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RADIATION-INDUCED GRAFT POLYMERIZATION OF STYRENE ONTO CELLULOSE ESTERS

City University of New York PH.D. 1980

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RADIATION-INDUCED GRAFT POLYMERIZATION OF STYRENE ONTO CELLULOSE ESTERS

by

JIUNN TSAY

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

1980

v

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 STYRENE ONTO CELLULOSE ESTERS

by

Jiunn Tsay

Adviser: Professor George Odian

The kinetics of mutual radiation graft polymerization of styrene onto cellulose acetate butyrate (CAB-171-40) has been studied over a range of radiation intensities and monomer concentrations. The reaction was diffusion-free under the experimental conditions as shown by the independence of the grafting rate on film thickness. The dependence of the grafting rate on monomer concentration increases from 3/2-order to slightly greater than 5/2-order with increasing radiation intensity. The dependence of the grafting rate on radiation intensity decreases from 1/2-order to 0-order with decreasing monomer concentration. The results does not follow the usual kinetic expression for free radical chain polymerization, $R_p = k_p[M](R_i/2k_t)^{1/2}$.

The preparation of the polymer film, and two possible mechanisms:

(1) Unusual initiation process.

(2) Combination of primary termination and bimolecular termination.

for these kinetic results are presented and discussed.

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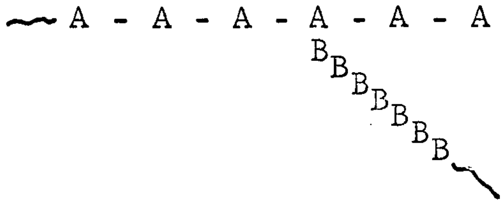
INTRODUCTION

A graft copolymer is a branched copolymer with a backbone of one type polymer A to which are attached one or more side chains of another polymer B.



Grafting is an attractive means for modifying base polymer because it frequently results in the superposition of properties relating to backbone (polymer A) and pendent chains (polymer B). Graft copolymerization by means of radiation is a convenient synthetic technique. During the last two decades, commercial availability of high energy radiation sources coupled with the ability to produce desirable chemical and physical modification in the properties of polymers brought forward extensive research in this area of polymer chemistry.

One of the most useful techniques for carrying out the reaction is the mutual irradiation technique: a base polymer is swelled and equilibrated in a monomer then subjected to ionizing radiation. It has been considered that the graft polymerization proceeds in a manner exactly analogous to the conventional free radical chain homopolymerization. Radiation causes excitation and bond breakage to form polymeric radicals.

$$P \xrightarrow{\gamma} P\cdot$$

The polymeric radical P• initiates the polymerization of the monomer,

$$P\cdot + M \xrightarrow{k_i} M\cdot$$

which then propagates.

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$$

Termination occurs by bimolecular coupling and/or disproportionation.

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} \text{dead polymer}$$

Using the usual kinetic analysis, one can derive the rate of graft polymerization R_p as $R_p = k_p(R_i/2k_t)^{1/2}[M]$; where [M] is monomer concentration, R_i is rate of initiation which depends on the radiation intensity I.

In the case of grafting of monomers on the solid polymeric film, one very important factor is the possible slowing of the grafting reaction owing to the slowness of monomer diffusion into the polymer. The reaction becomes diffusion-controlled and leads to different kinetics. Odian and coworkers[1] have established a mathematical model to describe the kinetics of diffusion-controlled reaction. Whether a reaction is diffusion-free or diffusion-controlled depends on the values of R_i, $k_p/k_t^{1/2}$, D and L as gathered in the parameter A,

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

where D is the diffusion coefficient for the monomer diffusing in the reaction system, L is the film thickness. Diffusion-free reaction occurs at low values of A and diffusion-controlled reaction occurs at higher values of A.

The experimental results by Odian and Derman show that rate of diffusion-free grafting of 4-vinylpyridine to high density polyethylene[2] is first-order in monomer concentration and 1/2-order in radiation intensity, corresponding to normal radical chain polymerization with bimolecular termination. However, the rate of diffusion-free grafting polymerization of styrene onto high density polyethylene[3] and low density polyethylene[4] does not follow normal radical chain polymerization kinetics. Instead, the dependence of the grafting rate on monomer concentration increases from 3/2-order to as high as 3-order with increasing radiation intensity. Simultaneously, the dependence of grafting rate on radiation intensity decreases from 1/2-order to almost zero order with increasing radiation intensity. The complete mechanism for this abnormal kinetic behavior has not been elucidated as yet. Various possible mechanisms responsible for these effects have been investigated, including the effects of viscosity on the initiation and termination reactions and the possibilities of ionic graft polymerization and energy transfer.

The purpose of this research is to extend the investigation of grafting kinetics to the styrene- cellulose esters grafting system. The major goals of this work consist of:

(1) Preparation of additive-free polymeric film and establishment of proper techniques to make uniform cellulose ester film.

(2) Selection of a monomer-polymer system which followed the diffusion-free route under mutual radiation graft polymerization. Different film thickness were examined to determine whether the reaction is diffusion-free or diffusion-controlled.

(3) Study the kinetics of the reaction by investigation of the dependence of grafting rate on monomer concentration and radiation intensity.

(4) Development of a better theory to account for all the experimental observations on graft polymerization.

BACKGROUND

1. Chemical Effects of Radiation Absorption

γ rays are emitted as the result of processes which occur within the nucleus, for example, the decay of radioisotopes. For γ rays the energy ranges from 40 KeV to 4 MeV. When electromagnetic radiation passes through a polymer[5,6,7] its intensity decreases, primarily as a result of scattering and energy absorption by some irradated molecules. Three major processes are operative: 1. The photoelectric absorption; 2. The production of a positron-electron pairs; 3. Compton scattering. In photoelectric processes, a photon with energy E_o transfers all its energy to the medium through the ejection of an electron with energy E_e, according to the relationship $E_e = E_o - E_b$; where E_b is the binding energy of the ejected electron in the atom. This process is important only for photons with relatively low energies. For organic polymers the contribution of this process to the overall absorption is less than 1% for photons with energies exceeding 0.1 MeV. Pair production, on the other hand, designates the process in which the photon energy is converted into a positron and an electron; the former eventually recombines with an electron, resulting in the emission of two photons, each with approximately 0.51-MeV energy. Since the conversion of energy into matter is involved, pair production process is inherently impossible when the energy of the photons is less than 1.02 MeV and does not contribute significantly ($<$10%) to the overall absorption coefficient in most polymeric or other organic materials unless the photon energy is at least on the order of 5 MeV. The predominant mechanism of radiation interaction for systems of polymeric materials is Compton scattering. This is the process in which the incident γ ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy. Both the electron and photon subsequently interact with the surrounding materials giving rise to essentially two processes, one of ionization ($A \longrightarrow A^+ + e^-$) and the other of excitation ($A \longrightarrow A^*$). The ions and excited molecules are very reactive; they either react with other materials present in the system or decompose into radicals. The ions and free radicals produced upon irradiation of polymeric system may initiate graft polymerization.

Cross-link formation is normally the predominate process upon the irradiation of polymers containing an α hydrogen in the unit structure, e.g. polyethylene or polystyrene. When polymers devoid of α-hydrogen and have the structure $-(CH_2-CR_1R_2)-$ such as polymethlystyrene or polyisobutylene are exposed to radiation, scission of the main chain is usually the predominant process. This is because the R_1 and R_2 produce a steric strain which weakens the bonds of the backbone chain.[5,6,7] Chain scission appears to be favored over cross-linking in cellulosic materials. Fortunately it is recognized that dose levels needed to encourage grafting are significantly below those likely to cause significant damage to the polymer[8].

2. Radiation-Induced Homopolymerization of Styrene

Reaction Mechanism

In radiolytic polymerization, a question often arises as to whether the mechanism is free radical, anionic or cationic. There are several pieces of evidence which distinguish among the mechanisms:

1. Evaluate the effect of variables such as temperature, dose rate, and solvent. The temperature coefficient and energy of activation are often smaller for ionic polymerization than for radical polymerization. Ionic polymerization are more sensitive to solvating power and polarity of the solvent.
2. Evaluate the effect of free radical or ionic scavengers at low concentration.
3. Study the reactivity ratio in copolymerization.

The earliest experiments in radiation-initiated polymerization of styrene show that the reaction was inhibited by traces of air and also by benzoquinone[5], which strongly suggested a free radical mechanism. The effect of dose-rate was investigated by Chapiro[9]. The results show the clsssical square-root relationship between the reaction rate and the activity of the source. Ballantine[10] studied the influence of reaction temperature at -18°, 25°, 72°C, and found the activation energy of 6.7 Kcal/mole which is slightly higher than the values derived from U.V. and thermal polymerization of styrene.

Early evidence for an ioic mechanism was obtained in the styrene-methylene chloride system for radiation-induced polymerization of styrene at -78°C. This reaction was not affected by the presence of air or benzoquinone and its rate was directly proportional to the radiation dose-rate. It was further found that the reaction was efficiently retarded by the addition of methanol, acetone, methyl acetate. An activation energy of -2.5 Kcal/mole was found in the study of the influence of the reaction temperature. These various results suggest strongly that the observed polymerization involves a cationic mechanism.

It has been noted that the radiation-induced cationic polymerization of isobutylene is very sensitive to small quantities of water[12,13]. Similar studies in the radiation-initiated polymerization of styrene in bulk was carried out in an extremely dry system by Okamura[14-17] and by Metz[18,19].

Metz use baked silica gel and high temperature bake-out of glassware to achieve rigorous dry condition. As the drying process is made more efficient, they observed the absolute values of the rates of polymerization increase and the dose rate dependence of the rate increases to 1. However, with the highest purity styrene the dose rate dependence of the rate shifts back to 0.65[20]. They proposed the probable relative importance of active species under different conditions of dryness of styrene as follows:

Relative water content	Relative rate of polymerization R_p	Dose rate dependence of R_p (n)	Possible propagating species
High	Low	$n = 1/2$	R•
Low	High	$n = 1$	R^+
very low	very high	$1/2 < n < 1$	R^+ and R^-

Okamura et al.[14] dried styrene by using sodium-potassium alloy. Wet monomer, dried by CaH_2, was used in comparison. The activation energy from molecular weight measurements in the dry system was estimated to be -0.9 Kcal/mole between -20 and +40°C, while in the wet system the molecular weight increased with temperature. The polymerization is strongly retarded by ionic scavengers, e.g., water, ammonia and amines. The copolymerization of styrene with α-methylstyrene was carried out and the results obtained were as follows:

Dry system:	$r_1(\mathrm{St})=0.25\pm0.20$;	$r_2(\mathrm{MSt})=8.5\pm4.0$
Wet system:	$r_1(\mathrm{St})=2.2\pm0.2$;	$r_2(\mathrm{MSt})=0.6\pm0.2$

These results can be compared with the values measured by conventional chemical-initiated polymerization.

Radical[21]	$r_1(\mathrm{St})=2.3$;	$r_2(\mathrm{MSt})=0.38$
Na-THF[22]	$r_1(\mathrm{St})=10.5\pm0.5$;	$r_2(\mathrm{MSt})=0.08\pm0.02$
$TiCl_4$-Toluene[22]	$r_1(\mathrm{St})=0.54\pm0.04$;	$r_2(\mathrm{MSt})=3.6\pm0.1$

These facts strongly suggest a free-cationic mechanism in the super-dry system and a free radical mechanism in the wet system.

Williams[17] provided a rather successful quantitative model for the radiation-induced ionic polymerization of certain vinyl monomers. In the case of super-dried styrene, the model can be summarized as:

Initiation

$$M \xrightarrow{\gamma} M^+ + Y^-$$

$$M^+ + M \xrightarrow{k_i} M\text{-}M^+$$

Propagation and Transfer

$$M_n^+ + M \xrightarrow{k_p} M_{n+1}^+$$

$$M_n^+ + M \xrightarrow{k_f} M_n + M^+$$

Termination by impurities $M_n^{+} + X \xrightarrow{k_{tx}} M_n + X^{+}$

Termination by recombination $M_n^{+} + Y^{-} \xrightarrow{k_t}$ product

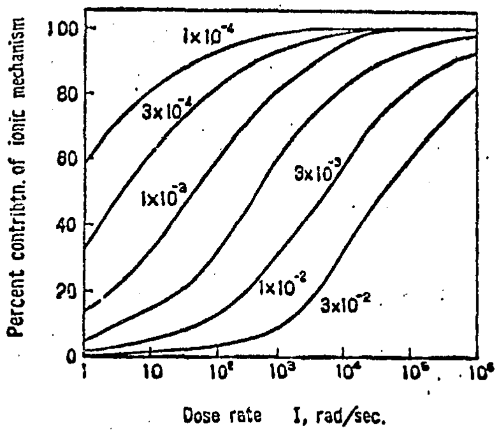
Invoking steady-state kinetics, the rate of polymerization can be expressed as:

$$R_p = \frac{R_i k_p[M]}{(R_i k_t)^{0.5} + k_{tx}[X]}$$

When the impurity level is insignificant, $(R_i k_t)^{0.5} \gg k_{tx}[X]$ and $R_p \propto R_i^{0.5} \propto I^{0.5}$. When the impurity level is quite high but still allows for predominating ionic propagation, $k_{tx}[X] \gg (R_i k_t)^{0.5}$ and $R_p \propto R_i \propto I$. In general, it is to be expected that $R_p \propto I^n$ and $0.5 \leq n \leq 1$ depending on the importance of impurity termination relative to ion-ion recombination. Williams[17] calculated dose rate dependence of R_p for styrene as a function of water concentration: $[X]=0$, $n=0.50$; $[X]=10^{-10}$M, $n=0.52$; $[X]=10^{-9}$M, $n=0.69$; $[X]=10^{-8}$M, $n=0.91$; $[X]=10^{-7}$M, $n=0.98$. Okamura et al.[23] found that the presence of water in excess of 10^{-2} mole/liter completely supresses the ionic mechanism, and thus only free-radical polymerization was observed in the earlier studies where no special precautions had been taken to remove the last traces of water from the styrene monomer.

Huang and Westlake [24-28] have shown that polymerization of styrene by radiation may occur simultaneously by both a free radical and a cationic mechanism for water concentrations of 10^{-2} to 10^{-3} moles/ liter. Evidence for this came from the results of kinetic studies and the resulting molecular weight distribution determined by gel-permeation chromatography. The dependence of the rate of polymerization on the dose rate at -10°C varied from 0.53- to 0.71- power as the water content of the sample varied from 7.5×10^{-3} to 1.0×10^{-3} mole/l. A value of 3.1 Kcal/mole was determined for the overall activation energy. The molecular weight distributions were bimodal in nature, each peak corresponding to one of the above mechanisms, and were found to be very sensitive to conditions of sample preparation and polymerization.

V. Stannett et al.[29] investigated radiation-induced polymerization of not rigorously dried styrene at higher dose rate up to 3 Mrad/sec., and a substantial contribution to the polymerization of concurrent cationic process was observed. J. Takezaki et al.[30] recently carried out similar experiments in a dose rate range of 4.2×10 to 2.1×10^{5} rad/sec. The water content of styrene wes varied between 3.2×10^{-3} and 3.5×10^{-2} mole/l. They estimated the contribution of radical and cationic mechnisms in the following figure (curves correspond to water contents mole/l.).



The figure shows that at a very high dose rate, such as 10^{6} rad/sec, the ionic mechanism is dominant, even in the case of water-saturated styrene.

Solvent Effect

In conventional free radical polymerization in solution, a number of cases are known where the solvent does not interfere with any of the reaction steps and solely acts as an inert diluent. However, in radiation polymerization, any added solvent is radiolysed and this leads to the production of additional free radicals, which may contribute to chain initiation. Accordingly, the simple dilution effect in radiation polymerization was defined as pertaining to a system in which effective energy transfer processes do not occur, i.e. in which the total rate of production of free radicals is a linear function of the mononer content in the mixture. ϕrel is defined as the ratio of the two rate constant of free radical production in the solvent and in the monomer. The radiation polymerization of styrene dissolved in aromatic hydrocarbons was studied by Chapiro[31] and 'ϕrel=1' was found in benzene system.

It was also shown that when the concentration of monomer (radical scavenger in the system) is lowered below a critical value, complete scavenging no longer occurs and a number of the primary radicals undergo recombination. The "critical concentration" of monomer increases with the dose rate. The influence of the dose rate of gamma-rays was also investigated in styrene-toluene solution over broad ranges of both dose-rate and monomer concentrations. The results show that the "critical dose-rate", above which the dose rate exponent drops below 0.5, steadily decreases when styrene is diluted in toluene.[32]

3. Graft Polymerization

Techniques

In general, two fundamental processes are available for radiation-induced grafting.

(a) Pre-irradiation method.

The polymer is irradiated, either in the presence of air or its absence, before being brought into contact with the monomer whether in liquid, gaseous or solution form. Irradiation produces trapped radicals in the polymer matrix that subsequently react with the monomer, giving grafting and some homopolymerization. This homopolymerization occurs through chain transfer to the monomer.

Difficulties often put forward against the use of pre-irradiation as a technique usually center around the sensitivity of the polymer to radiation damage and factors related to the monomer diffusion.

(b) Mutual irradation technique

The polymer is irradiated in the presence of a monomer and in the absence of oxygen. Usually the radiation step was carried out after the system has reached swelling equilibrium. Graft copolymerization of the monomer to the polymer is then initiated through the free radicals or active ions generated in the latter. However, ionizing radiation is unselective. Homopolymer is formed at the same time with the graft copolymer.

Diffusion Effect

In the mutual irradiation technique for carrying out graft polymerization, a solid polymer sample such as a film is immersed in and equilibrated with a liquid monomer and the mixture then exposed to radiation such as from ^{137}Cs or ^{60}Co gamma radiation. Radiation forms radical sites on the polymer and grafting of the monomer takes place at these sites. As the grafting reaction progresses, more monomer from outside the polymer diffuses into its interior to replace that which has reacted. The grafting reaction consists of a diffusional process followed by a polymerization process and may become diffusion-controlled under certain reaction conditions involving the interplay of diffusional and kinetic parameters. The diffusional parameters are those related to the ability of monomer to diffuse into the polymer: the polymer film thickness L and the diffusivity of the monomer in the polymer D. The kinetic parameters are those concerned with the chemical reaction: the equilibrium solubility M of monomer in polymer prior to irradiation, the rate constants k_p and k_t for propagation and termination, respectively, and the rate of initiation R_i of graft polymerization.

The rate of iniation is generally given by the expression

$$R_i = 2.9\mathrm{x}10^{-7} \; d \; G \; I \qquad (1)$$

where d is the sample density (g/ml), G is the number of polymer radicals produced per 100 eV of absorbed dose, and I is incident radiation intensity(Mrad/hr); the constant $2.9\mathrm{x}10^{-7}$ contains conversion factors to obtain R_i in units of moles/liter-second.

Earlier Odian and coworkers developed the expression[1]

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

where $$A = [(k_p/k_t^{1/2})(R_i^{1/2}/D)]^{1/2}L/2 \qquad (3)$$

to describe quantitatively the interaction of the kinetic and diffusional parameters in leading to diffusion-free or diffusion-controlled reaction according to the value of A. $\bar{R}_p$, the experimental graft polymerization rate, is the rate averaged over the film thickness.

Two limiting cases of eq.(2) arise depending on the interplay of the kinetic and diffusional parameters.

Case I. Diffusion-free reaction occurs at low values of A when chemical reaction is slow relative to diffusion of monomer, i.e., when R_i, k_p, and L are small and/or k_t and D are large.

Case II. Diffusion-controlled reaction occurs at higher values of A when diffusion of monomer is slow relative to chemical reaction, i.e., when R_i, k_p and L are large and/or k_t and D are small.

Under diffusion-controlled reaction conditions, a monomer concentration profile develops within the polymer film thickness. The concentration of monomer is M at the two surfaces and decreases as one moves toward the center of the film as monomer diffusion lags behaind chemical reaction. As diffusion control becomes more extreme (i.e., as A becomes larger), a progressively larger region develops in the center of the film which is almost devoid of monomer.

The original derivation of eq.(2) required specific assumptions on the dependencies of R_p and k_p, k_t, R_i and the monomer concentration under diffusion-free polymerization conditions. Specifically, the derivation of eq.(2) assumed

$$R_p = (k_p/k_t^{1/2})\, R_i^{1/2}\, C \qquad (4)$$

where C is the monomer concentration. Equation(4) is the usual situation in homopolymerization; it has also been assumed to apply to radiation-initiated graft polymerization. However, recent experiments by Odian and coworkers[3,4] indicate that eq.(4) is not valid for the radiation-initiated graft polymerization of styrene to polyethylene under diffusion-free conditions as has been assumed by workers with this system for over two decades. They have observed the following three situations depending on the value of the radiation intensity I:

Low I:	$R_p \propto C^{3/2}\, I^{1/2}$	(5)
Medium I:	$R_p \propto C^{5/2}\, I^{1/4}$	(6)
Higher I:	$R_p \propto C^{5/2}\, I^{0}$	(7)

These results were for diffusion-free reaction as shown by the fact that the reaction rates were independent of film thickness in the range 1-5 mils. (In these experiments $C \simeq M$) In these experiments, the styrene concentration was varied by dilution with benzene. Based on these results, it is clear that the previous derivation of eq.(2) was based on an invalid assumption as to the diffusion-free expression for the grafting rate.

Odian and coworkers[75] then presented a more general derivation of $\overline{R}_p$ based on fewer assumptions for the diffusion-free reaction. First, the derivation was more general in assuming that the initiation rate may be concentration-dependent, i.e., R_i is given by the expression

$$R_i = 2.9\text{x}10^{-7}\ d\ G\ I\ k\ C^n \qquad (8)$$

where n can have any value, and k would be an appropriate constant or rate constant or collection of rate constants and concentration terms (concentrations of species other than monomer which can react with primary radicals). Equation(8) becomes equivalent to eq.(1) when initiation is independent of monomer concentration, corresponding to the case of k=1 when n=0. Second, the expression for the rate of graft polymerization under diffusion-free conditions is assumed to be expressed by

$$R_p = (k_p/k_t^{\,z})(2.9\text{x}10^{-7}dGkI)^wC^v \qquad (9)$$

where z,w,and v can have any values. The value of the concentration exponent v in eq.(9) includes the value of n.

The choice of the values of z, w and v are based on a considerable range of possible kinetic situations one might reasonalbly encounter under different conditions, e.g., for radical polymerizations.

<u>Case A</u>. z=1/2, w=1/2, v=1, k=1 corresponds to the usual situation in polymerization (termination by coupling between propagating radicals; initiation independent of monomer, i.e., n=0).

<u>Case B</u>. z=1/2. w=1/2, v=3/2, k=k corresponds to the same situation as in case A except that initiation is first-order in monomer (n=1).

<u>Case C</u>. z=1, w=0, v=2, k=k corresponds to termination by the coupling of propagating radicals with primary radicals, and initiation is first-order in monomer (n=1).

<u>Case D</u>. z=1/2, w=1/2. v=5/2, k=k corresponds to the same situation as in case A except that initiation is third-order in monomer (n=3).

<u>Case E</u>. z=1, w=0, v=3, k=k corresponds to case C except that initiation is second-order in monomer (n=2).

As indicated, the above list of kinetic situations is for polymerizations initiated by radicals. Various kinetic situations can be envisioned if initiation were by ionic species, e.g., initiation would probably be first-order in radiation intensity (w=1); nonterminating ionic polymerization would involve z=0.

Assuming D is a constant, the grafting rate $\bar{R}_p$ averaged over the entire thickness of the polymer film is expressed by:

$$\bar{R}_p = (2D/L)(2a/D)^{1/2}[(M^{v+1}-C_o^{v+1})/(v+1)]^{1/2} \qquad (10)$$

where

$$a = (k_p/k_t^{z})\ (2.9\text{x}10^{-7}\ \text{dGkI})^{w} \qquad (11)$$

and C_o denotes the monomer concentration at the center of the film.

Two important limiting cases for graft polymerization can be identified: diffusion-free reaction and diffusion-controlled reaction.

Case I. Diffusion-Free Reaction. The monomer concentration profile is flat in this case. This may be due to various factors such as small film thickness, high diffusion constant, low radiation intensity, slow propagation, fast termination. In any case, sice C=M throught the film thickness, the diffusion-free reaction rate is obtained as

$$(\bar{R}_p)_{df} = a\,M^{v} \qquad (12)$$

Case II. Diffusion-Controlled Reaction. In this case, there is a sharp decrease in the monomer concentration profile as one proceeds from the film surface toward its center; the monomer concentration approaches zero very closely at the center. Thus by setting $C_o=0$ in eq.(10), the diffusion-controlled grafting rate is obtained as

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

These results reduce to those reported for the linear case in which the diffusion-free rate is linear in monomer (i.e., v=1). [Specifically, eqs. (12) and (13) reduce to eqs. (14) and (15), respectively.]. e.g., for Case A condition.

$$(\bar{R}_p)_{df} = (k_p/k_t^{1/2})\,R_i^{1/2}M \qquad (14)$$

$$(\bar{R}_p)_{dc} = 2(k_p/k_t^{1/2})R_i^{1/4}MD^{1/2}/L \qquad (15)$$

We see that the dependence of $\overline{R}_p$ on L is still the same as the linear case, namely, $\overline{R}_p$ is constant in the diffusion-free region and inversely dependent on the first power of L in the diffusion-controlled region. The dependence of $\overline{R}_p$ on the various kinetic and diffusional parameters in the term a is also analogous. In the diffusion-free region, the dependence of $\overline{R}_p$ on a is first order, which means that the dependencies of rate on the termination rate constant and initiation rate (i.e., the radiation intensity) are z-order and w-order, respectively, while there is no dependence on D. The dependence of $\overline{R}_p$ on a is 1/2-order in the diffusion-controlled region; i.e., the dependencies of rate on k_t and I are z/2-order and w/2-order, respectively, and the dependence on D is 1/2-order. However, it is clear that the dependence of $\overline{R}_p$ on M is different than in the linear case. If the diffusion-free rate is v-order in M, the diffusion-controlled rate shows a (v+1)/2-order dependence on M. To summarize, the effect of diffusion control is to change the dependence of rate on a from first order to 1/2-order and the dependence on M from v-order to (v+1)/2-order, irrespective of the particular values of n, w, z and v.

The mathematical calculations have been performed for the case in which D is assumed to be a constant. Although this may not be the case for many polymer-penetrant systems, it is a reasonable assumption for a system in which the monomer is diluted with a solvent which has the same properties as the monomer. e.g., styrene-benzene system.

Literature Review

The radiation initiated graft polymerization of styrene to polyethylene by the mutual irradiation technique is the most thoroughly studied radiation grafting system. However, the kinetics of the reaction are not well-established, especially the dependence of grafting rate on monomer concentration. For more than two decades, workers have assumed that this dependence is first-order as is normal in radical homopolymerization.

Silverman and coworker[33,34] varied the styrene concentration by diluting it with methanol, a non-solvent for grafted polystyrene and itself does not swell polyethylene at all. They observed that the grafting rate increased initially with monomer concentration, reached a maximum, and then decreased as monomer concentration increased further. The latter decrease has been attributed to a decrease in viscosity inside the polymer with increasing styrene concentration, resulting in an increased rate of termination relative to propagation. Similarly, Wilson[35] found the grafting rate to increase in the order polyethylene > polypropylene > poly(4-methylpentene) while the styrene concentrations increased in the reverse order -- results which are analogous to the previously described studies. Unfortunately, in all such studies the monomer concentration has been varied simultaneous with the viscosity inside the polyethylene since the latter varies with the amount of liquid absorbed.

Using styrene-alcohol-benzene mixtures, Wilson[36] attempted to vary the monomer concentration while keeping viscosity constant by varying the alcohol used and its relative amount to obtain solutions having the same value of the Hildebrand solubility parameter. But this promising approach was used with the assumption that the composition of the styrene-alcohol-benzene solution absorbed into a polymer sample (inside solution) was the same as the composition of the solution in which the sample was placed (outside solution) and, also, that the amount of solution absorbed by the polymer was independent of the composition of the outside solution. Previous work by Odian[37] and Silverman[33] indicate that both assumptions may not be true in styrene-methanol-polyethylene system.

Studying the styrene-polythylene grafting system, Chandler[38] found the k_p^2/k_t value to be 0.28 liter/mole-sec. On the other hand, Tobolsky and Baysal[39] obtained a value of 0.000114 liter /mole-sec. for the homopolymerization of styrene at the same temperature. Similar high k_p^2/k_t value has been observed for the styrene-PVC system.[40] Such a large difference is not surprising in view of the highly viscous nature of the grafting medium- the swollen polymer matrix. At higher viscosities, bimolecular chain termination of the radical chains is hindered, whereas the other steps in the polymerization process namely initiation, propagation and radical transfer processes are not affected to the same degree by increasing viscosity because the molecules involved are smaller and more mobile. This Trommsdorff effect (gel effect) is strongly solvent-dependent.

The swelling and diffusion ability of a monomer in a polymer are two major factors to determine whether the grafting will occur inside of polymer or on the surface only. If the monomer does not swell the polymer, a swelling agent will be needed to make the polymer available for monomer diffusion.

Huang and Rapson[41] found that in the absence of water as a swelling agent, no grafting was obtained in the styrene-cellulose fiber system. Guthrie[42] found that 2% of water in a monomer-solvent system greatly enhances the accessibility of the cellulose to the monomer solution. He studied the kinetics of grafting in the cellulose-styrene-dioxan-water system, and observed the first order dependence of the grafting rate on the inside monomer concentration. A high k_p^2/k_t (58 l/moles-sec.) value was obtained.[43]

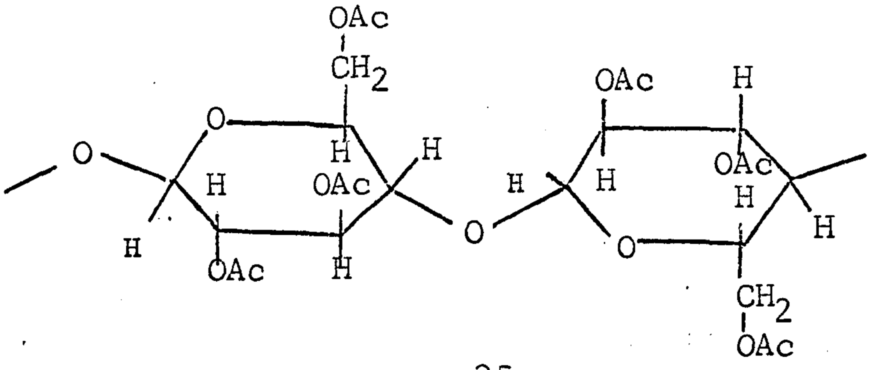
Secondary cellulose acetate is not soluble in styrene but is soluble in pyridine. The radiation grafting of the styrene-pyridine-cellulose acetate system has been investigated by Stannett [44,45]. The grafting yield goes through a maximum at a particular pyridine-styrene ratio. At low degrees of swelling insufficient monomer diffuses to the active centers (free radicals) created in the cellulose acetate substrate by the radiation. As the swelling is increased the availability of monomer to the radicals is facilitated but the termination rate is also enhanced. Consequently, a maximum in both the grafting yield and the molecular weight is reached. The grafting rate increases with both decreasing dose-rate and decreasing thickness. The results show clearly the diffusion controlled nature of the reaction. Yasukawa et. al.[46] have studied the kinetics of the grafting reaction of styrene to preirradiated cellulose acetate by labeling the active sites with bromine atoms. The dilution of styrene monomer with methanol affected grafting reactions remarkedly: e.g., as the concentration of methanol in monomer solutions increased, the growth rates of individual graft chains decreased while the average life time of the radicals increased. The amounts of graft chains were in proportion to the extents of swelling of cellulose acetate. Grafting rate for 50% styrene was higher than those for 25% styrene and 75% styrene.

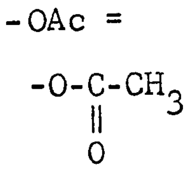
Recently Odian and coworkers have systematically studied the styrene-high density polyethylene[3,4], styrene-low density polyethylene, 4-vinylpyridine-polyethylene[2] grafting systems. The results have shown that the mechanism of the diffusion-free radiation graft polymerization of styrene to polyethylene is not well established. This is especially the case for the dependence of the reaction rate on monomer concentration which is much higher than previously assumed -- increasing from 3/2-order at low dose rates to 5/2-order at intermediate and higher dose-rate.

4. Cellulose Esters

Cellulose is one of the most abundant and widely used organic polymers in the world. Its principal sources are wood and cotton, and it is possible to modify it chemically so as to increase its usefulness. The first organic acid ester of cellulose was cellulose acetate, prepared by Schutzenberger[47] in 1865 by heating cotton and acetic anhydride to about 180°C in a sealed tube until the cotton dissolved. Franchimont[48], in 1879, acetylated cotton at lower temperatures with the aid of a sulfuric acid catalyst. In 1903, Miles [49] described partially hydrolyzed cellulose acetate and distinguished between his new product and the fully acetylated products.

Esterification is performed by mixing cellulose with the appropriate organic acids, acid anhydrides, and catalysts. This mixture is allowed to react until the triester is formed. In the triester form, the three hydroxyl groups per anhydroglucose unit have been replaced with the acyl groups of the organic acid. If two different organic acids are used simultaneously, the cellulose ester formed will be of the mixed ester type--e.g., cellulose acetate butyrate or cellulose acetate propionate. Cellulose triacetate has following chemical structure:





$-OAc = -O-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$

Polymer chemists have found the fully acylated cellulose esters to be of little value in the plastics and coatings industries. Some free hydoxyl groups along the chain are necessary to effect solubility, flexibility, compatibility, toughness, etc. Acylation directly to a predetermined degree less than the triester is not feasible, however, if a uniform, soluble product is desired. Therefore, the cellulose is fully acylated and then hydrolyzed back to the desired hydroxyl level. The secondary acetate contains an acetyl content of 36-42%.

Table 1

Amount of Acetyl Group in Cellulose Acetate

Degree of Substitution (DS)	% Acetyl (*)	% Combined Acetic Acid (**)
1.0	21.1	29.4
1.5	28.7	40.0
2.0	35.0	48.8
2.5	40.3	56.2
3.0	44.8	62.5

$$(*)\text{% Acetyl} = \frac{\text{Amount of } CH_3CO \text{ Group}}{\text{Weight of Repeat Unit}}$$

$$(**)\text{% Combined Acetic Acid} = \frac{\text{Amount of } CH_3COOH}{\text{Weight of Repeat Unit}} = \frac{60}{43} \text{ x(%Acetyl)}$$

The properties of unplasticized cellulose acetate are dependent on the amount and type of acetyl groups present and on the molecular weight. For instance, cellulose triacetate is soluble in chloroform but insoluble in acetone. Once the acetyl content decreases to 37-42% the substrate becomes soluble in acetone but insoluble in chloroform; 24-32% acetate is insoluble in acetone but soluble in 2-methoxy-ethanol; 13-19% cellulose acetate is insoluble in 2-methoxyethanol but soluble in water; a further decreasing to a less than 13% acetyl content, the substrate becomes insoluble in all the solvents just mentioned[50]. In short, as the acetyl content decreases, the solubility in polar solvent increases while the solubility in nonpolar solvent decreases.

Pure esters of bulkier alkyl radicals such as butyryl proved to be more soluble and more compatible than cellulose acetate, but were soft and low-melting. Consequently, they were not in themselves very useful in coating application. However, when cellulose was esterified with both acetyl and butyryl groups to form a mixed ester, cellulose acetate butyrate(CAB), it was found that many of the advantages and desirable properties of both esters could be obtained.

Low-butyryl esters are very simiilar to cellulose acetate in solubility, compatibility and performance, and are used primarily for wire coatings,airplane dopes and cements, and the preparation of photographic films. Esters with somewhat higher butyryl content,which are more compatible with resins and plasticizers, are used for much the same applications but only where solvent and grease resistance is not quite as critical. Solution grade CA are also used to make membranes for reverse osmosis applications such as artificial kidney, desalination of water, or the purification of industrial wastes.

EXPERIMENTAL

(A) CHEMICALS

1. Styrene and Benzene -- Monomer and Diluent

Styrene was chosen as the monomer in our grafting system because it was a well-studied monomer in other systems and unusual kinetic behavior has been observed in the diffusion-free polyethylene-styrene graft system. Styrene was washed three times with 10% sodium hydroxide solution to extract stabilizer, t-butyl catechol, and then washed with water until the washings were neutral. The monomer was dried over magnesium sulfate in the freezer (-10°C) overnight and then vacuum distilled before use.

In order to properly study the kinetics of grafting, it was necessary to choose the experimental system such that the inside styrene concentration could be varied without varying the inside viscosity. The use of benzene as a diluent for styrene was considered since benzene and styrene have similar solubility, diffusion, viscosity and radiation characteristics. Some of the physical properties of styrene and benzene are listed in Table II. δ values are the Hildebrand solubility parameters; η is the viscosity; n_D is the refractive index; G-value is the number of radicals produced per 100 e.v. of absorbed energy. One expects the extent of homopolymerization relative to graft polymerization to be the same for styrene-benzene mixtures as for styrene and that the presence of benzene should not introduce appreciable energy transfer processes due to the similarity of the two compounds.

Table II

Some Physical Properties of styrene and benzene [a]

Property	Styrene	Benzene
n_D^{20}	1.5468	1.5011
density(g/ml)	0.9060	0.87865
boiling point	145.2°C	80.1°C
melting point	-30.63°C	5.5°C
δ (cal/cc)$^{1/2}$ [b]	9.3	9.2
η (cp)	0.564(30°C)	0.587(38°C)
G [c]	0.69	0.74
molecular wt.	104.16	78.12

(a) all data from ref. 51 unless otherwise indicated.

(b) from ref.52.

(c) from ref. 5, p.260.

2. Cellulose esters -- parent polymer

Cellulose ester samples in powder form with different combinations of acetate and butyrate contents in different molecular weights and containing no additives were supplied by Eastman Kodak Company. polymeric films were cast from solution at our laboratory.

Since the acetyl content and the viscosity of a particular cellulose acetate greatly affect the properties of the product made from the ester, Eastman employs these values as the primary means of identifying the various types of cellulose acetate.[53] The identification system is shown with cellulose acetate CA-398-6 as an example. The acetyl content of the ester is indicated by 398 which follows the letter prefix-CA. This three-digit number expresses the average acetyl content of the ester as percentage by weight, but the decimal point which should appear between the second and third figures is omitted. Although not indicated in the code name, the hydroxyl content of a cellulose acetate may be readily determined from knowledge of the acetyl content: % Hydroxyl = (44.80 - % Acetyl) / 1.42. The viscosity of the ester, which is a function of its chain length or molecular weight, is shown by the fourth digit, 6 in the example. The higher the figure for viscosity, the greater the molecular weight; the lower the viscosity, the lower the molecular weight. Viscosity is determined by ASTM Method D-1343 in the solution described as Formula A, ASTM Method D-871. The result in poises is converted to ASTM seconds equivalent to values obtained under ASTM Method D-871. The viscosity term represents the time seconds required for a 5/16-inch steel ball to fall through 10 inches of a 20-percent solution in a 90:10 by weight mixture of acetone/ 2B denatured alcohol at 25°C in a 1-inch tube.

In naming the Cellulose Acetate Butyrate, however, the appoximate percentage of butyryl, only, is indicated. The nomenclature for CAB-381-0.1, for example, is shown as follows: the first two digits (38) indicate approximate butyryl content (38%) at the triester level--i.e., prior to hydrolysis. The extent of hydrolysis is indicated by the third digit, which represented the approximate number of hydroxyl groups per four anhydroglucose units in the cellulose ester chain. Viscosity is 0.5 seconds, determined by a falling-ball procedure identical to that used for cellulose acetate.

Table III

Number average molecular weights* of Eastman cellulose esters

CA	M_n	CAB	M_n
CA-383-40	52,000	CAB-171-2	43,000
CA-394-30	53,000	CAB-171-15	66,000
CA-394-45	58,000	CAB-171-25	74,000
CA-394-60	61,000	CAB-171-40	83,000
CA-398-3	27,000	CAB-272-3	45,000
CA-398-6	35,000	CAB-272-20	68,000
CA-398-10	37,000	CAB-381-0.1	20,000
CA-400-25	48,000	CAB-381-0.5	29,000
		CAB-381-2	46,000
		CAB-381-20	77,000
		CAB-500-1	42,000
		CAB-500-5	69,000
		CAB-531-1	44,000
		CAB-551-0.2	25,000

* data supplied by Eastman laboratory

The degree of substitution (x) can be calculated by the acetyl content of the cellulose acetate.

$$\frac{43\ x}{\%\ \text{Acetyl}} = \frac{157 + 1\ (3-x)}{100 - \%\text{Acetyl}} \quad (\text{for CA})$$

where 43 is the molecular weight of acetyl group CH_3CO-; 157 is the molecular weight of polymer backbone repeat unit $C_6H_5O_5$; 1 is the atomic weight of hydrogen for hydroxyl group. As for the cellulose acetate butyrate, the degree of substitution (DS) of acetyl (x) and the DS of butyryl (y) could be calculated by following equation:

$$\frac{43\ x}{\%\ \text{Acetyl}} = \frac{71\ y}{\%\ \text{Butyryl}} = \frac{157 + 1\ (\ 3 - x - y\ )}{100 - \%\ \text{Acetyl} - \%\ \text{Butyryl}} \quad \text{(for CAB)}$$

where 71 is the molecular weight of the butyryl group C_3H_7CO-. For instance, CAB-171-40 (Eastman batch AM1934B) has an acetyl content of 29.7 weight-percent, a butyryl content of 17.5 weight-percent, and can be translated to the DS of acetyl= 2.06; DS of butyryl= 0.73; DS of hydroxyl= 0.21.

(B) APPARATUS

1. Vacuum Distillation

The distillation apparatus is shown in Figure 1. The system consisted of a variable transformer a, a 1 liter or 500 milliliter distillation flask c with a inner ₸24/40 joint, a heating mantle b matched with the size of the flask , a 60 cm long Vigreaux distilling column d with ₸24/40 joints, a distillation head e, a collecting flask f, a cold trap t cooled by dry ice-acetone mixture, a vacuum gauge and a mechanical pump. The distillation head has a joint ₸10/30 for 3-inch immersion thermometer g and a 20 cm long separable cold-finger condenser h with joint ₸29/42. Tap water was circulated through the head at all times during distillation. It entered the distillation head at m exitted at n, reentered at o of the cold-finger

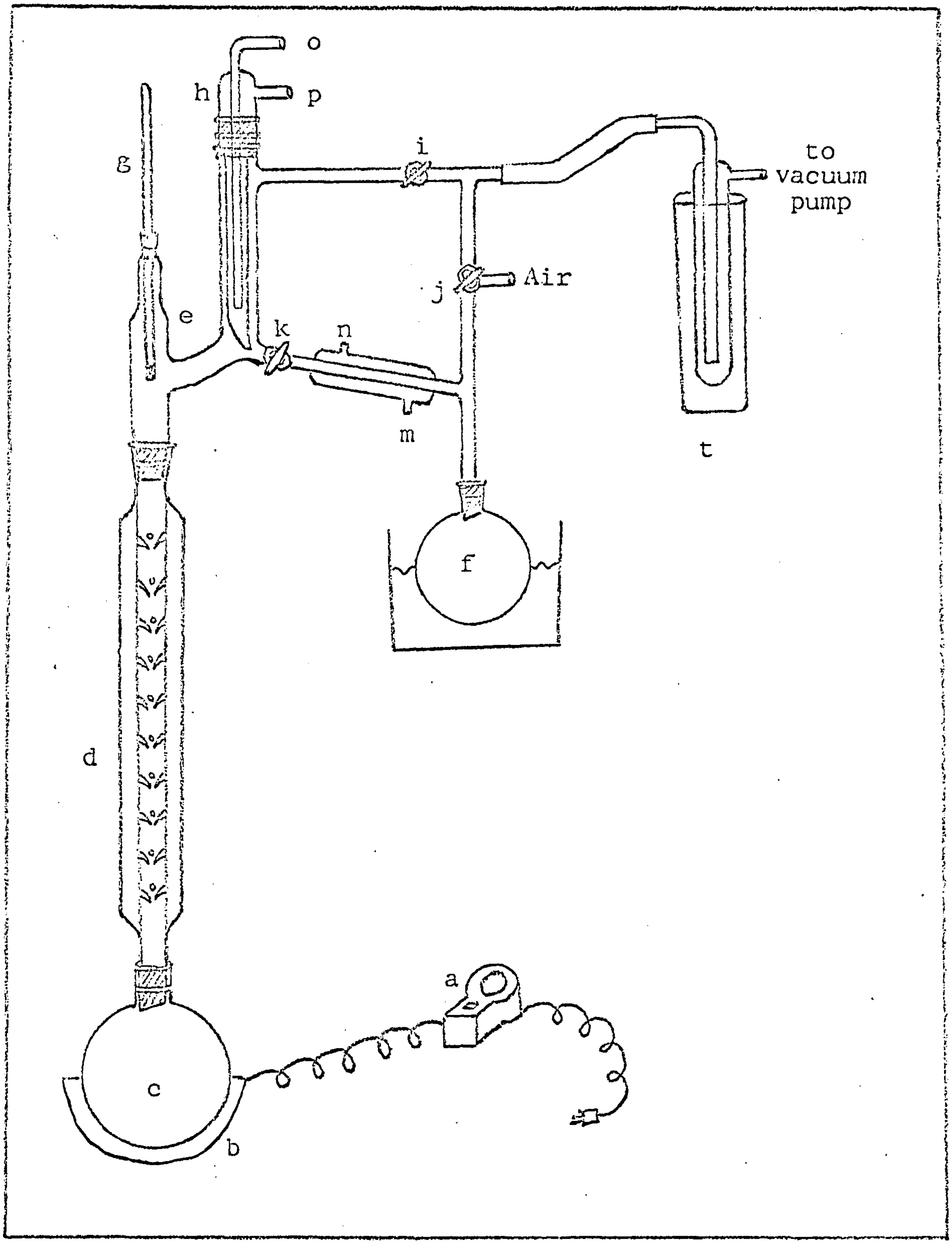


Fig. 1 The Vacuum Distillation Apparatus for purifying styrene

condenser and finally exited at p. The blue Teflon sleeve was used for the joint of the receiveing flask instead of grease. The receiver was always kept in ice-water bath to prevent evaporation. The stopcock manifold allows the contents of the receiver to be removed without disturbing the vacuum. This can be achieved by simply closing the valve k and opening the three-way valve j to the air. The collector can then be separated and replaced with another. The distillation can be resumed by opening valve j to vacuum and opening of the valve k. The distillation of styrene was carried out at a pressure of 10 mm Hg. The purest fraction of styrene can be collected at 33°C. The heating rate can be controlled by the variable transformer.

2. Vacuum line system with mercury diffusion pump

The vacuum system consisted of a mechanical pump, a screw-type Glocoil heater a connected with a variable transformer b, a mercury diffusion pump c, 3 cold traps d, 6 male ₸24/40 joints connected to the vacuum line e, and a McLeod vacuum gauge f. The entire sytem is shown in Figure 2. 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 cooled by liquid nitrogen was connected to the mercury diffusion pump through the same tubing, This diffusion pump was connected to the another two cold traps in series with a glass ball-joint §35/25 in between, then came the vacuum line which was fused to the other end of the

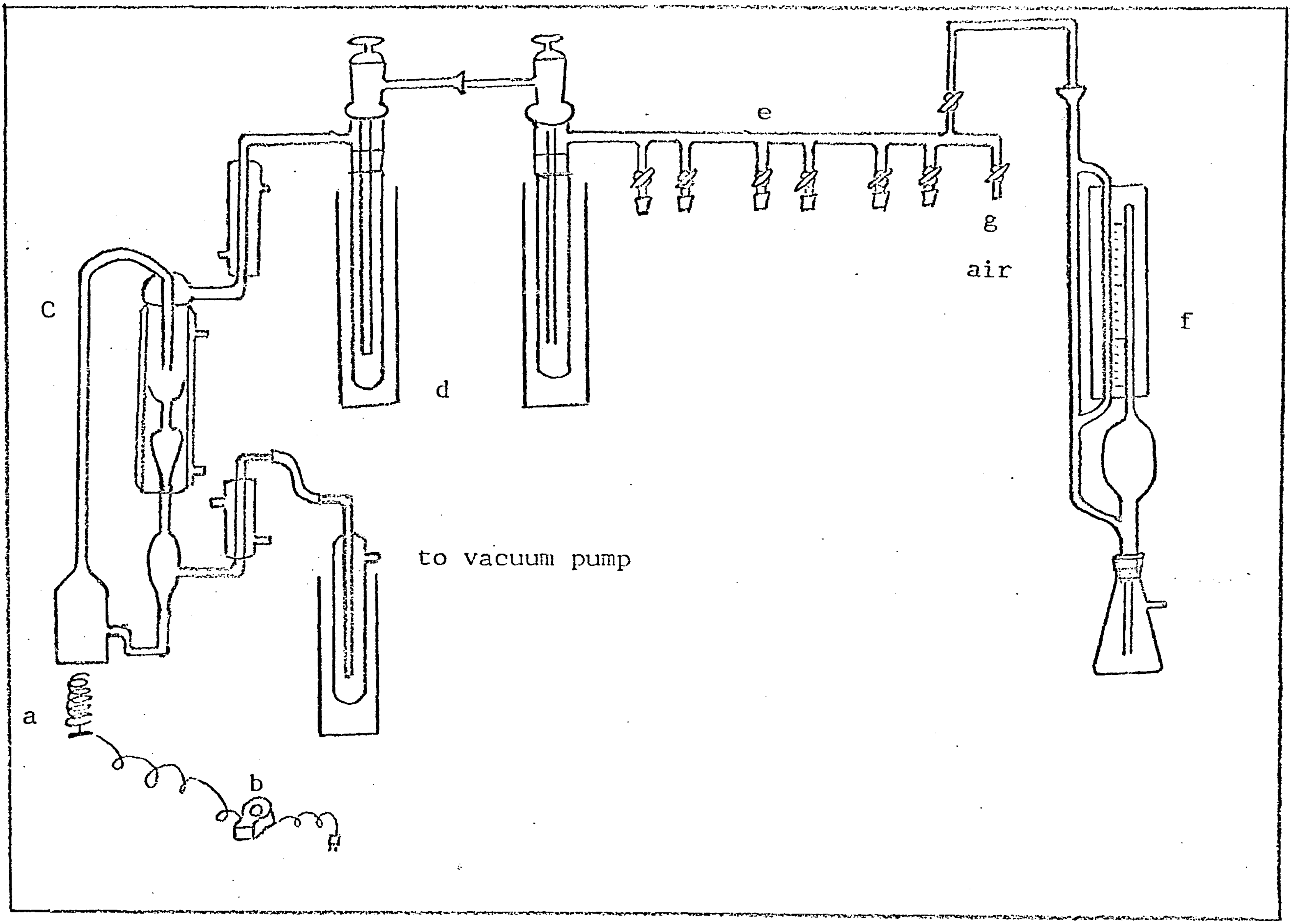


Fig. 2   Vacuum Line System with Mercury Diffusion Pump

traps. Finally the vacuum line was connected to the McLeod gauge through a §12/5 joint in between.

The vacuum line was a 3 cm o.d., approximately 120 cm long glass tubing. Three pairs of §24/40 male joints were fused to it through stopcocks and they were placed 20 cm apart from each other. Each individual joint in a pair was separated from the other by 8 cm. 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 _g_ used merely to let the air in when the operation is complete.

The McLeod gauge can read vacuum up to 10^{-6} mm Hg. Vacuum could be easily achieved at 10^{-4} torr with this system. the bottom flask of the gauge was connected to the water aspirator and air through a three way valve.

After completion of the operation, the Glocoil heater must be turned off first, the cooling dewar for the traps can then be removed after the mercury pump reaches room temperature, to avoid any mercury vapor entering the laboratory. Finally air is let into the system through the opening of valve _g_.

3. The Radiation Source

The gamma source used in this work was a 10,000 curies J.L.Shephered, Mark 1, Model 68, Cs^{137} irradiator, located at the College of Staten Island. The source and its components are shown in Figure 3.

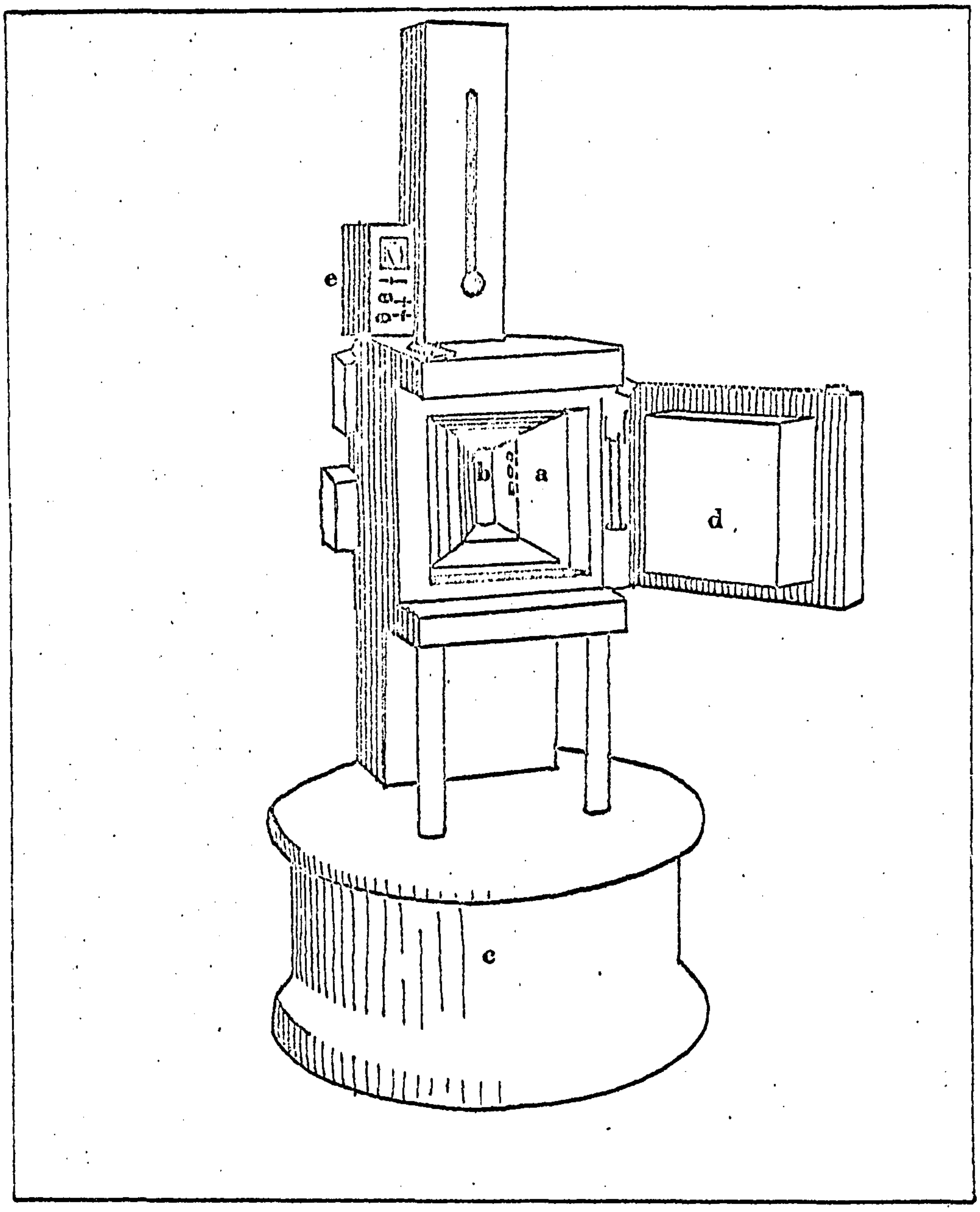
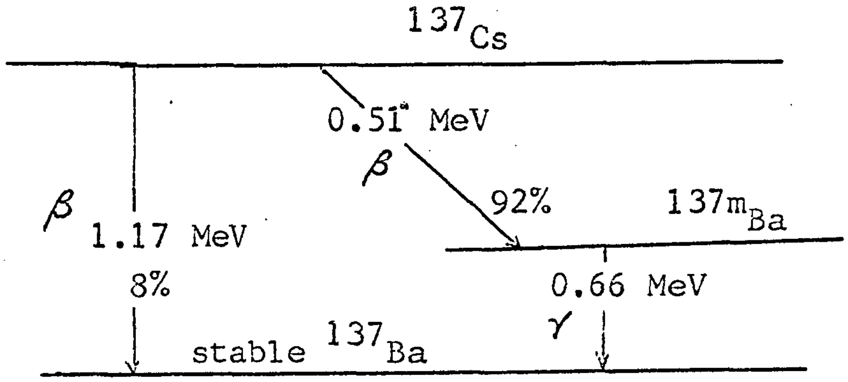


Fig. 3 Cs^{137} gamma irradiator "Mark 1, Model 68"

The source cavity has a triangular pyramid shape <u>a</u> with the source column located at the apex <u>b</u>. The source is kept in a shielded area <u>c</u> and can be pulled up manually into the source column for irradiation. During irradiation a safety mechanism locks the cavity door <u>d</u> 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 <u>e</u> 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. On these plates there are cylindrical holes where the sample holders can be placed. The sample holders are cylindrical glass tubes that are used to keep the samples vertically straight in the cavity. A sample holder containing a sample to be irradiated is placed into the desired hole on the sample plate and constant temperature water circulates around the sample during irradiation.

The dose rate can be varied by changing the distance between the source and the sample and/or adding the lead attenuators. The lead attenuators are half-hallow cylindrical in shape and are placed on the source column whenever reduction in the radiation intensity is desired. They can reduce the radiation dose rate in factors of approximately 2, 5, 10, and 50.

Cesium-137 is a source of gamma ray and has a half-life of about 30 years. Cesium-137 always contains some cesium-134, which is formed by (n,γ) reaction with cesium-133 resulting from fission. The amount of cesium-134 will depend on the irradiation conditions and the length of time the spent fuel was allowed to age. The following scheme shows that the gamma ray arises from a daughter isotope of the cesium-137:[54]



The calibration of the dose rate was done by other workers in our laboratory by using the Fricke dosimetry method[55]. The dosimeter contains 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 concentrations of the produced ferric ion are determined by spectrophotometric measurements at the wavelengths of 304 nm (Molar Extinction Coef. E = 2263.5) and 276nm (E_{276} = 1857)[56]. From the UV absorbance readings and the extinction coefficients for Fe^{3+}, one can determine the amount of dose received in a given period of time using the following relation:

$$I = 3777.0 \ A / (b \ E \ t \ d)$$

Where I is the dose rate (Mrad/hr.); A is the absorbance at 304 or 276 nms, b is the sample length (cm); E is the extinction coefficient(1/mole-cm), t is radiation time (min); d=1.024 is the density of the ferrous ammonium sulfate solution.

Using all the attenuators and the two sample plates, the dose rate for all the possible positions were determined and listed in Table 4.

Table 4

Radiation Intensities of Cs^{137} gamma source

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

All radiation work reported in this thesis was accomplished with using a constant temperature attachment controlled at 25 ± 0.2°C.

4. Differential Scanning Calorimeter (DSC)

The thermal analysis of the polymer film was done by using Du Pont 990 Thermal Analyzer with the DSC Cell. The cell base module provides electronic linerization of the calibration coefficient E. This coefficient is constant, over the entire temperature range, with the MODE switch at DSC CALIBRATED. With the switch at NORMAL, E will vary with temperature. The calibration coefficient of our cell was determined by using Indium (Heat of fusion: ΔH=28.4 J/g; Melting point T_f=156.6°C) as a standard.[57] (Table 5)

$$E = \frac{\Delta H \ m}{60 \ A \ B \ \Delta qs}$$

where ΔH=Heat of fusion in J/g; m=Sample mass in mg; A= Peak area in cm^2; B =Time Base setting in min./cm; Δqs = Y-axis Sensitivity setting in mV/cm; E in mW/mV. The peak areas were measured by using a K&E 620000 planimeter.

Table 5

Determination of the calibration coefficient by Indium

Sample: 19.50 mg Indium

Heating Rate (°C/min)	B (min/cm)	S	Δqs (mV/cm)	A (cm^2)	E (mW/mV)
1	0.5	1x	5	16.8	0.220
1	0.5	1x	10	8.7	0.212
1	0.25	1x	5	34.2	0.217
1	0.5	10x	50	17.4	0.212
2	0.5	1x	5	18.0	0.204
5	0.5	1x	10	9.1	0.203

Sample: 9.10 mg Indium

Heating Rate (^{o}C/min)	B (min/cm)	S	Δqs (mV/cm)	A (cm^2)	E (mW/mV)
1	0.5	1x	2	20.1	0.214
1	0.5	1x	5	8.2	0.210
1	0.25	1x	2	39.6	0.217
1	0.25	1x	5	16.0	0.215
1	0.5	10x	20	20.4	0.211
1	0.5	10x	50	7.8	0.221
2	0.5	1x	2	20.0	0.215
2	0.5	10x	50	8.2	0.210
5	0.5	10x	50	7.6	0.226

Sample: 1.55mg Indium

Heating Rate	B	S	Δqs	A	E
1	0.5	1x	1	6.8	0.216
1	0.25	1x	1	13.8	0.213
1	0.25	1x	2	6.7	0.219
1	0.5	10x	10	6.9	0.212
1	0.5	10x	20	3.6	0.203
1	0.25	10x	10	13.2	0.222
2	0.5	1x	2	3.3	0.222
2	0.5	10x	10	6.8	0.216
5	0.5	10x	20	3.3	0.222

AVERAGE E $\approx$ 0.216 mW/mV

The polymer films were cut into small dimensions (2mm x 2mm), and crimped in the aluminum pans and covers. For thinner samples, several layers of the film were needed to reach a measurable weight (ca, 5-10 mgs). Since cellulose esters have hydrophilic characteristic, its film always contains a certain amount of water molecules. An endothermic peak appeared on the DSC scan in the 85 - 105°C region due to water evaporation. The moisture peak could be avoided by heating the sample up to 110°C and holding there for three minutes, then cooling down to the room temperature , followed by measuring the sample weight and running the DSC. A heating rate of 10°C/min. was used for the polymer sample measurements. The heat of fusion ΔH of the polymer sample was calculated by:

$$\Delta H = \frac{A}{m} (60\ B\ E\ \Delta qs)$$

where A is the area of the melting peak.

(C) PROCEDURES

1. Film Casting

Cellulose ester film samples were prepared by solution casting on a glass plate or a mercury surface at room temperature.[58] The cellulose acetate powder sample was added to acetone solution and stirred until completely dissolved.

For the mercury surface method, a 5% w/v solution was spread on the mercury surface. After slow evaporation of the solvent, a film was made on the mercury surface which could be peeled off very easily. However, the film shrank to about 75% of its original dimension during the evaporation procedure and was non-uniform in thickness. This method was abandoned.

For the glass plate technique, the casting solution (ca. 10-20% w/v) was spread on a clean and levelled glass plate by using a Gardner casting knife. The final thickness of the dried film was controlled by adjusting the blade height of the casting knife. (The approximate settings were: 25 for 1.5 mil; 50 for 3.5 mil; 75 for 5 mil; 100 for 7.5 mil films). The solvent was then allowed to evaporate at room temperature and then the polymer film was peeled from the glass plate by immersing in a distilled water bath.

The proper concentration of the casting solution depends on the polymer itself. For instance, 20% CA-398-3 or 10% CA-394-30 could produce satisfactory film. Higher polymer concentrations led to the formation of bubbles in the cast film; lower concentrations yielded films of non-uniform thickness.

In our laboratory we found difficulty in making transparent films from acetone solution as we changed from cellulose acetate to cellulose acetate butyrate. Especially for CAB-171-40, it was almost impossible to avoid a cloudy appearance formed in the film during the solvent evaporation process. The opaqueness was developed at a very late stage of the evaporation. It was about 35 minutes after casting. The degree of opaqueness of the film was irreproducible and non-uniform.

It was first thought that the opaqueness was introduced by trace amounts of moisture in the polymer. Therefore, cellulose acetate butyrate powder sample was carefully predried in the oven and A.C.S. grade acetone was dried by magnesium sulfate and distilled, The film was made in a chamber which was predried by calcium sulfate drierite. But little improvement was observed.

The effect of evaporation rate was then under investigation by putting a polyethylene cover on the cast solution during the evaportion process. We found that only a small area at central part of the film showed opaqueness and this opaqueness developed about 5-8 hours after casting. A larger less opaque area was obtained when the film was made by evaporation without the cover. This result indicates that the evaporation rate of the solvent plays an important role on the optical appearance of the film.

Since the polyethylene cover over the casting solution does not provide good control of the evaporation rate, binary solvent systems were investigated to control the evaporation rate. 10% n-amyl alcohol (b.p. 138^{o}C) was added to acetone (b.p. 56^{o}C) and produced a less opaque film compared with the casting solution made by acetone alone. It indicates that the second solvent with a higher boiling point can reduce the evaporation rate of major solvent. But this acetone-alcohol system showed very poor reproducibility. It was found that the optical property of the film varied depending on the evaporation conditions such as temperature, pressure, and humidity. Several other binary solvent systems such as acetone-toluene(b.p. 110°C), acetone-cyclohexane (b.p. 80.7°C) were tried but showed similar poor reproducibility.

Dioxane (b.p. 101.3°C) instead of acetone was employed. Excellent transparent films were formed from this casting solution. This evidence does support our conclusion that the optical property of the film depend on the evaporation rate of the solvent. But the DSC diagram showed an exothermic peak at 175°C which might be due to peroxide formation from trace residues of dioxane in the film. Since radical grafting kinetics could be affected by the peroxides. Dioxane was not a proper solvent for casting.

Cyclohexanone (b.p. 154°C)-Cellulose Acetate Butyrate solution undergoes extremely slow evaporation. It took more than three days to dry the polymer film. However, cyclohexanone seems to be an ideal solvent to combine with acetone to control the evaporation rate. Upon several tests, the casting solution made by dissolving 25 grams CAB-171-40 powder in a mixture of 100 ml acetone and 100 ml cyclohexanone does produce quite satisfactory result. No enviornmental influence was observed on the optical appearance of the film. All CAB-171-40 samples were made following this recipe. The film samples were then soaked in toluene at room temperature for one day to extract any residual cyclohexanone or acetone, vacuum dried at ca. 1 torr at 110°C for three days and weighed. The dried CAB film samples were stored in a desiccator until used to minimize any absorption of moisture.

2. Study the CAB film Morphology

The morphology of the CAB film samples was examined by DSC and wide-angle X-ray diffraction. DSC experiments were performed using a calibrated DuPont 990 instrument at a heating rate of 10°C/min. Quantitative measuements involved weighing 5-8 mg. samples using a semi-microbalance and measuring the areas of endothermic peaks with a planimeter.

Wide angle X-ray diffractions were obtained with a Picker Diffractor using copper K_α radiation. These experiments were performed for us by Dr. Yoram Papir at the Chevron Research Center, Richmond, California.

3. Measurements of Swelling and Concentration of Inside Solution

The extent of swelling of cellulose esters was determined by equilibrating film samples with the styrene-benzene solution (referred to as "outside solution") at 25.0°C, removing, quickly blotting the surface liquid and then weighing. The percentage of swelling was calculated by

$$\%\ \text{Swelling} = (W_e - W_i) / W_i \times 100$$

where w_i is the dry weight of the polymer sample and w_e is the sample weight after equilibration with styrene-benzene.

The styrene-benzene solution absorbed into polymer (referred to as "inside solution") was vacuum distilled into a trap cooled by liquid nitrogen and the composition of the solution determined by refractive index measurements at 25°C using a Bausch and Lomb Abbe refractometer. A calibration curve for the refractive indexes of the styrene-benzene mixtures was shown in Fig. 4.

4. Grafting Procedure

The polymer films were cut rectangular in shape with different dimensions depending on the thickness, to attain a weight in the range of 0.4 - 1.0 grams. The films were folded in a zig-zag fashion and placed into the test tubes of 18 x 150 mm in dimensions. The tubes were then fused to $\mathfrak{T}$24/40 female joints through a glass tubing of 1/4 inch bore. During the process of glass blowing some water droplets condense in the tubes and it is essential to remove them. For this reason the samples were hooked to the vacuum line operating at 10^{-4} mm Hg for a period of one hour before the addition of monomer.

The styrene-benzene solution was added in the tube and the tube connected to the vacuum line. The liquid nitrogen dewar was immediately placed around the tube. After the samples were frozen, the stopcocks from the sample tube to the vacuum were opened. After the vacuum drops back to 10^{-4} torr, the stopcocks were closed and the liquid nitrogen dewar was removed, the samples were then placed in water bath at 25°C. When the

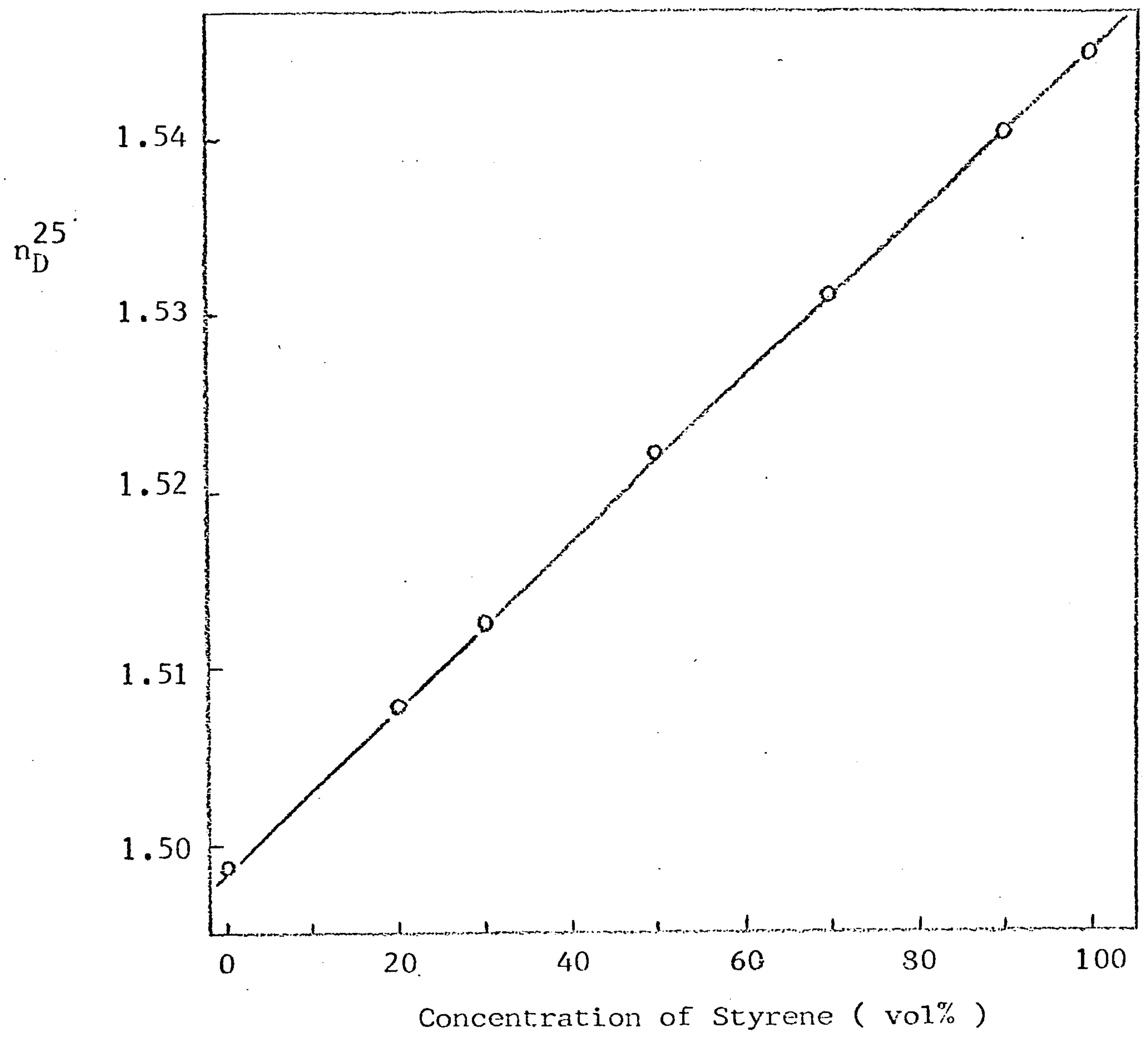


Fig. 4. Refractive indexes of Benzene - Styrene mixtures

samples reached room temperature, the tubes were wiped dry and placed again in liquid nitrogen. This freezing and thawing cycle was repeated three times. During the thawing process the samples were closed to the vacuum line to avoid solvent and monomer evaporation.

After the freeze-thaw cycles were complete, the tubes were sealed with an oxygen torch while the samples were in the frozen state. During the sealing process the stopcocks were still open to the vacuum.

The sealed tubes were placed into a water bath at $25 \pm 0.1^{\circ}C$ for 12 hours to reach equilibrium swelling. Following this treatment, the tubes were taken to the radiation source, placed in the sample holder and irradiated while water at $25 \pm 0.1^{\circ}C$ circulated around it. After irradiation the tubes were taken out of the source and cracked open immediately. The polymer film was soaked in toluene overnight to remove unreacted monomer and surface attached homopolymer, then vacuum dried at $110^{\circ}C$ for two days, and weighed.

The extent of graft polymerization in a sample was calculated as its percentage increase in weight:

$$\% \text{ graft} = (w_t - w_i) / w_i \times 100$$

where w_i and w_t are the dry weights of the sample before and after irradiation for a time t, respectively. All weight readings were the average values of three measurements by drying-weighing cycles.

RESULTS AND DISCUSSION

Film Morphology

To study diffusion-free graft polymerization, one must find conditions under which the grafting rate is independent of polymer film thickness. CAB-171-40 films of different thickness were prepared by solution casting and then examined by DSC and wide-angle X-ray diffraction. Figures 5 and 6 show the x-ray diffraction and DSC scans for 2.5, 5 and 7.5 mil thick CAB-171-40 films (1 mil = 0.001 inch = 0.00254 cm). The X-ray results show two broad diffuse halos which indicate the lack of long-range (large) ordered regions. There is little difference in the X-ray scattering observed for the different film thicknesses. However, the presence of some ordered regions is indicated by the endothermic peaks in the DSC. This behavior is generally observed for partially substituted cellulose esters.[59] The ordering is ascribed to "quasi-crystalline" structures, very small in size, which do not give rise to sharp X-ray diffraction peaks but are detected by DSC. The small endothermic peak at 147°C is due to residual cyclohexanone from the casting procedure. The peak disappears upon heating the CAB sample at 130-140°C for one-half hour. The thicker films (5 and 7.5 mil) show broad endothermic peaks centered at 190-193°C and 235°C. The two peaks are broader and less well-defined in the DSC

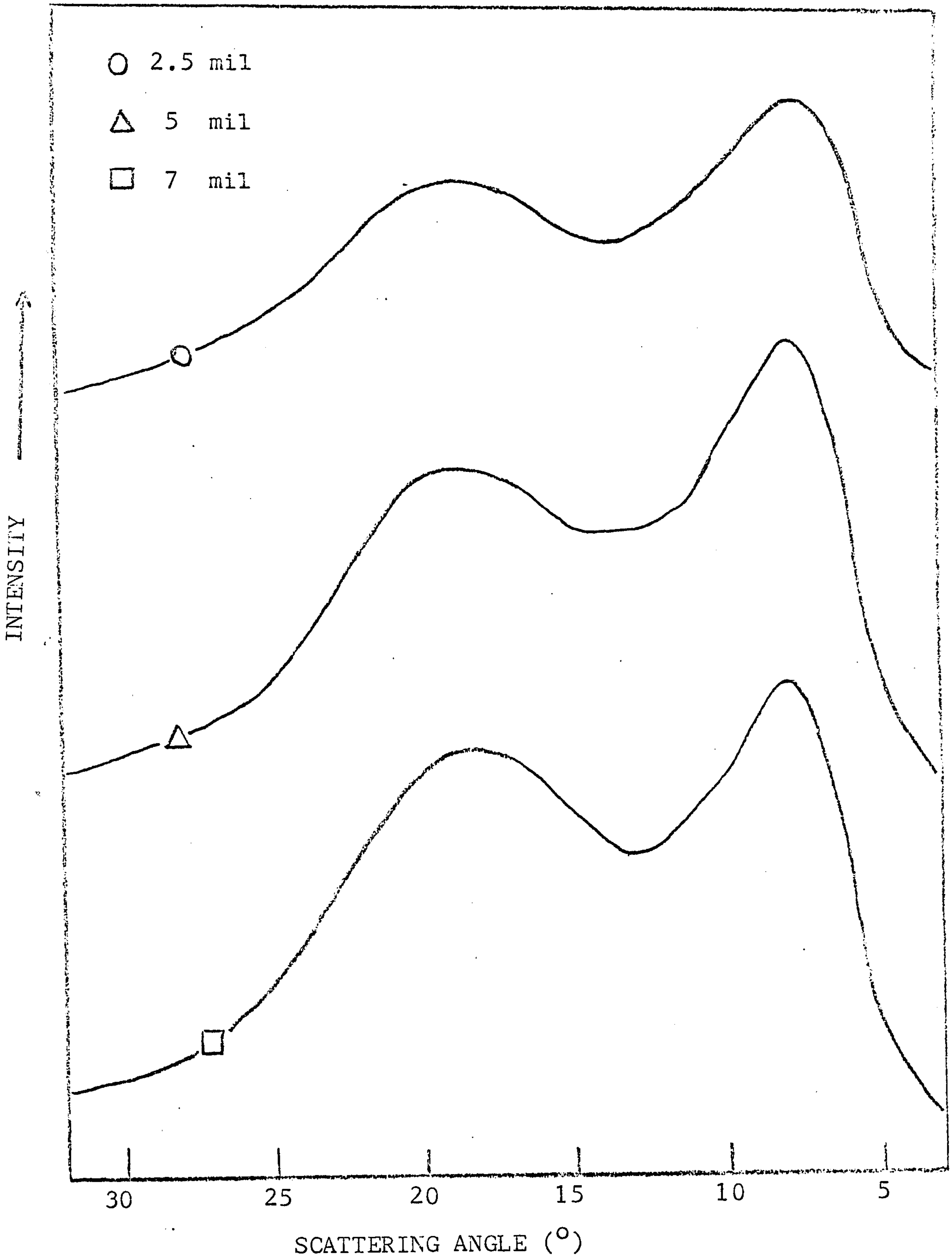


Fig. 5 X-ray scattering intensity versus scattering angle for CAB-171-40 films.

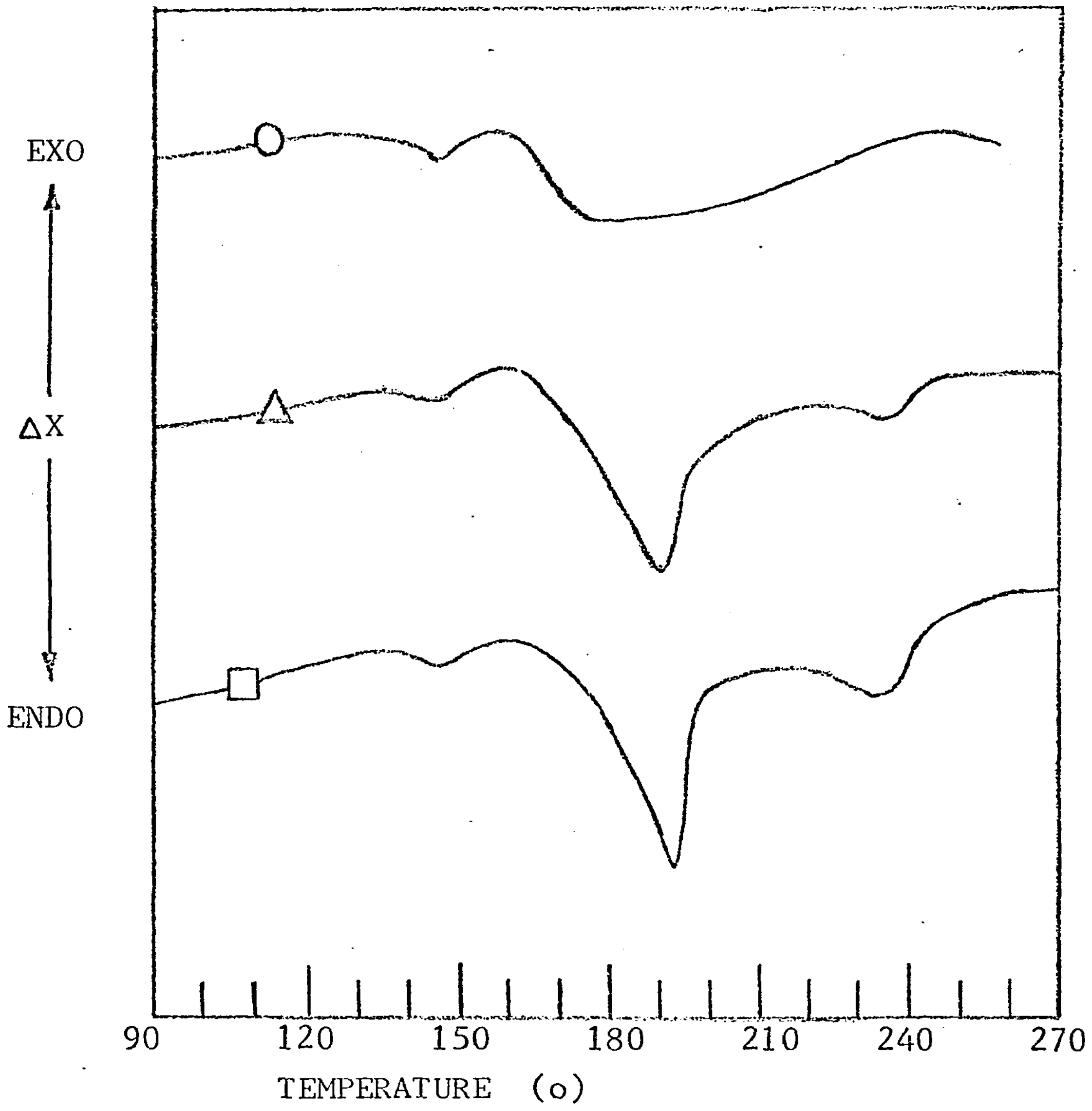


Fig. 6 DSC scans for CAB-171-40 films.
Film thickness: 2.5 mil (o), 5 mil (△), 7 mil (□).

scans of the thinnest film (2.5 mil). These differences in the DSC have been observed for other cellulose ester samples.[59,60] Although it indicates a difference in the exact morphology of the thinnest film relative to the others (probably due to the different rate of crystallization resulting from the more rapid evaporation of solvent), the gross morphology of all the CAB films is very close to the same as shown by heat of fusion data. The sum of the heats of fusion associated with the two endothermic peaks for the thicker films is 27 kJ/g while the heat of fusion for the broad endotherm in the region 160-245°C is 26 kJ/g.

The CAB-171-40 film samples employed in the above DSC and X-ray tests were cast from 25g CAB/(100ml acetone + 100ml cyclohexanone) solution and all were transparent. As mentioned in the experimental section, the evaporation rate is the key factor which affects the optical appearance of the film. Opaque film was produced if cast from a 25g CAB/200ml acetone solution and evaporated without any cover. When a polyethylene cover was used over the cast solution to slow down the evaporation rate, only a small area of opaqueness developed at the central part of the transparent film. The transparent region and opaque region on the same film made by this method were examined by DSC. Figure 7 shows the Du Pont 900 DSC scan (150 - 250°C) for the transparent and opaque regions of CAB-171-40 film cast by acetone solution.

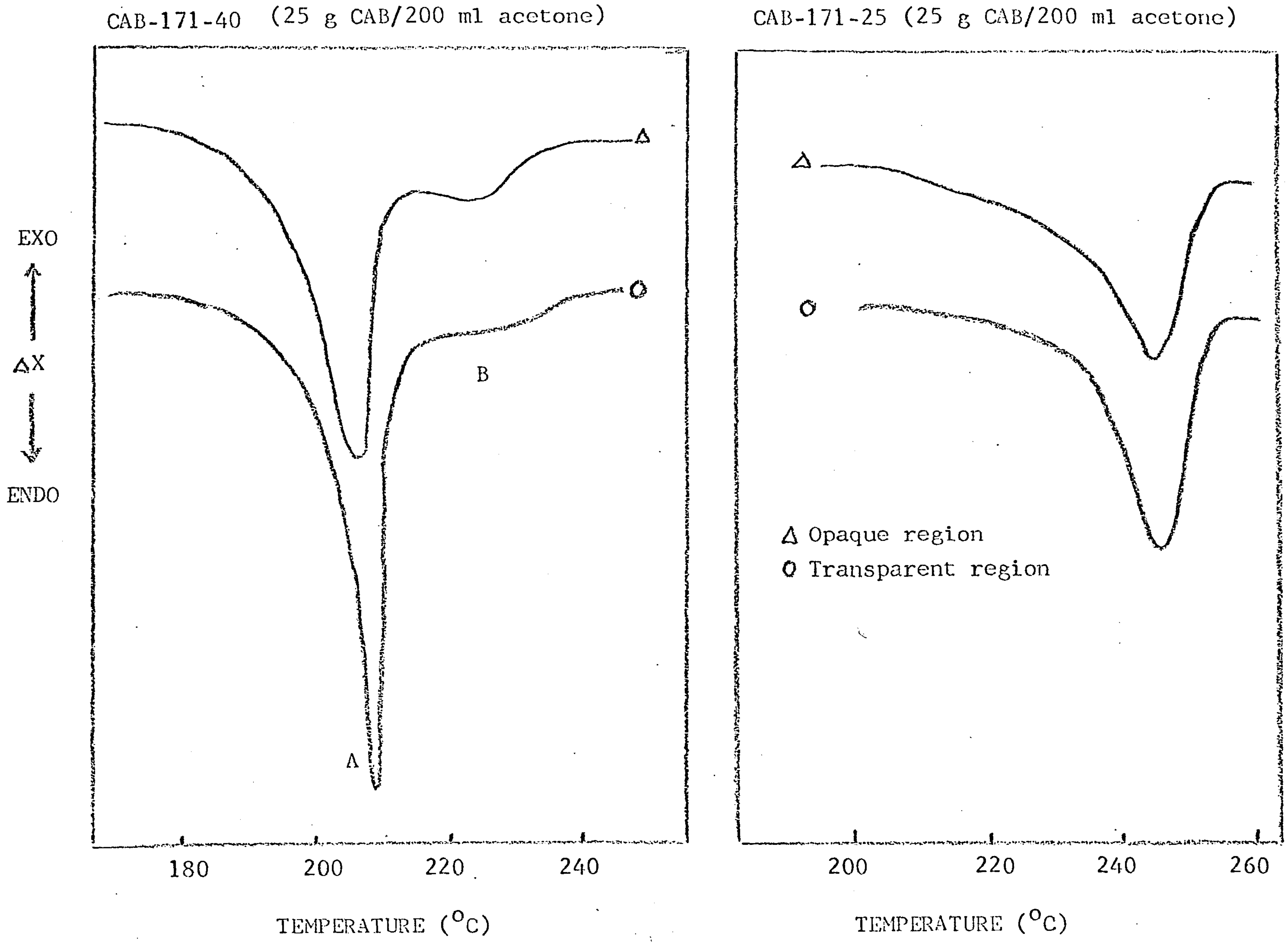


Fig. 7. Du Pont 900 DSC scans for transparent and opaque regions of CAB 171-40 and CAB 171-25 films cast by acetone solution and evaporated under cover.

The transparent region shows a sharp peak A centered at 210°C and a small shoulder B at 230°C. Broader and shorter peak A with a larger peak B was observed in the DSC scans of the opaque region. The ratios of area(A+B) to sample mass are approximately same for both region. The opaqueness might due to the scattering of light by micro-cavities[61] or crystalline spherulite in the film.

Three types of stress, present during the casting and evaporation procedures, are possible factors responsible for the molecular orientation in the film.

(1) The shearing stress of drawing the Gardner Knife (Doctor's blade).

(2) Escape of solvent from the cast solution.

(3) Adhesion to the glass plate, preventing the film from shrinking.

The shearing force of drawing knife on the solution might cause the surface molecules to lie in the plane of the membrane. The escape of solvent probably results in polymer molecules being oriented perpendicularly to the surface of the film. Adhesion of film on the glass plate prevents its shrinking after solvent evaporation. This interfacial stress can be determined by casting the solution on flexible substrates.[62] However, the function of this force on the film morphology is not clearly understood yet.

DSC scans of CAB-171-25 film, cast from 25g CAB/200ml acetone solution and evaporated under cover, shows only the 240°C peak for both opaque and transparent region. (Figure 7) The peak B is probably superimposed with peak A.

Film Properties

(A) Moisture Content

Since cellulose ester is a hydrophilic polymer, its film absorbs a certain amount of moisture under normal conditions. Cellulose diacetate has a higher moisture content than cellulose acetate butyrate due to its more polar character. Among the cellulose acetate butyrate materials the moisture content depends on the hydroxyl content of the ester. The measured weight of cellulose ester sample is very sensitive to the experimental environment. Results show that CAB-171-25 film has 2.1% moisture content at 70% relative humidity and 2.5% at 75% relative humidity at 25°C. When samples equilibrated with water, the percent swelling were 5.3 . This indicates the moisture content of the polymer film depends on humidity and temperature. However, its value varies depending on whether the equilibrium is approached from the dry or wet side.

The desorption of small molecules from the polymer film involves a two stage process. First, molecules diffuse from the interior of the film to the surface due to the concentration gradient. Second the surface molecules evaporate from the film.

After drying the film in the vacuum oven (10 mm Hg) without heating for two days, the polymer still contains high moisture content. This is probably due to vacuum being able to improve the evaporation rate of surface molecules but it has little effect on the diffusion rate through the film. Heating improves the efficiency of drying. Dry samples can be obtained by vacuum drying the film in the oven at 110°C for two days. DSC thermograms show no change on the nature of the melting peak indicating no annealing effect during this drying procedure.

(B) Infrared Test

Film reproducibility is a crucial requirement throughout entire research work. Attempts to make infrared bands assignments associated with crystallinity were not fruitful except that the O-H stretching band at 3,000-3,600 cm^{-1} indicated the relative amounts of free band and bonded band (in ordered region). But those bands are also seriously affected by the moisture content of the film. The O-H bands of cellulose acetate are much more sensitive to the moisture content than cellulose acetate butyrate which is due to CAB material having a lower hydroxyl group content and the relatively non-polar property of side chain.

(C) Swelling of Styrene-Benzene Solution

To determine the kinetic order of dependence of the grafting rate on monomer concentration, it is necessary to vary the monomer concentration inside the polymer without varying the viscosity. This can only be done by using monomer-diluent solutions with the nature of the polymer-monomer-diluent system being such that the amount of swelling of polymer is independent of the composition of the monomer-diluent solution. The choice of the diluent is critical for this purpose. Benzene was chosen as the diluent since it is very similar to styrene in solubility and viscosity characteristics. The extents of swelling of styrene-benzene mixture into CA-398-6 and CAB 171-4 film samples were determined and found to be independent of the composition of the mixture and film thickness (Table 6).

Table 6

Swelling of Cellulose Esters by Styrene-Benzene Mixtures

Composition of outside solution (vol.-% solution)	Extent of Swelling (Wt.-%)		
	CA 398-6	CAB 171-40	
	3.5 mil	3.5 mil	10 mil
0	0.1	49± 1	50.8 ± 0.4
50	-	-	50.7 ± 0.4
100	0.3	51± 1	51.4 ± 0.3

For comparison, one notes that cellulose diacetate (CA-398-6) film shows negligible swelling by styrene. The grafting can be achieved by so called "front grafting mechanism", grafting proceeds to the inner layers when surface grafted copolymer allows further penetration of the monomer. If a homogeneous inside grafted polymer was desired, certain swelling agents would be required in order to increase the inside monomer concentration. Pyridine was a very effective swelling agent for cellulose acetate-styrene grafting system.[44,45] The diffusion ability of monomer depended on the ratio of monomer-swelling agent ratio. However, the concentration and viscosity also varied at the same time which made the kinetics study more difficult. CAB is a much better choice for our studies since its extent of swelling is 50% without any added swelling agent. The experimental results show that the use of benzene-styrene mixtures allows one to vary the concentration of styrene inside the CAB-171-40 film while keeping constant the inside concentration of total liquid (benzene plus styrene). This then allows a variation of the inside composition without a significant effect on the inside viscosity. The inside viscosity is essentially constant since the viscosity of styrene-benzene mixtures varies less than 10% over the range of compositions.

An additional reason for choosing benzene as a diluent for styrene is the the G-values for radical formation are essentially the same (0.74 for benzene and 0.69 for styrene). Thus, the initiation rate and rate of homopolymerization relative to those of graft polumerization will be unaffected by the styrene-benzene composition. Further, energy transfer effects would also be expected to be independent of solution composition because of the similarity of benzene and styrene.

The extents of swelling of styrene-benzene mixture into other cellulose acetate butyrate film samples were also examined. CAB-272-3 film, cast from 30 g CAB/200ml acetone solution, has 33±1 % swelling of benzene and 34±1% swelling of styrene. CAB-272-20 film , cast from same concentration, has 35±2 % swelling of benzene and 36±2 % swelling of styrene. However, experimental results show that the extent of swelling of CAB-171-25 sample was sensitive to the composition of the cast solution. (Table 7)

Table 7

Effect of cast solution on the extent of swelling

Solution	Extent of Swelling (Wt-%)		
	CAB-171-25 (35/250)	CAB-171-25 (25/200)	CAB-171-25 (30/200+20)
Benzene	21±1	33±1	40±1
Styrene	20±1	32±1	42±2

Since these polymer films were not dried before examination, a certain error on W_i existed for its dependence on the humidity. However, the results does provide a reference of the swelling ability of the films made by different cast solution. 35/200 means 35g CAB-171-25 / 200ml acetone solution; 30/200+20 indicates the cast solution was made by dissolving 30g CAB-171-25 in 200 ml acetone and 20 ml n-amyl alcohol. The differences in the extents of swelling of styrene between different CAB samples might be due to different film morphologies which were controlled by concentration and evaporation rate of the cast solution.

Kinetics of the graft polymerization

(A) Inside homopolymerization vs. graft polymerization

The radiolysis of cellulose acetate butyrate to form CAB radicals was shown as

$$P \xrightarrow{\text{radiation}} P\cdot + H\cdot \qquad -1-$$

In the radiolysis of cellulose acetate butyrate in the absence of monomer, the fate of the hydrogen atom (which recoils from the C-H bond breakage with excess energy) is 1.-to form H_2 either by abstracting a hydrogen atom from a nearby C-H bond (to simultaneously form another CAB radical (P•) or unsaturation) or by coupling with another hydrogen radical formed by radiolysis, or 2- to react with alkyl radicals or 3- to add to double bonds (either present initially or formed during radiolysis). Considering the radiolysis of cellulose acetate butyrate in the presence of styrene, it is clear that one has often neglected the possiblity of the monomer scavenging hydrogen atoms to initiate inside homopolymerization

$$H\cdot + M \longrightarrow M\cdot \qquad -2-$$

The extent of involvement of hydrogen atoms in such reactions is generally not known but a number of workers[1,63,64] have found extensive amounts of inside homopolymerization, exceeding the limits which would be produced by the simple radiolysis of the monomer.

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

Before trying to determine the separate kinetics of the rate of graft polymerization and the rate of inside homopolymerization, let us define some terms:

1. kinetic graft: polystyrene formed in the matrix initiated by a cellulose acetate butyrate radical.
2. kinetic homo: polystyrene formed in the matrix initiated by a styrene radical, or benzene radical, or a hydrogen radical.
3. apparant graft: polystyrene with at least one end attached on the cellulose acetate butyrate backbone in the final form.
4. apparant homo: polystyrene in the cellulose acetate butyrate which does not have any chemical bond with CAB after reaction was complete.

It is quite clear that the kinetic graft and kinetic homo were not equivalent to the apparant graft and apparant homo, respectively, by following reasons:

1. Cross-termination; If termination occurs by bimolecular coupling of propagating radicals, one expected that the kinetic graft propagating radical may react with kinetic homo propagating radical to form a apparent graft.

$$\sim\!\sim G^{\bullet} + \sim\!\sim H^{\bullet} \longrightarrow \text{apparant graft} \qquad \text{-3-}$$

Compare "cross-termination" with the other two termination modes:

$$\sim\!\sim G^{\bullet} + \sim\!\sim G^{\bullet} \longrightarrow \text{apparent graft} \qquad \text{-4-}$$

$$\sim\!\sim H^{\bullet} + \sim\!\sim H. \longrightarrow \text{apparant homo} \qquad \text{-5-}$$

The probability of cross-termination is 50% assuming that the rate constants for all three terminations are the same, and the amount of the kinetic homo and kinetic graft propagating radicals are the same, and the termination occurs by bimolecular coupling exclusively.

2. Chain Transfer: In normal polymerization chain transfer results in a decrease in polymer size with little effect in the polymerization rate because chain transfer produce a new radical which then reinitiates polymerization. However in graft polymerization several chain transfer reactions are possible:

$\sim\!\sim G\cdot + XA \longrightarrow$ apparant graft $+ A\cdot$ (homo) -6-
$\sim\!\sim G\cdot + P \longrightarrow$ apparant graft $+ P\cdot$ (graft) -7-
$\sim\!\sim H\cdot + XA \longrightarrow$ apparant homo $+ A\cdot$ (homo) -8-
$\sim\!\sim H\cdot + P \longrightarrow$ apparant homo $+ P\cdot$ (graft) -9-

where XA may be monomer or solvent (benzene) and P is the cellulose acetate butyrate polymer. New radicals A· and P· would reinitiate homopolymerization and graft polymerization respectively. Apparantly chain transfer reaction in the graft system is equivalent to one termination step and one initiation step. Equations 7 and 8 are the examples of cross-transfer. If the separation of the graft polymer and inside homopolymer was desired, normal polymerization rate equation would not be valid for the grafting system. Part of the chain transfer reaction must be considered as a termination step.

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

The inside apparant hompolystyrene might be removed by extraction of an irradiated film with benzene or other solvents. But physical separation of the kinetic graft polymer and kinetic homopolymer is impossible. In this work, we have studied the overall kinetics of the graft polymerization under the assumption that both inside homopolymerization and graft polymerization mechanisms follow the same kinetic route. We did not attempt to physically separate the apparant homopolymer from the grafted polymer and study the separate kinetics of the rate of grafting polymerization and the rate of inside hompolymerization.

(B) Effect of radiation on cellulose acetate butyrate

Having chosen styrene-CAB 171-40 as the grafting system to be studied, control experiments were carried out to determine whether any degradation occured upon irradiation. Cellulose acetate butyrate film samples were placed into benzene, irradiated for a time period in excess of that for any grafting experiment with the highest dose rate, removed, dried, and weighed, There was no observable weight loss by cellulose acetate butyrate samples, indicating that radiolytic degradation of CAB was not important in the present study. Further, in the grafting system, monomer serves as a free radical scavanger and radiation degradation possibility is further reduced.

(C) Diffusion-Free Reaction

To establish that our studies have not involved diffusion-controlled reaction (in the sense of monomer diffusion into the polymer film not keeping up with polymerization), the graft polymerization rate was determined for different thicknesses (1.5, 3.5 and 7 mil) of cellulose acetate butyrate at two different dose rates (0.00769 and 0.0371 Mrad/hr.) for 50% styrene and 100% styrene. The results are shown in Table 8.

Table 8

Effect of Film Thickness on Grafting Rate

CAB 171-40 Film Thickness (mils)	R_p (% Graft/hr.) at I of		
	0.00769 Mrad/hr.	0.0371 Mrad/hr.	
	100% styrene	50% styrene	100% styrene
1.5	10.2	3.8	24.8
3.5	10.9	4.1	25.8
7	11.5	4.0	25.5

The small rate differences between 1.5, 3.5 and 7 mil thick samples may be due to experimental error. It is clear the results indicate that the graft polymerization reaction is diffusion-free for these film thicknesses. If the reaction were diffusion-controlled, the grafting rate would be inversely dependent on film thickness.

(D) Composition of Inside Solution

In conventional free radical homopolymerizations one can easily vary the monomer concentration by simply diluting the monomer to certain degrees with a proper solvent and study the effect on the polymerization rate. The nature of the diluent is not too critical at this condition. In radiation homopolymerization any added solvent is radiolysed and leads to the production of additional free radicals which may contribute to chain initiation. However, in mutual irradiation graft polymerization processes, the nature of the diluent is most important and crucial since the inside monomer concentration may differ from the outside solution because of different swelling and diffusion abilities of monomer and diluent.

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. 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. For our grafting system, styrene-cellulose acetate butyrate, benzene was used as a diluent for styrene since benzene and styrene have similar solubility, diffusion, viscosity and radiation characteristics. (see Table 1).

In a kinetic study, the determination of the inside solution composition is necessary to determine the dependence of graft polymerization rate on monomer concentration. If the outside and inside compositions were different, the kinetics order of dependence of grafting rate on monomer could only be determined from the dependence of grafting rate on the inside solution composition.

Composition of the inside styrene-benzene solution with cellulose acetate butyrate-171-40 film was determined by refractive index measurements after vacuum extraction from the swollen CAB samples. The results (Table 9) show that the composition of the inside solution is the same as that of the outside solution over the complete range of styrene-benzene composition.

Table 9

Composition of Inside Solution

Outside Solution (Vol. %-Styrene)	Refractive Index (n_D^{25})	
	Outside Solution	Inside Solution
0	1.4988	1.4988
30	1.5122	1.5124
50	1.5223	1.5224
70	1.5312	1.5312
100	1.5450	1.5450

(E) Effect of Monomer Concentration

The determination of the effect of monomer concentration on the grafting rate is one of the 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) 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,

(2) an order of 3/2 signifies that the initiation step is dependent on the monomer concentration to the first power and that termination is via a bimolecular termination.

(3) an order of 2 results mainly due to termination by primary radicals.

In between values of monomer order are also possible when several of the above modes operate at the same time. These modes of initiation and termination can also be extended to graft polymerization processes.

The effect of monomer concentration on the rate of graft polymerization was determined over the range of styrene composition from 30% to 100% at five different dose rates: 0.085 (Figure 8), 0.0371 (Figure 9), 0.0214 (Figure 10), 0.00769 (Figure 11), and 0.00368 Mrad/hr. (Figure 12) for 3.5 mil cellulose acetate butyrate 171-40 films. Each figure shows the extent of graft polymerization (percent of weight gain) as a function of irradiation time. The initial grafting rates were determined by least-squares calculations from slopes and are shown in Table 10.

Table 10

Effect of Monomer Concentration on Grafting Rate

Composition of inside solution (vol-% styrene)	R_p (% Graft/hr.) at radiation intensity (Mrad/hr.) of				
	0.085	0.0371	0.0214	0.00769	0.00368
100	36.4	22.0	17.5	11.0	8.2
75	16.3	11.5	10.2	6.9	-
50	5.8	5.0	4.0	3.3	2.6
35	-	2.2	-	-	-
30	1.4	-	1.3	-	1.2
25	-	1.0	-	-	-
Kinetic order dependence of R_p on [M]	2.69 ± 0.03	2.22 ± 0.03	2.14 ± 0.12	1.74 ± 0.06	1.60 ± 0.04

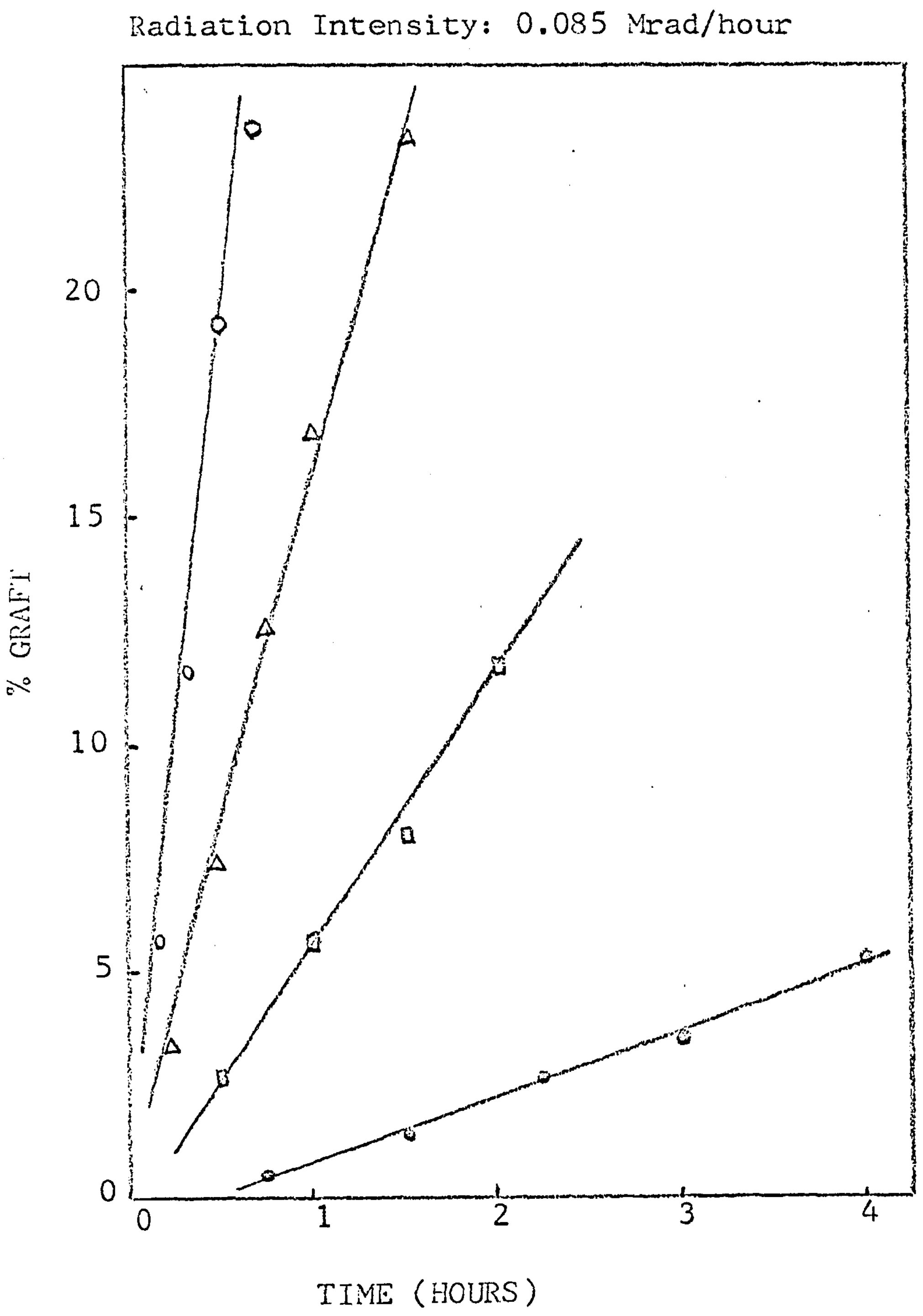


Fig. 8. Percent graft versus time for 0.085 Mrad/hr. Volume-percent styrene: 30%(●), 50%(□), 75%(▲), 100% (○).

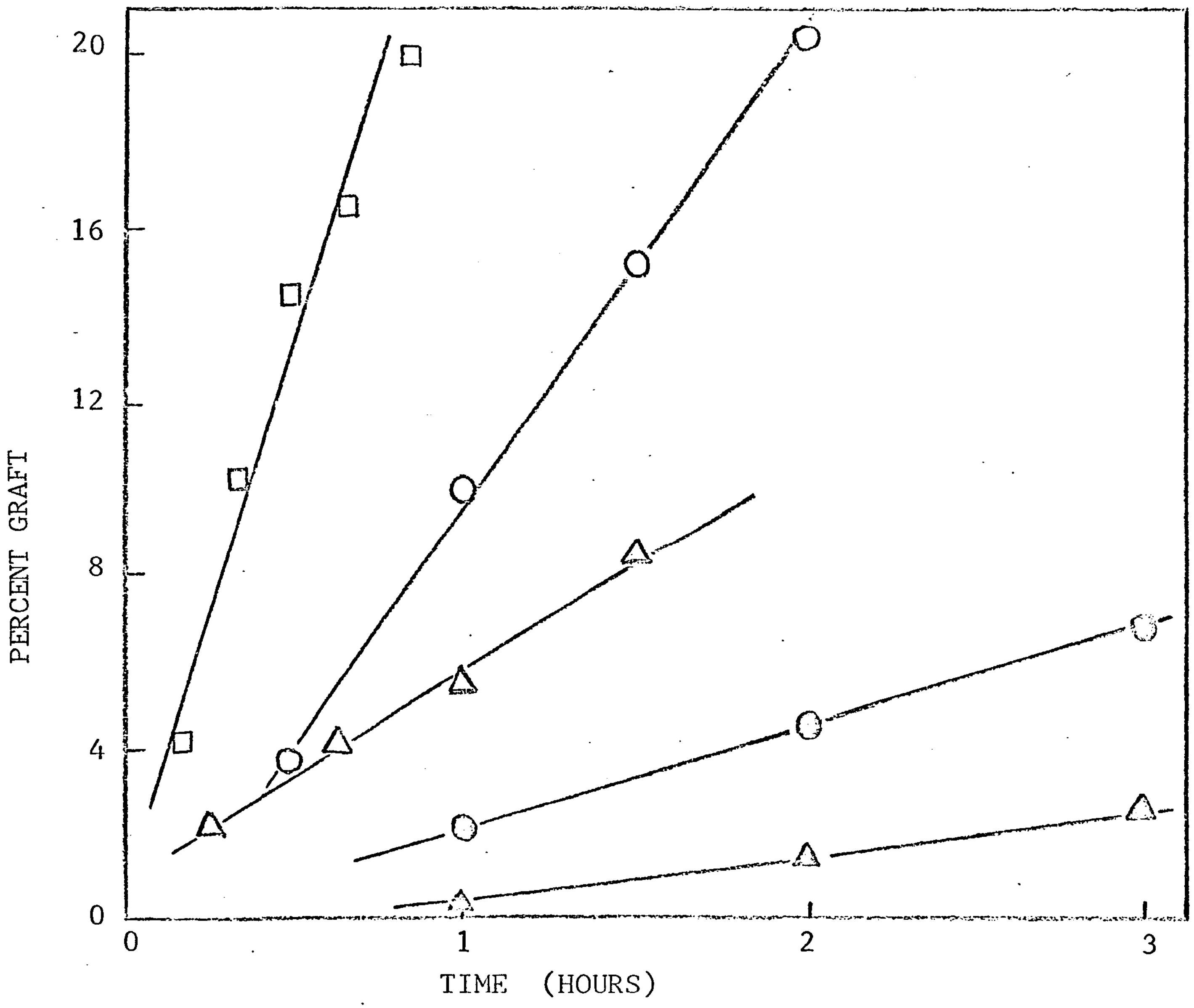


Fig. 9 Percent graft versus time for 0.0371 Mrad/hour
Volume-% styrene: 25(△), 35(○), 50(△), 75(○), 100(□).

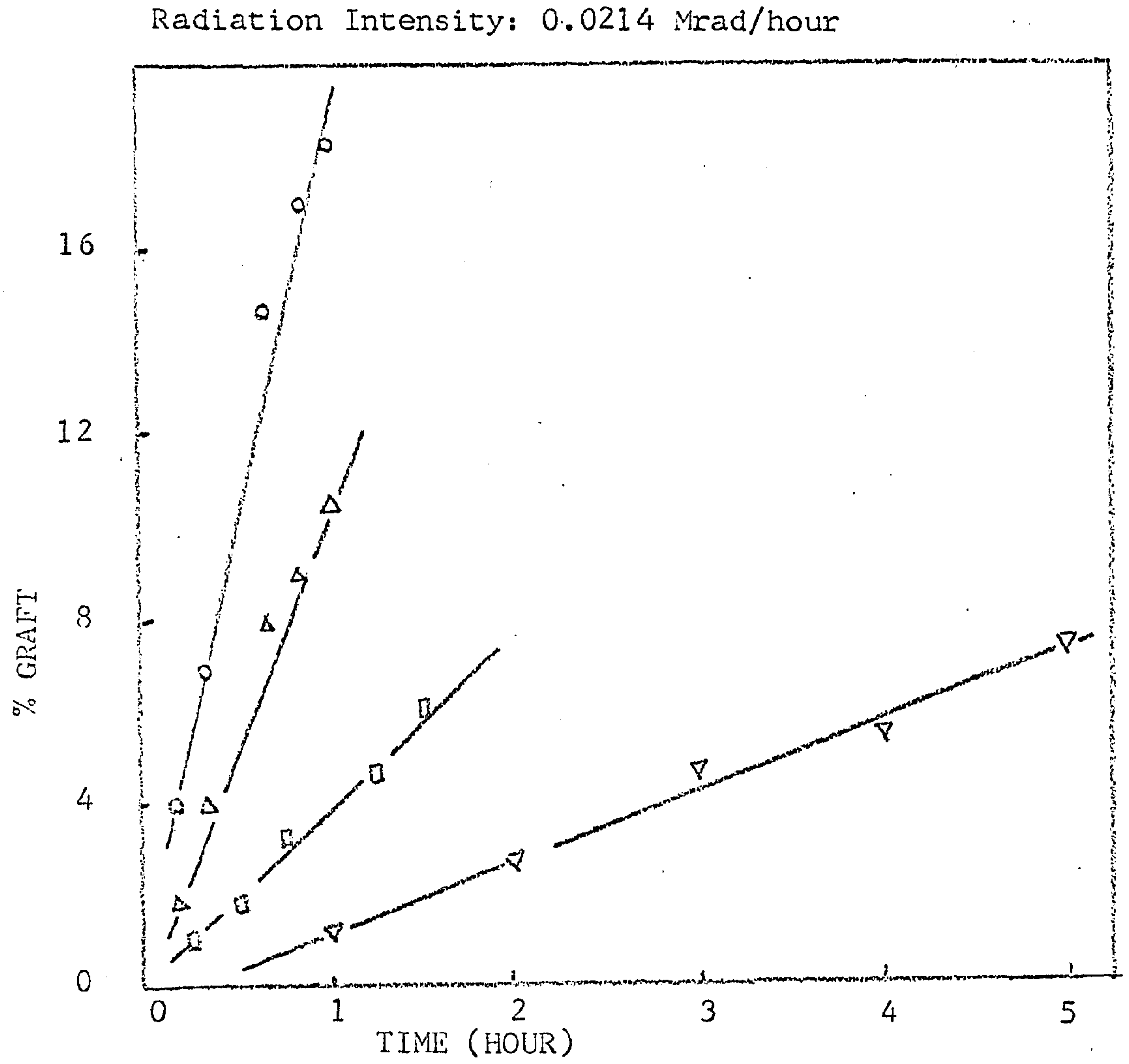
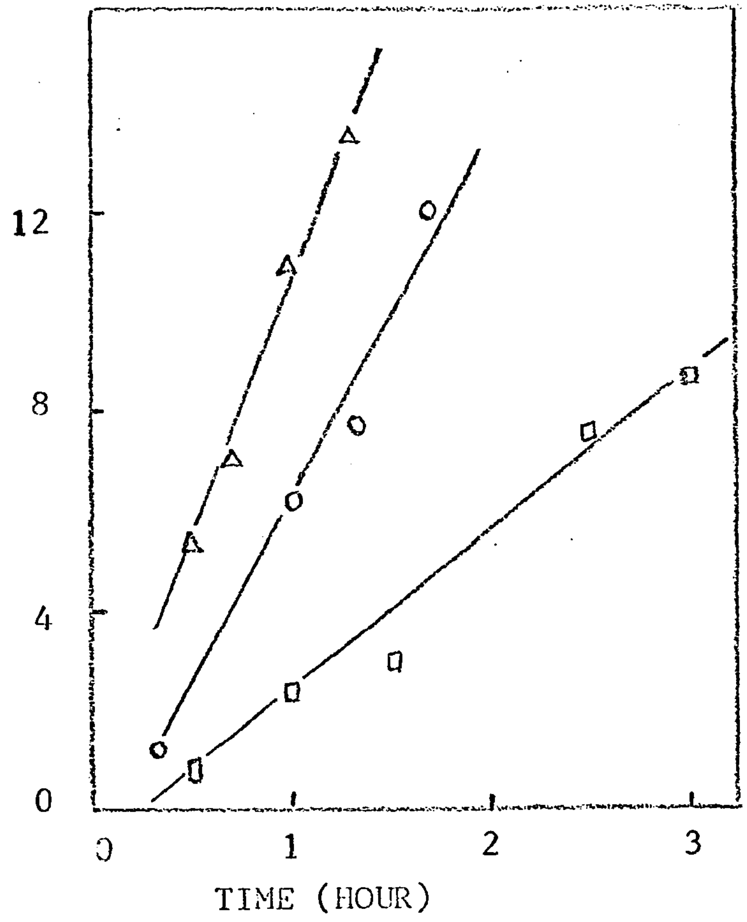

Radiation Intensity: 0.0214 Mrad/hour

Fig.10. Percent graft versus time for 0.0214 Mrad/hr. Volume-percent styrene: 30%(▽), 50%(□), 75%(△), 100%(○).

Radiation Intensity: 0.00769 Mrad/hr.

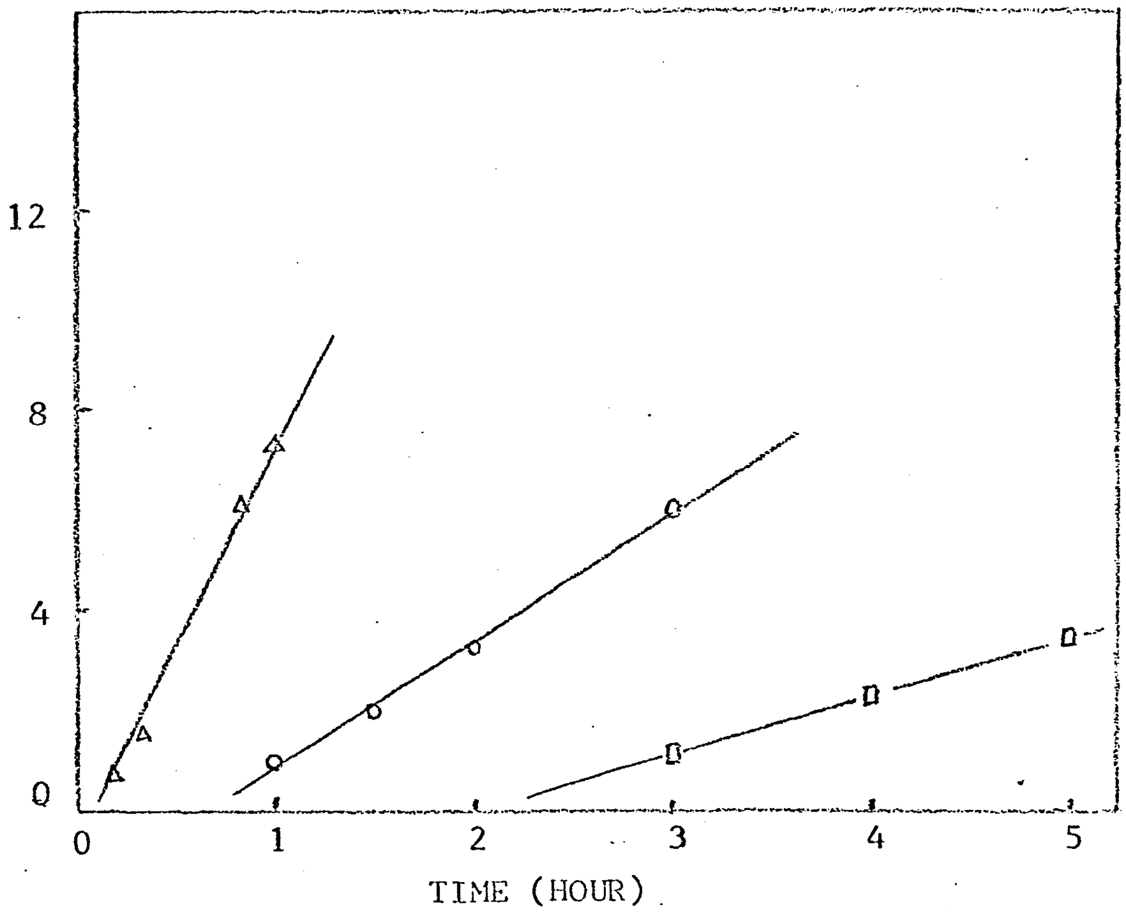


100% styrene(Δ)
75% styrene(○)
50% styrene(□)

Fig. 11

% Graft versus time for 0.00769 Mrad/hr.

Radiation Intensity: 0.00368 Mrad/hr.



100% styrene(Δ)
50% styrene(○)
30% styrene(□)

Fig. 12 .

% Graft vs. time for 0.00368 Mrad/hr.

Log-log values and plot of the graft polymerization rate versus inside monomer concentration for each dose rate are shown in Table 11 and Figure 13, respectively. The slopes of these plots, i.e., the orders of dependence of rate on monomer, were obtained by least squares calculations and are tabulated at the bottom of Table 10. The kinetic order of dependence of the graft polymerization rate on the monomer concentration increases from 3/2-order at the lowest dose rate to a 5/2- or slightly higher-order at highest dose rate.

(F) Effect of Radiation Dose Rate

One of the most important kinetic parameters in a polymerization reaction is the order of reaction rate on the initiation rate. In radiation induced polymerizations, ions are produced as well as radicals in the reaction medium, the nature of the initiating species could be determined by the initiation rate order. Generally, radical polymerizations show a half order dependence of grafting rate on R_i wheras ionic polymerizations exhibit a first order dependence at wet condition and a half order dependence at super-dry condition. (see Background Section).

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.

Table 11

Log-Log Values of Monomer Concentration and Grafting Rates

Composition of Inside Solution (Vol-% Styrene)		Dose Rate of									
		0.085 Mrad/hr.		0.0371 Mrad/hr.		0.0214 Mrad/hr.		0.00769 Mrad/hr.		0.00368 Mrad/hr.	
M	LogM	R_p	$\text{Log}R_p$	R_p	$\text{Log}R_p$	R_p	$\text{Log}R_p$	R_p	$\text{Log}R_p$	R_p	$\text{Log}R_p$
100	2.000	36.4	1.561	22.0	1.342	17.5	1.243	11.0	1.041	8.2	0.914
75	1.875	16.3	1.212	11.5	1.061	10.2	1.009	6.9	0.839	-	
50	1.699	5.8	0.763	5.0	0.699	4.0	0.602	3.3	0.519	2.6	0.415
35	1.544	2.2	0.342	-		-		-		-	
30	1.477	1.4	0.146	-		1.3	0.117	-		1.2	0.079
25	1.398	-		1.0	0.000	-		-		-	

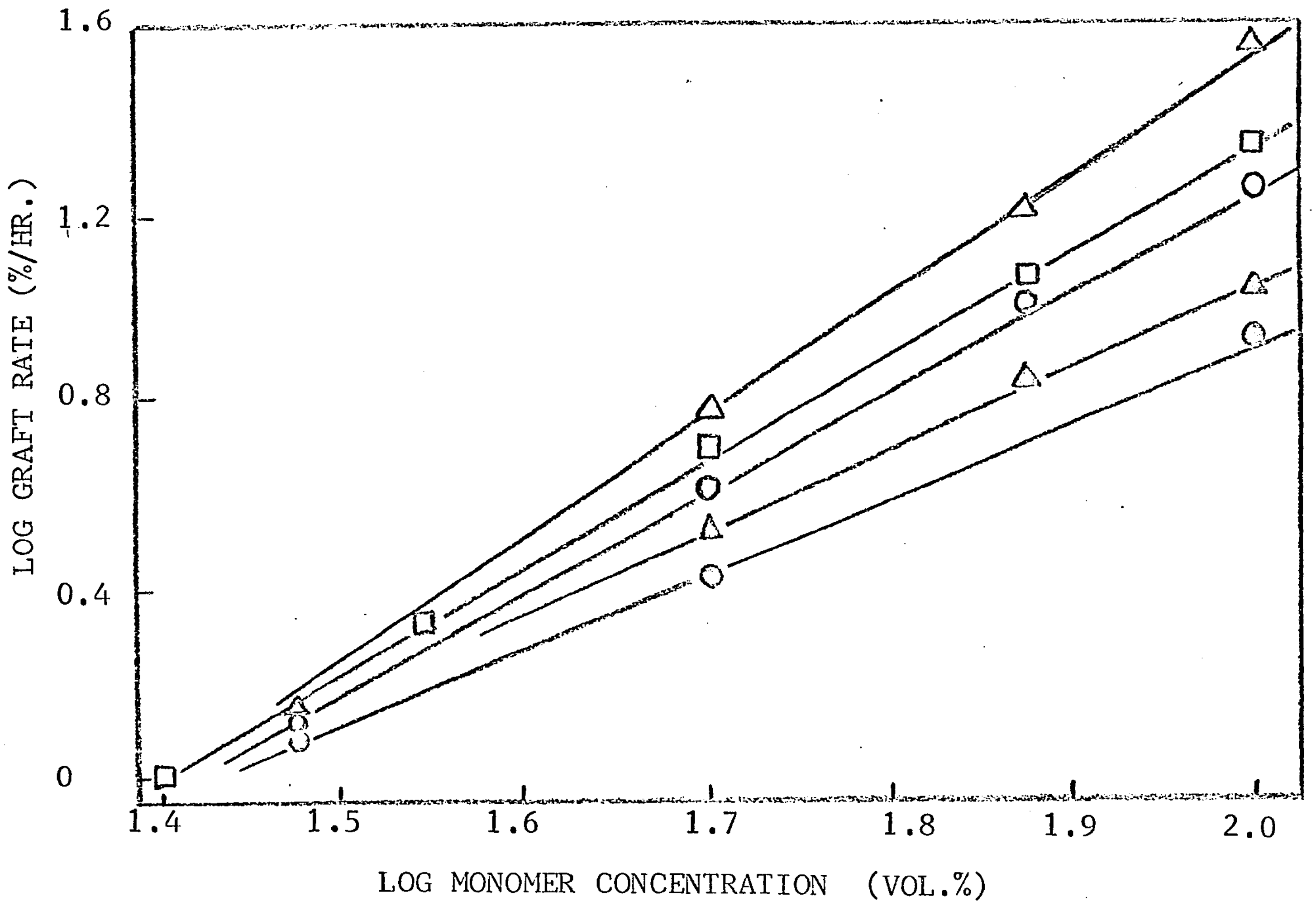


Fig. 13 Effect of monomer concentration on grafting rate for CAB-171-40 film.
Radiation Intensity (Mrad/hr.): 0.00368(○), 0.00769(△),
0.0214(○), 0.0371(□), 0.085(△).

The dependence of the graft polymerization rate on radiation intensity was determined at four different monomer concentrations over a wide range of radiation intensities from 0.00368 Mrad/hr. to 0.085 Mrad/hr. for 3.5 mil thick CAB-171-40 film. The initial grafting rates, obtained by least squares calculations, are shown in Table 12. Log-log values and plots of reaction rate against dose rate shown in Table 13 and Figure 14, respectively. The orders of dependence of grafting rate are tabulated at bottom of Table 12. The kinetic order of dependence of the graft polymerization rate on the radiation intensity decreases from 1/2-order at 100% styrene to a 0-order at 30% styrene.

Table 12

Effect of Radiation Intensity on Grafting Rate

	Grafting Rate (% graft/hr.) for			
Dose Rate (Mrad/hr.)	100% styrene	75% styrene	50% styrene	30% styrene
0.085	36.4	16.3	5.8	1.4
0.0371	22.0	11.5	5.0	-
0.0214	17.5	10.2	4.0	1.3
0.0111	13.2	-	-	-
0.00769	11.0	6.9	3.3	-
0.00368	8.2	-	2.6	1.2
Kinetic order dependence of R_p on I	0.47 ± 0.02	0.35 ± 0.02	0.26 ± 0.03	0.05 ± 0.001

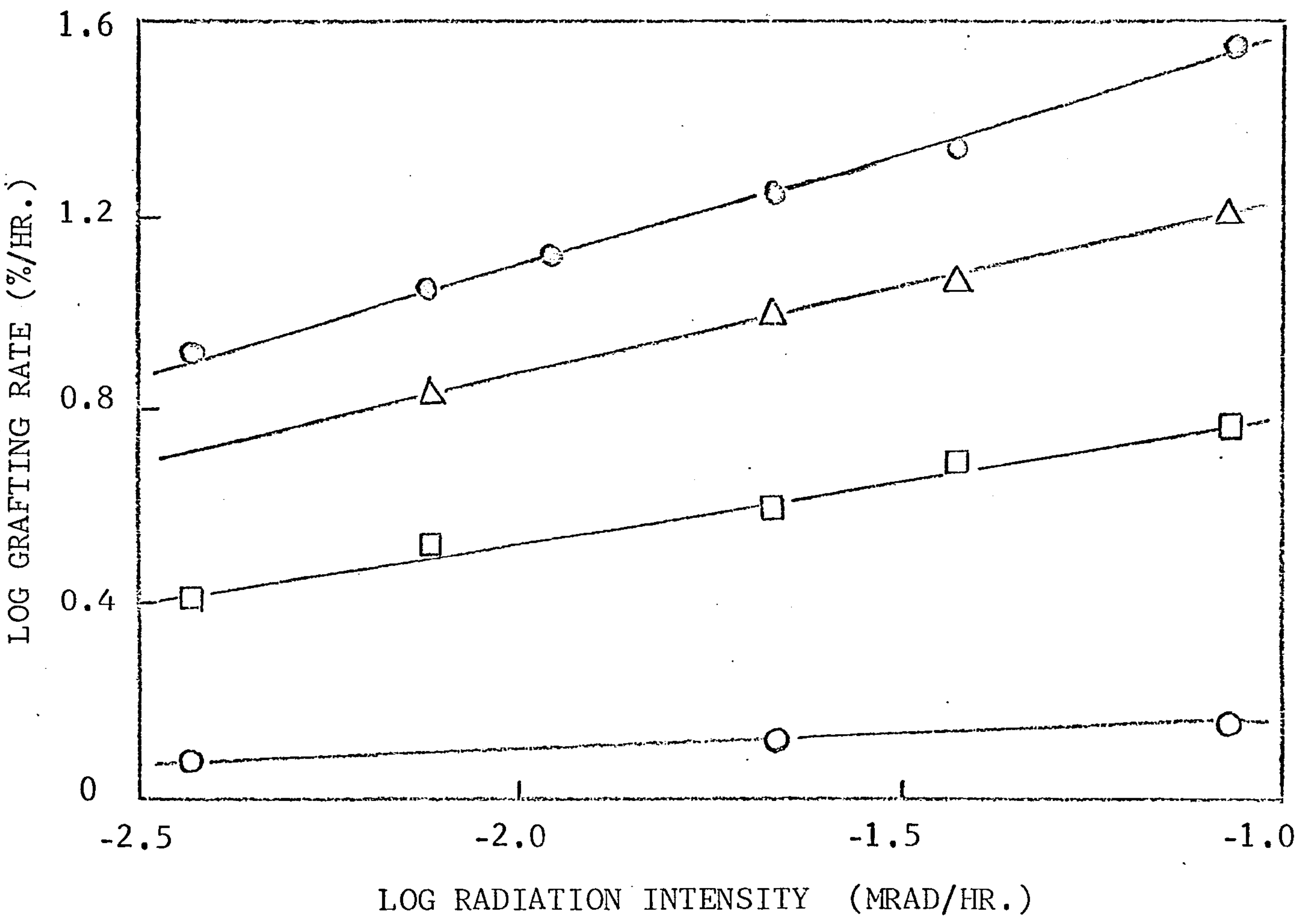


Fig. 14 Effect of radiation intensity on grafting rate for CAB-171-40 film. Volume-percent styrene: 30%(○), 50%(□), 75%(△), 100%(○).

Table 13

Log-Log Values of Radiation Intensity and Grafting Rate

Dose-Rate (Mrad/hr.)		Grafting Rates (%graft/hour) for 100% Styrene		75% Styrene		50% Styrene		30% Styrene	
I	LogI	R_p	$LogR_p$	R_p	$LogR_p$	R_p	$LogR_p$	R_p	$LogR_p$
0.085	-1.071	36.4	1.561	16.3	1.212	5.8	0.763	1.4	0.146
0.0371	-1.431	22.0	1.342	11.5	1.061	5.0	0.699	-	
0.0214	-1.670	17.5	1.243	10.2	1.009	4.0	0.602	1.3	0.117
0.0077	-2.114	11.0	1.041	6.9	0.839	3.3	0.519	-	
0.0037	-2.434	8.2	0.914	-		2.6	0.415	1.2	0.079
0.0111	-1.955	13.2	1.120	-		-		-	

(G) Comparison with Polyethylene-Styrene Grafting

The diffusion-free graft polymerization of styrene onto high density polyethylene[3] and low density polyethylene[4] by mutual irradiation method have been studied by Odian and coworkers.

In styrene-HDPE system, the grafting rates were plotted versus the inside monomer concentration on a log-log plot (Figure 15) to yield the monomer exponents. The dependence of graft polymerization on monomer concentration is 3/2-order at the lower dose rate, 5/2-order at the intermediate dose rate and between 5/2- and 3- order at the high dose rate. The dependence of rate on radiation intensity was observed over the complete range of dose rates from 0.00076 to 0.353 Mrad/hr. for pure and 50% styrene and the results are shown in Figure 16. Three different regions of behavior are defined: 1.-a low dose rate region where the grafting rate is 1/2-order in dose rate and 3/2-order in monomer, 2- an intermediate dose rate region where the grafting rate is intermediate between 1/2 and 0-order in dose rate and 5/2-order in monomer, and 3- a high dose rate region where the grafting rate is independent of dose rate and at least 5/2-order in monomer.

The diffusion-free graft polymerization of styrene-LDPE follows exactly the same kinetic behavior as found for styrene-HDPE. (Figures 17, 18). The reaction rate is 2-order in monomer and 1/2-order in intensity at the lower radiation intensities; at higher radiation intensities, the rate is 5/2-order in monomer and 1/4-order in intensity.

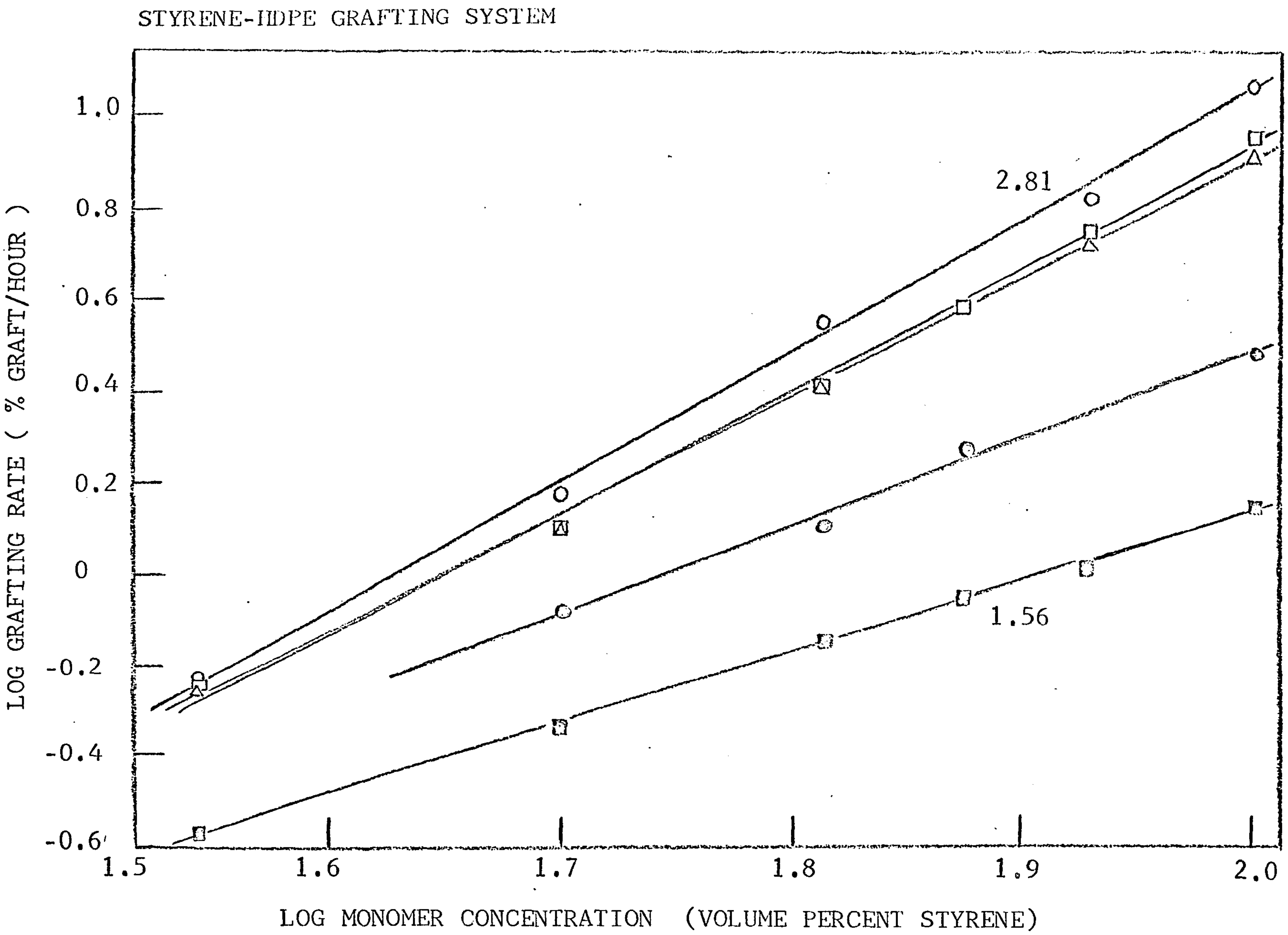


Fig. 15 Log-log plot of graft polymerization rate vs. monomer concentration for Styrene-HDPE grafting system.
Dose Rates (Mrad/hr.): 0.213(○), 0.0583(□), 0.0371(△), 0.00368(○), 0.000761(□).

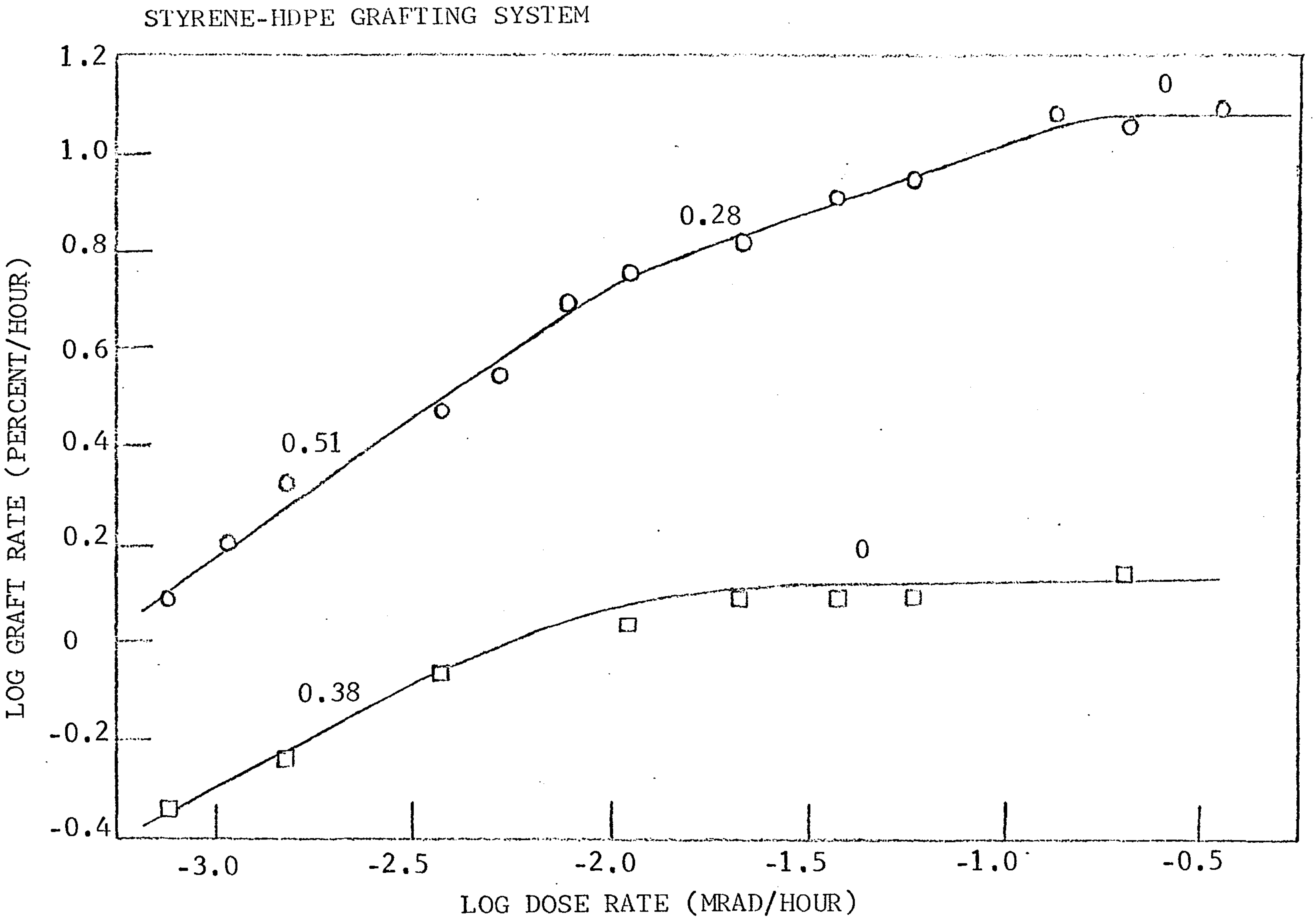


Fig.16 Log-log plot of graft polymerization rate versus dose rate for styrene-HDPE grafting system.

100% styrene (○), 50% styrene (□).

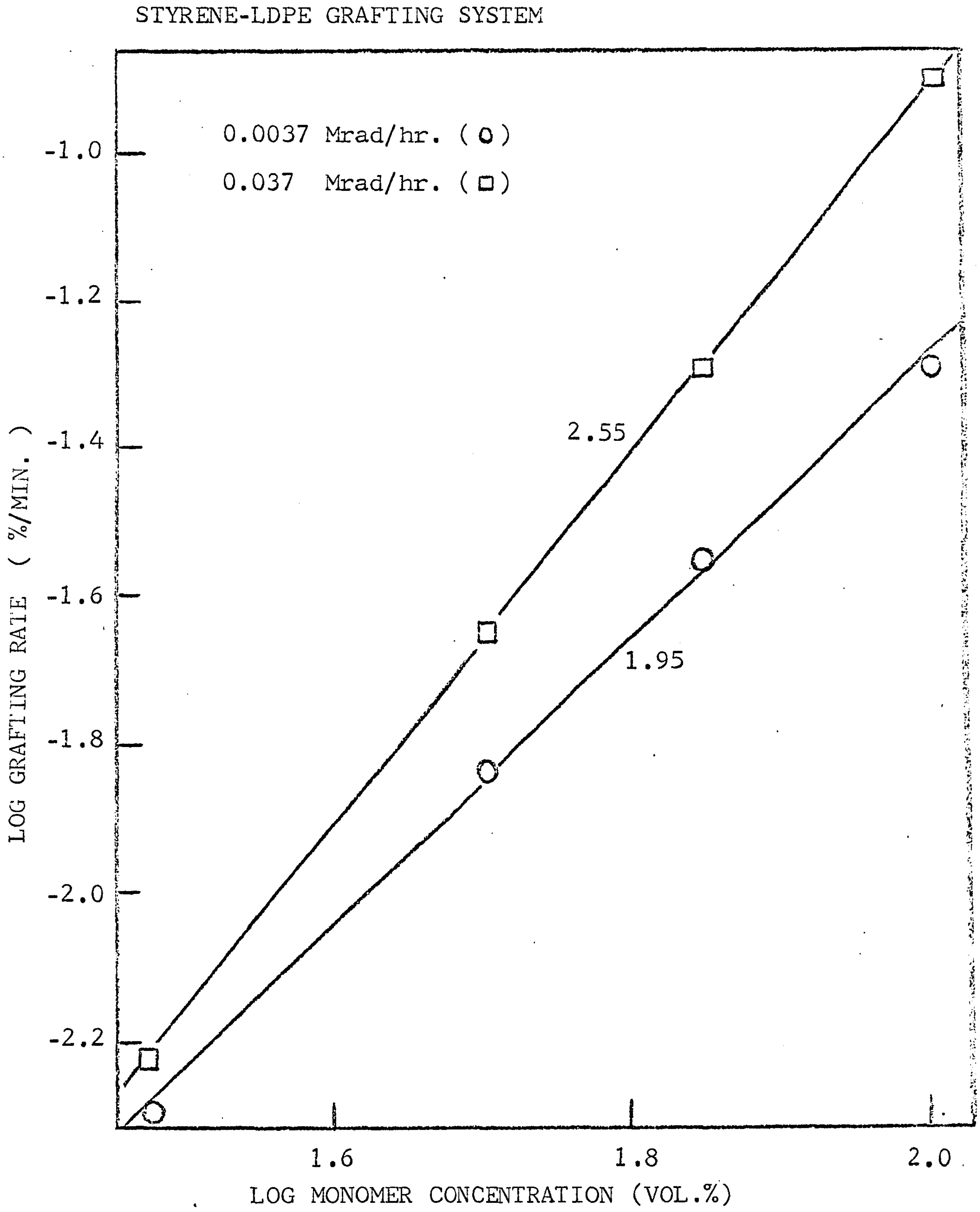


Fig. 17 Dependence of graft polymerization rate on monomer concentration for Styrene-LDPE system.

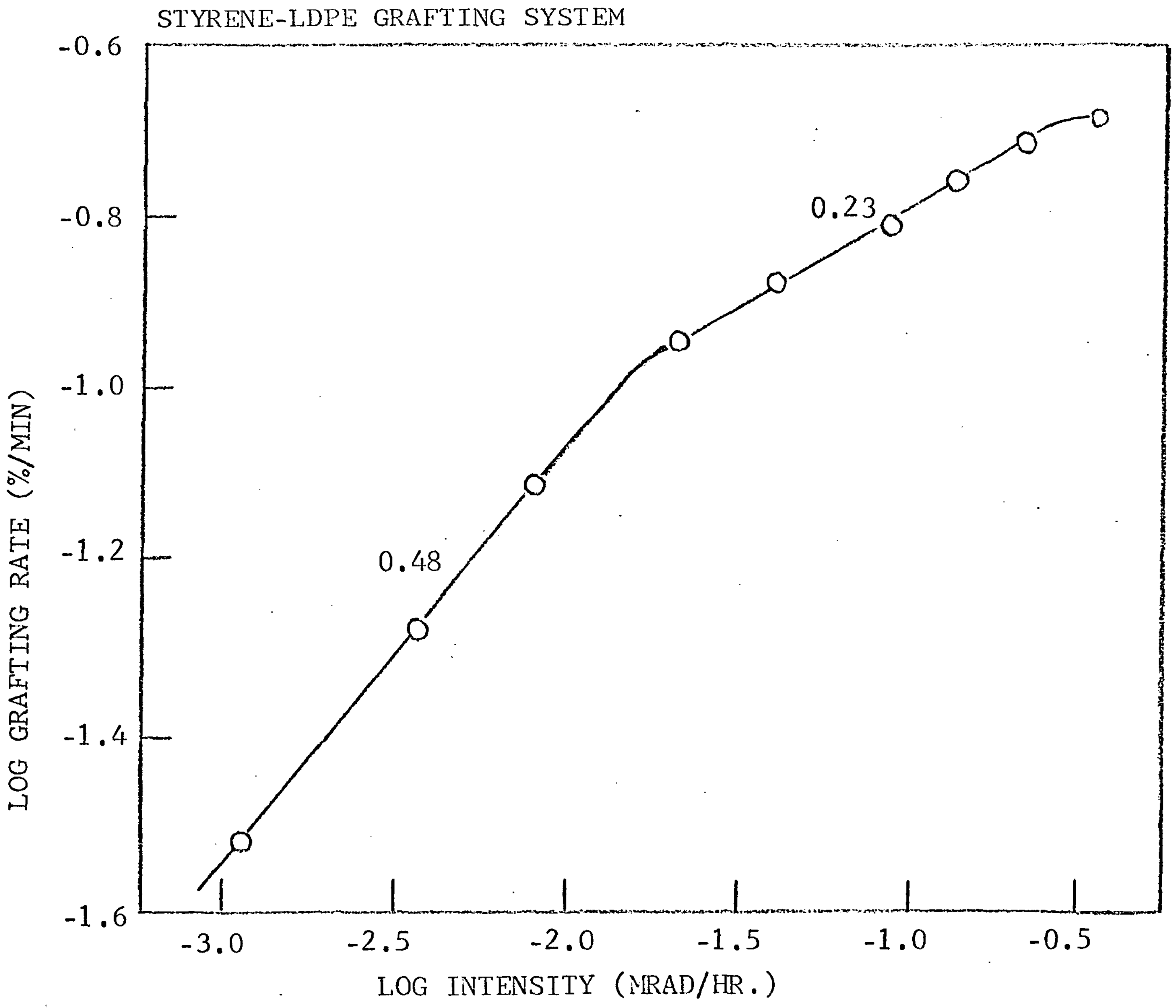


Fig. 18. Dependence of graft polymerization rate on radiation intensity for Styrene-LDPE grafting system.

Mechanisms of the Graft Polymerization

We have established the experimental dependence of the graft polymerization rate on monomer and intensity, the question arises as to the mechanism(s) responsible for the observed behavior. In this section, several possible mechanisms operating in the grafting system are presented and discussied.

(A) Dose-Rate Dependence

The dependence of the grafting rate on radiation intensity decreases from 1/2-order to 0-order with decreasing monomer concentration (see Figure 14). The result indicates different mechanisms operating with pure styrene and 30% styrene. The mode of termination is changing from the usual bimolecular termination, bimolecular coupling and/or disproportionation of propagating radicals, to primary termination, reaction of a propagating radical with a primary radical, as monomer concentration decreases,

Bimolecular Termination:

$$M\cdot + M\cdot \xrightarrow{k_{tb}} \text{dead polymer} \qquad (1)$$

Primary Termination:

$$M\cdot + P\cdot \xrightarrow{k_{tp}} \text{dead polymer} \qquad (2)$$

and rates of termination can be expressed as R_{tb} and R_{tp} respectively:

$$R_{tb} = k_{tb} [M\cdot]^2 \qquad (3)$$

$$R_{tp} = k_{tp} [P\cdot] [M\cdot] \qquad (4)$$

The initiation step of radiation grafting is considered to involve two reactions. The first is the production of primary radicals (polymeric radicals, hydrogen radicals, monomer and/or solvent radicals) P• by radiation,

$$P \xrightarrow{\text{radiation}} P\cdot \qquad (5)$$

followed by the addition of the primary radicals to monomer to form the propagating radical,

$$P\cdot \quad + \quad M \xrightarrow{k_i} \quad M\cdot \qquad (6)$$

The propagation step may be represented by

$$M_n\cdot \quad + \quad M \xrightarrow{k_p} \quad M_{n+1}\cdot \qquad (7)$$

The rates of initiation and propagation can be expressed as:

$$R_i = k_i \, [P\cdot] \; [M] \qquad (8)$$

$$R_p = k_p \, [M\cdot] \; [M] \qquad (9)$$

Using the steady-state assumption, $R_i = R_t$, one may get

$$[M\cdot] = (R_i/k_{tb})^{1/2} \quad \text{(if bimolecular termination)} \quad (10)$$

or $$[M\cdot] = k_i \, [M] \, / \, k_{tp} \quad \text{(if primary termination)} \quad (11)$$

Substitution into equation (9) yield

$$R_p = k_p \, [M] \, (R_i/k_{tb})^{1/2} \quad \text{(bimolecular termination)} \quad (12)$$

or $$R_p = k_p \, k_i \, [M]^2 \, / \, k_{tp} \quad \text{(primary termination)} \quad (13)$$

The kinetics of polymerization where termination occurs exclusively by primary termination show the grafting rate to be 2-order in monomer concentration and independent of dose rate. Whereas the grafting rate of usual bimolecular terminated polymerization was 1/2-order on radiation intensity.

Our styrene-CAB grafting results clearly show a continuous shift from bimolecular termination to primary termination as the monomer concentration decreases from 100%-styrene to 30%-styrene. (The dependence of R_p on I decreases from 0.47 to 0.05). With decreasing monomer concentration, the concentration of monomer is not high enough for all primary radicals to be scavenged by monomer as in the usual case in radical polymerization. Similar results have been observed in the polymerization of styrene dissolved in toluene.[65]

In styrene-HDPE grafting study, similar results at the intermediate dose rate region (ca. 0.00769 - 0.0583 Mrad/hr.) showed a 0.28 dose rate order for 100% styrene and a zero dose rate order for 50% styrene.(see Figure 16).

Primary termination may be especially important in high viscosity systems (such as a grafting system) where primary radicals have greater mobility than the larger-sized propagating radicals. Primary radical termination has been observed in homopolymerization of styrene carried out in high viscosity media.[66]

Chapiro[67] has pointed out primary termination becomes increasingly important at high dose rates as the concentration of primary radicals increases. In styrene-HDPE and styrene-LDPE system, the experimental data shows that the dependence of grafting rate on radiation dose rate changes from 1/2- to 1/4- to 0- order as the dose rate increases. (Figures 15 & 17)

It should be noted that the primary radical recombination

$$P\cdot \quad + \quad P\cdot \longrightarrow P_2 \qquad (14)$$

can be considered as a special case of primary termination (equation 2).

(B) 3/2-order Dependence of R_p on [M]

The 1.5-order dependence of rate on monomer at low dose rate (0.00368 Mrad/hr.) may indicate that the termination step of the graft polymerization proceed by bimolecular termination and primary termination simultaneously. In the usual free radical homopolymerization, initiation rate is independent of monomer concentration and R_p is first-order in monomer concentration for bimolecular termination, and R_p is second order in monomer concentration for primary radical termination. The reason for the contribution of primary radical termination may be due to the reaction being carryied out in the high viscosity system.

The other possible explanation is that the initiation rate is a function of monomer concentration and it lead to higher order dependence of R_p on [M]. (see page 96 for detailed discussion).

An alternate explanation is that initiation is independent of monomer as is usual but for bimolecular termination between propagating radicals the termination rate constant may depend on the viscosity of the reaction medium. The viscosity of styrene-benzene increases slightly with increasing styrene concentration; k_{tb} would decrease and the polymerization rate increase with concentration of styrene. This effect has been observed in some homopolymerizations where the rate has been found to be first-order in monomer and close 1/2-order in the viscosity of the system[68], that is

$$k_{tb} = k'_{tb}/\zeta = k''_{tb}/[M] \qquad (15)$$

which substituted into equation 12 yields

$$R_p = k_p[M](R_i \; /k'_{tb})^{1/2} = k_p[M]^{3/2}(R_i/k''_{tb})^{1/2} \qquad (16)$$

However, the range of viscosities of the benzene-styrene mixtures do not vary more than 10-15% at most over the range of compositions studied. It is doubtful that this range of viscosities would have a large enough effect on the termination rate constant to increase the dependence of the rate of graft polymerization on monomer from first-order to 3/2-order.

(C) 5/2-Order Dependence of R_p on [M]

The 5/2-Order dependence of graft polymerization rate on monomer at high dose rate is a most surprising result and more difficult to understand. Some possible mechanisms for this result are discussed below:

Grafting by ionic mechanism

Since radiation yields ions as well as radicals, the operation of an ionic mechanism, either completely or together with a radical mechanism, in the grafting system cannot be overlooked. Indeed, the first instance of radiation-initiated graft polymerization by ionic mechanisms has been reported by Kabanov and co-workers.[69] If graft polymerization occurs by an ionic mechanism, the 5/2-order dependence of rate on monomer could be due to monomer being involved in solvating the ionic initiating and propagating species in addition to its usual role in the initiation and propagation steps. This type of effect has been observed when ionic homopolymerizations are carried out in solvents of low solvating power such that the monomer is more polar than the solvent. The ionic species are solvated by monomer instead of solvent and the rate of polymerization shows much higher than normal orders of dependence on monomer; monomer is kinetically involved as both a reactant and solvating species.[70]

The presence of an ionic mechanism could also be responsible for the observed 5/2-order without the need to invoke such a large solvation effect to account for an additional 1- or 3/2- order dependence. Ionic grafting would be 2-order in monomer if the initiation step is first order in monomer. Solvation would then need to be invoked to account for only an additional 1/2-order dependence of rate on monomer.

However, we doubt that our reaction is occurring by an ionic mechanism for the following reasons:

1. Radiation-induced cationic polymerization of styrene required the super-dryness of the reaction medium ($[H_2O] < 10^{-2}$M) or high radiation intensity ($I > 1$ Mrad/sec.).

Our procedures used for drying styrene and benzene were far less exhaustive than those which appear to be necessary to observe ionic grafting. We also used relatively low dose rate ($I < 1$ Mrad/hr.) in these experiments.

2. Radiation-induced cationic polymerization of styrene showed 0.5 to first order dose rate dependence depending on the degree of dryness of the system. Our grafting kinetics do not show this effect. (The dependence of grafting rate on dose rate were between 0.47 to 0.05 in our system).

3. Cellulose esters are hydrophilic polymers which absorb moisture very easily. During the process of glass blowing, water molecules condensed in the reaction tubes and were not removed completely by vacuum alone according to DSC.

Energy Transfer

An energy transfer mechanism had been considered as being responsible either wholly or in part for the increased orders of dependence of rate on monomer and carefully examined in styrene-polyethylene grafting system by other people in our laboratory. This mechanism involving energy transfer (equation 17), from excited polymer to benzene, which competed with the formation of primary radicals (eq. 18) as shown below

$$\begin{tikzcd}
 & & P + B^{*} \arrow[r] & \text{energy dissipation by } B^{*} & (17) \\
P \arrow[r, "\text{radiation}"] & P^{*} \arrow[ur, "B"] \arrow[dr] & & & \\
 & & P\cdot \arrow[r, "M"] & \text{initiation} & (18)
\end{tikzcd}$$

where P^{*} and B^{*} are the excited polymer and benzene, respectively. Energy transfer results in a decrease in the initiation rate and its extent would increase with the concentration of benzene. The initiation rate would be inversely dependent on the benzene concentration and, therefore, directly dependent on the styrene concentration. Depending on the mechanism by which energy transfer occurs, whether by the Forster or Exciton mechanisms,[71] the initiation rate would be either 1- or 2-order in monomer. Energy transfer could account completely for the 3/2-order dependence at low dose rates; it might not be sufficient by itself to account for the 5/2-order dependence at high dose rate.

Odian and coworkers[72] indicated that energy transfer is not responsible for the increased dependence of grafting rate on monomer. n-Octane was substituted for benzene as the diluent in the grafting of styrene to polyethylene. Energy transfer from excited polyethylene to n-octane would not be expected to occur (or if it did, its extent should be very small compared to energy transfer with benzene) since both polyethylene and n-octane are alkanes. n-Octane was also chosen as the diluent since it is a reasonable solvent for polystyrene[73] in the concentrations used and a Trommsdorff-type effect would not be introduced by substituting it for benzene.

The graft polymerization rates were determined at 0.0076, 0.037, 0.213 Mrad/hr. and plotted against the inside styrene concentrations on a log-log scale to yield the kinetic orders of dependence of rate on monomer as 2, 3, and 3, respectively, when the non-aromatic n-octane was used as the diluent instead of benzene.

Since high orders of dependence of rate on monomer was not affected by the diluent, either benzene or n-octane, it is clear that energy transfer from excited polyethylene to diluent is not responsible for the observed results. If such energy transfer were occurring with benzene as the diluent, it would be absent when n-octane is used instead and the order of dependence of rate on monomer should decrease.

Unusual Initiation Process

The high order of dependence of grafting rate on monomer may be due to an abnormally high order of dependence of the initiation rate on monomer. The initiation step could be

$$\begin{tikzcd}
 & & Z \arrow[dr, "M"] & \\
P \arrow[r, "\text{radiation}"] & P\cdot \arrow[ur, "M"] \arrow[rr, "2M"'] & & R\cdot
\end{tikzcd} \qquad (19)$$

where Z is an intermediate species (PM•) which is inactive, R• is the active species to propagate polymerization and may have a structure P-M-M• or a complex structure.

The initiation rate in the above mechanism is 2-order in monomer concentration and this leads to 2- and 3- order dependences of grafting rate on monomer concentration for bimocular and primary termination, respectively.

The critical question in this mechanism is why Z is not the active species. The high viscosity of the reaction medium in which grafting takes place may decrease the mobility and, thus,the reactivity of the primary radicals to such an extent that the propagating radicals cannot be considered to be formed until a number of monomer molecules have added to the primary radicals. That is , radicals possess sufficient mobility to propagate only after several monomer molecules have added. This effect could be responsible partly or completely for the 5/2-order dependence of reaction rate on monomer concentration.

A 5/2-order dependence of reaction rate on monomer at high dose rate (0.085 Mrad/hr.) could result if the initiation rate is third-order in monomer and termination occurs by bimolecular reaction of propagating radicals; a 3/2-order dependence of rate on monomer at low dose rate (0.00368 Mrad/hr.) could be accounted for if initiation were first-order in monomer with bimolecular termination.

Referring to this unusual initiation mechanism, questions have arisen:

1. Why were the initiation rates third-order in monomer at high dose rate and first-order in monomer at low dose rate? Is this unusual initiation mechanism only shown at high dose rate? If that is so, then why?, the high viscosity of the reaction medium could not be responsible for this mechanism because the viscosity of the medium is not a function of radiation intensity.
2. Does this mechanism contradict Flory's principle of functional group reactivity being independent of size?, or, does this mechanism indicate a penultimate effect, i.e., the reactivity of propagating species is affected by the next-to-last or penultimate monomer unit.? Such effect has been observed in many radical copolymerizations where monomers contain highly bulky or polar substituents.[74] Or, is there a special complex structure required for primary radicals to gain activity to propagate?

Although some unanswered questions exist, the possiblity of an unusual initiation mechanism can not be overlooked since grafting is proceeding in an unusual condition (high viscosity of the reaction medium).

Primary Radicals Termination and/or Recombination

The primary radicals formed by radiation were all involved in the following reactions:

Initiation $P\cdot + M \longrightarrow M\cdot$ (20)

Primary radical recombination $P\cdot + P\cdot \longrightarrow P_2$ (21)

Primary radical termination $P\cdot + M_n\cdot \longrightarrow M_n$ (22)

where equation 21 might be considered as a special case of equation 22. As discussed in the previous section,a decrease in monomer concentration or an increase in radiation intensity should favor reactions (21) and (22) in their competition with reaction (20). Results show that the dependence of the reaction rate on radiation intensity decreases from 1/2-order to 0-order indicating a continuous shift from bimolecular termination to primary termination as the monomer concentration decreases from 100% styrene to 30% styrene.

Assume that the following kinetics apply

At high [M]: $R_p = k_p[M](R_i/k_{tb})^{1/2}$

At low [M]: $R_p = k_p k_i [M]^2/k_{tp}$

At intermediate [M]: mixture of bimolecular and primary terminations

For 30% styrene, reaction followed by primary termination chiefly and rate was independent of radiation intensity. We can see that the data points gathered at far left side of R_p vs. [M] plot (Figure 13). For 100% styrene, reaction proceeded by bimolecular termination predominantly and reaction rate was depend on 1/2-order of radiation intensity. In figure 13, data points at far right side of the plot were spread upward with increasing dose rate. The high order (2.69) dependence of grafting rate on monomer concentration at 0.085 Mrad/hr. might be an experimental artifact in which the two different mechanisms, namely bimolecular and primary radical terminations, were operating at the same time.

Depending on the contributions of these two mechanisms, the radiation intensity I, and the relative values of k_{tb} and k_{tp}, the overall grafting rate versus monomer concentration plot may be located in a way that the slope of the line drawn among all the experimental points is greater than that of either mechanism.

If there is a clear boundary between the two mechanisms, say 50% styrene, an S shape graph should be obtained instead of a staight line. For high monomer concentration region ($[M] > 50\%$), the slope should be close to 1 according to bimolecular termination. For the left portion of the log R_p vs. log [M] plot one may obtain 2-order dependence following primary termination.

However, our experimental data (the plot in Figure 13 for 0.085 Mrad/hr.) do not show an S curve. This might indicate an insufficient number of data points or a continuous shift of mechanism from primary termination for low styrene concentration to bimolecular termination for high styrene concentration.

An alternate explanation for the high order dependence of reaction rate on monomer concentration is that the initiation rate (equation 20) in a high viscosity medium is lowered compared to what one expected due to the competition from equations 21 and 22. This effect might show up kinetically in our work as a higher order of dependence of the rates of initiation and polymerization on monomer. This effect would be expected to be more exaggerated as the dose rate increases since primary radical recombination is 2-order in the radical concentration while initiation is only 1-order. This is exactly what is observed as the dependence of grafting rate on monomer increases from 3/2-order to 5/2-order with increasing dose rate.

CONCLUSIONS

In order to study the kinetics of diffusion-free radiation graft polymerization of styrene onto cellulose ester, it was desirable to use a polymer which would be swollen to a large extent by styrene so as to study the variation of grafting rate with monomer concentration over a wide range of concentration. Cellulose diacetate is not a proper polymer for this purpose since it shows negligible swelling by styrene. The polymer with a bulkier alkyl group such as cellulose acetate butyrate proved to be more compatible with styrene than cellulose acetate. Monomer concentration increases with decreasing acetyl and increasing butyryl content. The molecular weight of the cellulose ester was important in that the lower molecular weights resulted in brittle films which were difficult to handle. Evaluation of the various available cellulose esters led to a choice of CAB-171-40 (Eastman batch AM 1934B) as the polymer for our studies.

Cellulose ester film samples were prepared by solution casting. The use of acetone as a solvent did not produce uniformly reproducible films due to the very fast evaporation rate. Cyclohexanone was used as a co-solvent with acetone to slow down the evaporation rate. The casting solution was made by dissolving 25 grams of CAB-171-40 powder in a mixture of 100 ml. acetone and 100 ml. cyclohexanone. Higher polymer concentrations led to the formation of bubbles in the cast film; lower concentrations yielded films of non-uniform thickness. The swelling ability of the polymer film depended on the concentration and evaporation rate of the cast solution. CAB-171-40 films made by the above casting solution had an extent of swelling of styrene-benzene mixture equal to 50% and independent of the composition of the mixture and film thickness.

Styrene was the chosen monomer for this grafting study since it had been well studied in other systems. Benzene was employed as the diluent for styrene to vary monomer concentration since benzene and styrene have similar solubility, diffusion, viscosity and radiation characteristics.

The diffusion-free nature of the grafting reaction for our system was established by studying the reaction rate for various film thicknesses. The grafting rates were shown to be independent of film thickness for high and low radiation intensities and for both pure styrene and diluted styrene. This is the behavior expected for a diffusion-free reaction. For a diffusion-controlled graft polymerization, the reaction rate would be inversely dependent on film thickness.

Since our preparation of samples did not involve "super-drying"procedures, a requirement for radiation cationic polymerization of styrene, graft polymerization in this study should proceed by a radical mechanism chiefly.

The dependence of the graft polymerization rate on radiation intensity was determined at four different monomer concentrations over a wide range of radiation intensities from 0.0037 Mrad/hr. to 0.085 Mrad/hr. for 3.5 mil thick CAB film. The dependence of the grafting rate on radiation intensity decreases from 1/2-order for 100% styrene to 0-order for 30% styrene with decreasing monomer concentration. This indicates a continuous shift from bimolecular termination to primary termination as the monomer concentration decreases.

The dependence on monomer concentration of the rate of polymerization was determined at five different radiation intensities over the range of styrene compositions from 25 to 100 volume-percent for 3.5 mil thick CAB film. The dependence of the grafting rate on monomer concentration to increase from approximately 3/2-order to slightly greater than 5/2-order with increasing radiation intensity from 0.0037 to 0.085 Mrad/hr. The abnormally high order (2.69) dependence of grafting rate on monomer concentration at the highest radiation intensity is difficult to understand. We offer two possible mechanisms for the observed results:

(1) Unusual Initiation Process:

$$P \xrightarrow[M]{\text{radiation}} Z \xrightarrow{M} R\cdot$$

Polymerization propagates only after several monomer molecules have added to the primary radicals. The initiation rate is 2-order in monomer concentration and this leads to 2- and 3-order dependencies of grafting rate on monomer concentration for bimolecular and primary terminations, respectively. The high viscosity of the reaction medium in which grafting takes place might be responsible by decreasing the mobility and the reactivity of the primary radicals.

(2) Reaction involves a combination of primary and bimolecular terminations:

The high order dependence of grafting rate on monomer concentration may be an experimental artifact. The grafting rate versus monomer concentration plot may consist of two extreme cases--one for the higher monomer concentration and the other one for the lower monomer concentration. For 100% styrene, reaction proceeded by bimolecular termination predominantly and its rate depended on 1/2-order of radiation intensity. For 30% styrene, reaction follows primary termination mainly and its rate was independent of radiation intensity. For intermediate monomer concentrations, reaction involves a combination of primary termination and bimolecular termination. There is a continuous shift from bimolecular termination to primary termination as the monomer concentration decreases.

APPENDIX

DEFINITIONS

The rad - The amount of energy absorbed per unit weight of medium is known as the absorbed dose. The official unit of absorbed dose is the rad, defined as 100 ergs per g.

1 rad = 100 ergs/g

= 10^{-5} J g^{-1}

= 6.242×10^{13} eV g^{-1}

= 10^{-5} W s g^{-1}

Dose Rate - absorbed dose in unit time. e.g., Mrad/hr.

The curie (Ci) - a unit of radioactivity defined as the quantity of any radioactive nuclide in which the number of disintegrations per second is 3.700×10^{10}.

G-values - the number of molecules changed (formed or destroyed) per 100 eV of energy absorbed.

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