72-605

BLOCK, Ira, 1941-
   RADIATION-INDUCED GRAFTING OF BUTADIENE TO
   CHLORINATED POLYETHYLENE AND POLY(VINYL
   CHLORIDE).

   University of Maryland, Ph.D., 1971
   Engineering, nuclear

University Microfilms, A XEROX Company, Ann Arbor, Michigan

RADIATION-INDUCED GRAFTING OF

BUTADIENE TO CHLORINATED POLYETHYLENE

AND POLY(VINYL CHLORIDE)

by

Ira Block

Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
1971

APPROVAL SHEET

Title of Thesis: Radiation-Induced Grafting of Butadiene

to Chlorinated Polyethylene and Poly(vinyl

chloride)

Name of Candidate: Ira Block

Doctor of Philosophy, 1971

Thesis and Abstract Approved: _____

Joseph Silverman
Professor
Department of Chemical Engineering
Laboratory for Radiation and
Polymer Science

Date Approved: _April 1, 1971___

ABSTRACT

Title of Thesis: Radiation-Induced Grafting of Butadiene
                  to Chlorinated Polyethylene and Poly-
                  (vinyl chloride)

Ira Block, Doctor of Philosophy, 1971

Thesis directed by: Professor Joseph Silverman
                     Department of Chemical Engineering
                     Laboratory for Radiation and Polymer Science

The radiation-induced grafting of butadiene (BD) from methanol solution to thin films of chlorinated polyethylene (PECL) and poly(vinyl chloride) (PVC) was studied as a function of chlorine content, dose rate, irradiation time, and BD concentration at room temperature. A method for determining the crystal content of chlorinated films by IR measurements is described. The results for chlorination and grafting show the least scatter when expressed in terms of weight gain per unit weight of amorphous film. This indicates that both processes take place principally in the amorphous region.

The graft yield, expressed as percent graft, was found to increase with increasing weight percent of chlorine added to the amorphous fraction of the film (PCA), approaching a limiting value for grafting of BD liquid to polyethylene films with PCA greater than 45.

For grafting to PECL and PVC from methanol-butadiene

solutions, the graftyield was found to increase with increasing methanol concentration, reaching a maximum at from 77 to 85 vol-% methanol, depending upon the PCA, and rapidly decreasing thereafter.

Except for an early transient condition, the grafting rate from liquid butadiene to PVC was found to be almost independent of dose rate in the range from 3 - 300 krad/hr. However, the early graft rate is very high, and increases with increasing dose rate.

The results of the investigation show that chlorination of the amorphous PE increases the glass transition temperature of the polymer, and that greatly increased graft yields are obtained when T_g is made to approach the reaction temperature. Further increase in graft yield is obtained upon dilution of the monomer by providing conditions of monomer concentration and polymer viscosity that more closely approach an optimum. The results are explained in terms of the effect of the added chlorine and the sorbed monomer on the viscosity of the swollen amorphous polymer. The effect of chlorine content on the radical yield is shown to play a small role in the enhancement of the graft yield.

To Wendy

who stayed with me through thin

ACKNOWLEDGMENTS

To Professor Joseph Silverman, mentor and guide, without whom this work would have been neither possible nor necessary;

To Mr. Elbert Barrett for instruction and aid in the machinist's craft;

To Mrs. Donna Lichvar for her help in typing the manuscript;

To my fellow students for their helpful suggestions during the course of this work;

To the Faculty and Staff of the Chemical Engineering Department, University of Maryland for their contribution to my education;

To the Division of Isotope Development, and to the Division of Research, United States Atomic Energy Commission for their financial support,

<div align="center">Thank you.</div>

TABLE OF CONTENTS

LIST OF TABLES

vi

LIST OF FIGURES

vii

CHAPTER I

INTRODUCTION

The radiation-induced grafting rates of butadiene (BD) to poly(vinyl chloride) (PVC) are higher than those to low density polyethylene (LDPE) [1,2]. The saturation concentration of the monomer in both polymers is about 1 wt-%. In addition, it has been shown that chlorination of LDPE increases the rate at which various monomers can be grafted to it by factors of up to 40 [3]. Chlorine evidently plays a major role in these radiation-induced grafting reactions, and an understanding of this role is one of the major objects of this study. The increase in graft yield upon chlorination of LDPE can be due to either chemical or physical changes induced in the polymer. Changes that could bring about the reported effects are (1) increased radical yield upon irradiation, and (2) increased viscosity of the polymer.

This work is concerned with the radiation-induced grafting of BD to films of chlorinated, low-density polyethylene (PECL) and to poly(vinyl chloride) films. Particular emphasis is laid on the effects of chlorine content, monomer concentration, film crystallinity, and dose rate on the graft yield. This chapter describes the kinetic features of the grafting reaction in terms of these factors.

1

1.1 The Role of Chlorine

This section is concerned with basic definitions, and the possible mechanisms whereby chlorination of LDPE can give rise to increased graft yields. Analysis of chemical effects leads to the conclusion that increased radical yields can give rise to a twofold increase in graft yield. Reported results on other systems lead to the conclusion that increased viscosity of the polymer matrix is the major cause of increased graft yield. An experimental test of this hypothesis is presented.

The standard kinetic model for radiation-induced grafting (Appendix A) can be used to describe the steady-state grafting rate in terms of moles of monomer grafted per liter of swollen polymer per unit time. Integration of the graft rate over the time of reaction gives the graft yield in moles of graft per liter of swollen polymer. The kinetics, however, are measured by determining the weight gain of the base polymer after grafting, and the results are usually reported as the percent graft as a function of grafting time. The percent graft is defined as follows:

$$PG = [(W_f - W_i)/W_i] \times 100 \ * \tag{1}$$

where W_f = the weight of the grafted sample, and

W_i = the initial weight of the sample before grafting.

* All symbols are collected and defined in Appendix C.

The molar graft is defined as[2]

$$MG = \frac{(W_f - W_i)\ 1000}{M\left[\dfrac{W_i}{\rho_o} + \dfrac{W_f - W_i}{\rho}\right]}$$ (2)

where   MG = molar graft yield (mole/l);

W_f = weight of the grafted sample;

W_i = initial weight of the sample;

M = molecular weight of the monomer;

ρ_o = density of ungrafted sample (g cm^{-3}), and;

ρ = density of the grafted polymer (g cm^{-3}).

Equation 2 is based on the assumption that the molar volumes are additive. Although there is some evidence to show that this is not strictly true[4], the deviations are small enough to be neglected for the purposes of this study.

In this work graft yields are reported both as PG and as MG. The percent graft is of practical interest in cost analysis and plant design work. The molar graft yield is more useful in studies of reaction kinetics and mechanism. Where density effects are important the molar graft yield is required, as the PG is not sensitive to volume changes.

Chlorination of polyethylene films takes place almost exclusively in the amorphous region. The exothermic reaction can generate enough heat to cause localized melting of the crystals, which changes the crystal fraction of the material,

but the remaining crystals are essentially free of chlorine[5].
We may, therefore, consider chlorinated polyethylene (PECL)
as a composite consisting of crystalline polyethylene dis-
persed in a chlorinated amorphous matrix. For low to moderate
degrees of chlorination, the amorphous region is essentially
a random copolymer of ethylene and vinyl chloride[6] with
only a few units of each chain containing more than one
chlorine atom. The yield of radicals produced by ionizing
radiation in the crystalline regions should be that of pure
hydrocarbon crystals. Also, there is substantial evidence to
indicate that the radicals produced in the crystalline regions
migrate rapidly to the surface of the crystallites where they
may enter into reactions in the amorphous zone[7]. As a
first-order approximation these radicals may be assumed to
be homogeneously distributed throughout the amorphous re-
gion[7]. In the treatment that follows, this assumption is made.

1.1.1 Chemical Effects in Linear Independent Systems.

If the radiolysis of the two components of the amorphous
region proceeds independently the rate of radical production
obeys the relation

$$\frac{d[R \cdot]}{dt} = (\phi_A[A] + \phi_B[B]) \, I \qquad (3)$$

where $[R \cdot]$ = radical concentration in the amorphous

region (mole/l);

$\emptyset_A$ = molar yield of radicals from A* (moles of radical per mole of A per rad);

$\emptyset_B$ = molar yield of radicals from B (moles of radical per mole of B per rad);

[A] = concentration of A (mole/l);

[B] = concentration of B (mole/l);

I = dose rate (rad sec^{-1}).

If component A is polyethylene (PE) and component B is PVC, Equation 3 shows that the radical yield should increase linearly with the chlorine content, and, if the steady-state kinetic model (Appendix A) is applicable, the graft rate should be proportional to the square root of the radical production rate.

Equation 3 may be converted, after Nikitina and Bagdasaryan[8], to the following form:

$$\frac{d[R\cdot]}{dt} = \emptyset_A I ([A] + [B]) \left[\frac{1 + \emptyset_{rel}(x_B/x_A)}{1 + (x_B/x_A)} \right] \quad (4)$$

---

* The molar radical yield, $\emptyset$, is related to the G value for radicals by $\emptyset = G \frac{molecules}{100 \ eV} \times 0.6 \times 10^{12} \frac{eV}{erg} \times 100 \frac{erg}{g \ rad}$

$\times M \frac{g}{mole} \times \frac{1}{N}$, where N is Avogadro's number.

where $\emptyset_{rel}$ = the ratio of $\emptyset_B$ to $\emptyset_A$;

x_A = the mole fraction of A, and ;

x_B = the mole fraction of B.

The weight percent chlorine added to the amorphous region (PCA) is defined as

$$PCA = \frac{(w_f - w_i)}{f_a w_i} \times 100 \qquad (5)$$

where w_f = final weight of chlorinated sample;

w_i = initial weight of chlorinated sample;

f_a = amorphous fraction of chlorinated sample;

and, thus, the mole fraction of PVC is

$$x_{PVC} = \frac{PCA}{100} \times 27 \frac{gram}{(mole\ of\ ethylenic\ units)} \times \frac{1}{35.5}$$

$$\frac{(mole\ chlorine)}{gram} . \qquad (6)$$

The PCA for ordinary PVC is 131.

If in Equation 4, A is PE and B is PVC, then, since the G value for PVC, $G(R\cdot)_{PVC}$ is approximately twice the value for PE, $G(R\cdot)_{PE}$[9], it is to be expected that a PECL film with 40 wt-% chlorine added to the amorphous region, and with a crystal content of 30% will, have a radical production rate 1.7 times that of unchlorinated PE, and a graft yield 1.3 times that of the unchlorinated PE.

1.1.2 Chemical Effects Under Conditions of Energy Transfer

It is possible for absorbed energy to be transferred from the ethylenic units to the vinyl chloride units of the polymer and enhance the probability of scission of the C-Cl bond. Such energy transfer could cause the radical yield to increase more rapidly than the chlorine content. Effects of this type have been reported in which the G(R·) of binary solutions of chlorinated compounds is as high as $30^{(9)}$.

In the manner of Nikitina and Bagdasaryan, possible energy transfer effects are described in terms of the following model$^{(8)}$. For a reaction in which A and B are PE and PVC respectively, A* and B* intermediate excited states created by the absorption of radiation, P_{AB} the probability of energy transfer from A* to B*, P_{BA} the probability of energy transfer from B* to A*, the total radical production rate is

$$\frac{d[R\cdot]}{dt} = \phi_A I([A] + [B]) \left[\frac{1 + \phi_{rel} P_{rel} (x_B/x_A)}{1 + P_{rel} (x_B/x_A)} \right] \qquad (7)$$

where $P_{rel} = P_{BA}/P_{AB}$ and the other symbols are as previously defined (Appendix C).

Under steady-state conditions, the graft yield is proportional to the square root of the graft rate. A relative graft yield,

$$\left(\frac{(dR\cdot)}{dt} \middle/ [\phi_A I([A] + [B])] \right)^{1/2}$$ can be defined

which compares the yield in a chlorinated system to that of pure PE*. Figure 1 is a plot of the relative graft rate vs PCA with P_{rel} as a parameter. $\emptyset_{rel}$ is assumed to be 4.5, based on $G(R\cdot)_{PVC} = 14$ and $G(R\cdot)_{PE} = 7$ [9]. Note that for $P_{rel} = 1$, Equation 7 reduces to Equation 4. In the absence of density changes, the curve has a rapid rise which rolls off to approach a limiting value as the chlorine content increases. Equation 7 shows that for $P_{rel} \gg 1$, the relative graft yield approaches $[\emptyset_{rel}]^{1/2}$ as x_B approaches unity. For highly-chlorinated samples with 30% crystal content, an increase in radical production rate by a factor of 3.5, and an increase in the steady-state graft rate of 85% would be expected.

The above analyses show that an increase in radical yield due to chlorination may double the graft yield, but it cannot account for the factor of ten that is observed.

1.1.3   Viscosity Effects

Because of the magnitude of the change, it appears that the bulk of the increase in graft yield arising from chlorination of the polymer is due to physical processes. In their work on the grafting of styrene to PVC films Takamatsu and Shinohara[2] report a maximum in the grafting rate at a

_____

* ([A] + [B]) is a constant equal to the initial molar concentration of ethylene in PE.

monomer concentration in the film of 3.2 mole/l. The maximum

rate is 15 times the rate at the equilibrium monomer concen-

tration of 5.2 mole/l. Investigations of the elastic modulus

of the film as a function of sorbed monomer showed that the

modulus remains essentially constant up to 3.2 mole/l and

decreases rapidly to very low values as the monomer concen-

tration approaches the equilibrium value. They concluded

that the grafting rate increases with monomer concentration

as long as the polymer viscosity remains high, but that at

the higher monomer concentrations the monomer acts as a

plasticizer and allows the molecular motion of the polymer

to increase. This decrease in viscosity leads to higher

termination rates, and decreases the overall grafting rate.

Kamel[7] in his studies of the vapor-phase grafting of

styrene to polyethylene reached the same conclusions regard-

ing the effect of matrix viscosity on the grafting rate.

He shows that the graft yield after a 4-hr irradiation

increases with monomer concentration in the film to a maximum

at 4 wt-%, and decreases upon further sorption of styrene.

The maximum graft yield is approximately 4 times that ob-

tained at the equilibrium concentration of 15 wt-%.

Oswald and Kubu[11] in their investigations of the

physical properties of chlorinated polyethylene films found

that the elastic modulus increased with increasing chlorine content. Figure 2 is a plot of elastic modulus vs percent chlorine added, constructed from their results. The curve increases sharply at low chlorine concentrations and rolls off to an asymptotic value as the PCA is raised. It is reasonable to expect that the graft yield of butadiene to chlorinated polyethylene should increase with increasing chlorine content in much the same way that the elastic modulus increases with increasing chlorine content.

1.2 The Dilution Effect

This section discusses the results of investigations of the dilution effect in other monomer-polymer systems in the light of the model developed in this laboratory[12,13] to explain enhanced graft yield at decreased monomer concentration.

It has been shown for several systems that when a polymer is immersed in a solution of monomer the grafting rate of monomer to polymer can be increased over that obtained when the polymer is immersed in the pure monomer[10,13-16]. For example, grafting styrene to polyethylene from a 70 vol-% methanol solution increases the graft yield by approximately a factor of 3[13,14]. The increase in grafting rate appears to be a function of the particular monomer-polymer system, and data obtained from one system is not necessarily applicable

to others. In cases where the diluent and the monomer are absorbed in comparable amounts, the overall effect is a complex function of the following factors, which may or may not lead to an increase in graft yield: relative radical yields; propagation, termination and chain transfer constants; and viscosity effects.

When the diluent is not sorbed the grafting reaction appears to be controlled by the viscosity of the polymer. In their studies on the PE-styrene system, Machi, Kamel and Silverman[13] proposed that decreasing the monomer concentration in the polymer raises the matrix viscosity, thereby decreasing the termination rate and increasing the grafting rate. Dilution of the monomer beyond some critical concentration leads to a decrease in the graft yield since there is no longer enough monomer to support the reaction in the highly viscous polymer. This hypothesis is strongly supported by further work of Machi et al[12] on the styrene-polyethylene system, and the investigations of Kamel, and of Takamatsu and Shinohara cited above.

In the light of the foregoing, an investigation was performed to determine the degree to which the grafting of butadiene to PE, PECL, and PVC could be enhanced by dilution of the monomer with methanol.

1.3 Crystallinity

In this section the effect of the degree of crystallinity of partially crystalline polymers on graft yield is discussed. A method for determining the crystal content of chlorinated LDPE by measurement of the IR absorption peak in the region of 13.8 µm is presented.

Investigations on radiation-induced grafting of a variety of monomers to polyethylene show that the grafting rate is markedly affected by the degree of crystallinity of the polymer[1,12]. In general, the graft yield increases with the crystal content. Since grafting is believed to occur in the amorphous regions between crystallites it is at first glance surprising that a greater amount of material should be grafted to a polymer with a lower amorphous fraction. It has been shown, however, that the radicals created in the crystalline regions migrate to the surface of the crystals where they are able to initiate graft reactions[7]. This result, along with the increased viscosity of the denser polyethylene, has been advanced as the explanation of the ostensible anomaly[12].

Composite graphs which were first made from the data derived from experiments reported in this work showed considerable scatter. It was observed that the data for unchlorinated PE was more reproducible than that for PECL. This led to the

realization that the cause of the scatter in the PECL data was changes in the sample crystallinity upon chlorination. Keller, Matreyek and Winslow[5] in their investigations of the chlorination of PE crystals found that the chlorination destroyed some of the crystalline structure, and that the crystalline region does not transform gradually from an unchlorinated to a chlorinated material but contains regions of amorphous chlorinated material and regions of crystalline unchlorinated material.

Since the amorphous content of the films is affected by the chlorination procedure, calculations of the graft yield must take into account changes in the amorphous content. This requirement has two consequences, first Equations 1 and 2 must be modified to

$$PG = \frac{W_f - W_i}{f_a W_i} \times 100 \tag{8}$$

and

$$MG = \frac{(W_f - W_i) \; 1000}{M \left[\frac{f_a W_i}{\rho_0} + \frac{W_f - W_i}{\rho} \right]} \tag{9}$$

where f_a is the amorphous fraction of the sample; second, a means for measuring f_a is required.

It is well established that the absorption doublet exhibited by high molecular weight alkanes in the solid state

at 13.7 µm and 13.9 µm is due to crystallinity. Many studies have been performed[17-21] and it is generally accepted that the doublet is due to splitting of the $(-CH_2-)_n$ rocking motion by the forces within the crystal. The 13.7 µm absorption peak is due solely to the crystalline regions of the polymer, and the absorption at 13.9 µm is due both to crystalline and amorphous forms. Stein and Sutherland[19] in their studies of the IR absorption of PE in this region pointed out the difficulties in resolving the contribution of each component. To date, the contributions to the 13.9 µm absorption of the crystalline and amorphous forms of PE are still uncertain. Further difficulties in determining the polymer crystallinity from IR absorption arise from the fact that the absorbance at 13.7 µm is sensitive to stress, e.g., from quenching or cold drawing.

In order to determine the changes in crystallinity upon chlorination, a method based upon the absorbance at 13.7 µm and 13.9 µm relative to the absorbance of a "standard" sample was devised*. The absorbance of a number of strips of PE at 13.7 µm and 13.9 µm was measured. The average values were taken as the standard absorbance for PE. The density of the standard was determined by weighing a number of measured sheets. The crystallinity of the standard was determined

---

*   The absorption peak due to crystallinity at 7.5 µm could not be used in this work because of the strong absorption in this region arising from the chlorination.

from the relation

$$\rho' = (1-C_s) \, \rho_A + C_s \, \rho_C \tag{10}$$

where $\quad \rho' =$ density of the polymer (g cm^{-3});

$C_s =$ the crystal fraction;

$\rho_A =$ the density of the amorphous form (g cm^{-3}), and;

$\rho_C =$ the density of the crystalline form (g cm^{-3}).

The values of ρ_A and ρ_C were taken as 0.9 and 1.0 respectively.

The crystallinity of a sample was determined from IR

measurements by the formula

$$\text{Crystal Fraction} = \frac{1}{2} \left[\frac{A_1}{A_1^s} + \frac{A_2}{A_2^s} \right] C_s \tag{11}$$

where $\quad A_1 =$ the sample absorption at 13.7 µm;

$A_2 =$ the sample absorption at 13.9 µm;

$A_1^s =$ the absorption of the standard at 13.7 µm;

$A_2^s =$ the absorption of the standard at 13.9 µm; and

$C_s =$ the crystal fraction of the standard.

CHAPTER II

EXPERIMENTAL

This section describes the treatment of material and the manner of conducting the experiments.

2.1 Materials and Reagents

Strips of Dupont low-density polyethylene film 0.058 x 10 x 70 mm were soaked for 24 hours in n-hexane, dried and stored in vacuo at room temperature for 24 hours before use. Strips of Dow PVC film 0.050 x 10 x 70 mm were treated in a similar manner except for the addition of a 24 hour soak in liquid butadiene followed by storage in vacuo for another 24 hours before use. Chlorine was Fisher Scientific High Purity Grade. The butadiene, 99.5% pure, was supplied by Air Products and Chemicals Company; it was passed through a 20% sodium hydroxide solution and a silica gel column before use. The methanol, Mallinckrodt A-R grade, was used without further purification.

Chlorine and butadiene filling operations were carried out on a vacuum manifold apparatus. Samples were evacuated to less than 0.03 Torr before filling. Irradiations were conducted in the University of Maryland Gamma Laboratory.

16

2.2 Chlorination

Thermal chlorination of polyethylene films was carried out under air-free conditions. Approximately 1 ml of liquid chlorine at -78°C was distilled into the lower section of a pinched 25-ml tube containing the weighed sample in the section above the constriction. After freezing the chlorine in liquid nitrogen, the tube was sealed under vacuum, then raised to room temperature for a period sufficient to achieve the desired degree of chlorination.

The percent chlorine added was determined by Equation 5:

$$PCA = \frac{(w_f - w_i)}{f_a w_i} \times 100 \qquad (5)$$

2.3 Spectroscopy

The crystal fraction of the sample was determined by a method developed in the course of this work and described in section 1.3. It is based on measurements of the $(-CH_2-)_n$ absorption peaks at 13.7 and 13.9 µm with a Perkin-Elmer Model 137 Sodium Chloride Spectrophotometer and Equation 11. The values of A_1^s and A_2^s in Equation 11 were determined by taking the average of 70 PE samples. C_s was determined from the average of 10 samples of PE film from Equation 10. The crystallinity of each sample was taken as the average of the values of the films constituting the sample.

2.4 Grafting

Samples were prepared by adding methanol to a test tube containing a weighed sample of film, and measuring the height of the liquid in the tube. The methanol was then degassed by three freeze-thaw cycles under vacuum. After immersion in liquid nitrogen, butadiene gas was admitted to the tube where it was condensed and frozen in a layer above the methanol. The sample tube was evacuated and sealed, after which the sample was melted, shaken, and allowed to equilibrate for at least 10 hours at room temperature before the height of the butadiene-methanol solution was measured.

After irradiation the samples were frozen by immersion in liquid nitrogen and opened. The solution was melted and discarded. The films were wiped and placed in a vacuum chamber for 12 hours to remove unreacted monomer; post-grafting under these circumstances is trivial. The samples were weighed and the degree of graft was calculated from Equations 8 and 9.

2.5 Homopolymer Content

The infrared absorption peaks of the trans-1,4 and 1,2 polybutadienes in grafted films were measured at 10.3 μm and 11.0 μm respectively. Cis-1,4 polybutadiene is not produced in appreciable quantity at room temperature[22]. The films were soaked in cyclohexanone at room temperature for 36 hours to remove homopolymer. After removal from the

cyclohexanone, the samples were stored in vacuo for 60 hr to remove solvent and homopolymer. The IR absorbance was again measured. The change in polybutadiene content could then be calculated from the formula

$$\% \text{ loss} = \left[\frac{\alpha \, \delta A_{14} + \delta A_{12}}{\alpha \, A_{14} + A_{12}} \right] \times 100 \qquad (12)$$

where α = ratio of the extinction coefficient of the 1,2 configuration at 11.0 µm to the extinction coefficient of the trans-1,4 configuration at 10.3 µm;

δA_{14} = the difference in absorbance at 10.3 µm before and after soaking;

δA_{12} = the difference in absorbance at 11.0 µm before and after soaking;

A_{14} = the absorbance at 10.3 µm before soaking, and

A_{12} = the absorbance at 11.0 µm before soaking.

A value for α of 1.41 was used[23].

CHAPTER III

RESULTS

The results of this investigation are presented in
Figures 3-7. They show the dependence of graft yield on the
chlorine content of the polymer, monomer concentration, dose
rate and irradiation time. The graft yield to PECL was found
to increase rapidly with increased PCA of the amorphous region
up to 45 wt-%. Beyond this point, only a small increase in
graft yield was observed with increased chlorination. It was
found that the major portion of BD graft to PVC occurs under
non-equilibrium conditions at dose rates above 3 krad/hr.
The graft yield to PECL films of PCA = 45 and to PVC films was
found to increase upon dilution of the monomer with methanol
to a maximum at approximately 77 vol-% methanol, and to de-
crease upon further dilution. Measurements of homopolymer
content in the films showed that about 20% of the total weight
gain is due to homopolymer. Relevant physical data are listed
in Table II.

3.1 Homopolymer

The results of the homopolymer experiments are shown in
Table I. The samples were chosen so as to provide a wide
range of chlorine content and PG. In all cases the homopolymer
content was approximately 20% of the total weight gain. The

20

results reported in the other figures and tables are based on the apparant weight gains, i.e., they are not corrected for homopolymer content.

3.2 The Role of Chlorine

Figure 3 shows the apparent butadiene graft to PECL after a 5-hour irradiation as a function of chlorine concentration for two dose rates. Also shown is the average value of apparent graft yield for four samples of PVC irradiated at 340 krad/hr. The curves are characterized by a sharp linear rise in the graft yield until the PCA reaches 25. Beyond that point, the curve begins to level off. At a PCA greater than 60, the degree of graft reaches a limiting value of about 9 wt-%.

These are the most important features of Figure 3:

(1) the grafting rate of BD to amorphous PE can be increased threefold by the addition of 45 wt-% chlorine to the amorphous region of the polymer; (2) addition of chlorine beyond 45 wt-% contributes little to increasing the graft yield; and (3) at dose rates above 60 krad/hr the grafting yield is almost independent of dose rate. The fact that the graft yield can be increased threefold by the addition of only 45 wt-% chlorine to the amorphous region is of potential practical interest. The cost of chlorine is much less than 40% of the price of the polymer and it is relatively simple to achieve this degree of chlorination. Higher chlorine

contents require either much longer reaction times or a more complex process[24].

Figure 4 shows the apparent molar graft yield (MG) of butadiene to PECL, as derived from the data of Figure 3, and a plot of polymer density as a function of PCA based on the data of Oswald and Kubu[11]. The increase in MG with increasing chlorine content parallels the increase in PG up to about PCA = 45. However, at higher degrees of chlorination the molar graft yield increases linearly with increasing PCA of the polymer. This rise is due to an increase in density of the amorphous polymer as the PCA is raised. Examination of the slopes of the curves of polymer density and MG reveals that they are approximately equal.

3.3 Dependence on Time and Dose Rate

Figures 5 and 6 show the results of the grafting of butadiene to PVC films for irradiation times up to 10 hours at dose rates from 3 to 340 krad/hr. The yield is not proportional to time. In all cases there is an initial period during which the grafting rate has a relatively high value after which it decreases to a constant value. The transition period lasts from two to four hours, depending on dose rate. Of great importance is the result that it is during the transition period that most of the grafting occurs, e.g., at 340 krad/hr one obtains 5 wt-% graft in the first hour but

only 10 wt-% graft after 10 hours. Following the transient,
a steady-state condition is reached at which the reaction rate
is constant at 0.45 wt-% per hour at dose rates greater than
10^4 rad/hr. At lower dose rates the steady-state grafting
rate decreases with decreasing dose rate and the contribution
of the graft during the transient period to the total graft
decreases.

3.4 The Dilution Effect

Figure 7 summarizes the data on grafting BD from methanol
solutions to films of varying chlorine content. The curve
for PCA = 25 is constructed from the results of samples con-
taining between 20 and 30 wt-% added chlorine and adjusted to
25 wt-% by means of the data in Figure 3. The curve for
PCA = 45 is constructed from data from samples containing 30
to 60 wt-% added chlorine and normalized to 45 wt-% in the
same manner.

The apparent yield to unchlorinated, low-density poly-
ethylene remains constant up to 80 vol-% methanol, and de-
creases sharply with increasing dilution. In the case of the
chlorinated polymer, however, there is a large increase in
the degree of graft upon dilution of the butadiene to a maxi-
mum at a methanol concentration of 75 - 85 vol-%. A rapid
decrease in graft yield results from further dilution. The
same behavior is observed with PVC films.

Examination of the curves of Figure 7 reveals the following: (1) as the PCA increases, the peak in the curve shifts to solutions more concentrated in BD; (2) the ratio of graft yield at the peak to graft yield from the pure liquid BD decreases slightly with increasing chlorination, and (3) the graft yield of PE remains constant up to 80 vol-% methanol.

CHAPTER IV

DISCUSSION

It is shown that the graft yield increases with increasing polymer viscosity until the polymer glass transition temperature (T_g) is higher than the reaction temperature. Further increase in viscosity may be obtained by grafting from dilute monomer solution. (T) for T much less than T_g the matrix viscosity is so great that further increase in viscosity does not affect the grafting reaction. The transient condition and the dilution effect are discussed in terms of the matrix viscosity and monomer concentration.

4.1 The Role of Chlorine

Figures 3 and 4 provide strong evidence that the observed increase in graft yield upon chlorination of polyethylene is due to changes other than an increase in radical yield. As discussed earlier (1.1.2), energy transfer can increase the graft yield by no more than 85% when 40 wt-% chlorine is added to amorphous polyethylene. Figure 4 shows that the graft yield of the latter is five times that of unmodified PE. Also the increase in molar graft yield for samples with a PCA more than 45 is shown to be due to an increase in polymer density as the chlorine content increases. Because the energy levels of the (C-H) and (C-Cl) bonds are not well

25

matched and the spacing between the levels is relatively large, the efficiency of transfer is not expected to be high. A more fruitful approach is to investigate changes in the physical condition of the polymer.

Since butadiene is only slightly soluble in PE and PVC (about 1 wt-%), it is to be expected that the viscosity of the polymer will not be greatly affected by the absorption of monomer. For example Takamatsu and Shinohara do not find appreciable changes in PVC-styrene solutions until the styrene content reaches 12 wt-%. The viscosity of a polymer is reflected in its modulus and its glass transition temperature. Figure 2 contains plots of the elastic modulus (E) and the glass transition temperature (T_g) as a function of PCA of PECL films constructed from the data of Oswald and Kubu[11]. Two important points to be noted are as follows: (1) at a PCA = 45 T_g of the unswollen films is 30°C; and (2) E increases slowly with PCA up to 45 wt-%, but rises very sharply at slightly higher chlorine content. At a PCA of 60, E is 10 times its value at PCA = 45.

In Figure 8 the percent graft of butadiene to PECL, after a 5 hr irradiation, is plotted as a function of elastic modulus of the polymer. The graft yield rises linearly with modulus up to $E = 1.3 \times 10^4$ psi, corresponding to PECL of PCA = 40. Beyond this point, there is a sharp break, and the graft yield remains essentially constant with increasing

modulus. The break in the curve occurs at a modulus corresponding to a PCA of 40 rather than a PCA of 45 because of a reduction in T_g upon swelling by the monomer. In Figure 9 the PG after a 5 hr irradiation is plotted as a function of the difference between the reaction temperature and the T_g of the polymer. The graft yield rises with increasing slope as $(T-T_g)$ decreases. For T_g greater than 27°C the PG rises slowly with decreasing $(T-T_g)$. In Figure 10 the PG after a 5 hr irradiation to PECL with varying PCA is plotted vs relative viscosity of the polymer calculated from the Williams-Landel-Ferry (WLF) Equation (Appendix B). The graft yield rises linearly with the logarithm of viscosity for T_g less than the reaction temperature, becoming constant for polymers with T_g near the reaction temperature. The deviation from linearity is expected since in this region of high viscosity the graft yield is not sensitive to further increases in viscosity.

For PECL above its glass transition temperature, addition of chlorine raises T_g and the polymer viscosity, causing an increase in the graft yield. The increase in graft yield as the matrix viscosity increases is due to a decrease in the termination rate constant relative to the propagation rate constant. (This is discussed in Sections 1.1.3, 1.2, and Appendix A.) When T_g of the swollen polymer is well above the temperature at which grafting takes place the matrix is so viscous that further

increase in viscosity has little effect upon the grafting reaction. The slight rise in graft yield for films of PCA about 130 is believed to be due to an increase in radical yield in the highly-chlorinated material.

4.2 Dependence on Time and Dose Rate

As shown in Figures 5 and 6 the grafting rate is initially very high, but decreases to a much lower steady-state value as the reaction proceeds. Consider the data at dose rates above 10^4 rad/hr: 3, 4 and 5 in Figure 11. Initially, grafting proceeds at a high rate dependent upon dose rate, and decreases to a constant equilibrium value. This behavior may be explained by the following argument, illustrated in Figure 11.
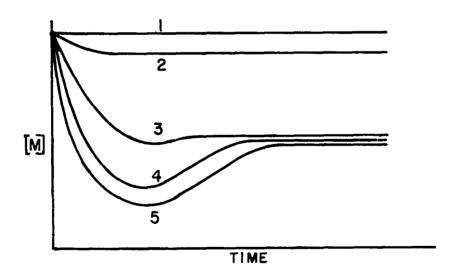
Fig. 11, Monomer Concentration Within the Polymer as a Function of Irradiation Time. Dose Rate: 1<2<3<4<5

At the start of irradiation the polymer contains the equilibrium concentration of monomer ($[M]_o$). The radical population quickly builds up to its steady-state value. (Machi[25] has observed the post-irradiation grafting rates of BD vapor to PVC powder under comparable conditions and found the lifetime of the chain radicals to be of the order of 5 minutes.) The initial grafting rate is higher than the rate of diffusion of monomer into the film, and the film becomes depleted in monomer. (Calculations based on the data of Morishima, et al[26], and Machi et al[12] show that the monomer concentration ([M]) must fall to 50% of its equilibrium value to bring about sufficient diffusion of monomer into the film to support the grafting rates shown in Figures 5 and 6.) The decrease in monomer concentration would decrease the grafting rate if the viscosity of the medium were to remain unchanged. However, the reduction in monomer content is also accompanied by an increase in viscosity which tends to increase the graft reaction rate value. Studies of gas phase grafting, where the time scale for the reaction is much greater, show that the grafting rate increases as the monomer concentration decreases[2,7,27].

As the percent graft in the film increases, the film becomes more rubbery, its viscosity decreases, and the reaction slows down. At the same time the solubility of the monomer

in the grafted film increases due to the presence of the graft copolymer. For the BD-PVC system the solubility is increased 60% at a PG = $4^{(28)}$. The increased driving force for diffusion of monomer into the film gives rise to a monomer current greater than that required to maintain the reaction, and [M] increases. The monomer concentration rises until ($[M]_o$ - [M]) is such that the input rate is equal to the rate of consumption. Under the new conditions, at which the monomer concentration is almost $[M]_o$, the reaction rate is constant.

At high dose rates the final monomer concentration and the steady-state reaction rate are not dependent upon dose rate because, under the conditions of high matrix viscosity and low monomer concentration that prevail, the primary radicals must compete for a limited amount of monomer. As the radical production rate is increased excess primary radicals are lost by rapid recombination processes, and the reaction rate is independent of dose rate. At lower dose rates, where the monomer concentration is higher, the critical number of radicals is not exceeded and the reaction is dependent upon dose rate at all times (Appendix A).

As the dose rate is decreased, the initial reaction rate is decreased, and the extent of the initial drop in monomer concentration decreases. Also the time of the transient drop in [M] is shortened as I is decreased. Under those conditions

where changes in [M] are less drastic, viscosity effects become negligible, and the graft rate becomes dependent upon dose rate. At very low dose rates, Figure 11 predicts that the transient will disappear, and steady-state conditions will prevail almost from the start, viscosity effects will not be significant, and the diffusion rate will not control the reaction rate.

4.3 The Dilution Effect

The results of Figure 7 may be explained by the same arguments advanced by Machi et al[12]. When grafting takes place from solutions of up to 50 vol-% methanol, the competing processes of monomer consumption and supply keep the monomer concentration constant. Beyond this point the butadiene flux into the film decreases, monomer concentration in the film decreases, the film viscosity increases, and the graft yield is increased. At about 80 vol-% methanol a maximum in graft yield is reached as the competing effects of viscosity and BD concentration reach an optimum. Continued dilution of the BD lowers the rate of diffusion of monomer into the film, decreasing the monomer concentration and decreasing the graft yield.

As the degree of chlorination of the polymer is increased, and its T_g is raised, the peak in the curve shifts toward

higher butadiene concentration because more monomer can be accommodated in the film before the viscosity falls to too low a value. The ratio of PG at the maximum to PG from pure monomer decreases slightly with increasing PCA because the change in viscosity is not as great for the more chlorinated polymer.

In the case of LDPE the graft yield remains constant with decreasing butadiene concentration up to 80 vol-% methanol, and decreases upon further dilution. This behavior is explained by the following argument. Low-density polyethylene is far above its glass transition temperature at all concentrations. The BD concentration is very low (less than 1 wt-%) and is not strongly affected by changes in methanol concentration in the solution. Under the conditions of low matrix viscosity and essentially constant monomer concentration in the film the graft yield remains constant. Figure 12 shows the variation of BD concentration in $g \; cm^{-3}$ as a function of vol-% methanol. Note that the BD concentration decreases linearly up to about 80 vol-% methanol, above this methanol content there is a sharp decrease in BD concentration. The concentration of BD in the film also decreases and the graft yield to LDPE is decreased.

CHAPTER V

CONCLUSIONS

This chapter is concerned with the significance of the results to the field of radiation-induced grafting, and their application to a system of potential practical importance.

The principal conclusion to be drawn from this work is that chlorination of low density polyethylene increases the viscosity of the amorphous region of the material, and raises the T_g of the polymer. This increase in viscosity provides the means whereby the graft yield increased. Recent work[2,7,13,29] has led to the realization that the viscosity of the polymer matrix plays a major role in determining grafting rates. Maximum graft yields are attained when the monomer concentration is high enough to convert primary radicals on the polymer backbone to grafted chain radicals, and yet low enough so that the matrix viscosity is very high and termination of growing chains is strongly inhibited; also the diffusion of monomer into the film must be high enough to support propagation. The optimum condition may be achieved by adjusting the temperature so that the reaction occurs near the T_g of the swollen polymer[29], or by adjusting the monomer concentration in the polymer to bring the T_g of the swollen material closer to the temperature of the reaction. This work adds a third method: adjusting the T_g of the polymer by chemical means to approach

33

the reaction temperature. This method is of particular importance for systems where the T_g of the polymer is near or below the freezing point of the monomer, e.g., styrene-PE.

In this investigation it was shown that for grafting at constant monomer concentration and constant reaction temperature, the graft yield increases as the T_g of the polymer approaches the reaction temperature. Schamberg and Hoigne[29], and Furuhashi and Kadonaga[1] show that the graft yield increases as the reaction temperature approaches the T_g of the polymer. Kamel[7] and Machi et al[13], show that a maximum in graft yield can be obtained by decreasing the monomer concentration even though the reaction temperature is far above T_g of the pure polymer, and Takamatsu and Shinohara[2] find the same effect even though the reaction temperature is far below T_g of the polymer. In this work it was found that although the reaction was conducted at T_g of the pure polymer, dilution of the monomer increased the graft yield. It is important to note that grafting at T_g of the pure polymer does not satisfy all of the conditions discussed above, but provides a good starting point. The increased radical yield upon chlorination of the polymer plays but a small role in the enhancement of the graft yield.

The conclusions of specific application to the grafting of butadiene to PVC and PECL are (1) the reaction should be conducted from dilute monomer solution at high dose rates in

order to obtain maximum production rates and (2) graft yields to PECL of PCA = 45 are essentially the same as those to PVC where PCA = 131.

Under conditions where the non-steady-state reaction is important, i.e., I greater than 3 krad/hr, the initial graft rate increases with increasing dose rate, and high graft yields are obtained with short irradiation times. Takamatsu and Shinohara[2] show that for grafting styrene to PVC, a MG of 2 is obtained with a 10 sec irradiation at 10^5 rad/sec, but requires 25 min at 10^5 rad/hr. At the higher dose rate, the yield per unit dose is only 2.5% of that at the lower dose rate, but the reaction rate is 150 times as great.

BD-grafted PVC and BD-grafted PECL are of potential industrial importance as they are tough viscoelastic materials. The fact that grafting yields to PVC and to PECL with PCA = 45 are essentially the same is of practical interest, since for applications where clarity is not critical a material with physical characteristics similar to PVC, but containing only 1/3 the chlorine can be used. BD-grafted PVC has advantages over ordinary PVC in that it does not require plasticizers which can be leached out of the material by e.g., blood. BD-grafted PECL is superior to low-density polyethylene in that its elastic modulus, yield strength and breaking strength are greater, and it retains its properties at higher temperatures.

It may also be used in place of PVC for applications in which clarity is not important. In addition, the polybutadiene grafted to the polymers is unsaturated, and may be cross-linked to yield a rubbery material of high gel content.

GRAFTING KINETICS

This section describes the kinetics of radiation-induced graft copolymerization by a free radical mechanism. The mathematical formulation of simultaneous diffusion and polymerization within a film is presented, and the work of Odian and Kruse[29] is discussed. For the systems examined in this investigation, steady state kinetics fit only the latter part of the grafting period, and an a priori analytical solution to the diffusion equation cannot be obtained.

A.1 Simplified Grafting Kinetics

For free radical addition polymerization in a field of ionizing radiation the reaction mechanism consists of initiation, propagation, and termination steps. These are usually described in the following manner:

Initiation $\quad$ A $\longrightarrow$ M$\cdot$ $\longrightarrow$ R_i (initiation rate)

Propagation $\quad$ $M_n\cdot + M \longrightarrow M_{n+1}\cdot$ $\quad$ $K_p[R\cdot][M]$ (propagation rate),

Termination

(a) by combination $\quad$ $M_n\cdot + M_m\cdot \longrightarrow P_{m+n}$

(b) by disproportionation $\quad$ $M_n\cdot + M_m\cdot \longrightarrow P_m + P_n$

$\quad K_t[R\cdot]^2$ (termination rate)

At steady-state the rate of loss of radicals by termination is equal to the rate of initiation of radicals. Thus,

$$R_i = k_t[R\cdot]^2, \text{ and}$$

$$[R\cdot] = (R_i/k_t)^{1/2} \tag{A1}$$

where $[R\cdot]$ = concentration of growing chains (mole/l),

R_i = initiation rate (mole l^{-1} sec^{-1}),

k_t = termination rate constant (l $mole^{-1}$ sec^{-1}).

The propagation rate can now be written as

$$R_p = k_p[R\cdot][M] = k_p k_t^{-1/2}[M] \tag{A2}$$

where R_p = propagation rate (mole l^{-1} sec^{-1}),

· k_p = propagation rate constant (l $mole^{-1}$ sec^{-1}),

$[M]$ = monomer concentration (mole/l).

In grafting reactions where the rate of production of radicals from the polymer is much greater than from the monomer,

$$R_i = \emptyset_p I[P] \tag{A3}$$

where $\emptyset_p$ = molar radical yield from the polymer (mole of radical $mole^{-1}$ rad^{-1}),

I = dose rate (rad sec^{-1}),

$[P]$ = polymer concentration (mole/l).

Equation A3 is valid in systems where $\emptyset_m[M] \ll \emptyset_p[P]$, e.g.,

BD-PE, BD-PECL, and BD-PVC systems. Equation A2 may now be written as

$$R_p = k_p k_t^{-1/2} (\phi_p [P])^{1/2} I^{1/2} [M] \qquad (A4)$$

The graft yield, MG, after time t is found by integration of Equation A4 to be

$$MG = k_p k_t^{-1/2} (\phi_p [P])^{1/2} I^{1/2} [M] t \qquad (A5)$$

if the monomer concentration remains constant.

At high dose rates, where the concentration of primary radicals [M·], is large enough to allow primary radical re-combination and primary radical termination to become significant the reaction scheme must be modified to provide for losses of primary radicals by

(c)   recombination   M· + M· ———► M_2 $k_{oo}[M·]^2$

(d)   addition to monomer   M· + M ——► M_2· $k_{po}[M·][M]$

(e)   termination of growing M_n· + M·——► P_{n+1} $k_{to}[M·][R·]$
       chains

It can be shown[9] that at the steady-state

$$R_p = \frac{k_p k_{to}[M·]}{2k_t} \left[\left(1 + \frac{4k_{po}k_t[M·]}{k_{to}^2[M·]} \right) - 1 \right] [M] \qquad (A6)$$

where k_{to} = rate constant for termination of chains by
           primary radicals (1 mole^{-1} sec^{-1}), and

k_{po} = rate constant for addition of primary

radicals to monomer (1 mole^{-1} sec^{-1}).

For very high dose rates, or very viscous systems, where the

initiation rate is much higher than the rates for steps (c),

(d) and (e).

$$R_p = k_p k_{po}[M]^2/k_{to} .$$ (A7)

Under these conditions, the polymerization rate reaches a

constant value which is independent of the initiation rate.

A.2 Simultaneous Diffusion and Polymerization

During a grafting experiment the process of monomer

diffusion into the polymer occurs simultaneously with the

polymerization reaction. For Fickean diffusion, the monomer

concentration within the film is described by

$$\frac{d[M]}{dt} = D\nabla^2[M] - R_p$$ (A8)

where [M] = monomer concentration in the film (mole/l),

R_p = grafting rate (mole l^{-1} sec^{-1}), and

D = diffusion coefficient for monomer into polymer

(cm^2 sec^{-1}).

For diffusion and reaction in a film, Equation A8 takes the

form

$$\frac{d[M]}{dt} = D \frac{d^2[M]}{dx^2} - R_p \qquad (A9)$$

In the usual grafting experiment, the polymer film is allowed to equilibrate in the monomer or a solution of monomer. After irradiation begins the monomer is depleted by the graft reaction and resupplied by the diffusion process. During this period, the monomer concentration profile and the reaction rate profile are interdependent; and are complex functions of diffusivity, reaction rate constants, dose rate, matrix viscosity and film thickness.

At the steady-state, the monomer concentration profile remains fixed, and Equation A9 becomes

$$R_p = D \frac{d^2[M]}{dx^2} \qquad (A10)$$

Using equation A2, Equation A10 may be written as

$$k_p k_t^{-1/2} (R_i)^{1/2} [M] = D \frac{d^2[M]}{dx^2} \qquad (A11)$$

Odian and Kruse[30] have investigated Equation A11 for the effects of diffusivity, film thickness and dose rate. They were able to derive a relation between the parameters of the form

$$B = \frac{\tanh A}{A} \qquad (A12)$$

where $\quad B = \bar{R}_p k_t^{1/2} k_p^{-1} [M]^{-1} R_i^{-1/2}$,

$\qquad A = (R_i^{1/2} k_p k_t^{-1/2} D^{-1}) L/2$,

$\bar{R}_p$ = average grafting rate within the film

$\qquad$ (mole 1^{-1} sec^{-1}), and

$\qquad$ L = film thickness (cm).

The derivation of Equation A12 assumes that $(k_p k_t^{-1/2})$ and D are constant throughout the film, and that the total graft during the transient period is negligible. These assumptions are valid where the polymer film is highly swollen with monomer or the polymer is far above its T_g, so that the matrix viscosity is low and essentially constant. For values of A $<$ 0.1 the reaction will be controlled by grafting kinetics, and Equation A12 reduces to Equation A2. For values of A $>$ 3 Equation A12 can be approximated by

$$\bar{R}_p = (k_p D k_t^{-1/2})^{1/2} R_i^{1/4} [M] (L/2)^{-1} \qquad \text{(A13)}$$

In this case, the reaction is diffusion controlled, and the bulk of the grafting takes place near the surface of the film.

The preceding model accurately predicts the grafting behavior of systems for which A $<$ 0.1, e.g., Acrylonitrile-styrene-PE[30], and for which A = 3, e.g., butadiene-LDPE[1], but it is not applicable (except for guidance) to systems in which viscosity effects predominate, such as BD-PVC. This investigation is concerned with a set of conditions under

which Equation A11 is not valid. Equation A9 must be written in the form

$$\frac{d[M]}{dt} = D \frac{d^2[M]}{dx^2} - k_p (M) [R\cdot] [M] \tag{A14}$$

[R·] is, from Section A.1, equal to the rate of initiation minus the rate of termination, or

$$\frac{d[R\cdot]}{dt} = R_i - k_t (M) [R\cdot]^2 \tag{A15}$$

Note that the propagation and termination rate constants have been written as functions of monomer concentration. This is due to the fact that the film viscosity, affected by the monomer concentration, controls the rate constants. Thus, in the absence of detailed data on the behavior of k_p and k_t, for systems where viscosity effects predominate, the grafting behavior cannot be predicted but must be experimentally determined.

APPENDIX B

THE WILLIAMS-LANDEL-FERRY EQUATION

William, Landel and Ferry[31], arguing that at T_g all polymers should have the same fractional free volume and should be equivalent in their flow behavior, proposed that the T_g of a polymer should be considered its characteristic temperature. Using the Doolittle Equation[32],

$$\ln \eta = \ln A + B(v/v_f), \tag{B1}$$

where η = polymer viscosity at temperature T,

v = specific volume of the liquid polymer,

v_f = polymer free volume, and

A and B are constants characteristic of each polymer, they expressed Equation B1 as

$$\ln \eta_t = \ln A + B(v_t/v_{ft}), \tag{B2}$$

where the subscript t refers to the glass transition temperature. Since B is approximately unity, Equation B1 minus Equation B2 is

$$\log \left(\frac{\eta}{\eta_t} \right) = \frac{1}{2.303} \left[\frac{1}{f} - \frac{1}{f_t} \right], \tag{B3}$$

where $f = v_f/v$, and

$f_t = v_{ft}/v_t.$

44

To a good approximation,

$$f = f_t + a(T-T_g) \quad , \qquad \text{(B4)}$$

where a = the difference in the coefficient of thermal

expansion of the polymer above and below T_g.

Then

$$\log \frac{\eta}{\eta_t} = - \frac{1}{2.303} \left[\frac{T-T_g}{(f_t/a) + (T-T_g)} \right] \qquad \text{(B5)}$$

Empirical data on a number of polymers established the WLF

Equation as

$$\log \frac{\eta}{\eta_t} = - \frac{17.44(T-T_g)}{51.6 + (T-T_g)} \qquad \text{(B6)}$$

The WLF Equation is suitable for use at temperatures above

the T_g of the material up to about $T_g + 100°C$. However,

deviations from experimental data become large at temperatures

close to T_g.

DEFINITION OF SYMBOLS

A_1	Absorption of chlorinated sample at 13.7 μm
A_2	Absorption of chlorinated sample at 13.9 μm
A_1^s	Absorption of polyethylene standard at 13.7 μm
A_2^s	Absorption of polyethylene standard at 13.9 μm
A_{12}	Absorption of 1, 2-polybutadiene at 11.0 μm
A_{14}	Absorption of trans-1,4 polybutadiene at 10.3 μm
BD	Butadiene
C_s	Crystal fraction of the polyethylene standard
E	Elastic modulus (psi)
$G(R\cdot)_i$	Number of radicals produced per 100 eV absorbed in material i
I	Dose rate (rad sec^{-1})
LDPE	Low density polyethylene
M	Molecular weight of monomer
[M]	Concentration of monomer within the polymer (mole/l)
$[M]_o$	Equilibrium concentration of monomer within the polymer (mole/l)
MG	Molar graft yield (mole of butadiene per liter of grafted sample)
PCA	Weight percent chlorine added to the amorphous

46

region of the polymer

PE	Polyethylene
PECL	Chlorinated low-density polyethylene
PG	Percent graft (g butadiene per g polymer)
P_{iy}	Probability of energy transfer from i to y
P_{rel}	Ratio of P_{iy} to P_{yi}
PVC	Poly(vinyl chloride)
[R·]	Chain radical concentration (mole/l)
R_i	Rate of initiation of chain radicals (mole l^{-1} sec^{-1})
R_p	Rate of propagation of chain radicals (mole l^{-1} sec^{-1})
T_g	Polymer glass transition temperature (°C)
W_g	Weight of grafted sample
W_i	Weight of sample before grafting
f_a	Amorphous fraction of chlorinated sample
[i]	Concentration of material i (mole/l)
k_p	Chain propagation rate constant (l $mole^{-1}$ sec^{-1})
k_t	Bimolecular chain termination rate constant (l $mole^{-1}$ sec^{-1})
w_f	Weight of chlorinated sample
w_i	Weight of sample before chlorination
x_i	Mole fraction of component i

α Ratio of the extinction coefficient of 1,2-polybutadiene at 11.0 μm to the extinction coefficient of trans-1,4 polybutadiene at 10.3 μm

η Polymer viscosity at temperature T

η_t Viscosity of the polymer at its glass transition temperature

ρ Density of the grafted polymer (g cm^{-3})

ρ' Density of the polyethylene standard (g cm^{-3})

ρ_A Density of the amorphous polyethylene (g cm^{-3})

ρ_C Density of the crystalline polyethylene (g cm^{-3})

ρ_o Density of the ungrafted polymer (g cm^{-3})

$\emptyset_i$ Molar yield of radicals from material i (mole of radicals per mole of i per rad)

$\emptyset_{rel}$ Ratio of $\emptyset_i$ to $\emptyset_y$

TABLE I

Homopolymer Content

Sample No.	Type of Material	Crystal Content	PCA	%* MeOH	PG	Homopolymer Content (%)
MC-76	PECL	0.12	129	0	8	19
P-25	PVC	0	131	0	13	22
MC-67	PECL	0.26	53	75	7	19

*   Vol-% methanol in monomer solution

TABLE II

Physical Data

PCA	%-Cl $\left(\dfrac{g\ Cl}{g\ Cl + g\ PE}\right)$	Cl/C $\left(\dfrac{atom\ Cl}{atom\ C}\right)$	PECL[a] (g cm^3)	x PVC	T_g [a] (°C)	Ex10^{-5} [a] (psi)	Apparent Graft Yield[b] PG 340[c]	PG 60	MG 340	MG 60
0	0	0	0.9	0	-25	(0) [d]	2.15	1.8	0.37	0.32
10	9	0.04	0.96	0.08	- 3	0.05	4.2	3.8	0.75	0.68
20	17	0.08	1.02	0.15	9	0.08	5.7	5.2	1.07	0.98
30	23	0.11	1.06	0.23	15	0.1	6.9	6.5	1.32	1.25
40	29	0.15	1.10	0.30	25	0.13	7.8	7.6	1.53	1.50
60	38	0.23	1.12	0.46	42	1.5	8.2	7.8	1.64	1.56
80	44	0.30	1.24	0.61	51	1.9	8.5	8.0	1.85	1.75
100	50	0.38	1.30	0.76	62	2.2	8.7	8.2	1.97	1.87
120	54	0.46	1.36	0.91	68	2.3	8.9	8.4	2.09	1.99
131	56	0.5	1.39	1.00	73	2.3	9.0	8.45	2.14	2.03
141	58	0.53	1.42	-	75	2.3	9.1	8.5	2.22	2.10

(a) From reference 11

(b) From Figures 3 and 4

(c) Dose rate in krad/hr

(d) Estimated

50

Fig. 1, Relative Graft Yield versus PCA

Fig. 2, Elastic Modulus and T_g versus PCA. (Calculations from the data of Reference 11.)
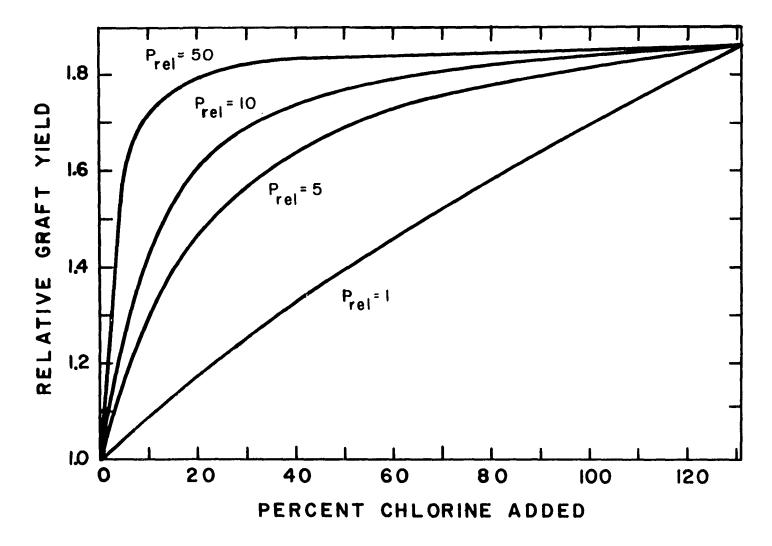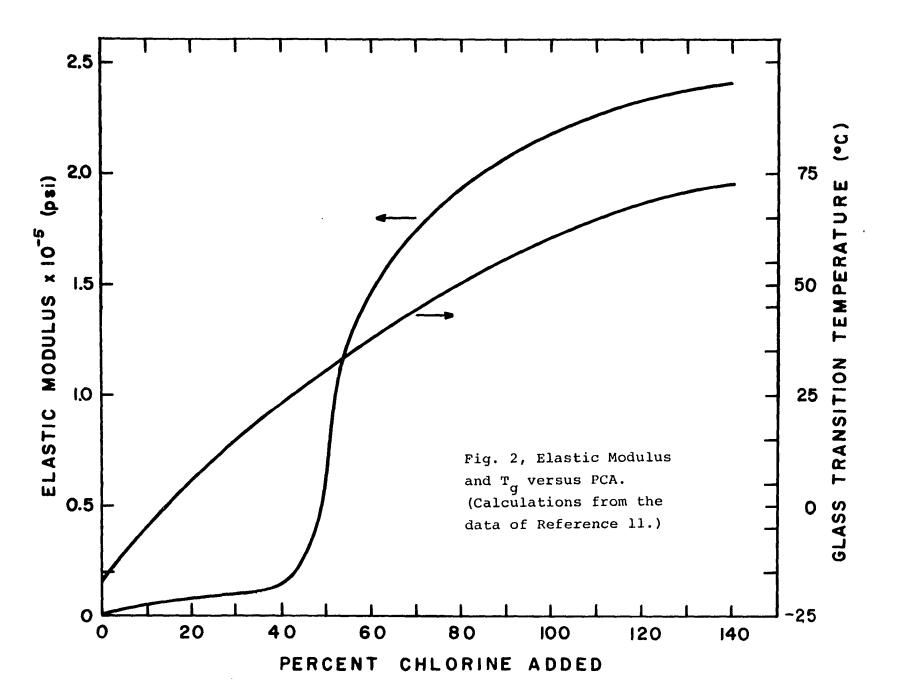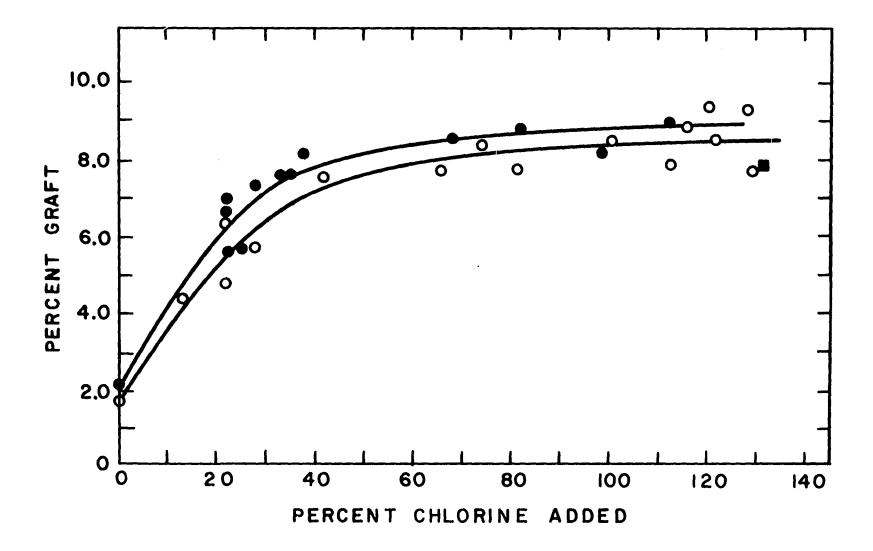
Fig. 3, Graft Yield from Liquid BD versus PCA. Polymer Irradiated at Room Temperature for 5 hr. ● 340 krad/hr; ○ 60 krad/hr; ■ poly(vinyl chloride)
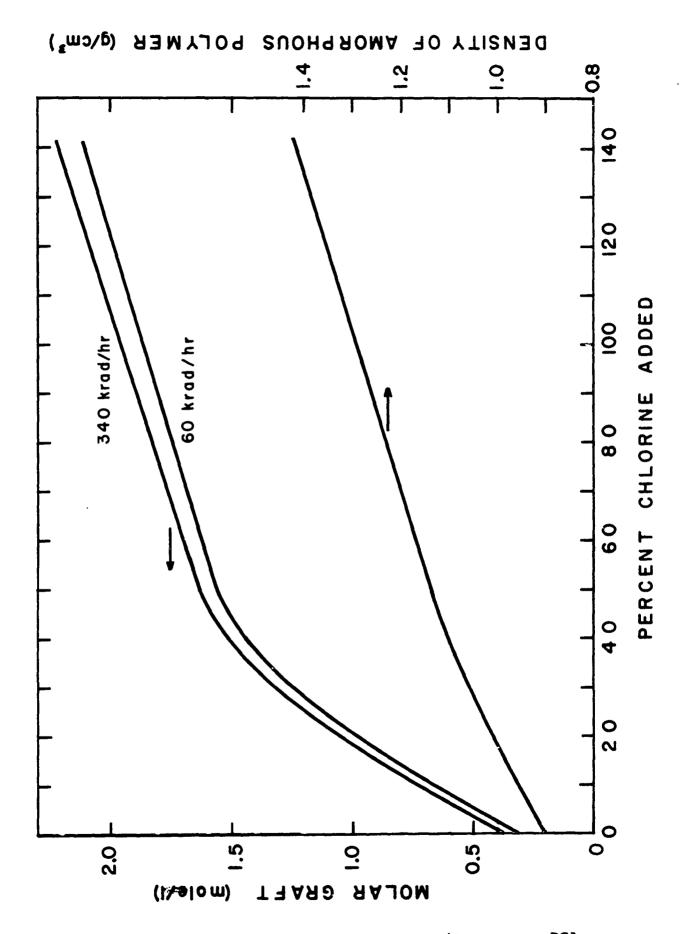
53

Fig. 4, Molar Graft Yield and Polymer Density versus PCA.
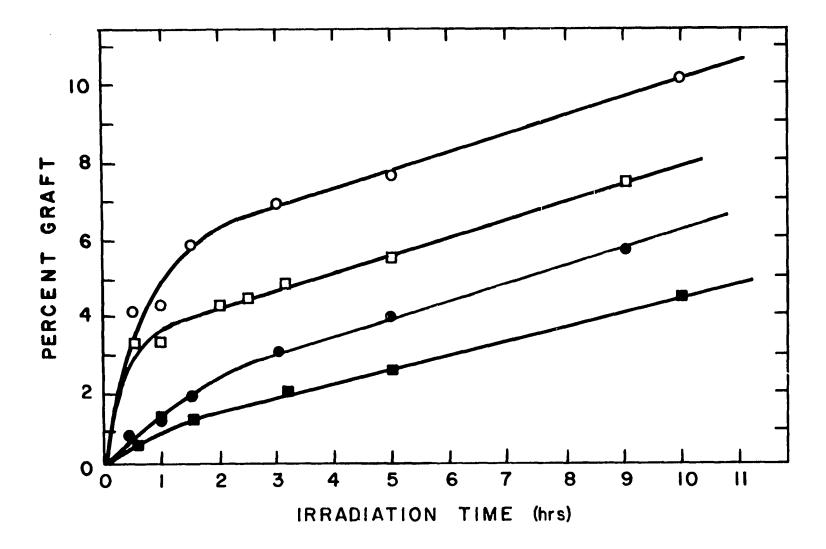(Polymer density from the data of Reference 11.)

Fig. 5, Percent Graft to PVC versus Irradiation Time. Polymer Irradiated in Liquid Monomer at Room Temperature. Dose Rate = O 340 krad/hr; ☐ 60 krad/hr; ● 10 krad/hr; and ■ 3 krad/hr
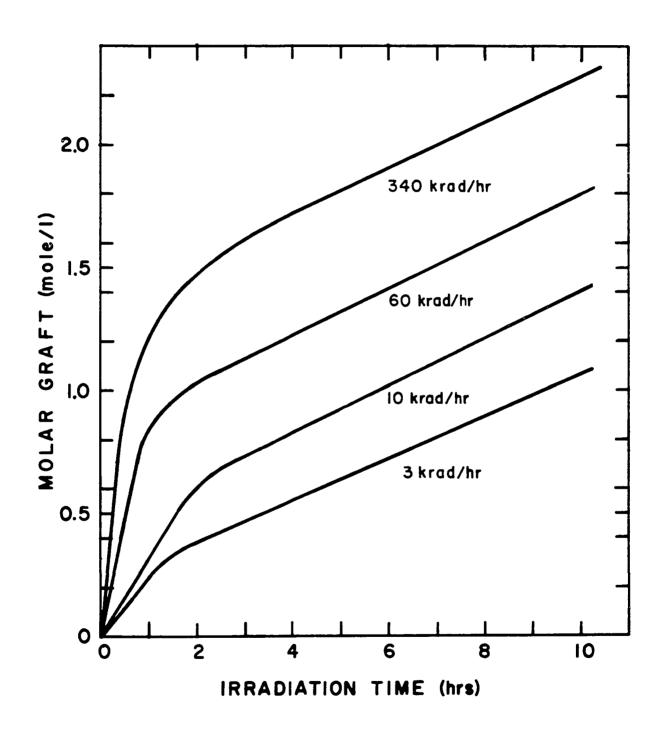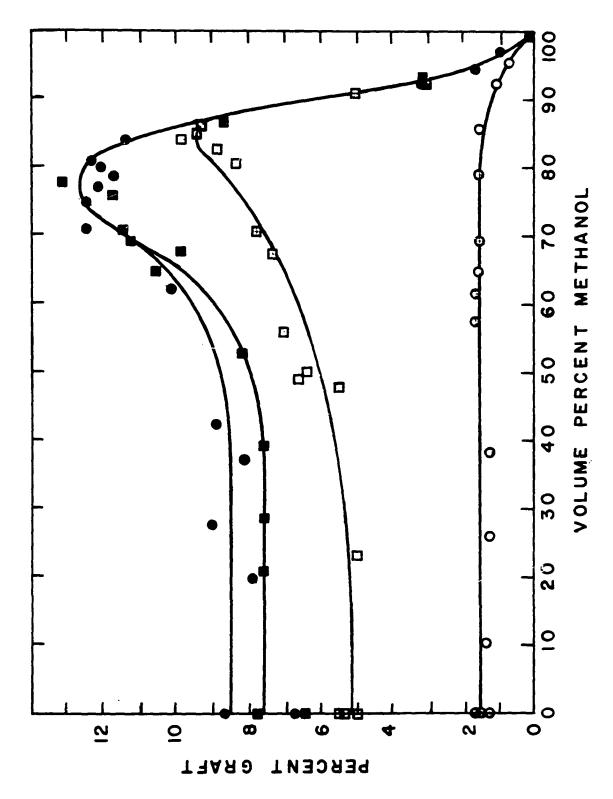
Fig. 6, Molar Graft Yield to PVC versus Irradiation Time.

Fig. 7, Percent Graft Yield to LDPE, PECL, and PVC from BD-
Methanol Solution. Polymer Irradiated in Monomer
Solution for 5 hr at Room Temperature. ● PCA=45;
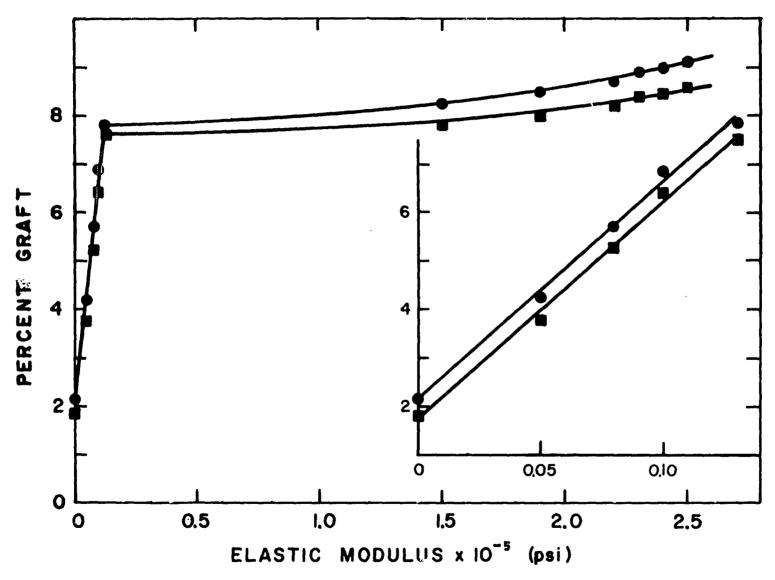■ PVC; □ PCA=25; O LDPE

Fig. 8, Percent Graft to PECL versus Elastic Modulus of Polymer. Dose Rate =
● 340 krad/hr; and ■ 60 krad/hr. Polymer Irradiated 5 hr at Room
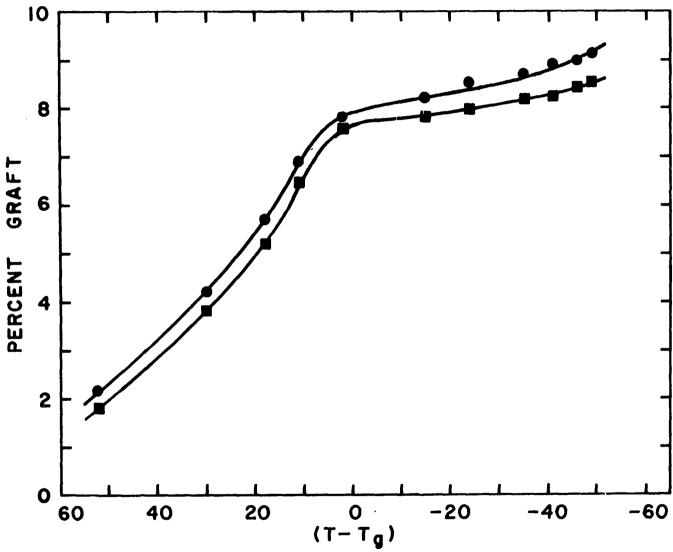Temperature in Liquid Monomer. Inset = Expanded Scale.

Fig. 9, Percent Graft to PECL as a Function of the Difference Between the Reaction Temperature and the T_g of the Polymer. Dose Rate = ● 340 krad/hr; ■ 60 krad/hr.
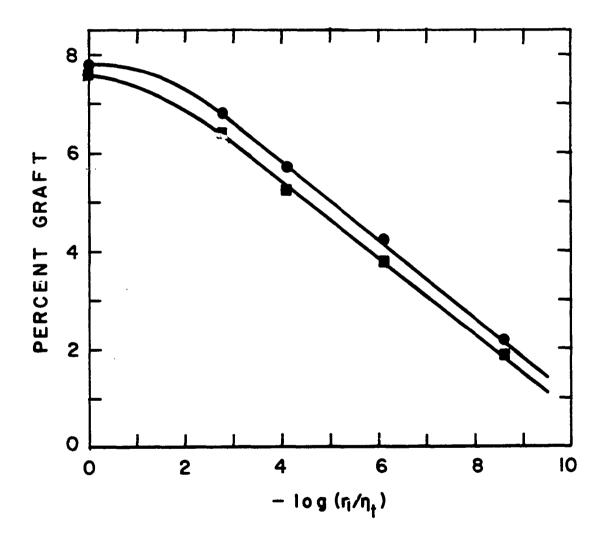
Fig. 10, Percent Graft to PECL versus Relative Viscosity of
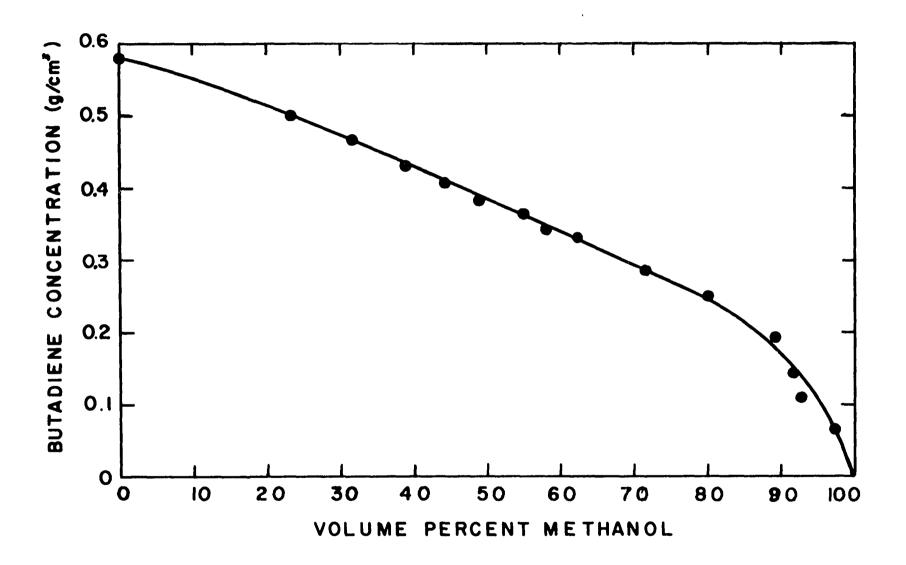the Polymer. Dose Rate = ● 340 krad/hr;
■ 60 krad/hr.

Fig. 12, Butadiene Concentration in BD-Methanol Solution versus Volume Percent Methanol.

BIBLIOGRAPHY

(1) Furuhashi, A. and M. Kadonaga, J. Appl. Poly. Sci.,
     10, 127 (1966).

(2) Takamatsu, T. and K. Shinohara, J. Poly. Sci.,
     A-1, 4, 197 (1966).

(3) Okamura, S., K. Hyashi, M. Hishi, and Y. Nokamura,
     Annual Report of the Japanese Association for
     Radiation Research on Polymers (AEC-tr-6231), 1,
     233 (1958).

(4) Harmer, D.E., "Irradiation of Polymers", Advances in
     Chemistry Series 66, American Chemical Society,
     Washington, D.C., p 203 (1967).

(5) Keller, A., W. Matreyek and F.H. Winslow, J. Poly.
     Sci., 62, 291 (1962).

(6) Nambu, K., J. Appl. Poly. Sci., 4 (10), 69 (1960).

(7) Kamel, I.L., Ph.D. Thesis, University of Maryland
     (1970).

(8) Nikitina, T.S., and Kh. S. Bagdasaryan, Sbornik Rabot
     po Radiatsionnoi Khimii, Academy of Science of the
     USSR, Moscow p 183 (1955).

(9) Chapiro, A., "Radiation Chemistry of Polymeric
     Systems", John Wiley and Sons, New York (1962).

(10) Odian, G., T. Acker and M. Sobel, J. Appl. Poly.
     Sci., 7, 245 (1963).

(11) Oswald, H.J. and E.T. Kubu, SPE Transactions, p 168
     (July, 1963).

(12) Machi, S. and J. Silverman, "Large Rad   ion Sources
     for Industrial Processing", International Atomic
     Energy Agency, Vienna, p 341 (1969).

(13) Machi, S., I.L. Kamel and J. Silverman, J. Poly.
     Sci: A-1 8, 3329 (1970).

(14) Matsuo, J., K. Iino, and M. Kondo, J. Appl. Poly.
     Sci., 7, 1833 (1963).

(15) Sakurada, I., N. Okada, and T. Takabayashi, Annual Report of the Japanese Association for Radiation Research on Polymers (AEC-tr-6372), 3, 135 (1961).

(16) Nakamura, Y., O. Hinojosa, and J.C. Arthur, Jr., Polymer Preprints, 10 (2), 788 (1969).

(17) Sheppard, N., and G.B.B.M. Sutherland, Nature, 159 (4048), 739 (1947).

(18) Rugg, F.M., and J.J. Smith, J. Poly. Sci., 11 (1), 9 (1953).

(19) Stein, R.S. and G.B.B.M. Sutherland,,J. Chem. Physics 22 (12), 1993 (1954).

(20) Tobin, M.C., and A.H. Wollett, J. Chem. Physics, 25 (5) 1044 (1956).

(21) Nielsen, J.R. and A.H. Wollett, J. Chem. Physics, 26 (5), 1044 (1956).

(22) Sakurada, I., T. Okada, and A. Torikai, Annual Report of the Japanese Association for Radiation Research on Polymers (AEC-tr-6520) 4, 127 (1962).

(23) Binder, J.L, Ind. Engr. Chem., 46 1727 (1954).

(24) Renfrew, A. and P. Morgan, "Polythene" - 2nd Edition, Interscience Publishers, Inc., New York p 391 (1960).

(25) Machi, S., Private Communication.

(26) Morishima, Y., H. Harayama, N. Sagana, Kobunshi Kagaku, 26, 689 (1969).

(27) Morishima, Y., H. Haragama, N. Sagana, Kobunshi Kagaku 26, 695 (1969).

(28) Higaki, H., Private Communication.

(29) Schamberg, E., and J. Hoigne, J. Poly. Sci: A-1 8, 693 (1969).

(30) Odian, G., and R.L. Kruse, J. Poly. Sci., Part-C, 22, 691 (1969).

(31) Williams, M.L., R.F. Landel, and J.D.,Ferry, J. Am. Chem. Soc., 77, 3701 (1955).

Name: Ira Block

Permanent Address: 120;616 Kinder Place
                      Bowowie, Maryland   20715.

Degree and date to be oconferred: Ph.D., 1971.

Date of birth: Novembeoer 11, 1941.

Place of birth: New Yoxork, New York.

Secondary education: 1 Baltimore Polytechnic Institute
                       1 Baltimore, Maryland - February, 1959.

Collegiate institutionos attended	Dates	Degree	Date of Degree
University of Maryland B	2/59-6/63	B.S.	1963
University of Maryland B	9/64-3/71	Ph.D.	1971

Major: Nuclear Engineering.

Minors: Chemical Engineering, Chemistry.

Positions Held: 1/71 · ~ Present, Faculty Research Associate,
                  Depoartment of Chemical Engineering, Lab. for
                  Radiation & Polymer Science, University of Md.
                  8/68—~1/71, Graduate Research Assista ~,
                  Depoartment of Chemical Engineerir
                  Uniiversity of Maryland.
                  9/64—~8/68, NDEA Fellow, Department of Chemical
                  Enggineering, University of Maryland.
                  7/63—~9/64, Process Development Engineer, E.
                  I. · duPont de Nemours & Co., Seaford,
                  Delüaware.

Professional Affiliation: Member, American Institute of
                                    Chemical Engineers.
                            Member, American Nuclear Society.
                            Member, Institute of Electrical
                                    and Electronic Engineers.