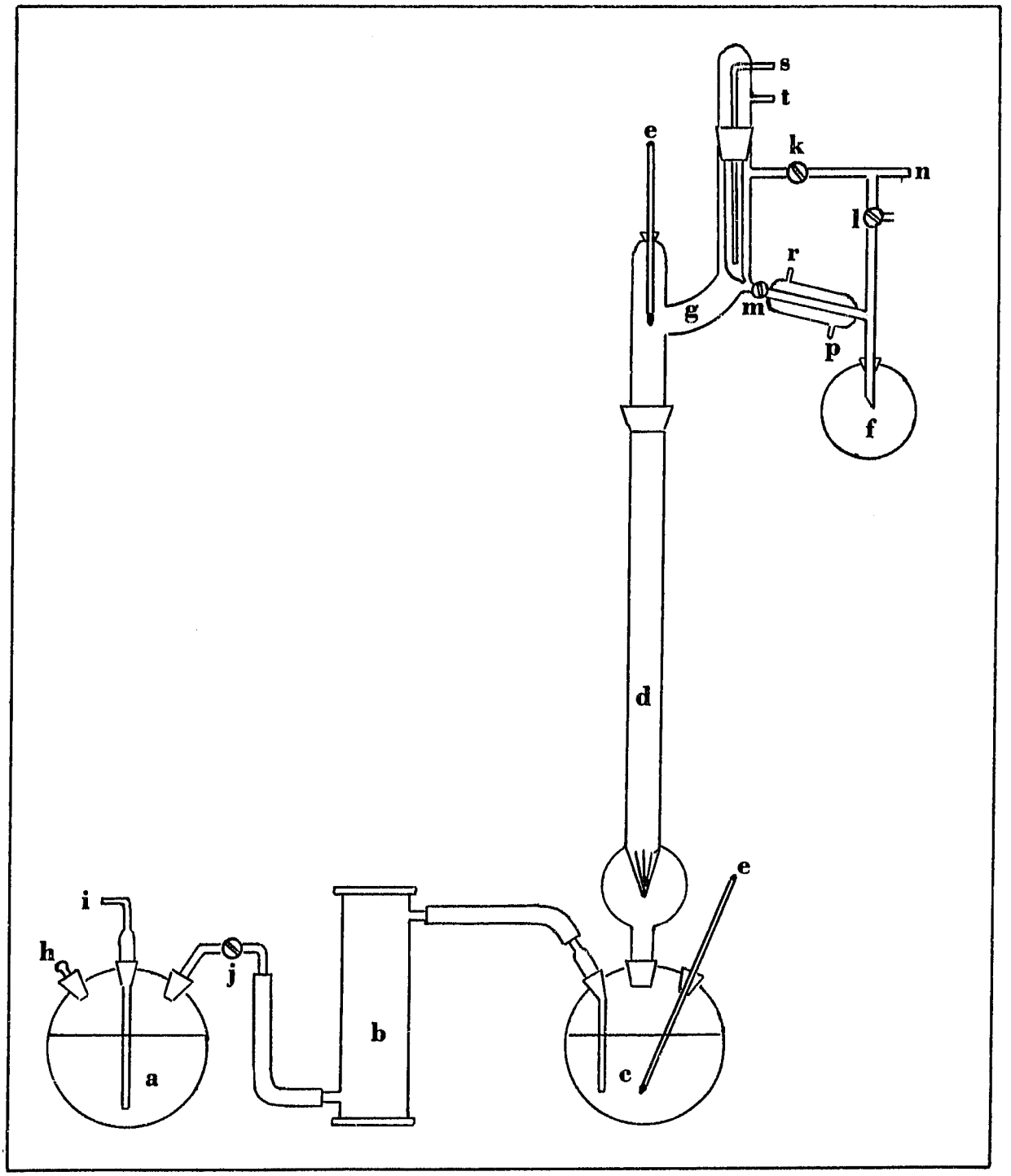



**FIG 1 THE DISTILLATION APPARATUS**

helices is increased. The column was made out of an 18 inch long, 3/2 inch bore glass tubing. Six pieces of 3 inch long, 1/8 inch diameter glass rod were fused at equal intervals to one end of the column. The rods were than tilted and fused to each other as shown in the figure. The bottom of a round-bottomed flask was then blown-out and a 24/40 male joint was fused to it at this point. After cutting the top joint off, it was fused to the tip of the column. In this way, when the column was filled with helices, the inverse pyramidal structure not only functioned as a support for the helices, but increased the area of contact. Normally, the distillation of 4-vinylpyridine is slow, as reported(43). But, using this column we were able to collect roughly 100 mls of the purest fraction in an operation period of about 10 hours.

A mechanical pump, manometer and a cold trap was connected to the system at (n). The valves (m, k and l) were kept open durig the distillation. At any desired time a fraction can be separated from the system without disturbing the distillation. This can be achieved by simply closing the valve (m) and opening the three-way valve (l) to the air. The collector (f) can then be separated and replaced with another. The collection can then continue by closing the valve (k), opening the valve (l) to the vacuum till all the air is removed and finally by opening valves (k and m). Tap water was circulated through the head at all times. It entered the head at (p) exitted at (r), re-entered at (s) and finally exitted at (t). The collector(f) was always kept in ice-water. The pot and head temperatures were observed by thermometers(e).

The distillation was carried out at a pressure of 50 mm Hg. At this pressure the purest fraction distilled at a temperature of 87.5 $^{o}$C. The pot temperature was 93-94 $^{o}$C. Onyon(43) reports the boiling point of 4-vinyl pyridine as 87.8 $^{o}$C at 50 mm Hg and in good agreement with our observation.

In contact with small amounts of oxygen, this monomer tends to get

colored(44, 45) and therefore the distilled fractions were always purged vigorously with nitrogen before storage and kept under nitrogen atmosphere during storage. The samples were stored in dark-colored, air tight(the storage bottle caps had plastic cushions in them for tight seal) bottles at a temperature of -10 °C and always used within a week. No polymerization was detected during the storage time.

The purity of the distilled fractions were checked with Gas Chromatography under the following conditions:

Gas Chromatograph: Hewlett & Packard, F & M Scientific 5750.

Column: 12 feet, 10% diethyl glycol succinate, 60-80 mesh, W. AW, DMSC.

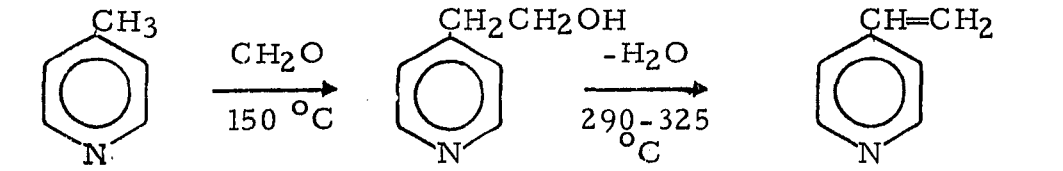
Column Temperature: 150 °C.

Injection Port Temperature: 225 °C.

Carrier: Helium.

The first and middle third fractions of each distillation boiling at constant temperature contained some impurities. The last third fraction was pure. This fraction was used for all graft polymerization studies.

Commercially, 4-vinylpyridine is synthesized from 4-picoline in the following manner(15):




4-picoline — 4-ethylhydroxy pyridine — 4-vinylpyridine

Therefore, several picolines, ethylhydroxypyridines and vinylpyridines were simultaneously injected with 4-vinylpyridine to determine the nature of the impuruties. Although no quantitative determination was attempted, the impurities qualitatively were identified as 2-picoline, 4-picoline and 2-vinyl pyridine. One other impurity was unidentified.

4-vinyl pyridine is a very corrosive monomer. In contact with skin it produces severe burns and irritation. It has a very unpleasant odor and therefore all experimentation was carried out under highly ventilated hoods and handling of the material was carried out using thick neoprene gloves.

(b) pyridine - This solvent was supplied by Fisher Co. as a colorless liquid and distilled from KOH at atmospheric pressure prior use. The boiling point was 116 $^{o}$C, as reported in the literature(48). The distillate was stored at room temperature, in dark colored bottles and under nitrogen atmosphere. Some of the physical properties of 4-vinylpyridine and pyridine are listed in Table 1.

(c) alkaline pyrogallol solution - The following recipe was used for the preparation of alkaline pyrogallol solution(42).

15 grams of pyrogallol was dissolved in 25 mls of water and mixed with 150 mls of aqueous 30% KOH solution.

The absorption of oxygen is reported to be satisfactory for concentrations less than 25%, at higher concentrations the absorption is slow.

(d) polyethylene - High density polyethylene films of thicknesses ranging from 1 to 10 mils were supplied by Gulf Oil Co. and reported to have the following properties:

Gulf Oil Company Resin Number : 9614

$M_w$ : 157600

$M_n$ : 18985

$M_w/M_n$ : 8.3

$\rho$ : 0.96 gram/ml

% crystallinity : 83

The crystallinity of the films were re-determined by Differential Scanning Calorimetry using Dupont 900 Analyser. A heating rate of 10 $^{o}$C/min

was used. The films were washed with acetone and dried overnight under vacuum at room temperature. They were then cut into dimensions to fit the sample cup and encapsulated. For thinner samples, severel layers of film was needed to reach an accurately measurable weight(i.e. 10 mgms). Nitrogen gas flowing at a rate of 0.2 liters per minute was passed through the DSC cell during all runs. Indium, Galium and Tin obtained from Fisher Co. were used for instrument calibration. The calibration constant (E) for the reference standards were calculated from the equation below,

$$E = (\Delta H_f M a)/(A \Delta T T) \qquad (20)$$

where $H_f$(cal/mgm) is the heat of fusion,

M(mgm) is the sample weight,

a($^{o}$C/min) is the heating rate,

$\Delta$T($^{o}$C/inch) is the temperature difference between the sample and reference cups per inch of thermogram,

T($^{o}$C/inch) is the temperature of an inch of thermogram

and A(inch$^2$) is the area under the thermogram.

6.79, 19.1 and 14.2 cal/mgm were used as the heat of fusion of Indium, Galium and Tin, respectively(49). A typical thermogram of Indium is shown in Figure 2(a). The areas under the thermograms were measured using a K & E 620000 planimeter. An alternative technique is to trace these areas on a uniform weight paper(such as Mylar paper), cut the area and find its weight relative to the weight of an inch$^2$ of uniform weight paper. This technique was also used and yielded the same results as that of the planimeter.

The calculated E values were averaged over 5 runs and plotted against the peak temperatures of the respective standards. This calibration curve is shown in Figure 2(b). The peak temperature of high density polyethylene varied slightly with thickness in the range 144-148 $^{o}$C. In this

TABLE 1

Some Physical Properties of 4-vinylpyridine and pyridine[a]

| Property | 4-vinylpyridine | pyridine |
|---|---|---|
| $n_D$(25 °C) | 1.5500 [c] | 1.50745 [c] |
| $\rho$25°C(gm/ml) | 0.979 | 0.978 |
| $\eta$(c.p.) | 1.22(20°C) [b]<br>0.98(40°C) | 0.884(25°C) |
| Boiling Point (°C) | 65(15 mm Hg) | 115.5 [c] |
| Molecular Weight | 105.14 | 79.1 |

(a) all data from ref. 48 unless otherwise indicated,
(b) from ref 49,
(c) same values observed in this work.

TABLE 2

Crystallinity of Gulf High Density Polyethylene(Resin-9614)

| Film thickness (mils) | Crystallinity(% w/w) | Average |
|---|---|---|
| 1 | 77.6, 76.3, 76.5[a], 77.4[a] | 77.0 |
| 2 | 78.2, 76.9, 78.9[a], 78.6[a] | 78.2 |
| 3 | 76.4, 77.9, 75.7, 77.2[a], 75.9[a] | 76.6 |
| 5 | 79.9, 78.3, 79.1 | 79.1 |
| 6 | 76.3, 76.4 | 76.3 |
| 8 | 75.8, 74.2, 75.1 | 75.0 |
| 10 | 79.6, 78.3, 77.3, 78.2[a] | 78.4 |

(a) crystallinity determinations by the DSC technique done by other workers in our laboratories(9)

range from the calibration curve the E value of high density polyethylene was calculated to be 136.5 ± 0.5 cal/min-°C. Substituting this calibration constant into equation (15) with the other necessary data from polyethylene thermograms(a typical polyethylene thermogram is shown in Figure 3) one can calculate the heat of fusion($\Delta H_f$).

If the heat of fusion($\Delta H_f^*$) of a perfectly crystalline polyethylene is known then the percent crystallinity can be calculated, i.e.

$$\% \text{ crystallinity} = (\Delta H_f(\text{experimental})/\Delta H_f^*)100 \quad (21)$$

It is rarely possible to prepare polymers with 100 % crystallinity and therefore the heat of fusion of perfectly crystalline polyethylene is estimated either from high molecular weight hydrocarbons(e.g. from the heat of fusion of crystalline dotriacontane(59)) or by plotting specific volume versus heat of fusion for a number of samples and extrapolating to the perfect crystal specific volume calculated from X-ray lattice parameters. Lately, Wunderlich(50) prepared perfect crystals of polyethylene by high pressure crystallization from the melt. All of the results from the various methods described above lead to a value of 69 cal/gram. Using this value and equation (16), percent crystallinity for all the available thicknesses of polyethylene were determined and listed in Table 2.

From the data in Table 2 one can conclude that, considering the precision in the DSC technique, the difference in the crystallinities calculated for different thicknesses is small and that all films of different thicknesses can be considered to have the same crystallinity. Averaging the averages of each thickness, a value of 77.2 % crystallinity has been calculated for Gulf high density polyethylene.

Density determinations, an alternative technique for the calculation of percent crystallinity, has also been done on this particular polyethylene(9) and the results confirmed the DSC data. It should be noted that this calculated

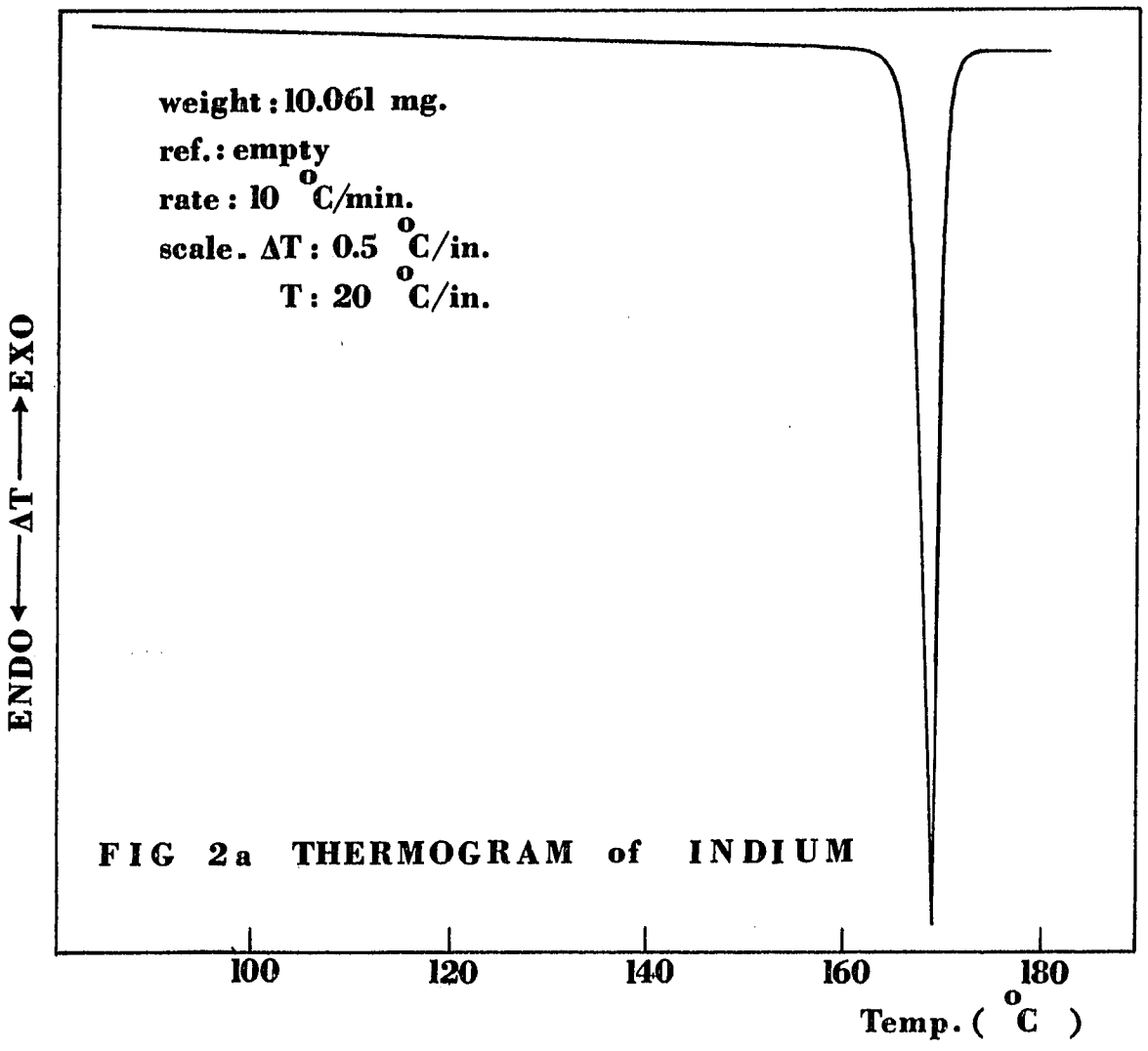



FIG 2a THERMOGRAM of INDIUM

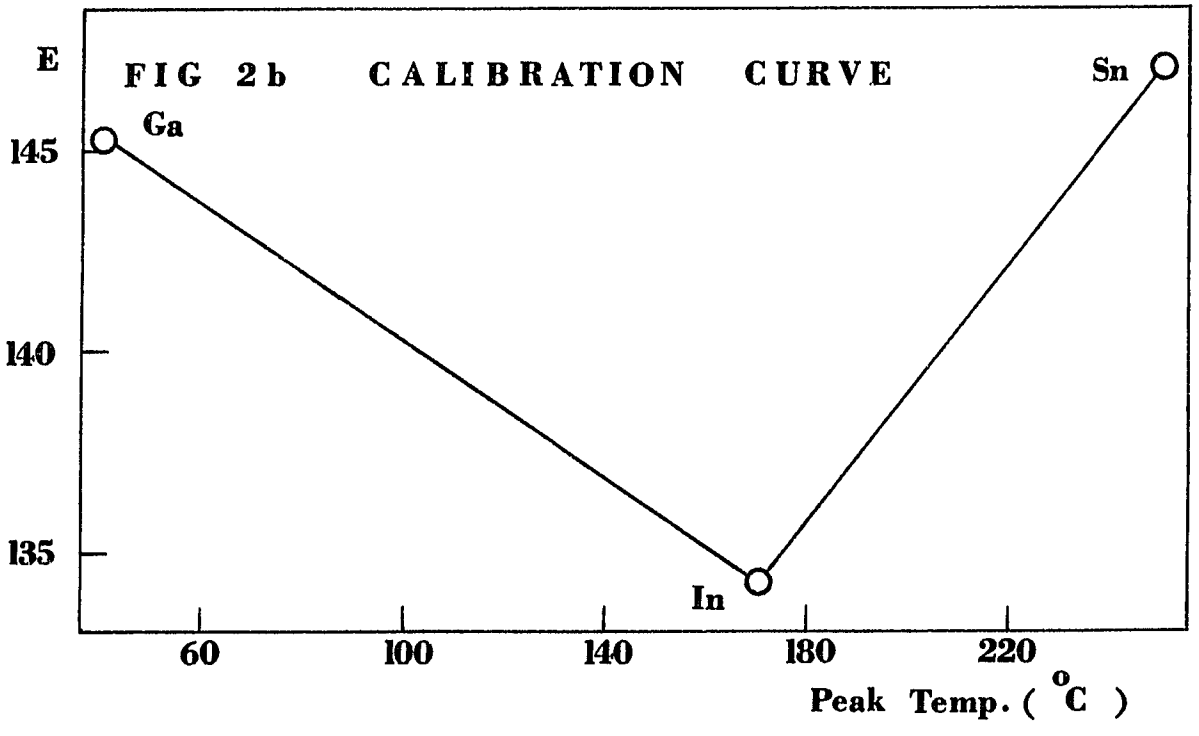



FIG 2b CALIBRATION CURVE

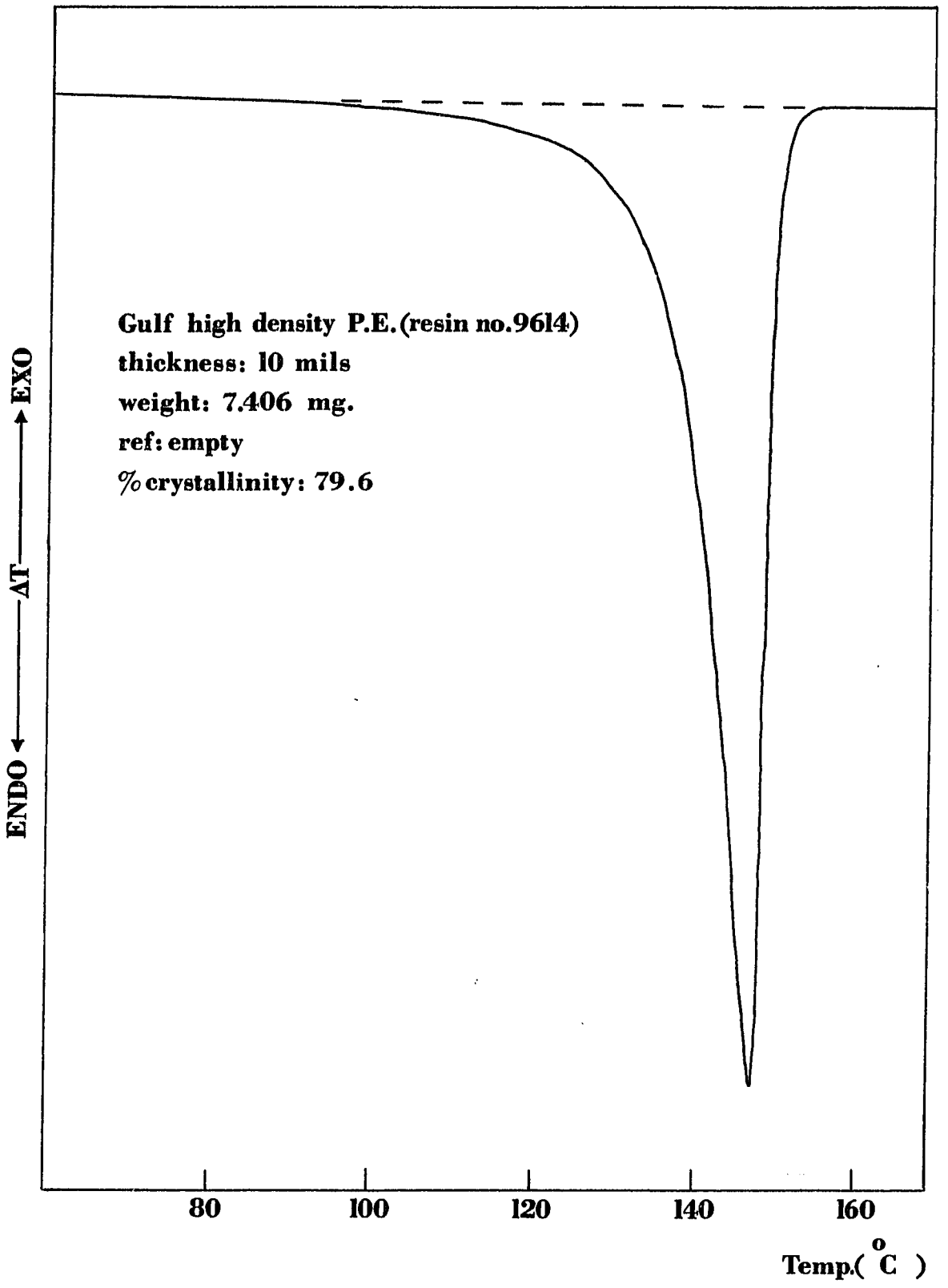



FIG 3 THERMOGRAM of POLYETHYLENE

value of 77.2 % crystallinity is considerably lower than that reported by the Gulf Oil Company(see page 21).

B - THE SOURCE

The gamma source used in this work was a J. L. Shepherd, Mark 1, Model 68, $Cs^{137}$ irradiator, loaded with 10000 curies. It was designed quite different than the more popular $Co^{60}$ Gamma-Cell and have several advantages over the latter.

The cavity is much larger than the Gamma-Cell and therefore enables one to radiate several samples at the same time. The dose rate can be varied at least 500 fold without the loss of the necessary cavity space for sample placement. Also, in this dose rate range, one can use 14 different positions with varying dose rates. At each position 4 samples can be irradiated at the same time. However, using the Gamma-Cell one can only vary the dose rate about 10 fold with great reduction in the cavity space.

The source and its components are shown in Figure 4. The cavity has a triangular pyramid shape(a) with the source column located at the apex(b). The source is kept in a shielded area(c) and can be pulled up manually into the source column for irradiation. During irradiation a safety mechanism locksthe cavity door(d) and therefore this door can only be opened when the source is not in operation. After irradiation the source can either be returned to the shielded area automatically by the expiration of the time preset on the digital timer(e) or manually. Two sample plates were provided for use with and without the lead attenuators. These plates can be installed into the source cavity at any desired height.Also on these plates there are cylindrical holes where the sample holders can be placed. The sample holders are cylindrical tubes that are used to keep the samples vertically straight in the cavity. A sample holder containing a sample to be radiated is placed into the

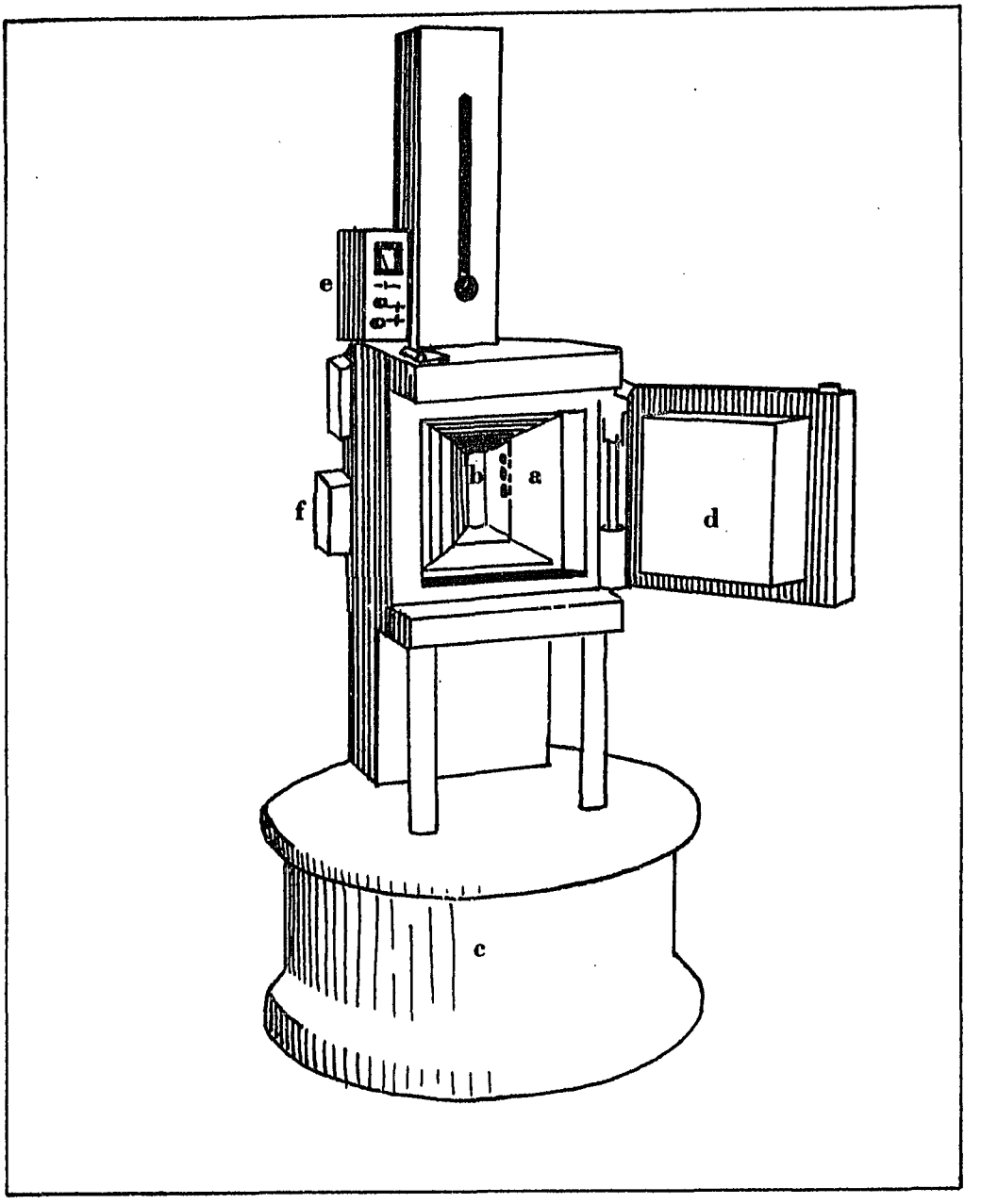



**FIG 4** $Cs^{137}$ **gamma irradiator "Mark 1, Model 68"**

desired hole on the sample plate and during irradiation rotated through a chain mechanism built in the plate by a motor (f) located on the left side of the source.In this way the samples receive homogeneous and uniform dose throughout the irradiation.

The lead attenuators are half-hollow cylindrical in shape and are placed on the source column whenever reduction in the radiaton intensity is desired. They can reduce the radiation dose in factors of approximately 2, 5, 10, 50 and 100.

The calibration of the source was done by the Fricke dosimetry method(52). The dosimeter usually consists of a 1 millimolar ferrous sulfate solution made up in oxygen saturated 0.4 M sulfuric acid . Upon irradiation ferrous ions are oxidized to ferric and the concentration of the produced ferric ions are determined by spectrophotometric measurements at the wavelengths of 304 and 276 nms. The procedure followed in this calibration was as follows;

(a)Extinction Coefficients(E), the determination of extinction coefficients at respective wavelengths was accomplished using potassium chlorate as standard. A known amount of chlorate oxidizes ferrous ions to ferric according to the following equation;

$$ClO_3^- + 6Fe^{+2} + 6H^+ \longrightarrow Cl^- + 6Fe^{+3} + H_2O \qquad (22)$$

The standard potassium chlorate solution was prepared after drying the compound in a vacuum oven at 75 $^{o}$C for overnight. The concentration of the standard was $1.22 \times 10^{-4}$M.

0.001 M ferrous ammonium sulfate solution was prepared fresh daily. It contained 1 millimoles of NaCl. The addition of chloride has been shown to supress the side reactions of ferrous ions(54). Also, use of ferrous ammonium sulfate instead of ferrous sulfate has been shown to yield more

reproducible results(53).

Final solutions for the determination of extinction coefficients were prepared by mixing the above solutions and a sulfuric acid solution in varying proportions and kept overnight in a temperature bath maintained at 25 ± 0.5 °C. The prepared solutions were 0.4 M with respect to sulfuric acid concentration.

The absorbance determination of these final solutions were carried out using Cary 118 spectrophotometer. The absorbances were than plotted versus the related ferric concentrations and the extinction coefficients($E_{304}$ and $E_{276}$) were calculated from the respective slopes(Figure 5). These coefficients were found to be $E_{304}$=2263.5 and $E_{276}$=1857.0 . The values correlate well with the literature results(55).

(b) Dose rates: test tubes of 3/4 o.d. were cleaned with chromic acid, washed and dried. They were marked 3 inches from the bottom and ferrous ammonium sulfate solutions were filled up to these marks and stoppered. A sample plate was positioned 3 1/4 inches from the bottom of the cavity. In this way, when the test tubes were fitted on the sample plates, the middle point of the solutions coincided with the middle point of the cavity height where the dose rate variation with vertical displacement is minimal. Under the above conditions, considering the solution height in the test tubes (about 3 inches), this variation was found to be not more than 5 %. All graft polymerization data reported in this thesis was carried out with the sample plates positioned as described.

Oxygen was bubbled through the sample solutions for 1/2 an hour before they were placed for irradiation. After this operation the samples were placed into the cavity and irradiated for a pre-determined time. After irradiation the tubes were shaken to compensate for vertical dose variations

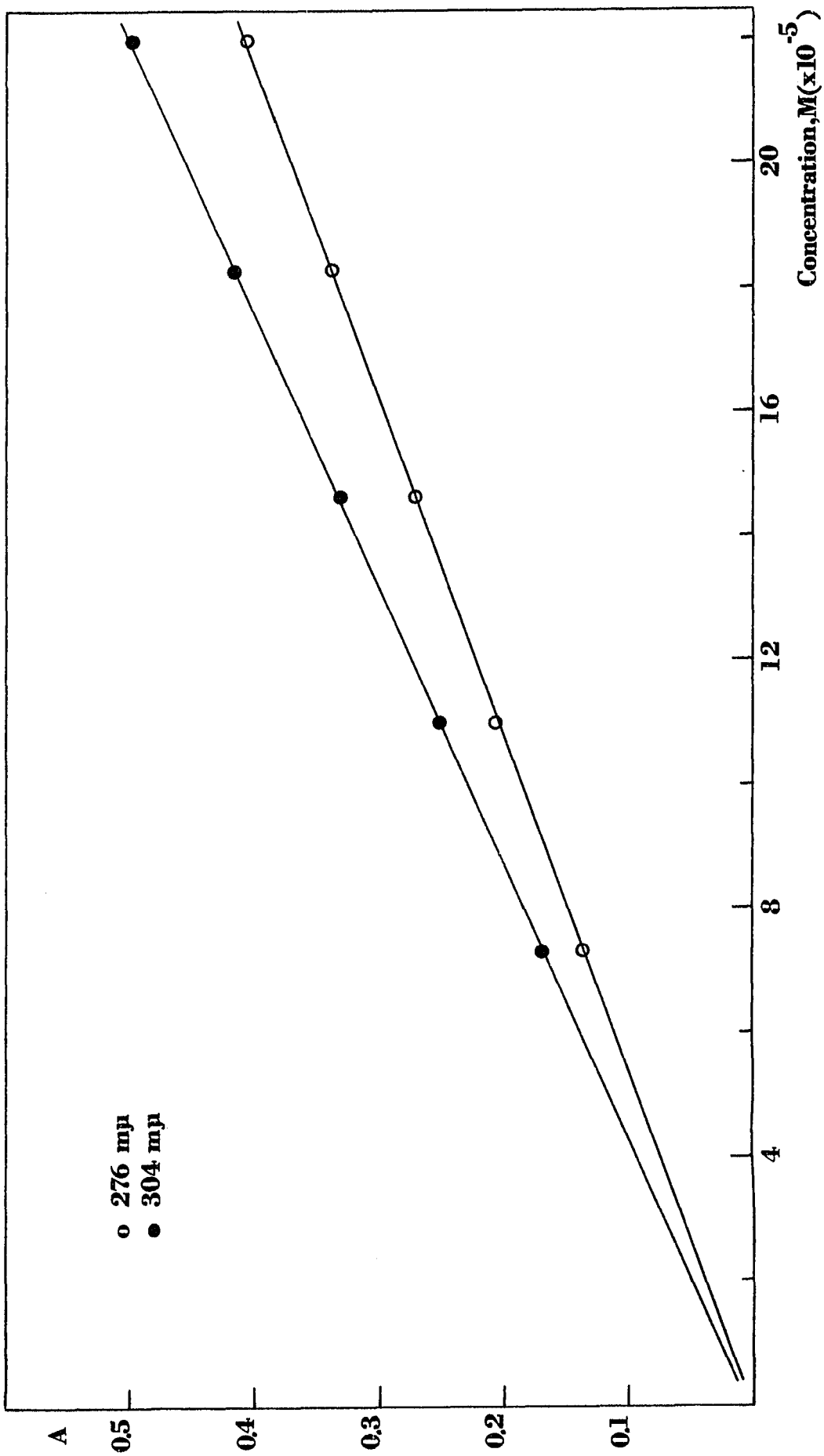



FIG 5 ABSORBANCE versus FERRIC ION CONCENTRATION

and were taken to a constant temperature bath at 25 ± 0.5 °C. The UV spectra was taken against a blank consisting of unirradiated ferrous ammonium sulphate solution which was kept in stoppered tubes for the same length of time as the irradiated samples. The samples and blanks were diluted when necessary to obtain an absorbance reading below 0.6 .

From these absorbance readings and the calculated extinction coefficients, one can determine the amount of dose received in a given period of time using the following relation:

$$I = 3777.0\ A/(bEt\rho) \qquad (23)$$

where I is the dose rate (Mr/hr),

A is the absorbance at 304 or 276 nms,

b is the cuvette diameter(cm),

E is the extinction coefficient(1/mole-cm),

t is time(min),

and $\rho$ =1.024(56), is the density of the ferrous ammonium sulphate solutions(gm/ml).

The constant(3777.0) in the above equation includes the $G(Fe^{+2} \rightarrow Fe^{+3})$ value for $Cs^{137}$ gamma rays(in this case the G value is defined as the number of ferric ions produced per 100 e.v of radiation absorbed) and other conversion factors for converting e.v's into Mrads, etc. The $Cs^{137}$ gamma rays have a mean energy of 0.662 mev and a $G(Fe^{+2} \rightarrow Fe^{+3})$ value of 15.3 ± 0.3 molecules/100 e.v.(57).

Using all the attenuators and the two sample plates, dose rate determinations for all the possible positions were done and the results are summarized in Table 3. The values listed in the table are mean values of at least ten individual determinations for each dose rate position. It is observable that in the range of 0.35 to 0.00076 Mr/hr, there are 14 different

TABLE 3

Radiation Intensity of $Cs^{137}$ gamma source

| Attenuator | Position | Radiation Intensity(Mr/hr) |
|---|---|---|
| - | I | 0.35 |
| - | II | 0.21 |
| - | III | 0.13 |
| - | IV | 0.085 |
| - | V | 0.058 |
| - | VI | 0.037 |
| x2 | III | 0.021 |
| x5 | II | 0.011 |
| x5 | III | 0.0077 |
| x10 | II | 0.0053 |
| x10 | III | 0.0037 |
| x50 | II | 0.0011 |
| x50 | III | 0.00076 |

dose rate positions.

During the irradiation it is also possible to maintain constant temperature. Although the source itself is not equipped with such attachment, one can easily build sample holders with outlets and inlets to pass the constant temperature water through. One disadvantage of using such a system is that the sample holders cannot be rotated during the circulation of water. Nevertheless, the dose rate variation, even at the highest dose rate position under this condition, is calculated to be no more than 5 %( dose rate decreases as one moves away from the source column and this decrease

is more pronounced at the highest dose rates between the front and the back of a sample).

All radiation work reported in this thesis was accomplished using a contant temperature attachment at a temperature of 25 ± 0.1 $^{o}$C.

## C- EXPERIMENTAL METHODS

### (a) graft polymerization techniques:

(i) sample preparation: a general procedure was followed for the preparation of samples for graft polymerization.

Test tubes of 18x150 mm in dimensions were cleaned with acetone and dried before use. All the tubes are then constricted at a height of 3 inches from the bottom. This was done to prevent the polyethylene samples from sticking out of the monomer solutions. 4-vinylpyridine has a slightly higher density than polyethylene, 0.979 versus 0.96 at 25 $^{o}$C.

The polyethylene films were cut rectangular in shape with varying dimensions depending on the thickness. To attain a weight not less than 1/4 grams, the films were cut to constant width, 6 cms but varying length, 15 cms for 1 mil to 3 cms for 10 mils. The films were then washed with acetone, dried in a vacuum oven overnight at room temperature, weighed to the nearest tenth of a milligram, folded in a zig-zag fashion lengthwise and placed into the test tubes. The tubes were then fused to 24/40 female joints through glass tubing of 1/4 inch bore. During the process of fusing some water droplets condense in the tubes and it is essential to remove them before the addition of monomer. For this reason the samples were hooked to a vacuum line operating at $10^{-6}$ mm Hg for a period of one hour. After this treatment the samples were taken from the vacuum line and stoppered.

It has been mentioned earlier that the monomer 4-vinylpyridine is air sensitive and in contact gets colored. Due to this property handling of this material was done at all times under nitrogen atmosphere.

The sample tubes that were prepared as described above, freshly distilled monomer and two 2-liter dewars full of liquid nitrogen were placed in a glove bag and nitrogen gas was purged through for half an hour. The samples were then filled with monomer or monomer solutions through the joint, with a long funnel, stoppered and immediately placed in liquid nitrogen. They were kept in the glove bag, in liquid nitrogen until ready to be transferred to the vacuum system. The vacuum system consisted of a mechanical pump, a mercury diffusion pump, 3 traps, a McLeod gauge and 6 male 24/40 joints connected to the vacuum line through two-way stopcocks. The sequence in which the above apparatus joined to each other was: the mechanical pump was connected to a trap through 2 inch thick rubber tubing, the trap was connected to the diffusion pump through the same material, this pump was connected to the two traps in series with glass ball-joints then came the vacuum line which was fused to the other end of the traps. Finally the vacuum line was connected to the McLeod gauge.

The vacuum line was a 3/2 inch o.d., approximately 4 feet long glass tubing. Three pairs of 24/40 male joints were fused to it through stopcocks and they were placed 8 inches apart from each other. Each individual joint in a pair was separated from the other by 3 inches. In this way six samples can be frozen and thawed at one time with the requirement of only three dewar flasks of liquid nitrogen for the freezing process. At one end of the vacuum line there was a stopcock used merely to let the air in when the operation is complete.

The McLeod gauge was a stationary type(there are rotating types available) and read vacuum up to $10^{-6}$ mm Hg. Once the system operated, the mercury line was between $10^{-6}$ and 0, indicating a vacuum bettter than $10^{-6}$ mm Hg.

When the vacuum system was ready, the samples were taken from the

glove bag and connected to the joints on the vacuum line while remaining in the liquid nirogen. The stopcock were then opened till the vacuum drops back to normal. They were then closed, liquid nitrogen dewars were taken off and the samples were placed immediately in water supplied from a constant temperature bath at 25 ± 1 °C. When the samples reached this temperature, they were wiped dry and placed again in liquid nitrogen. This freezing and thawing cycle was repeated 3 times. During the thawing process the samples were closed to the vacuum line to avoid bumping.

After the cycles were completed, the samples were sealed with an oxygen torch while they were cold(i. e. the liquid nitrogen dewars were lowered from 2 samples at a time and the samples sealed immediately while the monomer is in the solid state). During the sealing process the stopcocks were open to the vacuum.

The samples were then transferred to a freezer at -10 °C and stored until ready to use. The storage time was not more than a week and during this time no homopolymerization was detected(this was done by cracking a sample tube and mixing some of the monomer with a non-solvent for poly(4-vinylpyridine), e. g. acetone. A clear solution indicates no homopolymerization.)

(ii) irradiation and after-treatment: the samples to be irradiated were taken from the freezer and placed into a water bath at 25 ± 0.1 °C. They were kept in the water bath for 10 to 12 hours and during this time they reached equilibrium swelling state. It should be pointed out that this step is a crucial one and the time necessary for swelling equilibrium depends on the film thickness and on the physical properties of the monomer and polymer in question. For 4-vinylpyridine-polyethylene 10 hours were more than sufficient for the thin films( 1, 2 and 3 mils), 10-12 hours were adequate for other thicknesses.

Following this treatment, they were taken to the source, placed in the water jackets (i.e. sample holders with inlets and outlets) and irradiated while water at 25 ± 0.1 °C circulated around them. At the end of the irradiation period they were taken out of the source individually, the tubes cracked immediately and the grafted polyethylene films were washed with methanol (a good solvent for poly(4-vinylpyridine) (58)) for about five minutes and placed in a vacuum oven. They were kept under vacuum (about 0.01 mm Hg) at room temperature for overnight and then weighed to the nearest tenth of a milligram. The relative increase in weight was taken as the extent of grafting.

(b) monomer concentration measurements:

In the mutual grafting technique, there are mainly two experimental techniques to vary the monomer concentration:

(a) by diluting the monomer with a proper solvent and

(b) by swelling the monomer to different degrees with the monomer vapor.

The former technique has been used throughout this study and the monomer 4-vinylpyridine was diluted with the solvent, pyridine. The dilutions were done as follows: 100 ml volumetric flasks were taken and while nitrogen gas was purging continuously into the flasks, proper amounts of 4-vinylpyridine was pipetted into them. The flasks were then filled to a point slightly lower than the 100 ml mark with pyridine, mixed and placed in a bath at 25 ± 1 °C. They were kept in the bath for about 15 minutes, taken out and the solution level brought to the 100 ml mark. They were then mixed again and stored at -10 °C for about 2 hours and used within this time. The refractive indices of the mixtures were taken prior to storage and compared with a calibration curve to double check the prepared concentrations. The calibration curve is

shown in Figure 6. This curve covers the whole concentration spectrum of the 4-vinylpyridine-pyridine mixtures.

These mixtures were then used to fill the sample tubes as described earlier.

When a polymer swells a monomer-solvent mixture, depending on the swelling and polar properties of the monomer, solvent and polymer, the composition inside the polymer matrix(inside composition) may not be the same as that of the outside solution(outside composition). It is therefore necessary to experimentally determine the inside composition of the monomer-solvent mixtures.

The determination of the inside composition of 4-vinylpyridine-pyridine mixtures was accomplished in the following manner: the thickest film i.e.10 mils was cut into dimensions of 12x24 cms,folded in a zig-zag fashion, washed with acetone and dried overnight in a vacuum oven at room temperature. It was then immersed in a particular 4-vinylpyridine-pyridine mixture and kept overnight in a bath at 25 ± 0.1 $^{o}$C. A vacuum system was assembled as shown in Figure 7. It consisted of a three-neck round bottomed flask, a vacuum trap and a mechanical pump. Nitrogen gas entered the system at (a) and exitted at the three-way stopcock(e). The system was flushed with nitrogen for about half an hour before the experiment started. The polymer film was then taken out of the mixture, blotted rapidly to get rid of the excess mixture on the surface of the film and placed into the round bottomed flask through (c). During this operation nitrogen was flowing through the system but instead of exitting through (e), it exitted through (c). In this way no air entered the system while placing the film into the flask. Once the film was in the flask, stopcock (a) was closed and the system was opened to the vacuum at (e). A dewar containing liquid nitrogen was placed

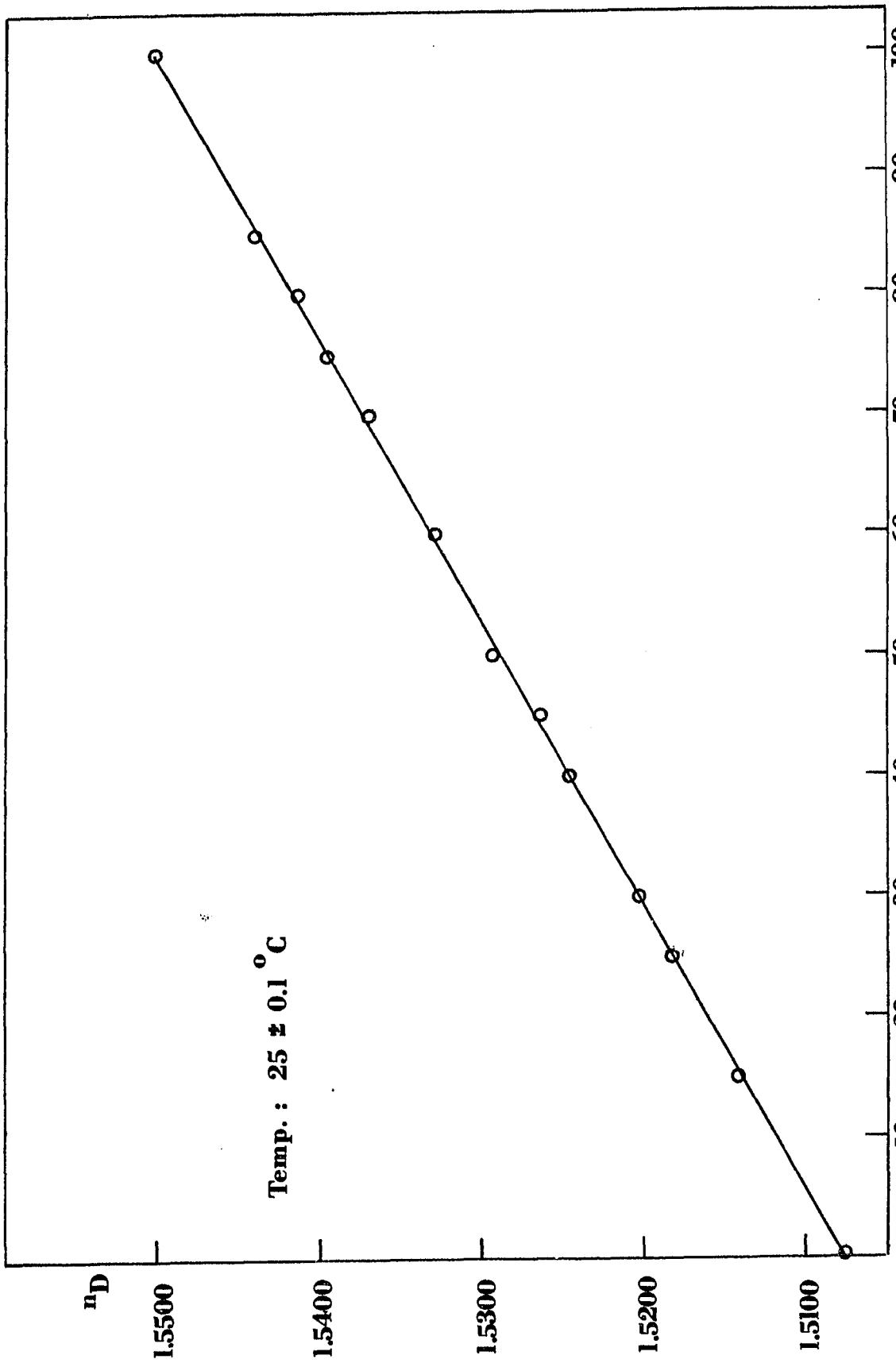



FIG 6 Refractive indices of 4-vinylpyridine - pyridine mixtures

at trap(d). At the same time flask(b) was placed in warm water. In this way the desorption of the inside mixture is speeded up.

Approximately 2 hours later, the system was closed to vacuum at (e), liquid nitrogen dewar was removed and after the trap(d) reached room temperature, nitrogen gas was admitted to the system at (a). The refractive index of the distillate in the trap was then measured at 25 $^{o}$C using a Baush & Abbe refractometer. The observed value was compared to the calibration curve(Figure 6).

This technique of determination of the inside composition has been applied to other monomer-polymer systems in our laboratories(9, 60) and is proven to be effective. U. V Spectroscopy has also been used, yielding the same results as observed with this technique(9, 60).

(c) determination of the parameter - d

The d value appearing in equation 18, has been determined for 4-vinylpyridine and pyridine using the desorption technique described elsewhere(59).

Polyethylene films of 10 mils were cut in a circular fashion to gain an optimum weight of approximately 3 grams and weighed to the nearest one hundreth of a milligram. The films were then swelled with 4-vinyl pyridine or pyridine overnight at 25 ± 0.1 $^{o}$C to attain swelling equilibrium. They were then taken out of the solution, blotted to dry the surfaces, immediately weighed and placed in the diffusion chamber. At specific time intervals, they were taken out of the chamber and weighed. The decrease in weight with time was measured. The diffusion chamber was a rectangular box of 3x4x5 dimensions maintained at a constant temperature of 25 ± 0.1 $^{o}$C.

The d value for 4-vinylpyridine and pyridine was estimated by comparing the experimental desorption curves with the theoretical ones given in reference 59.

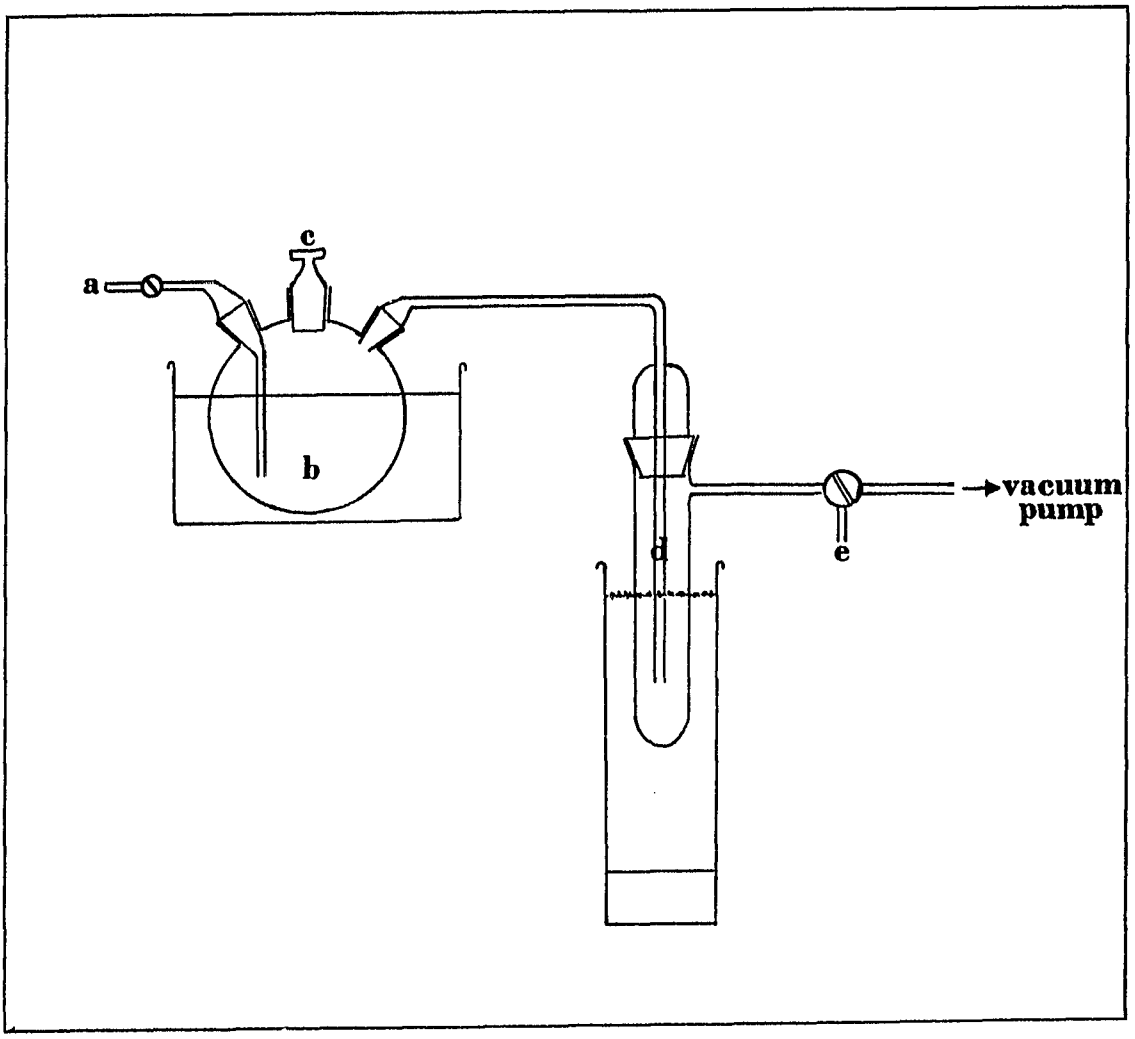



**FIG 7 Apparatus for the determination of "inside concentration"**

## RESULTS AND DISCUSSION

In radiation induced graft polymerization of a liquid monomer to a solid polymer backbone, the grafting process takes place in a highly viscous heterogeneous medium. Generally, the reaction kinetics in such media are quite complex and the use of a semi-crystalline polymer like polyethylene adds more to this heterogeneity. In the mutual irradiation technique a polymer film is swelled by monomer(not dissolved in it) and therefore the grafting system is constituted of three physically different states of matter. A liquid monomer and a solid polymer with amorphous and crystalline regions. A kinetically important question is the effect of this morphology on the grafting reaction and whether the reaction is confined in regions of a particular morphology or take place uniformly throughout the solid in both the amorphous and crystalline regions.

When high energy radiation impinges on such a system, amorphous as well as the crystalline parts of the polymer will simultaneously be radiolysed, the net effect being the production of radicals that initiate the grafting reaction. After receiving a certain dosage of radiation, although the population of radicals per unit volume of polymer is probably higher in the crystalline regions than that in the amorphous parts of the polymer, it is considered to be highly unlikely that any grafted chain is initiated in the crystalline parts. The highly dense packed nature of these regions are thought to be impenetratable for the monomer molecules. Studies on the permeation and solubility of uncondensable gases in polyethylene confirmes this view(61).

A question that directly follows the above discussion is the effect of grafting and radiation dose on the percent crystallinity of the film, that is, what effect does the increase in the extent of grafting and radiation dosage have on the percent crystallinity during the course of the reaction. Generally,

one expects a decrease in the percent of crystallinity due to the destruction by radiation and if this is the case then all the data points in a given grafting reaction have to be corrected to compensate for this variation.

Earlier studies on the styrene-polyethylene system in our laboratories and elsewhere(13, 62) has shown that even up to 100 % grafting, the percent crystallinity remained constant. Additionally, Dole(63) and his workers studied the effect of gamma radiation on high density polyethylene and detected no change in the crystallinity up to doses of 10 Mrads. It should be pointed out at this time that our limits of experimentation were well below the preceeding values due to reasons that will be discussed shortly we have confined our experiments in the region of 0-10 % grafting and to achieve this amount of grafting not more than 0.2 Mr of radiation dosage is needed.

Thus, with the fore-going literature facts in hand, we have analysed our kinetic results assuming that:

(a) the grafting reaction takes place solely and isotropically in the amorphous regions of the polyethylene and that crystalline regions act only as impenetratable fillers and

(b) the percent crystallinity of the film is not effected by the grafting process.

When polyethylene is exposed to gamma radiation, the major effect is the cleavage of the C-H bonds yielding a polymeric radical and a hydrogen atom

$$\sim CH_2\text{-}CH_2\sim \xrightarrow[\text{radiation}]{\text{gamma}} \sim CH_2\text{-}\dot{C}H\sim + H\cdot \qquad (24)$$

At first, it seems surprising that the frequency of C-H bond cleavage is much higher than that of the C-C bond since the bond strength of C-H is considerably higher than C-C, 98 and 83 kcal/mole, respectively(64). However,

the situation is not so simple, other factors such as cage effects could slow down the scission reaction and bring forward the C-H bond cleavage as the main effect of the radiolysis. Moreover, it is speculated that the energy deposited at a C-C bond is dissipated along the chain without chain scission whereas the deposited energy at a C-H bond is localized in the pairs of C-H bonds attached to the same carbon atom with the resultant experimentally observed $H_2$ gas evolution(65).

The produced polymeric alkyl radicals(equation 24) are involved in several reactions such as cross-linking by reaction with other polymeric radicals, migration along or across the chain and vinylene double bond formation, etc. On the other hand, the hot hydrogen atoms are involved in a series of reactions, the main one being the production of hydrogen gas. Although hydrogen atoms were never detected even by ESR studies at 4 $^{o}$K(66), it is speculated that these atoms must have been liberated during irradiation with enough kinetic energy to overcome the activation energy barrier for H atom abstraction from a neighboring methylene group.

In graft polymerization, the radiolysis of polyethylene in the presence of monomer is of concern and it has been demonstrated by ESR that the produced polymeric alkyl radicals are mainly consumed in the initiation of the grafted chains(19). What about the fate of the hydrogen atom ? In this case hydrogen atoms, too, can react with the monomer that is swelled by the amorphous parts of the polymer and lead to the production of undesirable homopolymer. The extent of involvement of hydrogen atoms in such reactions is generally not known but a number of workers(13, 35) have found extensive amounts of inside homopolymerization, exceeding the limits which would be produced by the simple radiolysis of the monomer.

Generally, the amount of homopolymer produced inside the polymer

matrix by the radiolysis of monomer depends on the $G_R$ value of that monomer. Usually, the $G_R$ value of aromatic compounds and of monomers containing aromatic side groups are small compared to the $G_R$ value of polyethylene( $G_R$=6-8 (5)). For example, the $G_R$ value of benzene and styrene, using DPPH (diphenylpicrylhydrazyl) as the free radical scavanger, has been determined to be 0.66 (67, 68). For our case, although we have failed to find the $G_R$ value of 4-vinylpyridine in the literature, it is probably close to the $G_R$ value of pyridine, which is reported to be about 0.3(69). Considering the above values it is clear that the radiolysis of the above monomers should produce negligible homopolymer compared to graft polymer.

Besides the radiolysis of monomer and the hydrogen atom produced in reaction (24) other phenomenon such as energy transfer and chain transfer reactions can lead to the production of inside homopolymer.

It is not yet known whether the kinetics of the homopolymerization reactions follow the same route as that of the grafting reaction. Both processes take place in the same medium, the only difference being is the initiation step. A grafted chain is initiated by a large, higly immobile polymer radical whereas homopolymer chains are initiated by mobile, smaller species.

In this work, we have studied the overall kinetics of the graft polymerization under the assumption that both homopolymerization and graft polymerization mechanisms follow the same kinetic route. We did not attempt to physically separate the grafted polymer from the homopolymer and study the separate kinetics. The techniques available for such a separation are not well-established(13, 70).

Effect of film thickness(L)

The effect of film thickness on the grafting rate was studied at a dose rate of 0.0077 Mr/hr. Figure 8 shows the extent of grafting of 4-vinyl

pyridine with respect to time for all available thicknesses( it should be pointed out that the phrases "extent of grafting" and "rate of grafting" may be misleading because of the possibility of formation of homopolymer in the polymer matrix. Nevertheless, these phrases will be used throughout this work).

The grafting curves are linear up to 10-12 % grafting and then tend to level-off(this levelling-off is shown by the broken lines in the figure since this behavior is observed in experiments carried to conversions well over 12 %). One can think of several reasons for this behavior:

(a) with increasing conversion, the system can become clogged-up with grafted chains, decreasing the diffusion rate of the monomer which will bring forward a diffusion-controlled reaction and therefore lower grafting rates or

(b) in the reaction medium, the monomer may become more soluble with conversion, due to the formation of polar poly(4-vinylpyridine) grafted chains. Increase in the monomer concentration may have a plastisizing effect, increasing the value of $k_t$ and thus lowering the overall rate of grafting. Such an effect is observed in styrene-polyvinyl chloride system(23).

This levelling-off effect is not unique for this particular graft polymerization system, it is observed in several other systems including styrene-polyethylene but appear at higher conversions.

The rates of graft polymerization has been calculated from the slopes of these curves and tabulated(Table 4). From the table it is seen that for films below 3 mils the rate of grafting is essentially constant and is not effected by thickness. However, for thicknesses above 2 mils, the rate of grafting decreases with increasing film thickness. A log-log plot of rate versus film thickness clearly displays this behavior(Figure 9).

TABLE 4

The dependence of rate on the film thickness*

| L(mils) | Log L | $R_p$(% graft/min) | Log Rp |
|---|---|---|---|
| 1 | 0.000 | 0.1123 ± 0.0033 | -0.950 |
| 2 | 0.301 | 0.1140 ± 0.0036 | -0.943 |
| 3 | 0.477 | 0.0903± 0.0039 | -1.044 |
| 5 | 0.699 | 0.0524± 0.0023 | -1.281 |
| 6 | 0.778 | 0.0369± 0.0025 | -1.433 |
| 8 | 0.903 | 0.0277± 0.0026 | -1.558 |
| 10 | 1.000 | 0.0212 ± 0.0011 | -1.673 |

(*) dose rate: 0.0077 Mr/hr.

The non-dependency of the rate of grafting on thickness for the thin films clearly displays that the grafting reaction is diffusion-free in this region and the kinetics are governed by equation (12). In this region the monomer concentration profile is constant and uniform throughout the film thickness. For films thicker than 2 mils the dependence of grafting rate on the film thickness is close to inverse linearity with a calculated slope of -1.20 ± 0.034. This slope is reasonably close to the theoretical slope of -1.0 required by equation (13). In this region, the grafting kinetics are diffusion-controlled and therefore the monomer concentration profile is no longer uniform but curved, with the highest concentration at the surface of the film, gradually decreasing towards the middle and close to zero at the middle of the film.

The difference between the experimental and theoretical slopes is within the limits of the plot, as will be shown subsequently. Let us now take a look at equation 17(later, it will be clear that for 4-vinylpyridine-poly-

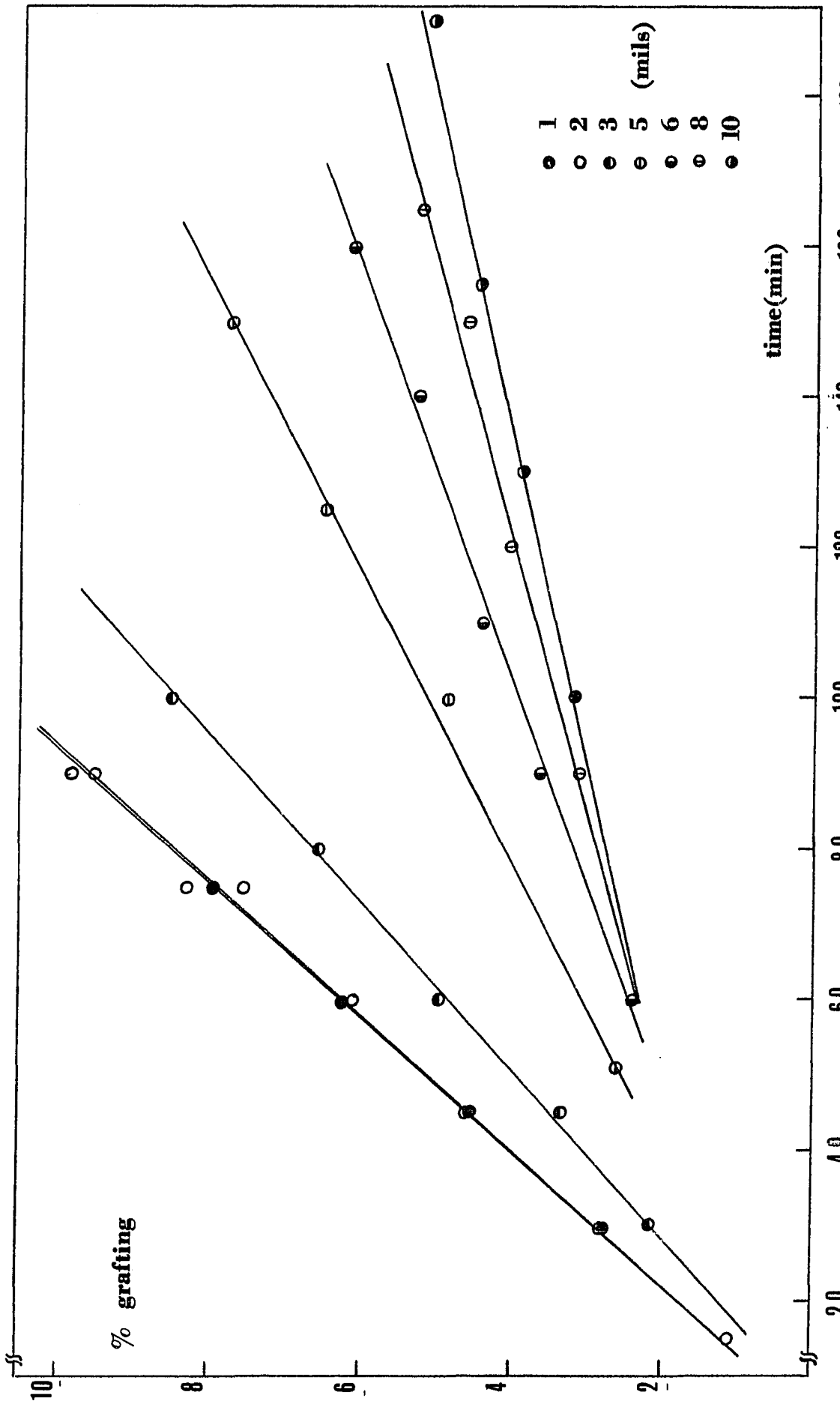



FIG 8 Dependence of Rp on film thickness (L)

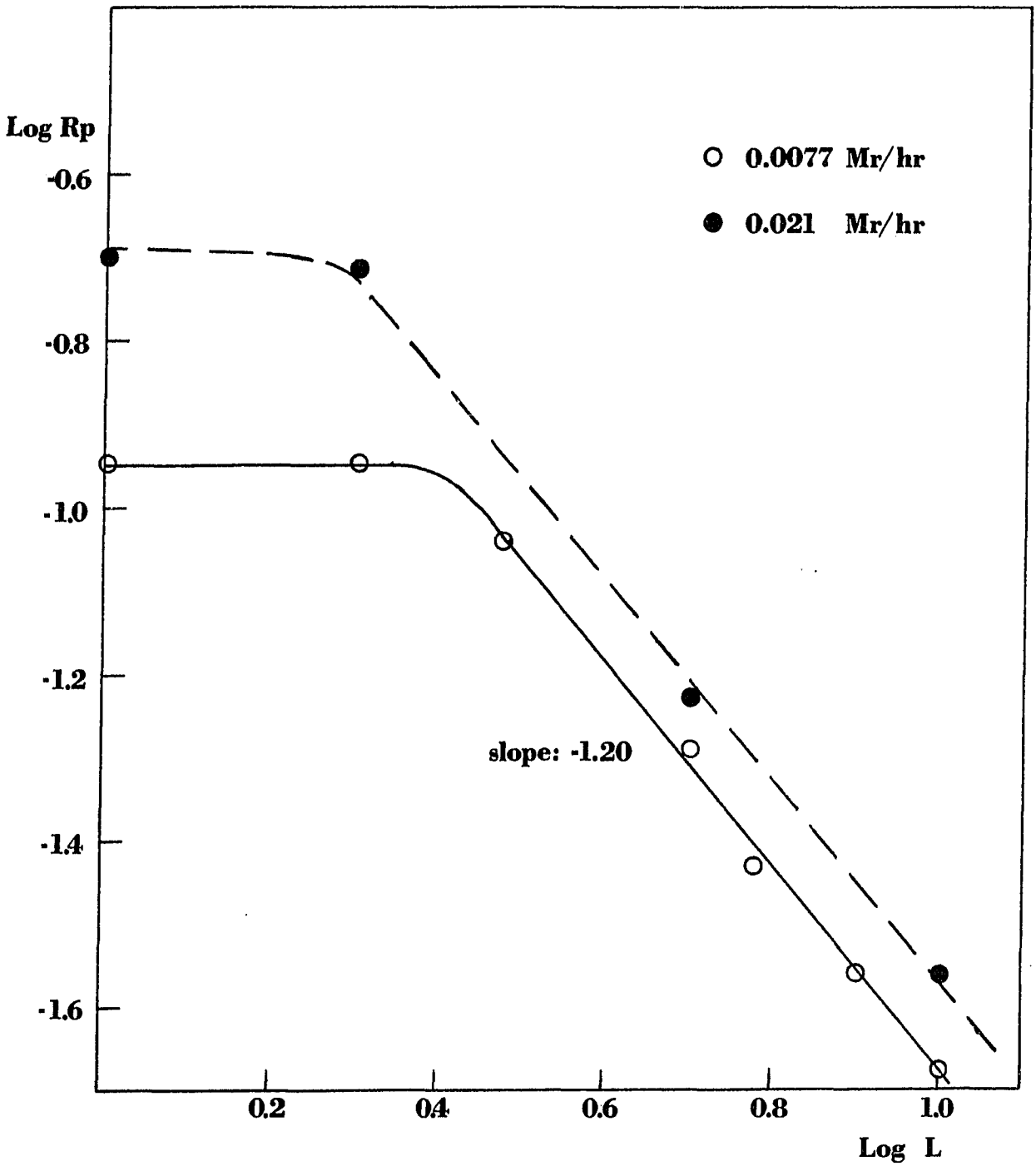



**FIG 9 LOG Rp versus LOG L**

ethylene system, v=1 and the kinetics are governed by equations (14) through (17). ).

According to the equation (17) a plot of $R_p$ versus L assumes that M, $k_p/k_t^{1/2}$, D and $R_i$ are constant and do not depend on thickness, L. The rate rate of initiation($R_i$) is directly proportional to dose rate (I) and therefore must be constant. Since all films possessed almost the same crystallinity, variation of M with thickness can be assumed to be negligible. At the first glance, one can also think that the other variables D and $k_p/k_t^{1/2}$ are constant and independent of thickness. However, earlier investigations on the styrene-polyethylene system(13) have shown that this is not the case. The diffusion coefficient of styrene increased with increasing thickness. This result indicated that although the percent crystallinity is the same for all films, the films differed in crystallite size with thicker films having larger size crystals. For thinner films, the smaller sized crystallites can possibly act as physical cross-links, restricting the motion in the amorphous regions(61, 71). The difference in the crystallite size may be due to differences in the crystallization rates during the manufacture of the films. Even if the crystallization rates were the same for thicker films the inner layers may cool slower than the surface, resulting in larger crystallite sizes.

The $k_p/k_t^{1/2}$ values changed accordingly, decreasing with increasing film thickness. This is logical since a decrease in diffusivity may indicate an increase in viscosity, therefore lower $k_t$ and consequently higher $k_p/k_t^{1/2}$ values.

To compensate for these variations in D and $k_p/k_t^{1/2}$ values, the experimental data was re-plotted( i.e. instead of plotting log $R_p$ versus log L, log( $R_p/(Mk_p/k_t^{1/2}D)$ ) was plotted versus log L ). The dependence of $R_p$ on L then changed from a value of -1.24 to -0.96.

Although we have not corrected our data for such variations, this is exactly the same direction which would yield a closer value than -1.20 to the theoretical value of -1.0 . At this point it is sufficient to add that, coupled with the earlier results on the styrene-polyethylene system, these results on the 4-vinylpyridine-polyethylene system are more than satisfactory for the verification of our theoretical predictions on the effect of film thickness on the grafting rate.

Furthermore, from independent experiments done for other purposes, data at a higher dose rate of 0.021 Mr/hr are gathered together and shown in Figure 9. Although there are not enough data points for a slope calculation, the behavior is similar to that at the lower dose rate of 0.0077 Mr/hr. One should also note that with increasing dose rate the range of the diffusion-free region decreased. This is in line with the theoretical predictions, an increase in $R_i$ should increase the characteristic parameter A (equation 15) and shift even the thinnest films more close to the diffusion-controlled region. In the subsequent sections it will be seen that at a dose rate of 0.037 Mr/hr there is no diffusion free region and even the kinetics of 1 mil film is partially under diffusion-control, governed by equation (17).

The dependence on $R_i$

One of the most important kinetic parameters in a polymerization reaction is the initiation rate order. Depending on its value one can have an idea of the polymerization mechanism and the mode of termination.

In radiation induced polymerizations, because ions as well as radicals are produced in the reaction medium, the value of the initiation rate order is directly related to the nature of the initiating species.

Generally, radical polymerizations show a half order dependence of $R_p$ on $R_i$ whereas ionic polymerizations exhibit a first order dependence.

The difference in the behavior is a consequence of different modes of termination. In radical polymerizations termination is usually second order with respect to propagating species but in ionic polymerizations it is first order.

In radiation induced graft polymerization, the rate of initiation is directly related to the dose rate(I), thus, studying the rate of grafting at various dose rates one can determine the value of the initiation rate order.

Figure (10) shows the effect of dose rate on the grafting rate for polyethylene film of 1 mil thickness. The dose rate is varied 300 fold from 0.00077 to 0.21 Mr/hr. As usual the extent of grafting is followed up to 10 % and the grafting curves are linear in this range. The study is not extended to the highest dose rate since it took less than 10 minutes to reach 10 % grafting and this involves a high margin of error. An increase in the grafting rate with increasing dose rate is apparent(Table 5) but is most marked at the low dose rate region. A plot of log $R_p$ versus log I is shown in Figure 11. The logarithmic curve is linear between the dose rates, 0.00076-0.021 Mr/hr, with a slope of 0.56 ± 0.02. At higher dose rates than 0.021 Mr/hr, this dependence decreases from the half-order behavior(this decrease is evidenced by the deviation from the dotted extention of the curve).

The decrease in the dose rate order at high dose rates can be attributed to a number of phenomenon:

(a) if the mode of termination changes from the usual bimolecular coupling and/or disproportionation of propagating radicals to a reaction involving a polymeric radical and a primary radical(A·), i.e.,

$$P\text{-}M_n^{\cdot} + A^{\cdot} \xrightarrow{kto} P\text{-}M_n\text{-}A(\text{dead polymer}) \qquad (25)$$

where A· may be a hydrogen atom, monomer radical, etc., then the kinetics will follow a different pattern in which the rate of polymerization is indepen-

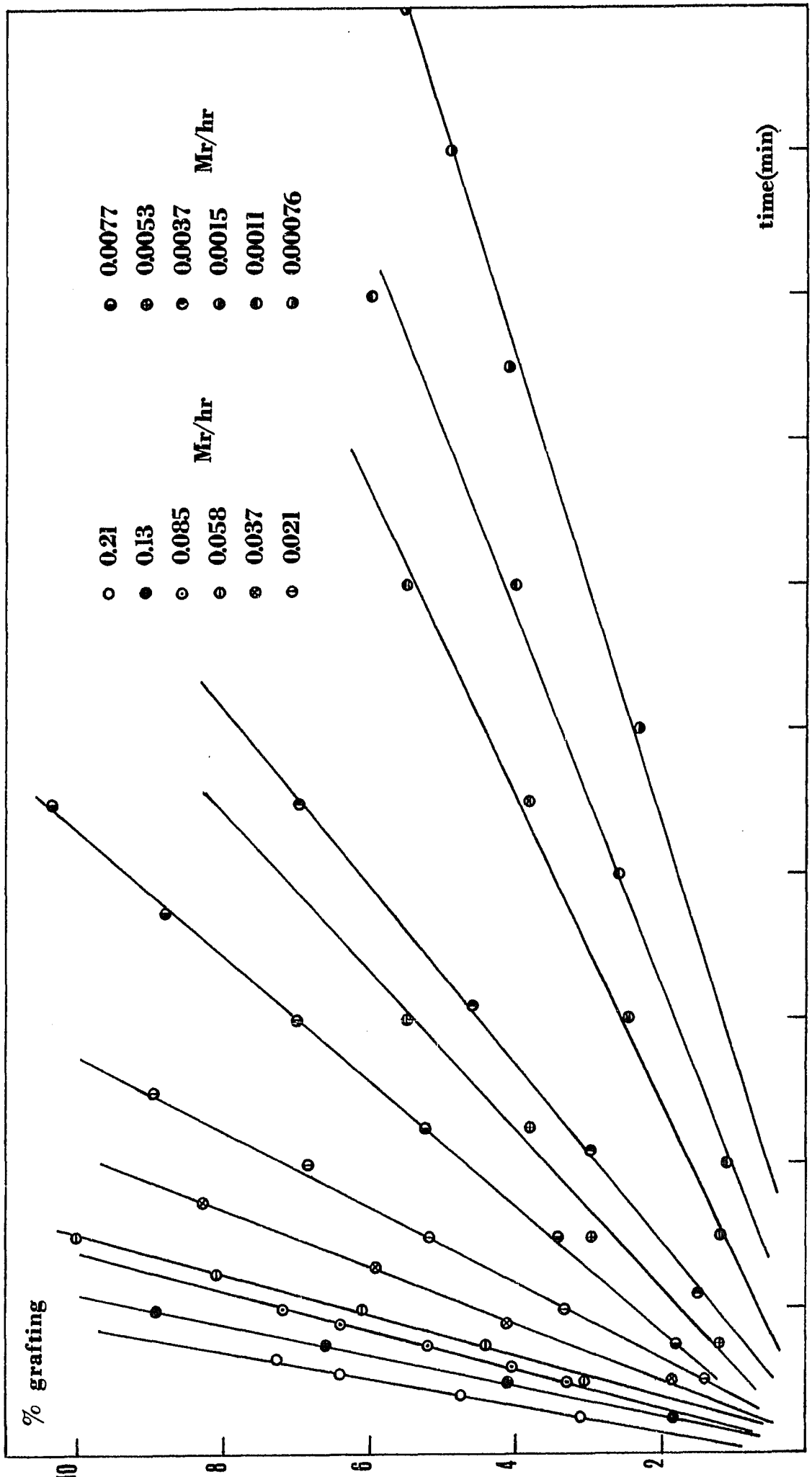



FIG 10 Dependence of Rp on dose-rate "I" ( 1 mil film )

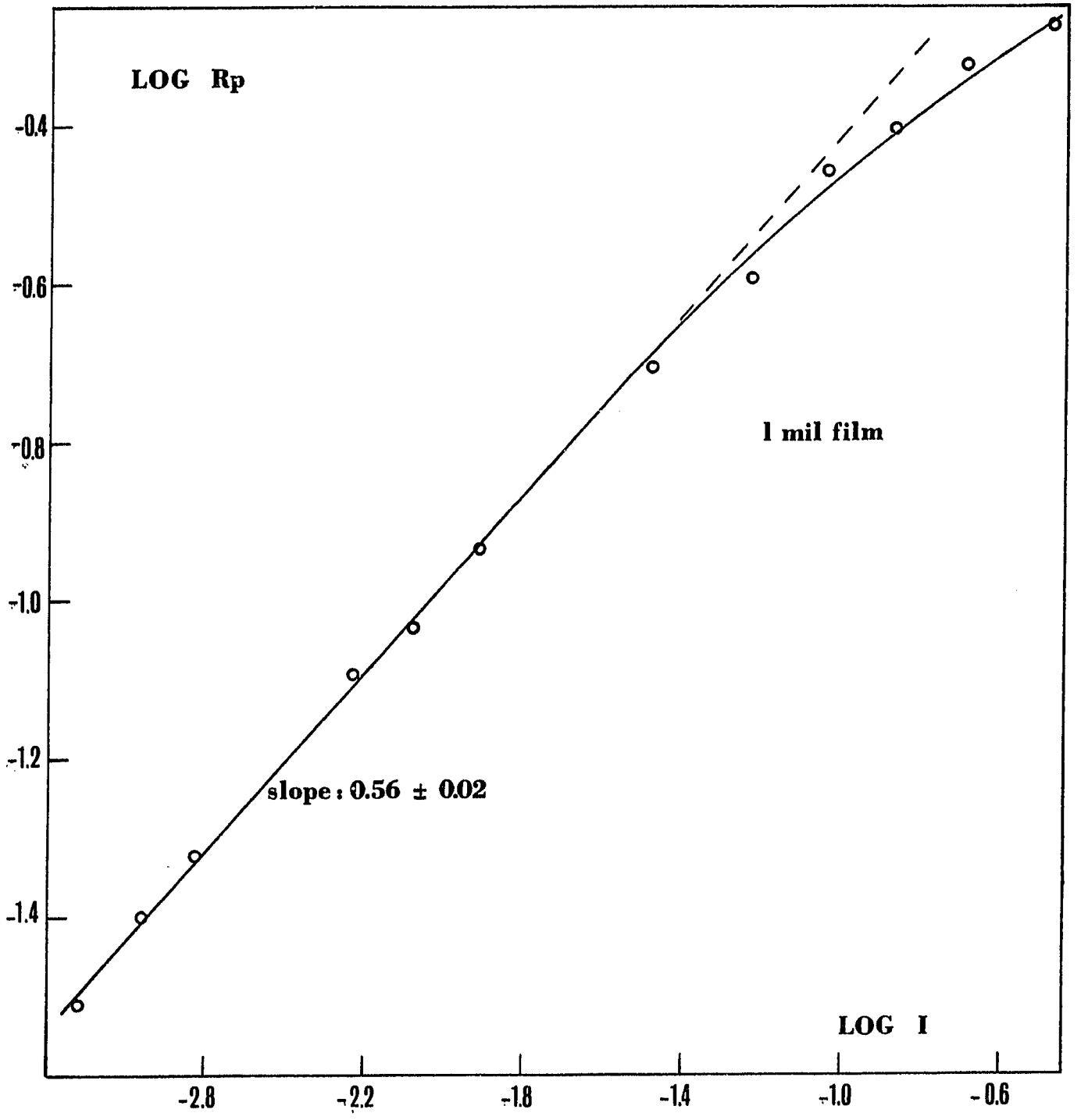



FIG 11 LOG Rp versus LOG I

TABLE 5

The dependence of $R_p$ on dose rate(I)*

| I(Mr/hr) | LogI | $R_p$( % graft/min) | Log $R_p$. |
|---|---|---|---|
| 0.00076 | -3.1192 | 0.0304 ± 0.0014 | -1.518 |
| 0.0011 | -2.9590 | 0.0402 ± 0.0014 | -1.396 |
| 0.0015 | -2.8240 | 0.0476 ± 0.0023 | -1.323 |
| 0.0037 | -2.4320 | 0.0809 ± 0.0023 | -1.092 |
| 0.0053 | -2.2760 | 0.0917 ± 0.0083 | -1.038 |
| 0.0077 | -2.1140 | 0.1152 ± 0.0013 | -0.939 |
| 0.011 | -1.9590 | - | - |
| 0.021 | -1.6780 | 0.1969 ± 0.0047 | -0.706 |
| 0.037 | -1.4320 | 0.2545 ± 0.0072 | -0.594 |
| 0.058 | -1.2370 | 0.3506 ± 0.0160 | -0.455 |
| 0.085 | -1.0710 | 0.3913 ± 0.0013 | -0.408 |
| 0.130 | -0.8860 | 0.4730 ± 0.0067 | -0.325 |
| 0.210 | -0.6780 | 0.5262 ± 0.0170 | -0.279 |
| 0.350 | -0.4560 | - | - |

(*) 1 mil film.

---

dent on the initiation rate(1),

$$R_p = k_p M^2 / k t_o \qquad (26)$$

Chapiro has pointed out that primary termination may become increasingly important at high dose rates where the concentration of primary radicals are high and also that this kind of termination may be especially important in highly viscous systems, such as a grafting system, where primary radicals would have greater mobility than the large sized polymeric radicals.

In the bulk polymerization of styrene by ordinary free radical initiators, DeSchrijver and Smets(72) increased the viscosity of the reaction medium by simply adding polystyrene in varying amounts to styrene and studied the effect on the initiation and monomer order. They have found that with increasing viscosity the initiator order dropped from 0.5 to 0.3 and monomer order increased from 1.5 to 2.0 . These results are in line with the above kinetics.

(b) secondly, the decrease in the dependence of $R_p$ on I at high dose rates could be solely due to diffusional effects. In the preceeding sections it was shown theoretically that, when the kinetics of graft polymerization is shifted under complete diffusion-controlled conditions, the initiation rate exponent dropped from 1/2 to 1/4 for the case where v=1(compare equations 16 and 17).

Experiments in this laboratory on the styrene-polyethylene system has shown that(9) at high dose rates between 0.13-0.35 Mr/hr, the grafting rate is independent of dose rate and furthermore at these dose rates the grafting reaction is not diffusion-controlled(this was evidenced by comparing the grafting rates of 1, 2, 3 mil films. Under complete diffusion-control, the grafting rates would be inversely dependent on thickness and the relative rates for these three films would be 1:1/2:1/3, respectively. Experimentally observed rates were about the same). At the same time, increasing the dose rate increased the monomer order from 3/2 to 5/2. These results were explained by assuming a contribution from primary termination kinetics(eq. 26).

The same line of reasoning is thought to hold for the decrease in the dose rate order at high dose rates for our 4-vinylpyridine-polyethylene system since:

(a) 4-vinylpyridine is more viscous than styrene( 0.98 cp at 40 $^{o}$C (48), 0.59 at 37.8 $^{o}$C(58), respectively),

and (b) 4-vinyl pyridine swells polyethylene to a lesser degree, thus the over-all viscosity in the amorphous regions of the polyethylene must be higher for the 4-vinylpyridine grafting system. It should be noted that the same grade polyethylene, same radiation source and dose rate range was used in this work and in the styrene-polyethylene work reported in ref. 9 .

Surprisingly, our expectations did not come true. Figure 12 shows the grafting curves of 4-vinylpyridine to 2 mil polyethylene film in the dose rate range of 0.0037 to 0.35 Mr/hr. An increase in the grafting rate with dose rate is apparent from Table 6. A log-log plot of $R_p$ versus I is shown in Figure 13 . Although we did not cover the whole dose rate spectrum, at low

TABLE 6

The dependence of $R_p$ on dose rate(I)*

| I(Mr/hr) | Log I | $R_p$(% graft/min) | Log $R_p$ |
|---|---|---|---|
| 0.0037 | -2.4320 | 0.0752 ± 0.0022 | -1.124 |
| 0.0053 | -2.2760 | 0.0956 ± 0.0028 | -1.020 |
| 0.0077 | -2.1140 | 0.1140 ± 0.0036 | -0.943 |
| 0.0110 | -1.9590 | 0.1440 ± 0.0098 | -0.840 |
| 0.0210 | -1.6780 | 0.1910 ± 0.0047 | -0.719 |
| 0.0370 | -1.4320 | 0.2600 ± 0.0043 | -0.585 |
| 0.0580 | -1.2370 | 0.3110 ± 0.0062 | -0.507 |
| 0.0850 | -1.0710 | 0.3590 ± 0.0085 | -0.445 |
| 0.1300 | -0.8860 | 0.4053 ± 0.0170 | -0.392 |
| 0.2100 | -0.6780 | 0.4393 ± 0.0091 | -0.357 |
| 0.3500 | -0.4560 | 0.5064 ± 0.0500 | -0.296 |

(*) 2 mil film

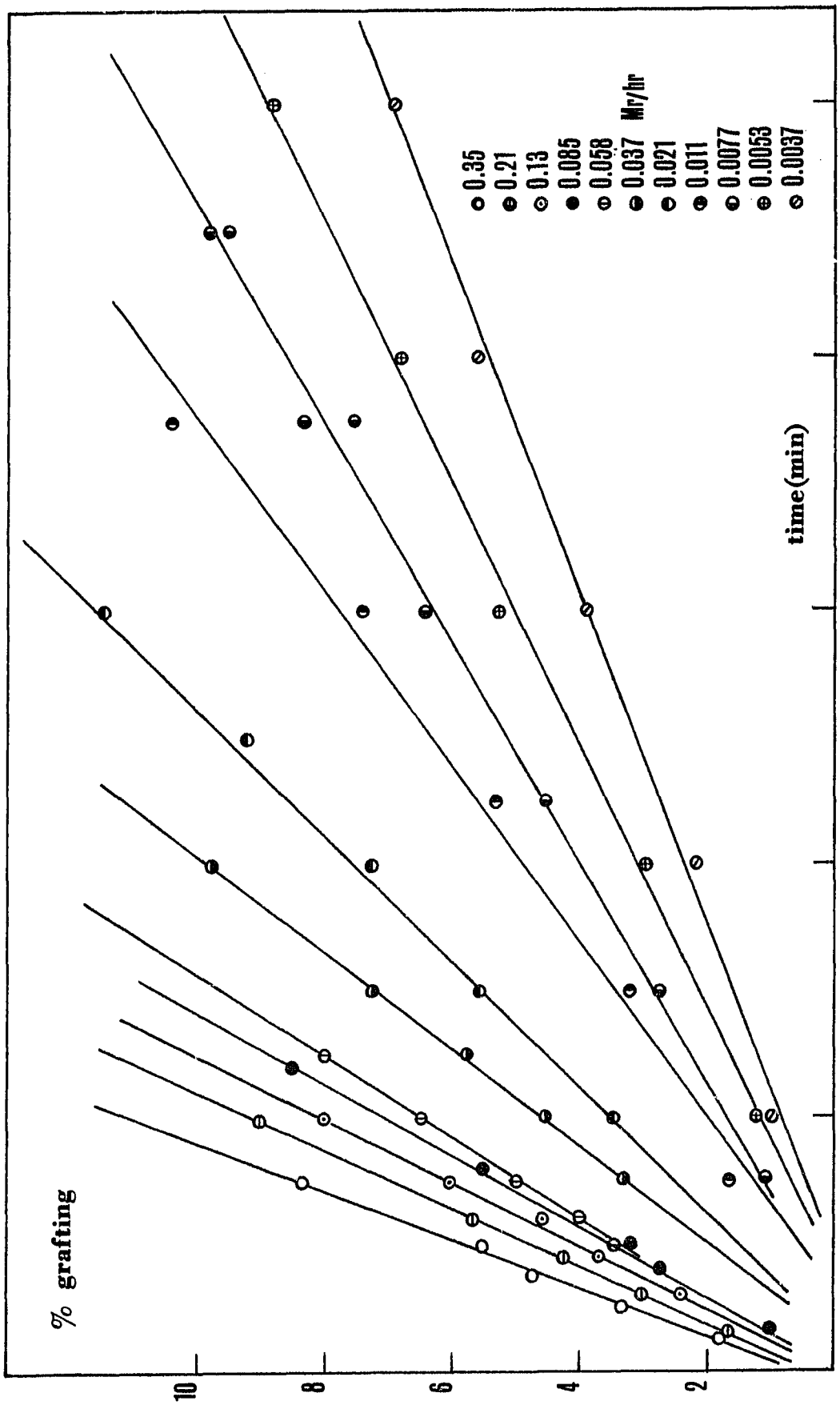



FIG 12 Dependence of Rp on dose-rate "I" ( mil film )

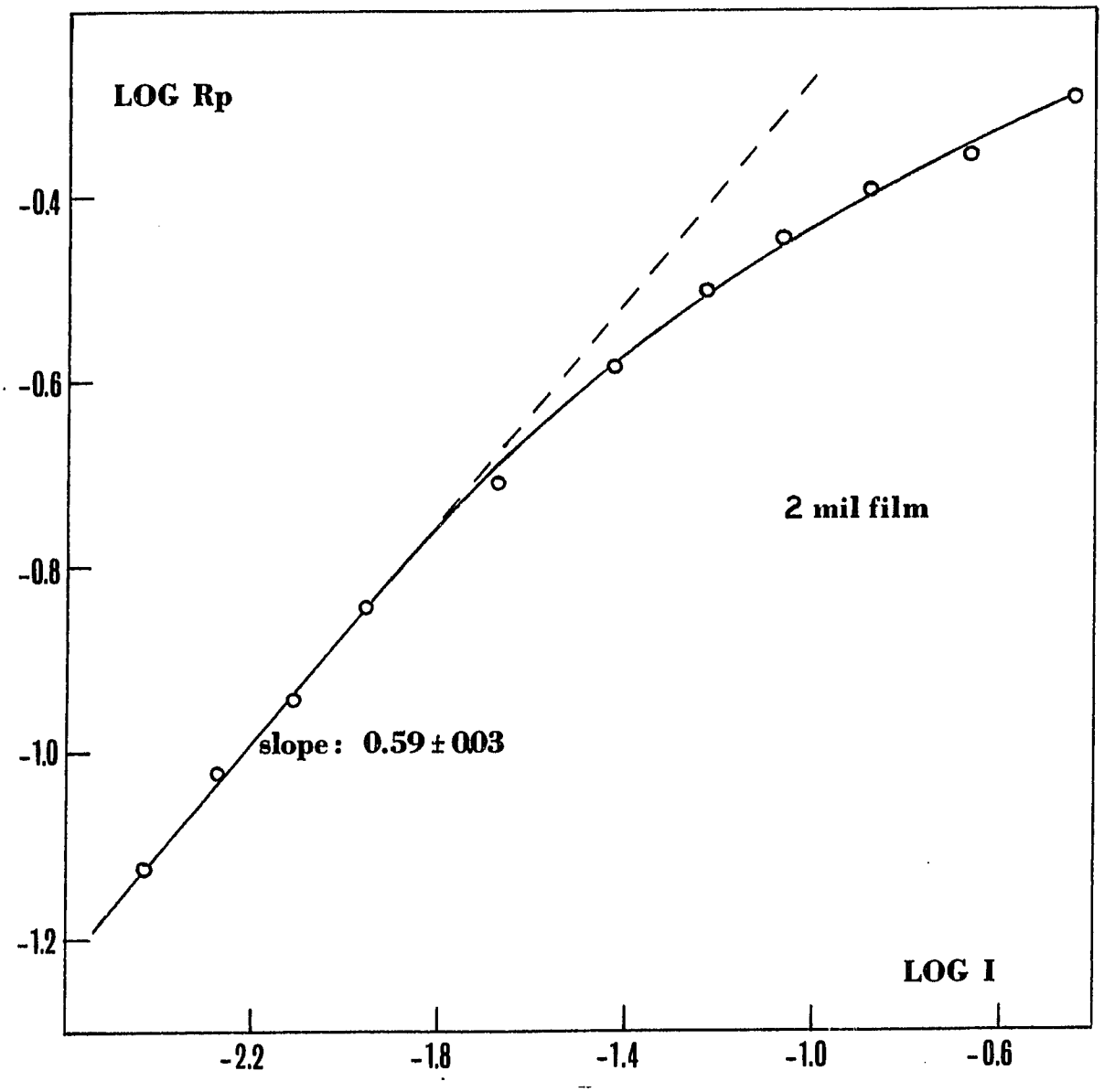



**FIG 13 LOG Rp versus LOG I**

dose rates from the four data points, the calculated slope is 0.59 ± 0.03 , quite close to that observed for the 1 mil film. On the other hand, all of the four data points in this region have approximately the same grafting rates as that of the 1 mil film(compare the grafting rates at 0.0037, 0.0053 and 0.0077 Mr/hr in Tables 5 and 6).

At high dose rates, similar to 1 mil data, the curve slopes below 1/2 order and also, surprisingly, the rates of 1 mil film are higher than that of the 2 mil film. This behavior is quite opposite to that observed for the styrene-polyethylene system(9).

Meanwhile, at high dose rates, not only the grafting rates of 2 mil film are lower than that of the 1 mil film but the difference in the grafting rates increase with increasing dose rate. This behavior can only be explained by assuming diffusion control in this region.

When $v \simeq 1$, a characteristic parameter A was defined and given in equation (15). With increases in A, a grafting system can be shifted from the diffusion-free region ($0.1 \geq A$) to the transition region ($0.1 < A > 6$) and with further increase in A to the complete diffusion-controlled region ($A \geq 6$). Increase in A with increasing I and consequently $R_i$ is rather slow since A is dependent on $R_i$ to the 1/4 th power.

Let us assume that at a dose rate of 0.021 Mr/hr A is equal to 0.1 . Increasing the dose rate from this value to the highest attainable value of 0.35 Mr/hr would produce approximately a 16-fold increase in the dose rate and this merely increases A from 0.1 to 0.2 . Thus, at this high dose rate region the grafting system is in the transition region and the relative ratio of the grafting rates of 1 and 2 mil films slowly but gradually increases with dose rate. Table 7 demonstrates this behavior with slight deviations due to experimental error.

TABLE 7

Grafting behavior at high dose rates

| I | $R_p$(1 mil)/$R_p$(2 mil) | $R_p$(1 mil) | $R_p$(2 mil) |
|---|---|---|---|
| 0.021 | 1.030 | 0.197 | 0.191 |
| 0.037 | 0.980 | 0.255 | 0.260 |
| 0.058 | 1.132 | 0.351 | 0.311 |
| 0.085 | 1.086 | 0.391 | 0.360 |
| 0.130 | 1.170 | 0.473 | 0.405 |
| 0.210 | 1.200 | 0.526 | 0.439 |
| 0.350 | - | - | 0.506 |

Theoretically, further increases in the dose rate should increase the relative ratio and at a value of 2, the grafting kinetics will be completely under diffusion-control(it should be remembered that in the diffusion controlled case, when v=1, the kinetics are governed by equation (17), where the grafting rate is inversely proportional to film thickness(L) and thus the relative rates for 1 and 2 mil films should be 1:1/2, respectively).

Unfortunately, since our highest experimentally attainable dose rate is 0.35 Mr/hr, we have no means of further increasing the relative ratio. Nevertheless, an alternative approach for bringing the system under complete diffusion control is by repeating the above study at high dose rates using thicker films.

Figure 14 shows the grafting curves of 4-vinylpyridine on 10 mil thick polyethylene within a dose rate region of 0.0077-0.13 Mr/hr. From the figure it can be seen that some curves are not linear at the initial periods of the grafting reaction and therefore the grafting rates were determined from the slopes in the linear regions of the curves(Table 8). This non-...

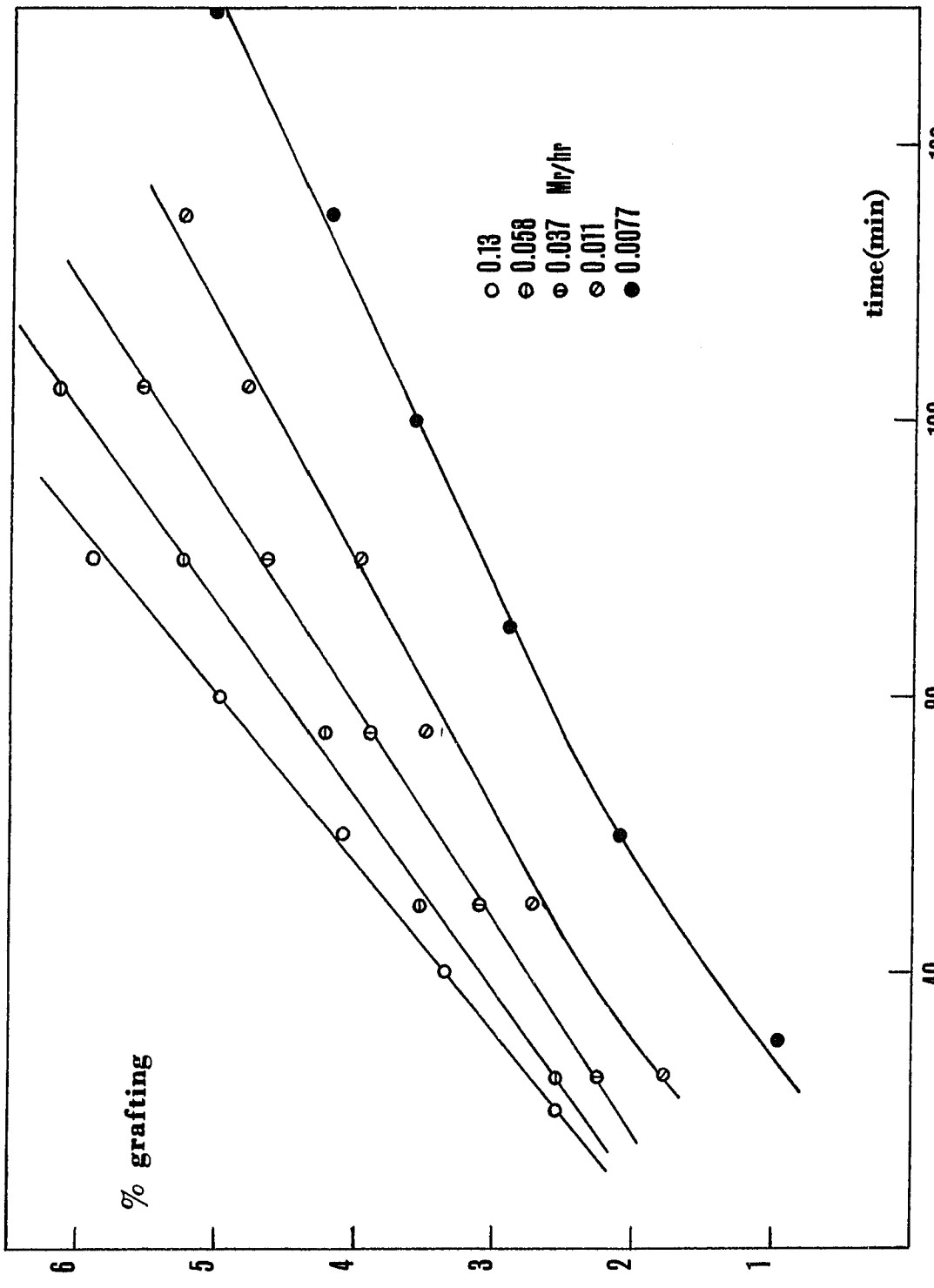



FIG14 Dependence of Rp on dose-rate "I"(10 mil film)

linearity is explainable; under diffusion control the grafting reaction can only reach the steady state after approximately half of the initial amount of monomer present in the polymer matrix is consumed(for 4-vinylpyridine, after about 1.5 % grafting). The steady state here does not only mean that the propagating radical concentration reached a constant value but it also refers to the fact that the monomer concentration profile is established throughout the film thickness.

TABLE 8

The dependence of $R_p$ on dose rate(I)*

| I(Mr/hr) | LogI | $R_p$(% graft/min) | Log $R_p$ |
|---|---|---|---|
| 0.0077 | -2.114 | 0.0212 ± 0.0011 | -1.673 |
| 0.0110 | -1.959 | 0.0235 ± 0.0010 | -1.630 |
| 0.0210 | -1.678 | 0.0276 ± 0.0014 | -1.559 |
| 0.0370 | -1.432 | 0.0324 ± 0.0009 | -1.489 |
| 0.0580 | -1.237 | 0.0356 ± 0.0011 | -1.448 |
| 0.1300 | -0.886 | 0.0415 ± 0.0010 | -1.383 |

(*) 10 mil film.

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A log-log plot of $R_p$ versus I for 10 mil film is shown in Figure 15. Earlier shown data on 1 and 2 mil films is also included in the figure for comparison. The 10 mil curve is a straight line with a slope of 0.23 ± 0.01. This slope is strikingly close to the theoretically predicted dependence of $R_p$ on $R_i$ under completely diffusion controlled conditions, namely 1/4(eq. 17). Comparing the three curves, at any constant dose rate, it is apparent that the rate of grafting of 10 mil film is much smaller than either 1 and 2 films. It is thus evident that at high dose rates monomer diffusion is the rate

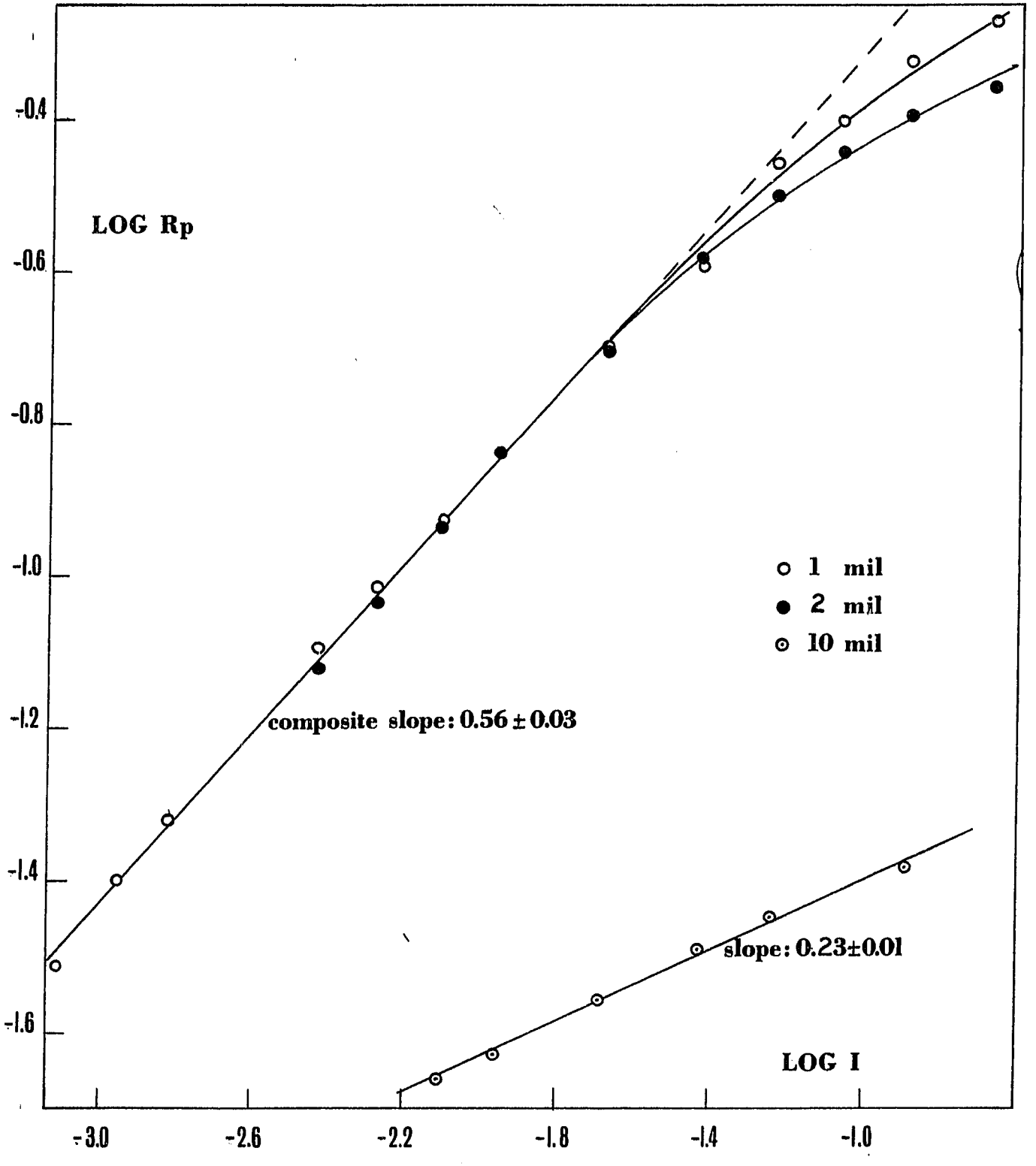



FIG 15 LOG Rp versus LOG I (composite)

controlling phenomenon and any contribution from primary termination kinetics is not observable. This point can further be substantiated by the results of our investigation on the effect of monomer concentration on the grafting rate at high dose rates. We will come back to this point later.

At this point it should be mentioned that in the range of dose rates used in this study, in comparison to styrene work in reference 9, the rates of grafting of 4-vinylpyridine are higher than that of styrene in all stages and coupled with the fact that 4-vinylpyridine swells polyethylene to a lesser degree than styrene, it is highly possible that even for the thinnest films the rates are effected by monomer diffusion and the decrease from the half order is purely a diffusional phenomenon.

Finally, as a last comment we would like to add that, throughout this discussion in all the figures and tables we have not converted the units of grafting and initiation rates to the more appropriate units of moles/liter-sec(these conversions are shown in Appendix II). This was not necessary since the curve patterns and the slopes would have not been effected.

Effect of Monomer Concentration(M)

The determination of the effect of monomer concentration on the grafting rate is one of the most crucial investigations in the elucidation of the mechanism of graft polymerization. Although the establishment of monomer order would not be of help in the understanding of the nature of the polymerization process, i.e. whether the polymerization proceeds via a radical or an ionic route, it has great significance in the determination of the nature of initiation and termination steps.

In radiation induced free radical chain homopolymerization processes(1),

(i) a monomer order of 1 is an indication that the initiation step

is independent of monomer concentration and that termination is via bimolecular coupling and/or disproportionation of the propagating radicals,

(ii) an order of 3/2 signifies that the initiation step is dependent on the monomer concentration to the first power and that termination is as in (i), and

(iii) an order of 2 results mainly at high dose rates due to termination by primary radicals. In between values of monomer order are also possible when several of the said modes operate at the same time.

The above modes of initiation and termination can also be extemded to graft polymerization processes.

In free radical homopolymerizations, one can easily vary the monomer concentration by simply diluting the monomer to several degrees with a proper solvent and study the effect on $R_p$. At the same time, the nature of the diluent is not too critical(10). However, in graft polymerization processes by the mutual irradiation technique, although the monomer concentration is varied in a similar manner, the nature of the diluent is very important and crucial. The following factors should be taken into account for the proper selection of a diluent:

(a) the diluent should swell the polymer to a certain extent. In graft polymerization, the polymerization process takes place inside the polymer matrix and therefore the monomer concentration inside this matrix is of effectual importance while the monomer concentration of the surrounding medium(outside concentration) has no influence on the grafting rate. Thus, the concentration of the monomer inside the polymer matrix can only be varied if the diluent is swelled by the polymer to a certain degree.

(b) the diluent should be a good solvent for the grafted chains. The determination of monomer order can only be established properly if

the other kinetic parameters are kept constant while varying the monomer concentration. The use of a bad solvent or a non-solvent for the grafted chains may effect the termination rate and consequently the rate of grafting. In the presence of such a solvent the growing polymeric radicals tend to coil up making it difficult for the propagating radicals to terminate. The net result is a decrease in the termination rate followed by an increase in the rate of grafting. Such solvent effects were observed in free radical homopolymerization systems(10) as well as in graft polymerization.

(c) the intrinsic viscosity of the diluent should be close to that of the monomer. In free radical polymerizations the viscosity of the reaction medium is of paramount importance. In ordinary homopolymerization reactions with free radical initiators drastic increases in the rate of polymerization with increasing conversion is a well-known phenomenon. One normally expects a decrease in the polymerization rate with increasing conversion since both the monomer and initiator concentrations decrease. This exactly oppsite behavior; autoacceleration in the polymerization rate is termed 'gel effect' or 'Trommsdorff effect' and has been established to be due to decreases in the termination rate as the viscosity of the system increases with conversion. The said behavior has been observed in the homopolymerization of many monomers, especially styrene(80), methyl methacrylate(73) and various methacrylates(74, 75).

In homopolymerization reactions, either in bulk or in solution, rate determinations are usually made at the initial stages of the reaction where viscosity effects would be minimal. However, in graft polymerization in all stages, the reaction is liable to viscous effects due to the nature of the reaction medium. Although such effects are not as drastic as in the case of homopolymerization reactions one should be careful not to vary the overall viscosity

while varying the monomer concentration. This can only be accomplished if the diluent has similar intrinsic viscosity to that of the monomer.

(d) structural similarity between the diluent and monomer is desirable. In ordinary free radical polymerizations it is possible to dilute the monomer with a chemically inert solvent that does not interfere with any of the reaction steps involved. In radiation polymerization, however, such a situation never arises since no chemical substance is inert to radiation and any added diluent will simultaneously be radiolysed. In radiation polymerization, therefore, there are no ideal diluents and addition of diluent will effect the initiation rate, i.e. additional free radicals will be produced that can initiate chain propagation. At this point one might think that a diluent close to ideality is the one with considerably lower $G_R$ value than that of the monomer. As will be shown shortly, such a conclusion might be misleading.

When a binary mixture, such as a monomer and a solvent, is radiolysed it is often found that the rate of production of free radicals in the monomer and/or solvent is modified, i.e. energy absorbed by monomer is transferred to the solvent or vice-versa. Such energy transfer processes can further complicate the reaction kinetics.

Although there are no general trends that one can follow to predict whether transfer processes will be observed for a particular mixture or not, from gathered literature work, it seems that for mixtures in which the monomer and diluent are structurally similar and consequently have similar $G_R$ values, energy transfer processes are not detected. For example; in the radiation-induced homopolymerization of methyl methacrylate in methyl and ethyl acetate(76), the relative polymerization rate(rate in the diluent/rate of pure monomer) with change in the mole fraction of monomer yielded linear

plots indicating no energy transfer processes. Similar plots were obtained for styrene and benzene(77).

In graft polymerization the situation is more complex since we have a ternary system, namely polymer, monomer and diluent. Nevertheless, without giving regard to the possibility of energy transfer reactions between the polymer and the monomer, if a diluent structurally similar to the monomer is choosen, then, the possibility of additional transfer processes while varying the monomer concentration may be eliminated.

We have discussed above the important factors that should be considered for the proper selection of a diluent in radiation induced graft polymerization. For our grafting system, 4-vinylpyridine-polyethylene, the diluent that fits the above requirements was simply pyridine.

Pyridine is structurally similar to 4-vinylpyridine and swells polyethylene to the extent of 2.25 % w/w(at 25 $^{o}$C). It is a good solvent for poly(4-vinylpyridine)(58) and has comparable intrinsic viscosity to that of 4-vinylpyridine(see Table 1).

When polyethylene is swollen by mixtures of 4-vinylpyridine and pyridine, it is important to know if the inside composition for a particular mixture is the same as the outside composition. In the range of the mixtures used one also has to determine the extent of swelling. Table 9 shows the swelling properties of the monomer-solvent mixtures.

From the table it can be seen that the refractive indices of the outside and inside compositions of the mixtures in the range of 15 to 100 vol % are about the same indicating that for a particular mixture the composition inside the polymer matrix is the same as that of the outside. At the same time, the variation in the extent of swelling in this range is not more than 5 % and therefore no corrections on the monomer concentration are

TABLE 9

Swelling properties of 4-vinylpyridine-pyridine mixtures

| Composition(vol %)* | $n_D^{25}$(outside) | $n_D^{25}$(inside) | % swelling(% w/w)** |
|---|---|---|---|
| 100 | - | - | 2.52 |
| 75 | 1.5394 | 1.5390 | 2.53 |
| 60 | - | - | 2.47 |
| 50 | - | - | 2.37 |
| 40 | 1.5247 | 1.5247 | 2.46 |
| 25 | 1.5180 | 1.5178 | 2.36 |
| 15 | - | - | 2.34 |
| 0 | - | - | 2.26 |

(*) vol % of 4-vinylpyridine,

(**) average of 4 individual determinations.

needed. If there had been appreciable differences in the inside composition and in the extent of swelling then all mixture compositions should have been converted to the more proper units of moles of 4-vinylpyridine per liter of amorphous swollen polyethylene(this conversion is shown in Appendix II) in the $R_p$ versus M data.

The effect of monomer concentration on the grafting rate at the dose rate of 0.00076 Mr/hr is shown in Figure 16. The grafting curves are linear and the slopes increase with increasing monomer concentration. At this dose rate, at low concentrations the reproducibility was rather poor therefore we have not gone below 30 vol % composition. Probably at low concentrations some interference by thermally catalysed homopolymerization takes place. The rates of grafting are calculated from the slopes of the curves

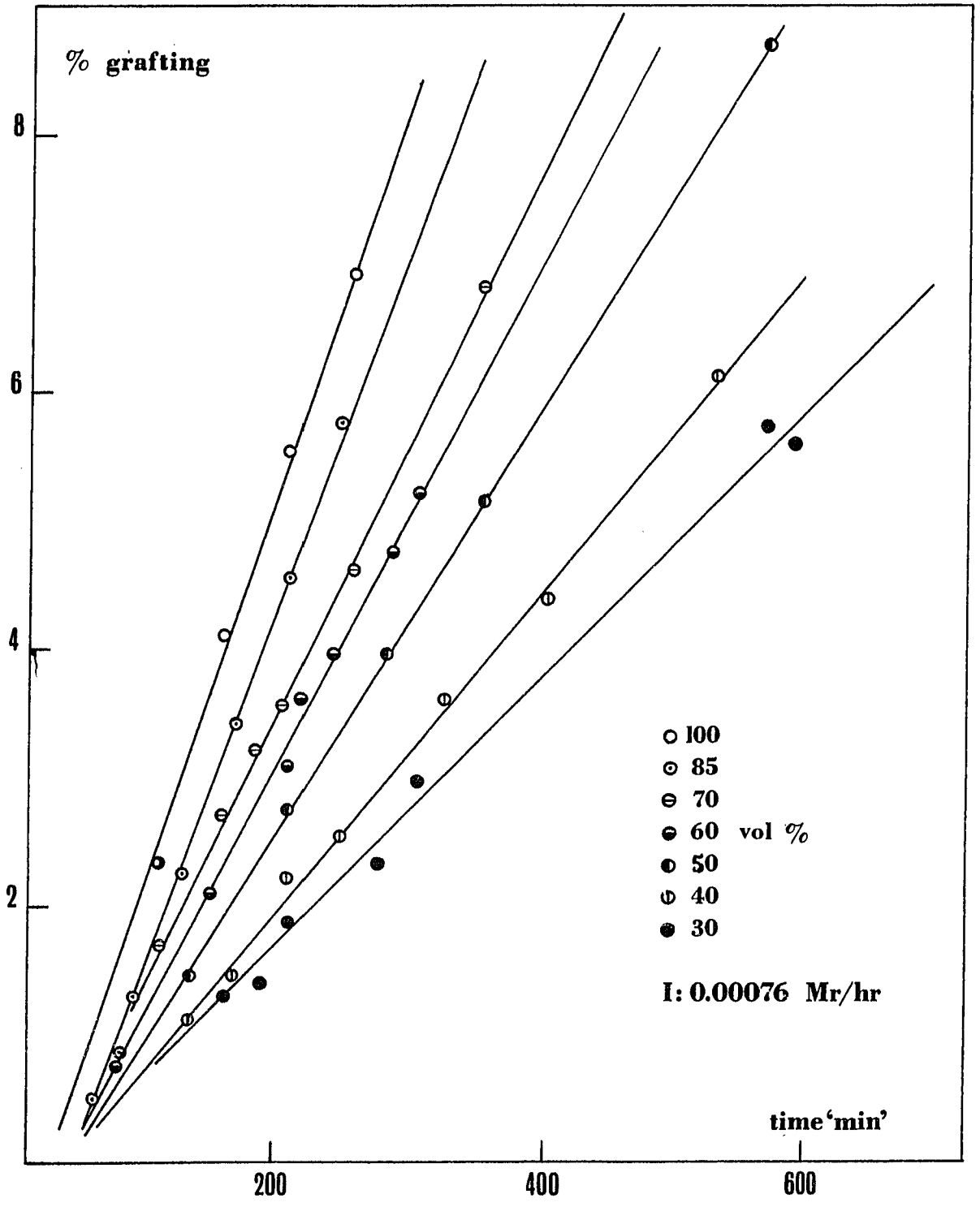



**FIG. 16 Dependence of Rp on monomer concentration " M "**

and are shown in Table 10.

TABLE 10

Dependence of $R_p$ on monomer conc. (M)*, **

| M(vol %) | Log M | $R_p$(% graft/min) | Log $R_p$ |
|---|---|---|---|
| 100 | 2.000 | 0.0303 ± 0.0014 | -1.518 |
| 85 | 1.929 | 0.0280 ± 0.0006 | -1.553 |
| 70 | 1.845 | 0.0206 ± 0.0003 | -1.687 |
| 60 | 1.778 | 0.0190 ± 0.0005 | -1.721 |
| 50 | 1.699 | 0.0162 ± 0.0001 | -1.791 |
| 40 | 1.602 | 0.0121 ± 0.0003 | -1.916 |
| 30 | 1.477 | 0.0103 ± 0.0004 | -1.989 |

(*) 1 mil film

(**) I=0.00076 Mr/hr

A log-log plot of $R_p$ versus M appears in Figure 17. The curve is linear with some scatter in the data points. The slope of the curve is calculated to be 0.944 ± 0.05, very close to unity. It should be remembered that the dose rate at which this study is done falls into the region where the initiation exponent is 1/2. Hence, from these results it is clear that in the diffusion-free region 4-vinylpyridine-polyethylene system follows the ordinary free radical polymerization mechanism where v=1, w=1/2 and z=1/2. Therefore the grafting kinetics are governed by equations 14 through 17.

It is interesting to note that under similar conditions styrene-polyethylene system follow a different kinetic pattern with v=3/2, w=1/2, z=1/2 and at this dose rate although styrene swells polyethylene about 2 times more than 4-vinylpyridine, it has a lower rate of grafting, 1.37 and 1.82

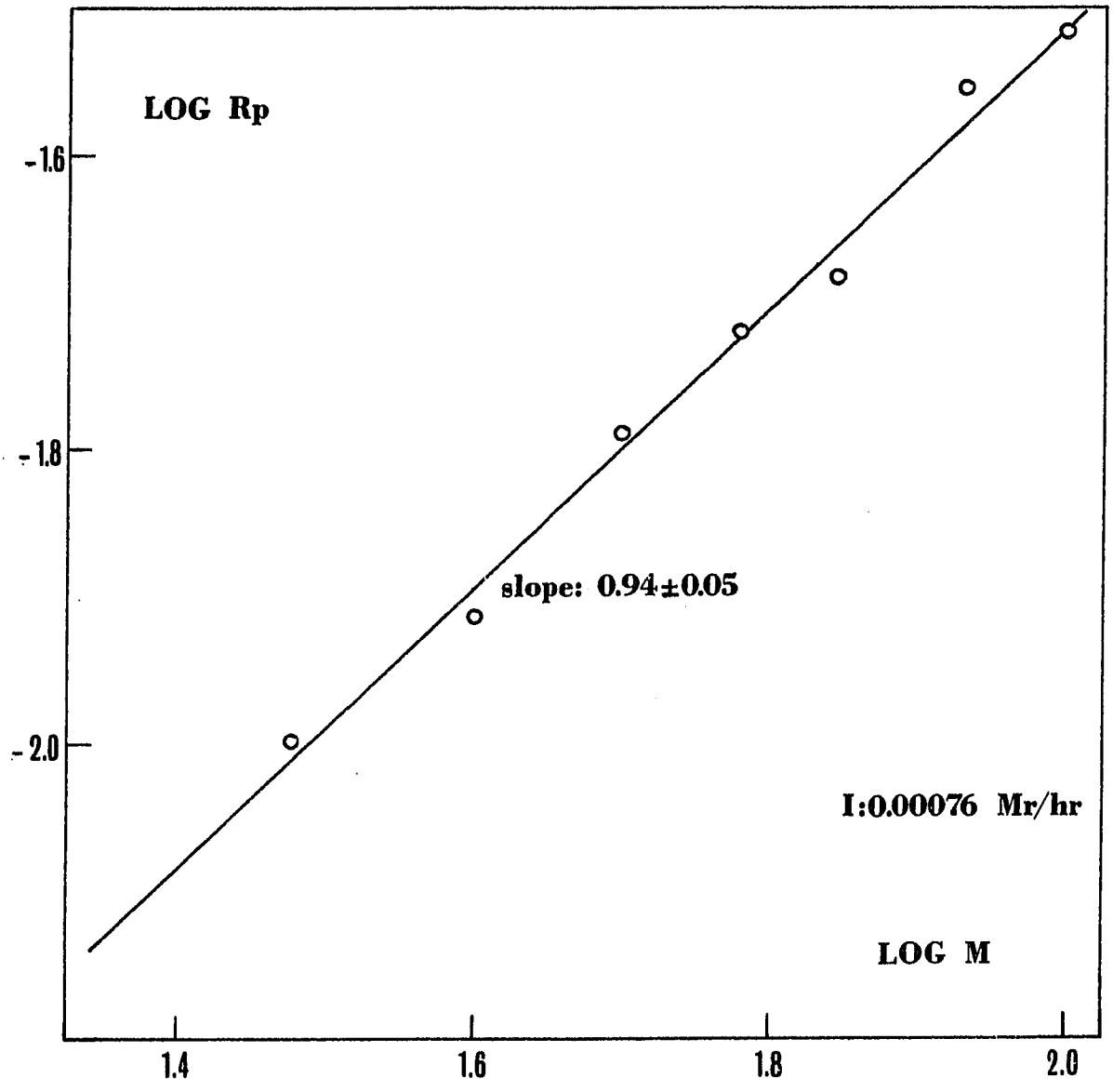



**FIG 17 LOG Rp versus LOG M**

% graft/hr, respectively(9).

At high dose rates, we have repeated the monomer order work and to our surprise the kinetic behavior was different. Figure 18 shows the grafting curves for 1 mil polyethylene film at a dose rate of 0.021 Mr/hr. At this dose rate there was no problem of reproducibility and we have extended the range of monomer composition down to 15 vol %. The grafting curves were linear and as usual the rate of grafting increased with monomer composition(Table 11). 70 and 60 vol % composition curves coincide at low conversion probably due to different induction periods.

TABLE 11

Dependence of $R_p$ on monomer conc. (M)*, **

| M(vol %) | Log M | $R_p$(% graft/min) | Log $R_p$ |
|---|---|---|---|
| 100 | 2.000 | 0.1969 ± 0.0047 | -0.706 |
| 85 | 1.929 | 0.1792 ± 0.0040 | -0.747 |
| 70 | 1.845 | 0.1623 ± 0.0022 | -0.790 |
| 60 | 1.778 | 0.1469 ± 0.0020 | -0.833 |
| 45 | 1.653 | 0.1085 ± 0.0014 | -0.965 |
| 35 | 1.544 | 0.0900 ± 0.0029 | -1.046 |
| 25 | 1.398 | 0.0640 ± 0.0007 | -1.194 |
| 15 | 1.176 | 0.0373 ± 0.0008 | -1.428 |

(*) 1 mil film

(**) I=0.021 Mr/hr

A log-log plot of $R_p$ versus M is shown in Figure 19. Strikingly, the logarithmic plot is not linear and shows two regions of different kinetic behavior. At low compositions up to 60 vol % the curve has a slope of 0.98

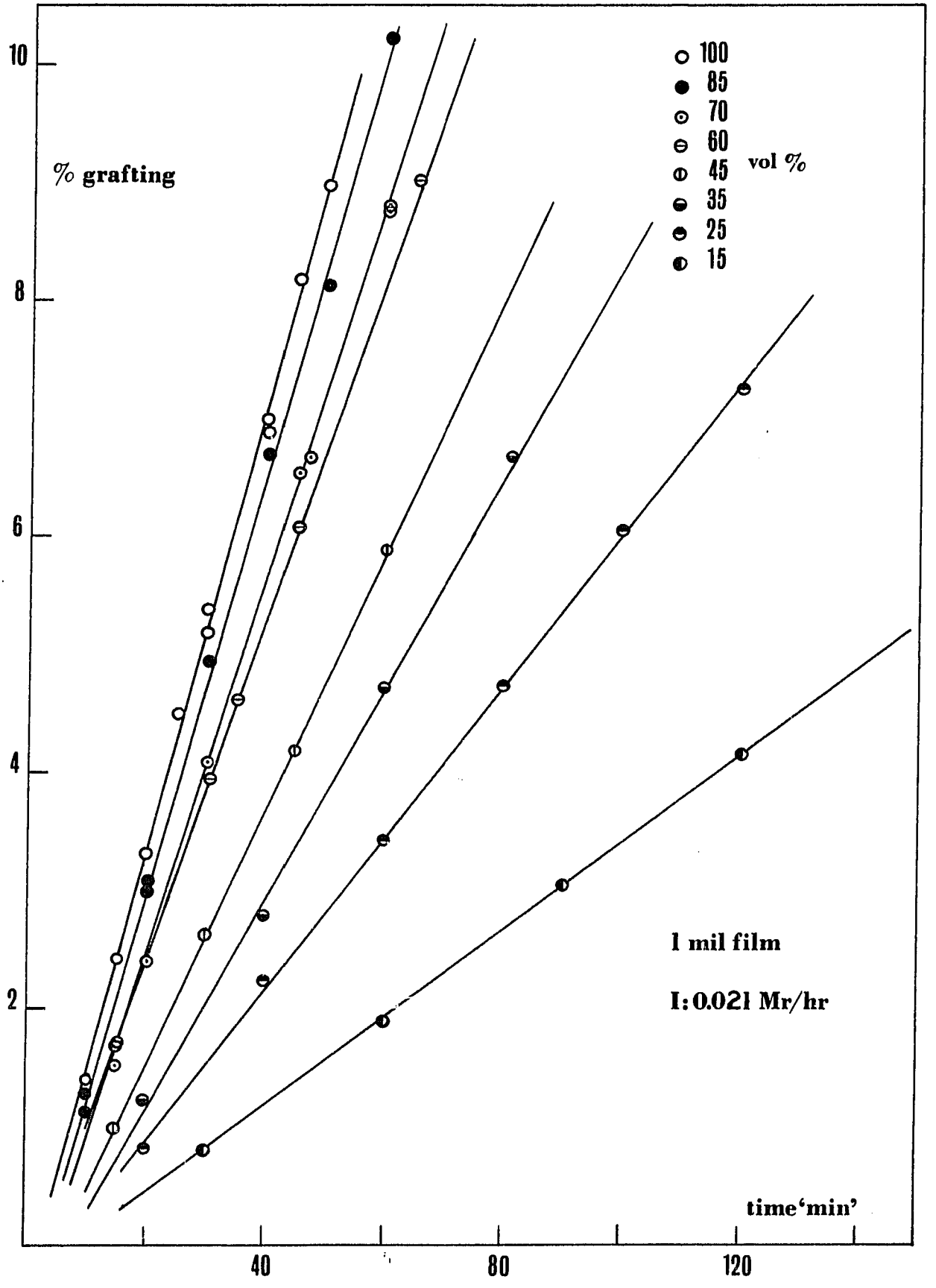



**FIG 18 Dependence of Rp on monomer conc."M"**

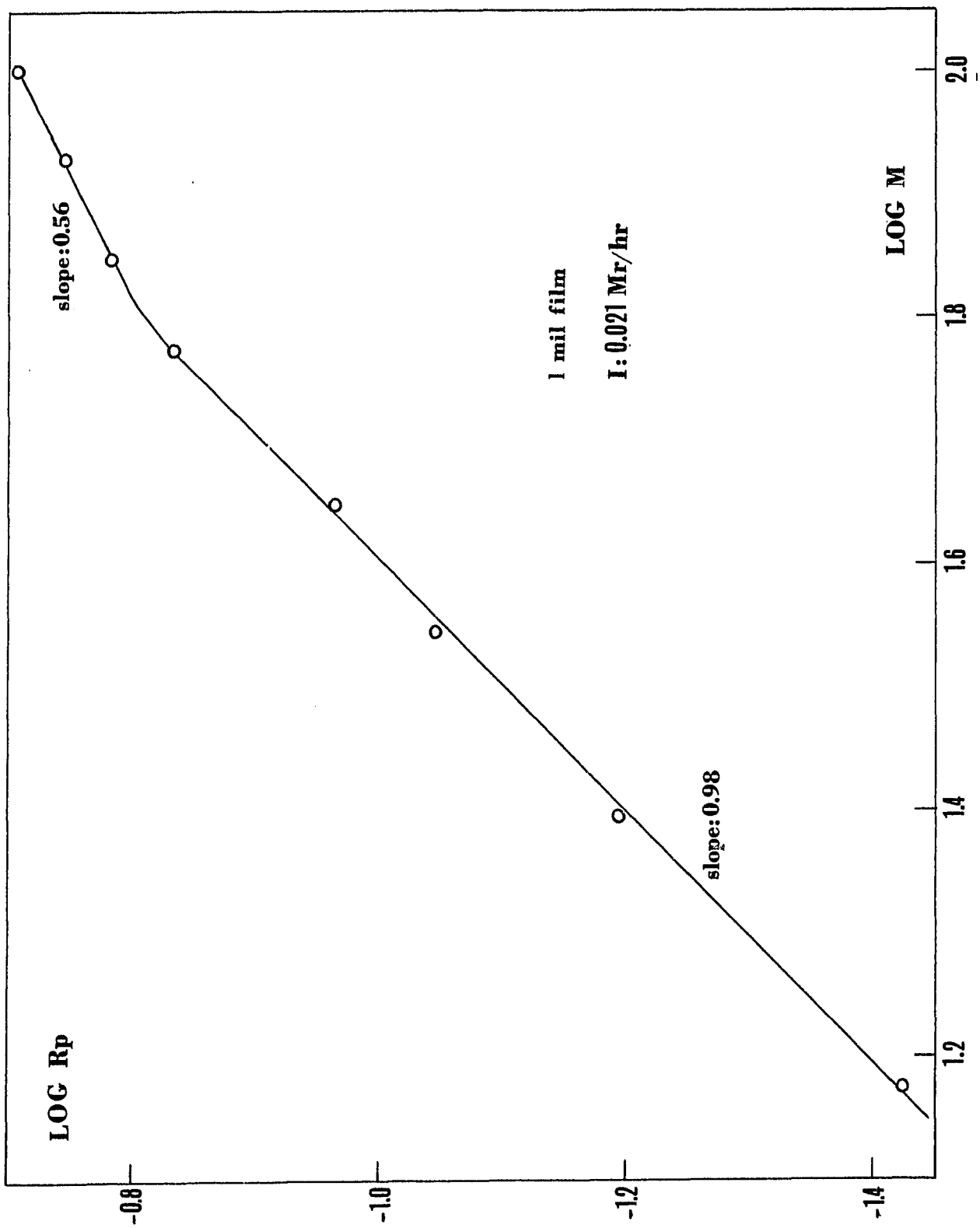



FIG 19 LOG Rp versus LOG M

± 0.03 and for compositions over 60 vol % the slope reduces to 0.50 ± 0.04. At first the drop from the first-order behavior is thought to be due to experimental error but repeated work at high compositions showed that this is not the case. The deviation from first-order to half-order at high monomer compositions has never been observed in the literature and there are no known kinetic schemes that can explain this behavior.

Turning back to the $R_p$ versus I data for 1 mil film(Figure 11), it can be seen that the dose rate at which this study is done(0.021 Mr/hr) is located at the start of the deviation from half order behavior and therefore the kinetics could probably be in the transition region to the diffusion-controlled kinetics and this behavior could possibly be a diffusional effect. To study this point further we investigated the monomer order:

(a) at a higher dose rate than 0.021 Mr/hr and

(b) at this dose rate using thicker films.

The grafting curves of 1 mil polyethylene film at a dose rate of 0.21 Mr/hr is shown in Figure 20. It is apparent that the rate of grafting increases with monomer composition(Table 12). A log-log plot of $R_p$ versus M(Figure 21) displays similar pattern as observed before. In this figure, the earlier shown data at 0.00076 and 0.021 Mr/hr are re-plotted for comparison. It can be seen that although a ten-fold increase in the dose rate did not effect the monomer order at the corresponding regions, this increase brought forward a change in the range of the different kinetic behavior regions. An increase in the dose rate decreased the range of the first-order region and increased the range of the half-order region. This behavior can be explained if one assumes that the half-order dependency is purely a diffusional phenomenon. An increase in the dose rate should shift the system closer to the diffusion-controlled state and therefore the effect of diffusion on the rate

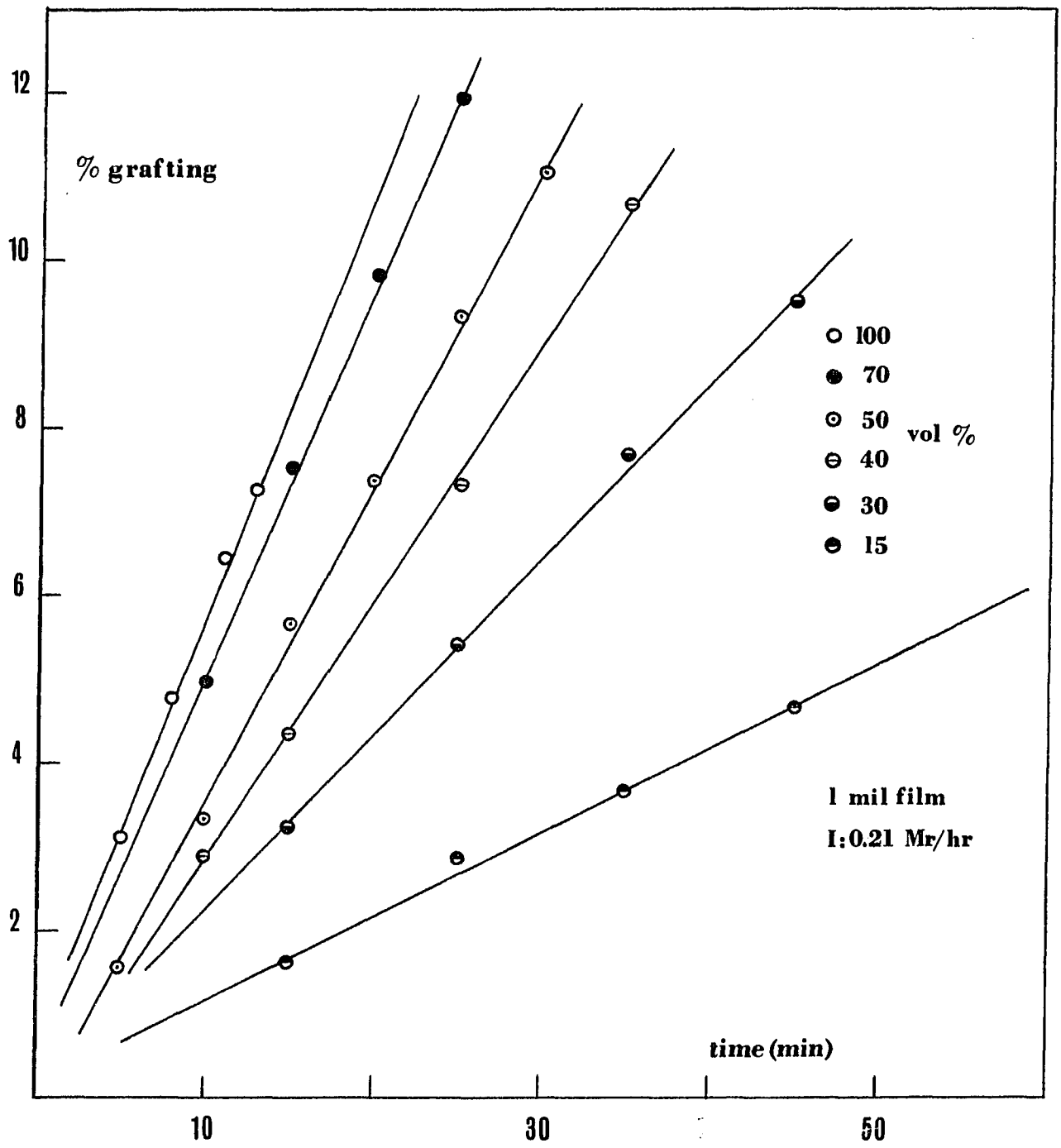



**FIG 20 Dependence of Rp on monomer concentration"M"**

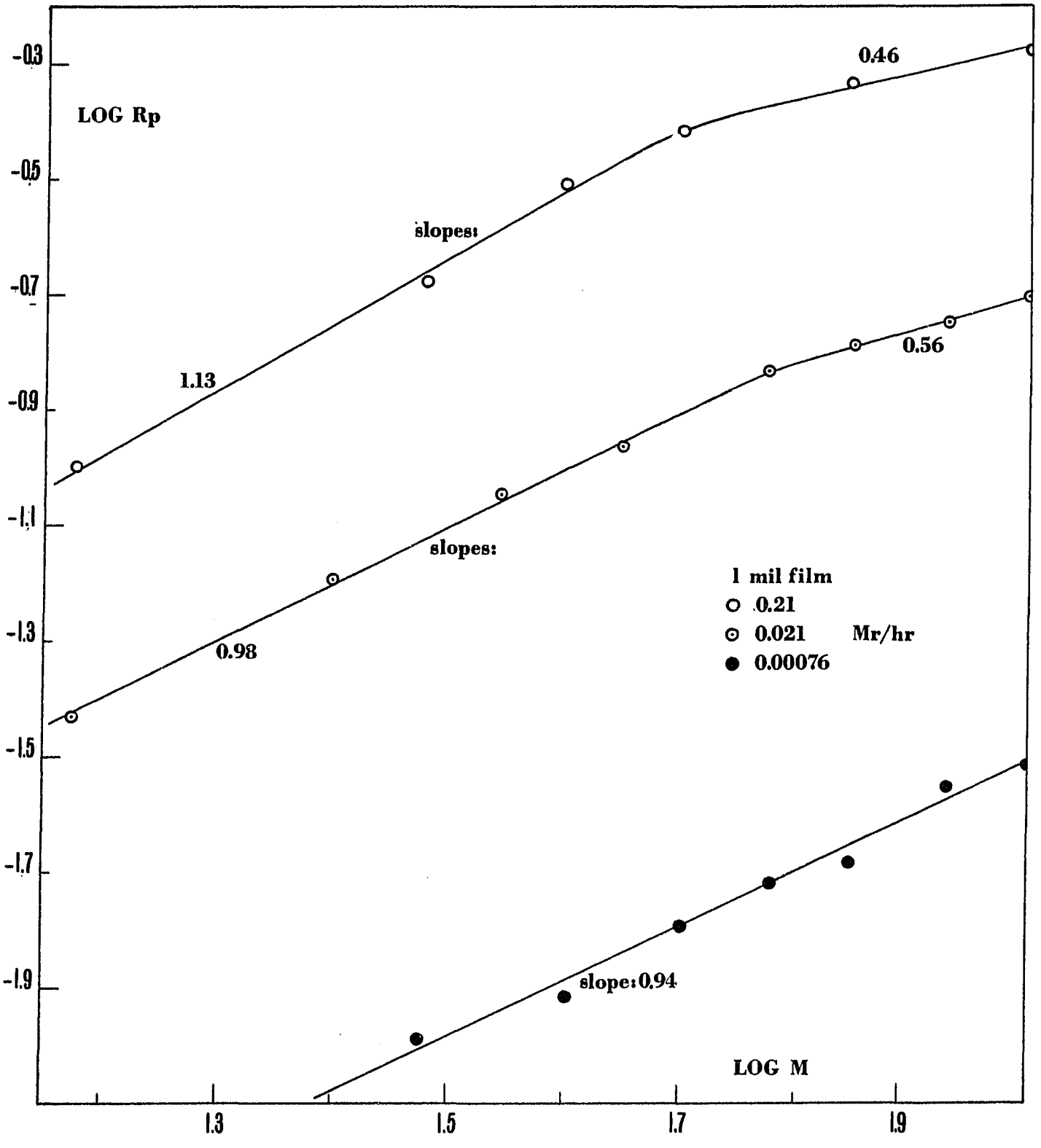



**FIG 21 LOG Rp versus LOG M "effect of dose-rate"**

TABLE 12

Dependence of $R_p$ on monomer conc. (M)*, **

| M(vol %) | Log M | $R_p$(% graft/min) | Log $R_p$ |
|---|---|---|---|
| 100 | 2.000 | 0.5262 ± 0.0170 | -0.279 |
| 70 | 1.845 | 0.4634 ± 0.0140 | -0.334 |
| 50 | 1.699 | 0.3817 ± 0.0077 | -0.418 |
| 40 | 1.602 | 0.3089 ± 0.0077 | -0.510 |
| 30 | 1.477 | 0.2093 ± 0.0069 | -0.679 |
| 15 | 1.176 | 0.0997 ± 0.0067 | -1.001 |

(*) 1 mil film

(**) I=0.21 Mr/hr

of grafting should start at a lower monomer composition.

Let us, now, look at the effect of film thickness on the dependence of $R_p$ on monomer concentration. Figures 22 and 23 show the grafting curves at 0.021 Mr/hr of 5 and 10 mil polyethylene films, repectively. Grafting studies with thick films are experimentally difficult since longer times are necessary for the samples to reach swelling equilibrium. Consequently, formation of thermally catalysed homopolymer during this period is unavoidable. In both figures positive intercepts at 0 % grafting for most of the monomer compositions are probably due to this effect. The intercepts approach towards the origin as the monomer concentration decreases. It is obvious that less homopolymer will be produced during the swelling period as the monomer gets more and more diluted.

The grafting rates are determined from the slopes of the curves and tabulated(Table 13). A log-log plot of $R_p$ versus M is shown in Figure 24.

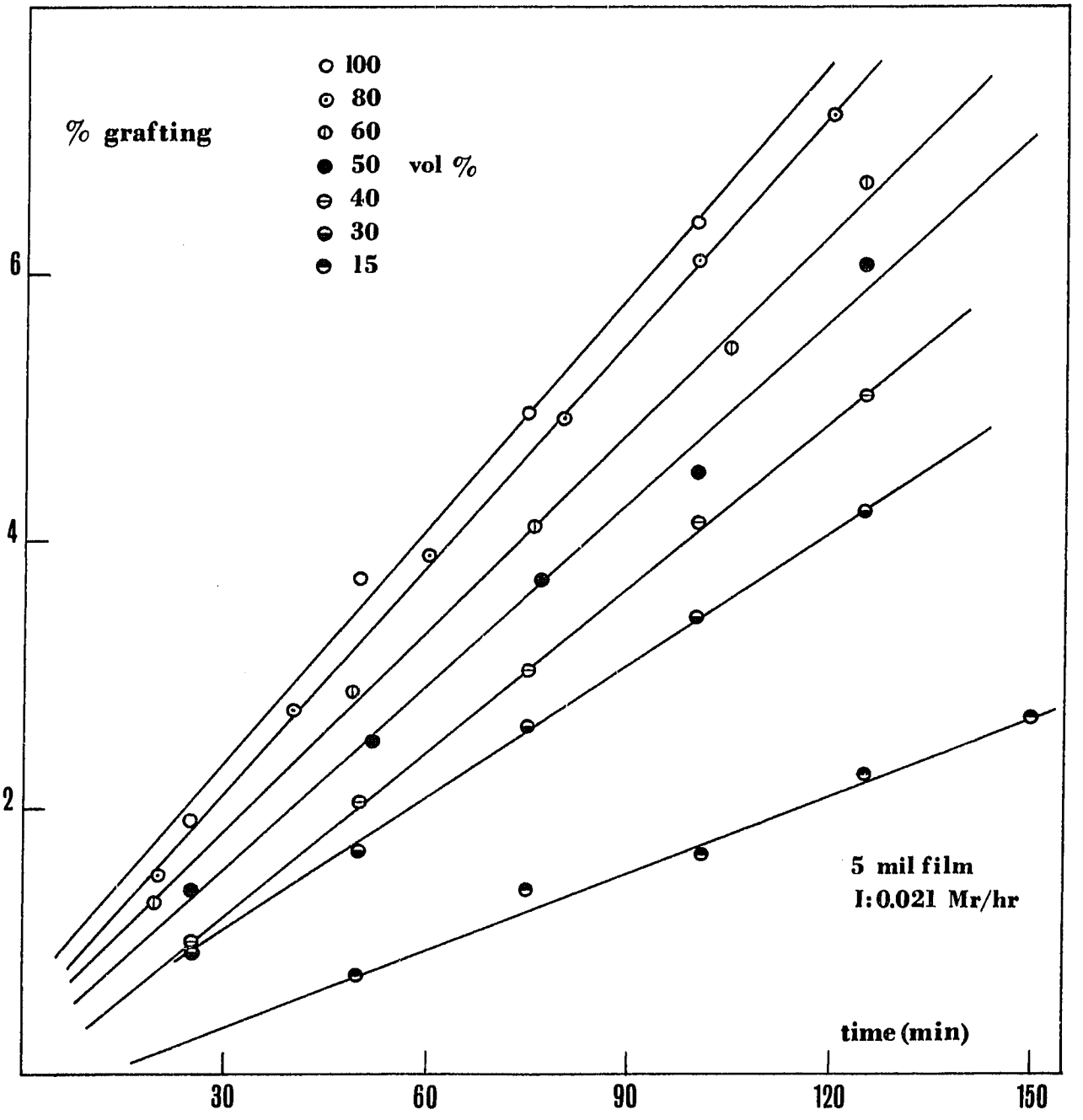



**FIG 22 Dependence of Rp on monomer conc."M"**

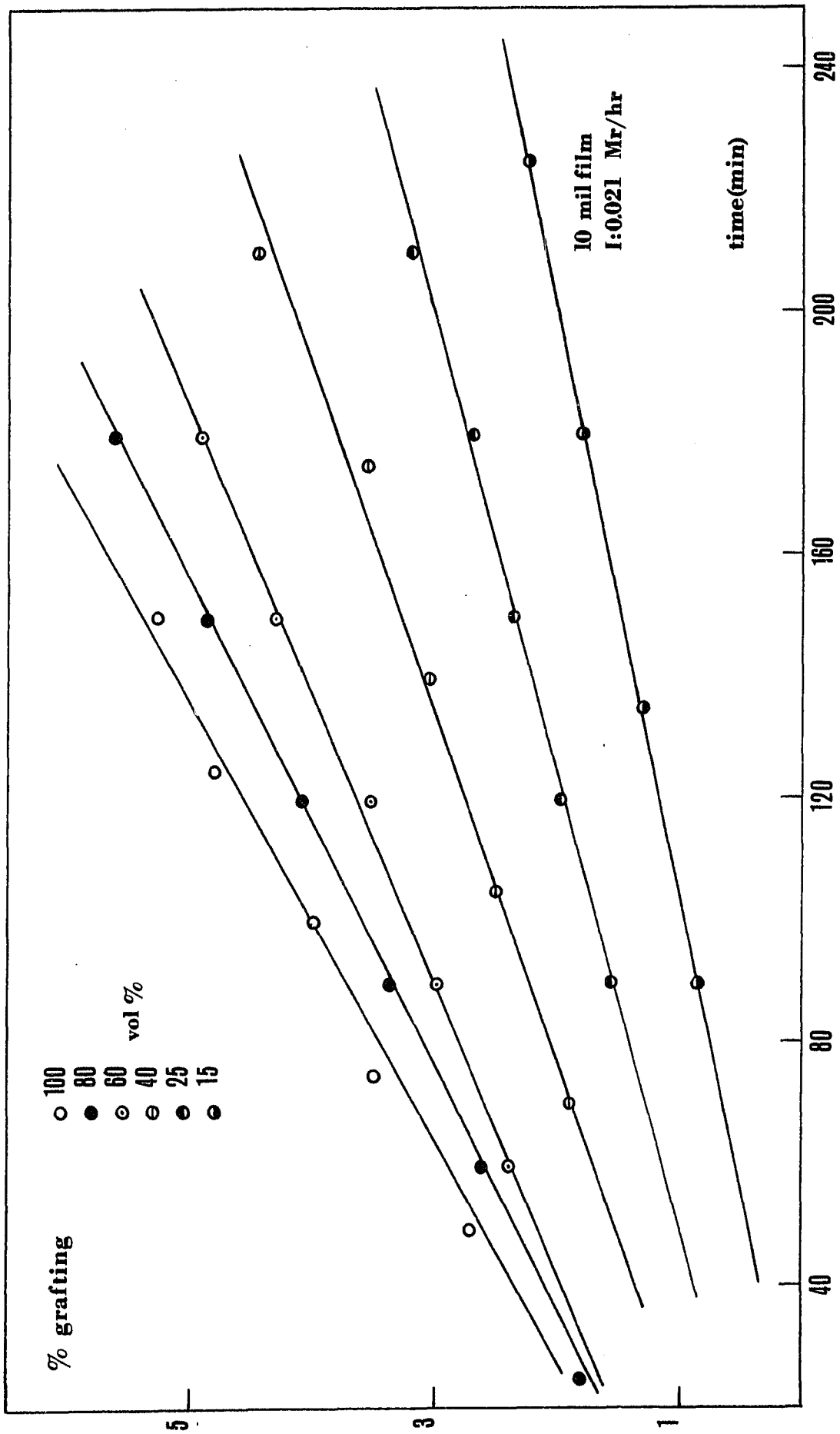



FIG 23 Dependence of Rp on monomer concentration "M"

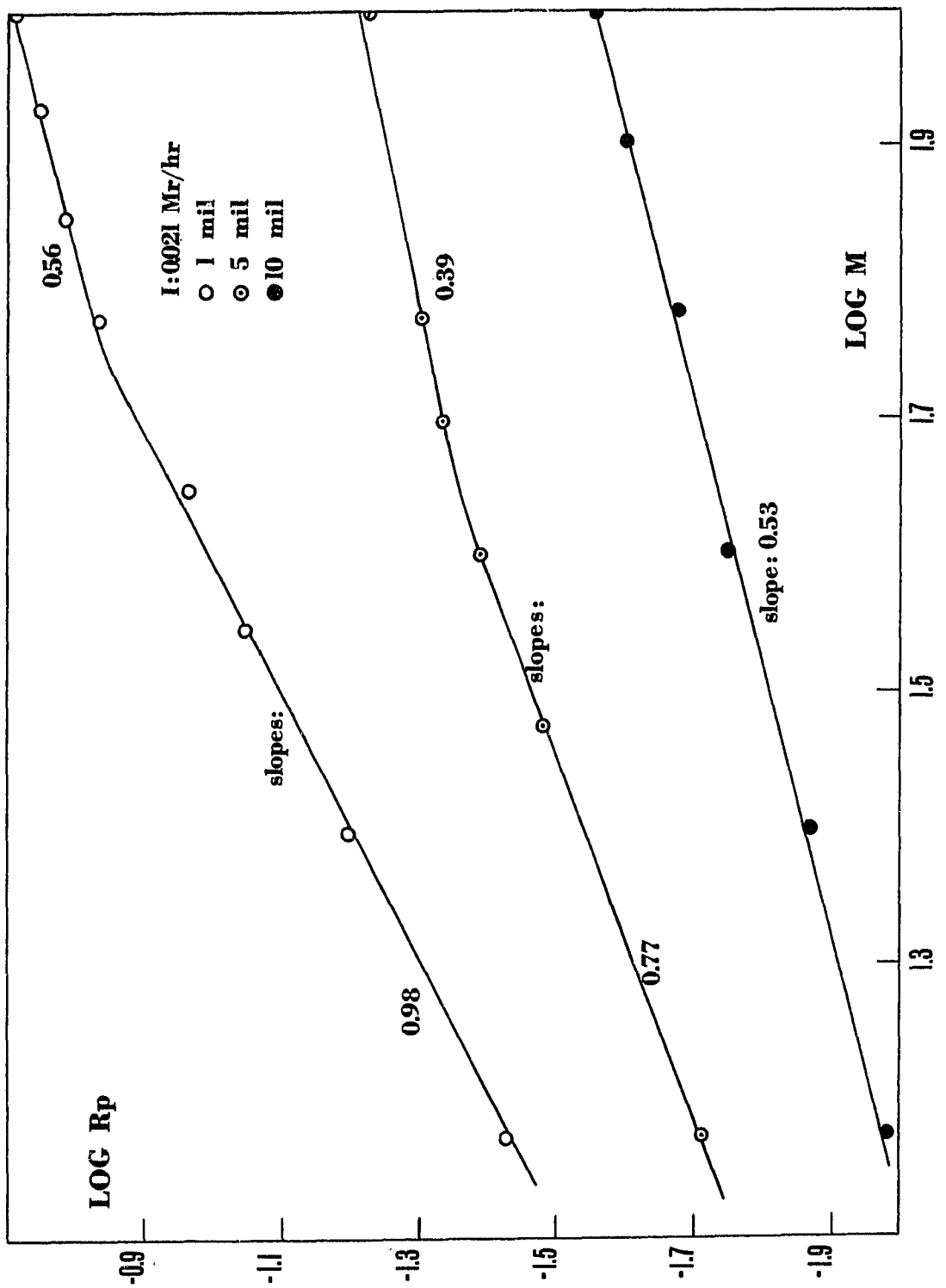



FIG 24 LOG Rp versus LOG M "effect of film thickness"

TABLE 13

Effect of film thickness on the dependency of $R_p$ on M**

| M(vol %) | $R_p$*(5 mil) | $LogR_p$ | $R_p$*(10 mil) | $LogR_p$ |
|---|---|---|---|---|
| 100 | 0.05852 ± 0.0031 | -1.233 | 0.02760 ± 0.0014 | -1.559 |
| 80 | 0.05667 ± 0.0008 | -1.247 | 0.02500 ± 0.0003 | -1.602 |
| 60 | 0.05002 ± 0.0036 | -1.301 | 0.02117 ± 0.0007 | -1.674 |
| 50 | 0.04572 ± 0.0023 | -1.340 | - | - |
| 40 | 0.04088 ± 0.0004 | -1.389 | 0.01769 ± 0.0011 | -1.752 |
| 30 | 0.03288 ± 0.0007 | -1.483 | - | - |
| 25 | - | - | 0.01340 ± 0.0005 | -1.873 |
| 15 | 0.01926 ± 0.0008 | -1.715 | 0.01043 ± 0.0001 | -1.982 |

(*) % graft/min

(**) I=0.021 Mr/hr

Earlier data at this dose rate using 1 mil film is also included for comparison. The slopes of the respective regions are shown on the curves. It is observable that the half-order dependency region extends with increases in the film thickness. For 5 mil film the slope of this region is appreciably lower than 1/2 probably due to scarcity of experimental points in the grafting curve(figure 22) of 100 vol % composition leading to a slope error in this figure. Also, the slope of the first-order dependency region decreased appreciably. With further increases in the film thickness, the first-order dependency region diminishes as seen from the data of 10 mil film, the curve is a straight line with a slope close to 1/2. One should also note that for thicker films the grafting kinetics are under the control of diffusional effects as evidenced from the drop of the grafting rate with increasing film thickness

in the whole range of monomer compositions studied.

Returning back to our $R_p$ versus $R_i$ data for the 10 mil film(figure 15) it was shown that at the dose rate in which the above study is done(0.021 Mr/hr) the rate dependence on the dose rate is close to 1/4-order and according to the theoretical analysis(equation 17) it indicates complete diffusional control. Therefore, it is possible that the 10 mil data presented in the figure above is under complete diffusion control and that the observed half-order dependency is a purely diffusional phenomenon. The theoretical analysis presented earlier indeed accounts for such a change in the dependence of $R_p$ on the monomer concentration(M).

For the case when the monomer diffusion coefficient(D) is dependent on the concentration of monomer(equation 18), it was shown that under complete diffusion-controlled conditions the monomer order( $v_{dc}$) is a function of d and expressed as in equation 19.Since for our system $v_{df}$ =1.0, a shift to 1/2-order is exactly what the theory predicts for high values of d.

The Parameter 'd'

The diffusion coefficient of many liquid-polymer systems depend on the liquid concentration and is expressed as,

$$D=D_o\, e^{dc/c_o} \qquad (18)$$

The parameter d in this equation is a measure of the dependence of D on the concentration of liquid and its value for a particular liquid-polymer system can be estimated by desorption studies.

The mathematical analysis of the kinetics of desorption of liquids from a polymer slab involves the solution of a non-linear differential equation which have been succesfully approximated by numerical methods(59). The resulting theoretical curves for each d value have been published in reference 59 and can be applied to the desorption data of any liquid-polymer system.

In the desorption technique, the relative weight loss of liquid from a saturation-swelled polymer film is measured with respect to time and the experimentally observed $t_{1/2}$ ( the time necessary for the desorption of half the amount of the total liquid in the polymer matrix) is matched to the theoretical $t_{1/2}$'s for various d values and the resulting curves are superimposed on the experimental curve. The curve that closely matches to the experimental curve gives the d value for that particular liquid-polymer system.

Figure 25(a & b) shows the desorption curves for 4-vinylpyridine and pyridine, respectively. The solid lines represent the actual experimental desorption curves. The circled points are the theoretically calculated data points for 4-vinylpyridine and pyridine for the specified d values. A larger circled data point at the relative weight loss of 0.5 signifies that all the theoretical curves pass through this point(on the figure, for a better view, the theoretical curves are not drawn but the reader can have an idea of the pattern by simply following the data points for a particular d value. For both 4-vinylpyridine and pyridine the best fit between the experimental curves and the theoretical points is obtained for a d value of 4.

Although McCall(59) claims that the accuracy in the value of d obtained using this technique is within $\pm$ 0.5, it is the belief of this author that the accuracy is less than 0.5, probably around $\pm$ 1.0 and also that the actual value of d is somewhat higher than that experimentally estimated.

Experimentally, at the start of a desorption run, the swelled polyethylene film is taken out of the monomer or solvent solution, blotted dry rapidly to get rid of excess liquid on the surfaces of the film by rubbing with a paper tissue, both surfaces exposed to alpha-radiation from a 10 microcurie $Po^{210}$ source for a short period of time(since polyethylene is a good insulator some static charge builds up due to the rubbing process and each

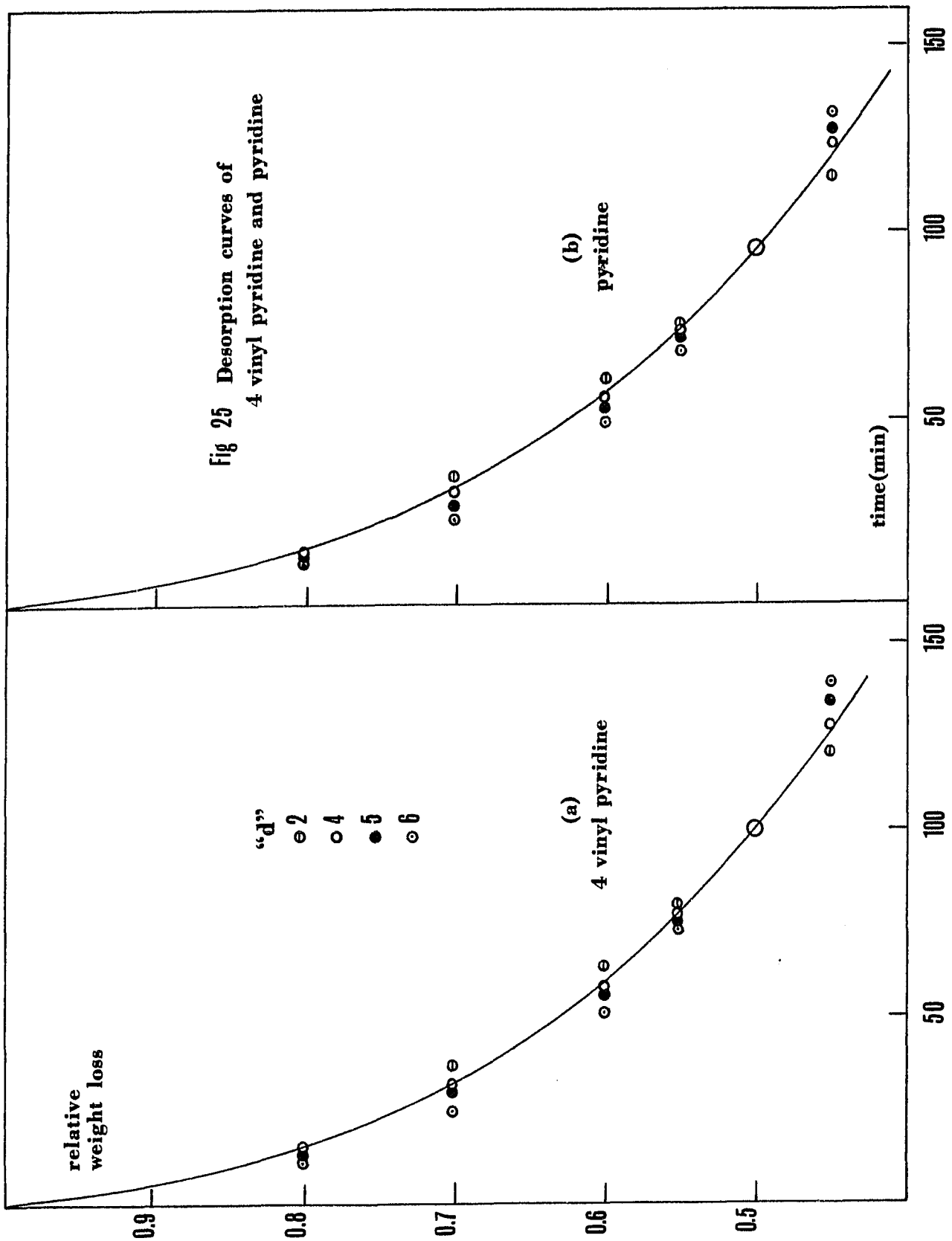



Fig 25 Desorption curves of 4 vinyl pyridine and pyridine

sample has to be discharged before weighing) and weighed. This whole operation takes up about a minute and since the highest rate of weight loss in a desorption experiment is at the start, the observed initial weight ($w_i$) should be somewhat lower than the actual value. Consequently, since the relative weight loss is given as:

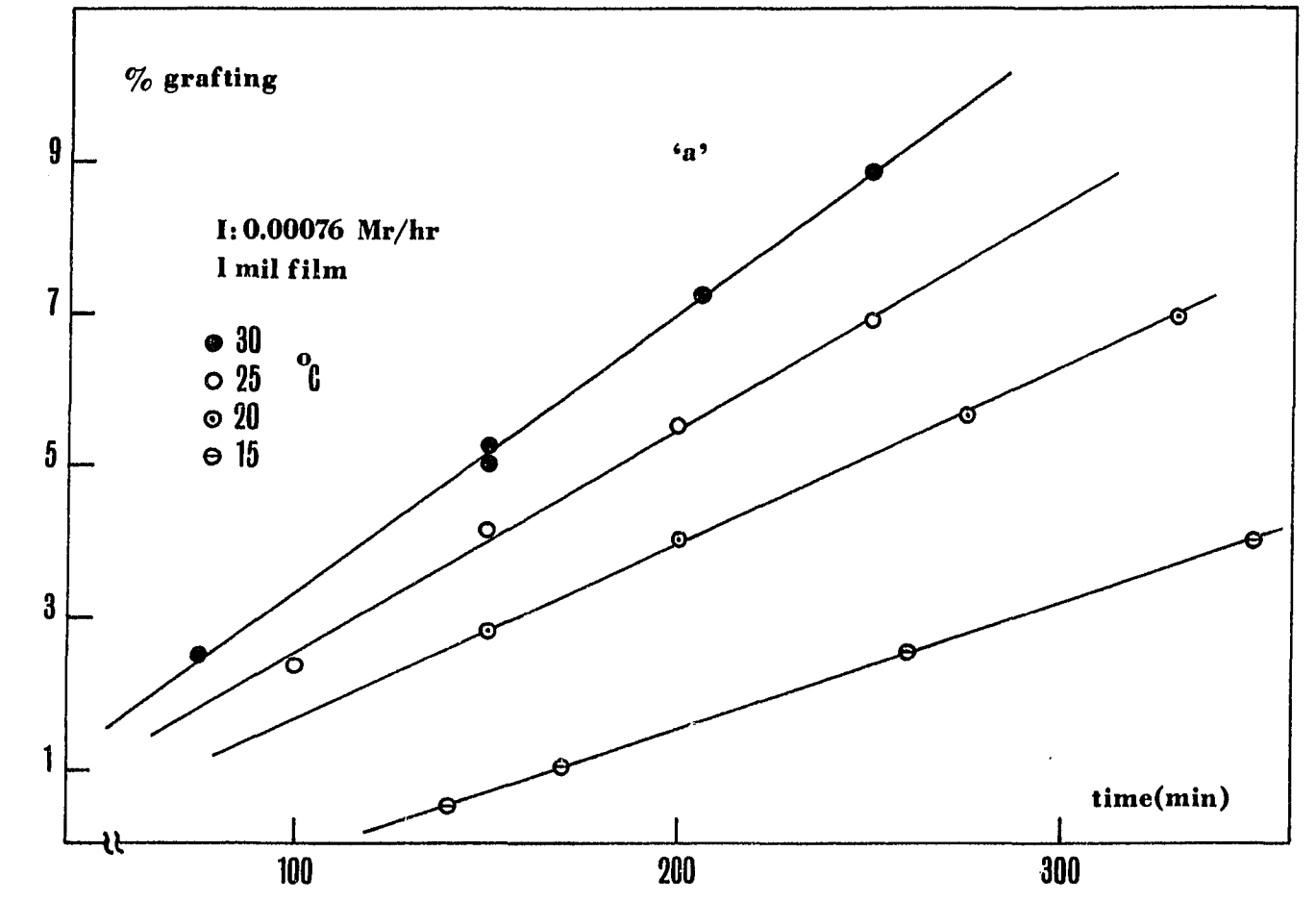
$$\text{relative weight loss} = (w_t - w_o)/(w_i - w_o) \qquad (27)$$

where $w_t$ is the weight of the sample at any time t and $w_o$ is the initial weight of the polymer alone, in actuality, all the data points on a given desorption curve should be lower than that observed. This unavoidable error in the technique is felt highly only at the initial stages of the experiment where the value of d is determined with a resultant lower than actual determined d value.

Considering the above discussion, the actual value of d for 4-vinyl - pyridine, pyridine and the mixtures of the two is probably in the range of 4 to 5. Substituting a value of 5 for d in equation 19 with $v_{df}$=1.0, $v_{dc}$ is calculated to be 0.633 . This value is highly close to the experimentally observed value of 0.53 for the monomer order of the 10 mil film at the dose rate of 0.021 Mr/hr(figure 24).

Activation Energy ( $E_A$ )

The activation energy of grafting of 4-vinylpyridine to polyethylene was determined by studying the grafting rate at various temperatures. Since at high dose rates the grafting reaction is under the influence of diffusional effects, this study was done at the lowest possible dose rate of 0.00076 Mr/hr. At this dose rate the grafting curves of 1 mil thick polyethylene film is shown in Figure 26(a). The curves are linear in the studied range with some inhibition due to dissolved oxygen. It is apparent from the figure that the grafting rate increases with increasing temperature. The rates are calculated



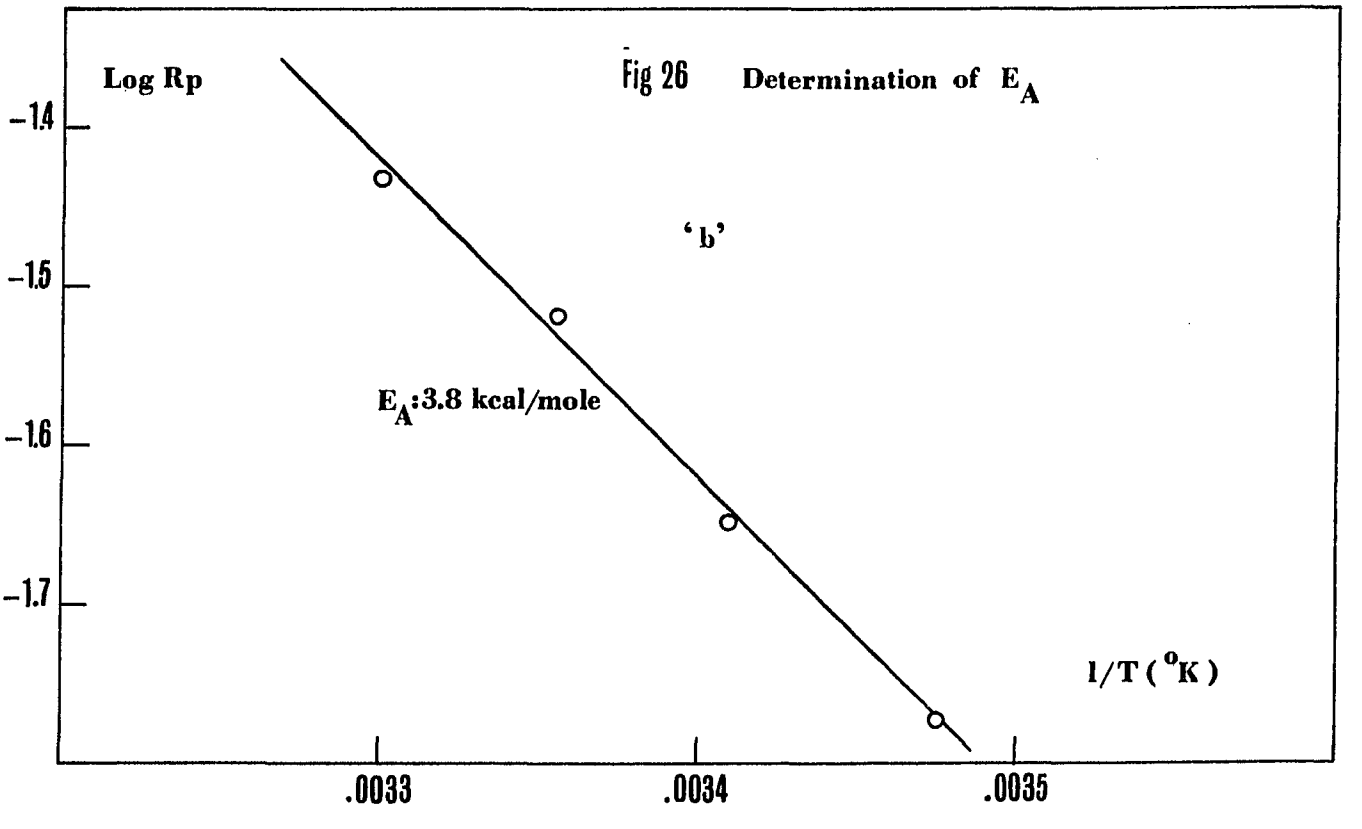




Fig 26 Determination of $E_A$

TABLE 14

Effect of temperature on the rate of grafting ($R_p$)*,**

| T(°C) | 1/T(°K$^{-1}$) | $R_p$(% graft/min) | Log$R_p$ | % swelling*** |
|---|---|---|---|---|
| 30 | 0.003300 | 0.0369 ± 0.0030 | -1.433 | 2.65 |
| 25 | 0.003356 | 0.0304 ± 0.0014 | -1.518 | 2.56 |
| 20 | 0.003410 | 0.0223 ± 0.0022 | -1.652 | 2.49 |
| 15 | 0.003472 | 0.0168 ± 0.0018 | -1.774 | 2.41 |

(*) 1 mil film

(**) I=0.00076 Mr/hr

(***) w/w, average of 6 determinations.

from the respective slopes and shown in Table 14. This study is carried in a rather narrow range of temperature since the extent of swelling is effected by the variation in temperature. In this temperature range, from the table, it can be seen that the variation in the extent of swelling is negligible and therefore the grafting rates are not corrected to compensate for this variation.

An Arrhenius plot of log $R_p$ versus 1/T is shown in Figure 26(b). Since the slope of the curve is equal to $-E_A/R$ where R=1.987 cal/deg.-mole, the activation energy is calculated to be 3.8 kcal/mole.

Comparing this value to that for the styrene-polyethylene system, it is considerably lower, the reported activation energy of radiation-induced grafting by the pre-irradiation technique of styrene to high density polyethylene(78) and low density polyethylene(79) are 18, 8.7 kcal/mole, respectively.

# CONCLUSION

The kinetic behavior of the radiation-induced graft polymerization of 4-vinylpyridine-polyethylene system can be summarized as follows:

(a) at low dose rates, between 0.00076 and 0.021 Mr/hr, the reaction kinetics are free of diffusional effects as evidenced from the similar rates for 1 and 2 mil films. Under these conditions the rate of grafting is proportional to the square-root of the initiation rate and the monomer order is unity.

(b) at intermediate and high dose rates, from 0.021 Mr/hr to 0.35 Mr/hr, even for the thin films the reaction kinetics are influenced by diffusional effects. In this region the 2 mil film has a lower grafting rate than 1 mil film at any particular dose rate. The dependence of $R_p$ on $R_i$ drops 1/2-order to a lower order and the monomer order varies between 1 and 0.5, decreasing with increasing monomer concentration. For thicker films, particularly for 10 mil film the reaction kinetics are under complete diffusion control and the rate of grafting is dependent on the initiation rate to the order of 0.25 . The variation in the monomer order steadily flattens with increasing film thickness and for 10 mil film the monomer order becomes 0.53 .

(c) under diffusion-free conditions the activation energy for the grafting reaction is 3.8 kcal/mole.

From the results above, it is clear that kinetically 4-vinylpyridine-polyethylene system follow ordinary free radical polymerization mechanism,

$$R_p = k_p / k_t^{1/2} R_i^{1/2} M \qquad (28)$$

A radical initiation is evidenced by the square-root dependence of $R_p$ on $R_i$. If initiation was ionic, then this order would have been unity. Moreover, in radiation-induced graft polymerizations(11) as well as in radiolytic homopolymerizations(81, 83), evidence for an ionic mechanism has only been observed when the monomer and all glass apparatus are passed through rigorous drying procedures. In our case, the procedures for drying were hardly rigorous.

The rate constants that appear in equation 28 can be calculated if $R_p$, M and $R_i$ are converted to their appropriate units. At a dose rate of 0.00076 Mr/hr, the grafting rate of 1 mil film is 0.0304 % graft/min. Converting to the units of moles per liter of swollen amorphous polyethylene-sec, $R_p = 1.65 \times 10^{-4}$ moles/liter-sec. Since M= 0.814 moles/liter and at this dose rate, $R_i = 1.336 \times 10^{-9}$ moles/liter-sec,

$$k_p^2/k_t = 30.76 \text{ liter/mole-sec.}$$

From free radical homopolymerization of 4-vinylpyridine in bulk(43), $k_p^2/k_t$ is given as $4.8 \times 10^{-5}$ liter/mole-sec. The vast difference in the values is immediately evident. Such drastic increases in the $k_p^2/k_t$ values has also been observed in other systems such as styrene-polyethylene and has been attributed to the nature of the reaction medium. The graft polymerization proceeds in highly viscous surroundings and the rate of termination is highly effected since it requires the diffusion and reaction of two macromolecular radicals with each other. On the other hand, the propagation rate constant, $k_p$, should not be effected as highly since it involves the reaction of a polymeric radical with a monomer molecule.

Earlier, while comparing the kinetics of grafting 4-vinylpyridine and styrene, we have stressed tha fact that under similar conditions the rate of grafting of 4-vinylpyridine is higher than that of styrene though styrene

swells polyethylene approximately twice as much as 4-vinylpyridine. From reference 9, under similar conditions as above, i.e. at 0.00076 Mr/hr and using 1 mil film, the rate of grafting of styrene to the same polyethylene is found to be 1.23 % graft/hr. Converting this value to moles/liter-sec, $R_p$ is calculated to be $1.058 \times 10^{-4}$. Since M= 1.68 moles/liter and $R_i = 1.336 \times 10^{-9}$ moles/liter-sec (same as above), one can calculate $k_p^2/k_t$ as,

$$k_p^2/k_t = R_p^2/(R_i M^3) = 1.79 \text{ liter/mole-sec}$$

It should be noted that, the monomer concentration term above is raised to the third power since at this dose rate the monomer exponent has been determined to be 3/2(9).

Comparing the $k_p^2/k_t$ values, it is quite clear that the value of this parameter for 4-vinylpyridine is at least 15-fold higher than that of styrene and is responsible for the difference in the grafting rates.

If one makes the crude assumption that the propagation rate constant, $k_p$, is not effected severely by the viscosity of the reaction medium and that $k_p$ in grafting is about equal to that in bulk, 12.0 liter/mole-sec(43), the termination rate constant ($k_t$) can be estimated as 4.68 liter/mole-sec. Comparing this value to that in bulk, $3 \times 10^6$ liter/mole-sec, approximately 100,000-fold decrease in the $k_t$ value in the grafting medium is observable. This vast difference in the $k_t$ values is a clear indication of the effects of viscosity in a given polymerization reaction.

Turning back to the initiation rate order at high dose rates, the drop from half-order is clearly a diffusional phenomenon since there is no experimental evidence for any contribution by primary radical termination kinetics. If there had been ..... contribution, then although this effect should have also lowered the initiation rate order for 0.5, the monomer order at high dose rates would have been higher than unity.

At intermediate and high dose rates, the drop in the monomer order from first-order with increasing monomer concentration is also attributable to diffusional effects. For thin films, at low monomer concentrations, since the grafting rate is low, the grafting kinetics should not be under the effects of diffusion. For 1 mil film at 0.021 and 0.21 Mr/hr this is exactly what we observed. With increase in the thickness of the film, the effect of diffusion should shift to lower and lower concentrations of monomer and with further increases in the film thickness the whole range of monomer concentration should be under complete diffusion control. The data for 10 mil film at the dose rate of 0.021 Mr/hr clearly displayed this behavior. Also, the observed monomer order, 0.53, is highly close to that predicted by the theoretical analysis, namely, for $d=5$, $\nu_{dc}=0.63$ .

Considering all that is said and reported in this thesis, there is no doubt that diffusional effects play a dominant role in the kinetics of graft polymerization. Without a knowledge on the mechanism and boundaries of these effects one can easily make the mistake of considering them as purely kinetic.

In this work we have not only demonstrated systematically the effects of diffusion in a given grafting system but we have also methodically outlined the direction in which the kinetical parameters are influenced. Additionally, this work was more than succesfull in the verification of our theoretical analysis on the mechanism of graft polymerization.

## APPENDIX I - Definitions

Dose - amount of energy imparted to matter, expressed in rads(r) or million rads(Mr).

Dose Rate - absorbed dose in unit time, expressed as Mr/time.

G-value - number of individual chemical events occuring per 100 e.v. of absorbed energy.

$G_R$-value - number of radicals produced per 100 e.v. of absorbed energy.

The rad - unit of absorbed dose. 1 rad is 100 ergs/gram or $6.25 \times 10^{13}$ e.v./gram.

The curie - is the unit of radioactivity. It is the amount of radioactive material which disintegrates at a rate of $3.7 \times 10^{10}$ disintegrations per second(at the same rate as radium).

Hildebrand solubility parameter($\delta$) - is the square root of the energy of vaporization per unit volume of a liquid ( cohesive energy desity).

## APPENDIX II - Conversions

### Rate of graft polymerization($R_p$)

$$R_p(\text{moles/liter-sec}) = R_p(\%\ \text{graft/min})/(60\text{x}100) \times \left[\frac{0.855\ \text{gm APE/ml APE} \times 10^3\ \text{ml/l}}{105\ \text{gm/m} \times 0.228\ \text{gr APE/gm PE} \times 1.0957\ \frac{\text{ml SAPE}}{\text{ml APE}}}\right]$$

where 0.855 gmAPE/mlAPE is the density of amorphous polyethylene(13),

105 gm/m is the molecular weight of 4-vinylpyridine,

0.228 gmAPE/gmPE is the weight fraction of amorphous parts in PE

and 1.0957 mlSAPE/mlAPE is the calculated increase in the volume of amorphous regions upon swelling(assuming additivity of volumes).

### Monomer concentration(M)

$$M\ (\text{moles/liter}) = \frac{(0.025\ \text{gm/gm PE} \times 0.855\ \text{gm/ml} \times 10^3\ \text{ml/l})}{(105\ \text{gm/m} \times 0.228\ \text{gm/gm} \times 1.0957\ \text{ml/ml})}$$

$$= 0.814\ \text{moles/liter}$$

where 0.025 gm 4-VP/gm PE is the extent of swelling of 4-VP at 25 °C.

### Rate of initiation($R_i$)

$$R_i(\text{moles/liter-sec}) = 2.9\text{x}10^{-7} \times d \times G_R \times I$$

where $2.9\text{x}10^{-7}$ is a conversion factor,

d is the density of the swelled polyethylene, calculated to be 0.8658 gm/ml,

$G_R$ is the G-value of radical production in PE(a value of 7 is used(1))

and I is the dose rate in Mr/hr.

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