RADIATION GRAFTING OF DISPERSE DYSES
TO POLYPROPYLENE FIBERS

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The Faculty of the Graduate Division
by
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SUMMARY

Isotactic polypropylene has many outstanding fiber qualities which make it desirable for use in many textile applications. One of the main problems concerning its use as a textile material is its dyeability.

One method of dyeing the polymer makes use of solvent soluble dyes applied from an ethanol-water dyebath. The major drawback of this method is that the fastness properties of the dyed polymer are very poor.

In this work several of these solvent dyes containing an amine group were selected and reacted with acryloyl chloride to form acrylamide derivatives. These derivatives were then used to dye polypropylene. An attempt was then made to graft the dye to the polymer in the presence of gamma radiation.

Grafting was accomplished to some degree but further investigation is needed to determine optimum conditions.
CHAPTER I

INTRODUCTION

Polypropylene Fiber

Using the aluminum alkyl titanium chloride catalysts discovered by Ziegler (1) in 1954, a new class of stereo-specific polyolefins was produced having superior properties to any formerly made. Isotactic polypropylene has proven to be of particular interest due to its excellent film and fiber forming properties, and the low cost of the propylene monomer. Polypropylene can be melt-spun into textile fibers having outstanding physical properties. Such fibers are light, strong, resistant to abrasion, chemically non-reactive (under normal conditions), and hydrophobic.

The latter property coupled with the fact that polypropylene is non-polar presents a problem which is of great importance in the processing of textile fibers, i.e., its dyeability.

The Dyeing Problem

In order for a textile fiber to be generally marketable, it must be applicable to many varied end uses such as apparel, carpeting, industrial, and others. But before a fiber can be acceptable for many of these end uses, it must have the ability to be dyed to permanent colors which are stable to washing, dry-cleaning, and treatments normally applied to textile materials.

In this light, polypropylene has presented the textile industry
with its most challenging opportunity. The relatively low cost and excellent properties of polypropylene make it a superior choice for many end use applications. However, many of the physical and chemical properties of the polymer which impart the extraordinary qualities to fibers, are also the basis of a number of problems when used as a textile material.

One of these problems is the low melting point (176°C.) of polypropylene, which is not the subject of discussion in this paper. Perhaps the major problem in textile uses of polypropylene is that, not only is it difficult to dye, but it is also difficult to obtain shades which have good fastness to light, washing, and dry-cleaning.

The dyeing of polypropylene has become the subject of much research in recent years. Many attempts have been made to color the polymer, some of which are discussed briefly below.

Pigmentation

Perhaps the most successful coloration of polypropylene has been achieved by mixing pigments with the polymer before it is extruded into fibers. Although good fast colors are obtained by this method, colors are not easily tailored to the requirements of the customer and some sacrifices of strength and tenacity must be made with higher amounts of pigmentation.

Modification of Fibers by Pretreatments

Many and varied pretreatments have been suggested to provide dye sites for various types of commercial dyes and to improve diffusion of dyes into the polymer matrix.

The surface of fibers may be treated to cause cracking of the
surface (2), therefore increasing the ease of penetration of swelling agents, dye receptors, or dyes. Dye receptors may therefore be infused into the fiber and later be used as sites for various dyes (3).

Many attempts have been made to **graft** polymerize onto the polypropylene chains, compounds having sites which will attract dyes. This may be achieved by normal chemical methods (4) or by irradiation (5).

**Modifications by Admixing Dye Receptors to the Polymer**

Certain chemical compounds which act as dye receptors may be mixed with the polymer prior to melt-extrusion into fibers.

Polyalkylvinylpyridine compounds have been successfully incorporated into polypropylene fibers. Fibers containing these compounds may be dyed with disperse dyes or after a suitable acid-protonation treatment (6) may be dyed with acid dyes.

Organometallic compounds which are soluble in the polymer have been suggested as additives to improve dyeability (7). These compounds have the ability to chelate with selected dyes.

**Attempts to Dye the Unmodified Polymer**

Because of the high crystallinity of isotactic polypropylene, dyes of large molecular weight cannot be made to penetrate the intermolecular spaces in the polymer. Even by employing dyebaths or emulsions containing hydrocarbon or chlorinated hydrocarbon swelling agents (8) the size of the dye molecule is limited. Also, because the only attraction between the dye molecule and polymer is Van der Waal's attraction, the fastness properties of the dyed materials are very poor.

Disperse dyes may be applied to unmodified polypropylene. These dyes give only a limited range of shades and have very poor fastness
Unmodified polypropylene may be dyed with solvent colors to a wide range of shades. These colors are applied as dispersions from solvent-containing baths. However, with practically no exceptions they have very poor fastness to dry-cleaning (9).

**Purpose of the Research**

From the brief survey given above, it is fairly evident that, although polypropylene can be dyed by many and varied methods, one of the main problems concerning the resultant dyeing is the fastness properties. The purpose of this research is therefore to investigate the possibility of preparing a new class of dyes or modifying existing dyes, such that after having been dyed onto the polymer, have the ability to react with polypropylene under the influence of ionizing radiation. This investigation is to determine the feasibility of preparing reactive dyes for polypropylene. These dyes could be reacted with and thus become a part of the polypropylene molecule, therefore having superior fastness properties.

It is not the author's intention to make the results of this research a commercially applicable process, but to lay the groundwork which may stimulate further investigation of this possibility.

**Approach to the Research**

Selected solvent dyes of the amine type were applied to a purified polypropylene fiber. Acrylamide derivatives of these dyes were prepared and applied to the fiber in the same manner. The dyed samples were then exposed to varying doses of gamma radiation. The irradiated
samples were allowed to remain in contact with a commercial dry-cleaning solvent for a period of 24 hours. The amount of extracted dye was then measured employing ultraviolet spectrophotometry. By this method the effectiveness of the radiation treatments was compared.

**Review of Literature**

Much literature is available concerning the grafting of monomers or other reactive materials to polymers using ionizing radiation. Much of this literature applies directly to polypropylene. A survey of all literature in this subject area would be much too voluminous to report here, and is not directly pertinent to the subject presented in this paper.

Literature concerning itself with the effects of radiation on the dyeing of polypropylene or, more specifically, the grafting of dyes to polymers is practically non-existent. A United States patent awarded to Koble and Goldtrap of Phillips Petroleum Company (10) cites the use of ionizing radiation to prevent bleeding of dyes from polyolefins colored with certain low molecular weight dyes. In this instance, however, the coloring matter was incorporated into the polymer matrix before the articles (fibers, films, moldings, etc.) were extruded. The effect of the radiation treatment was merely the crosslinking of the polymer and subsequent entrapment of the dye. There was no claim to chemical reaction between the dye and the polyolefin, i.e., the dye is held mechanically.
Nature of Gamma Radiation

Gamma radiation is emitted from a radioactive substance when the radioactive nuclei of the atom decays with the emission of an alpha or beta particle. After such an emission of a particle the nucleus is left in an excited state. It then returns to the ground state by emission of gamma radiation. This form of radiation is highly penetrating. Gamma rays consist of electromagnetic radiations having wavelengths in the range 50 to $1 \times 10^{-3}$ Å and energies in the range $5.7 \times 10^{5}$ to $3 \times 10^{8}$ kcal mole$^{-1}$. They produce ionization in all solids and this is their most important effect (11). In insulators, chemical reactions that cannot be induced by other means can be initiated using gamma radiation.
CHAPTER II

INSTRUMENTATION, APPARATUS AND SPECIMENS

Fiber Specimen

Isotactic polypropylene (See Figure 1) is now commercially available in fiber form from a number of United States companies. However, no commercial fiber now available consists of pure polypropylene polymer. As received, they contain "impurities" such as light stabilizers, finishes, and additives to improve dyeability. The fiber used in this work was type 60 Herculon, manufactured by Hercules Powder Corporation. This fiber was purified before use as described in the section Purification of the Fiber.

Chemical Specimens

Dyes

Two dyes of the solvent type were selected for this work and obtained from commercial sources. These dyes are of low molecular weight and are soluble in most common organic solvents.

C.I. Solvent Yellow 3 (See Figure 2) was obtained from E.I. du Pont de Nemours and Company under the name Oil Yellow. C.I. Solvent Brown 1 (See Figure 3) was obtained from the Imperial Chemical Industries under the name Lithofor Brown A. The purification and use of those compounds will be discussed in Chapter III.

Acryloyl Chloride

The acid chloride of acrylic acid, i.e., acryloyl chloride was...
Figure 1. Isotactic Polypropylene

Figure 2. C.I. Solvent Yellow 3
M.W. 225.3

Figure 3. C.I. Solvent Brown 1
M.W. 262.3
used to prepare the dye derivatives. This chemical is a colorless liquid, has a boiling point of 75.5°C, a density of 1.15 g/ml, and is an extremely powerful lacrymator. Extreme care is required when handling this compound.

The acryloyl chloride used in this work was obtained from the Aldrich Chemical Company of Milwaukee, Wisconsin. The chemical was received packed over hydroquinone as a stabilizer and was used as received.

The Dyeing Apparatus

General Description

Dyes were applied to the fiber employing a constant temperature, constant volume type dyeing apparatus. The dyeing vessel is immersed in a temperature-controlled oil bath and is fitted with a condensing unit of the reflux type to return evaporated liquid to the dye bath. The sample to be dyed is agitated by the movement of a glass rod carrying the sample. The rod is attached to a motor-driven eccentric. (See Figure 4).

Temperature Control Section

Heat is transferred to the dyeing vessel by a mineral oil bath heated by an electrically controlled heating mantel. The oil bath is stirred constantly with a motor-driven stirring device regulated to a speed necessary to keep the temperature of the bath as constant as possible. The oil bath is contained in a one liter Pyrex beaker fitted with a suitable heating mantel. The heating mantel is electrically connected to a variable transformer which remained set at 25 volts after the desired bath temperature was initially reached. Regulation of the
Figure 4. Constant Temperature - Constant Volume Dyeing Apparatus
set temperature is achieved by connecting the variable transformer to a Thermocap relay. The sensing lead of this relay is connected to a sliding collar attached to a mercury thermometer. The thermometer is immersed in the oil bath to the same level to which the dye vessel extends into the bath. The temperature of the bath can be set by sliding the collar to the desired temperature on the thermometer. The variable transformer is activated through the relay until the temperature reaches the set value. The relay mercury column sensor then detects the column of mercury and interrupts the flow of current to the variable transformer and thus to the heating mantel. When the mercury falls below the set value, the sensor detects the absence of the mercury column and activates the relay which then supplies power to the transformer and to the heating mantel. In this manner the temperature of the bath can be regulated to any set temperature ±0.5°C in the range 40 to 100°C when a 0 to 100°C, 0.1°C divisions thermometer is used.

Dyeing Section

The vessel in which the actual dyeing operation is carried out consists of a 3/4 in. X 5 in. test tube which is immersed in the mineral oil bath. The mouth of the test tube is provided with a rubber stopper having one hole large enough to accommodate the male end of a 14/20 male, 24/40 female standard taper ground glass adapter. The female 24/40 end is then provided with a 24/40 standard taper 12 inch straight-wall condensing unit having a suitable Teflon sealing sleeve. The condenser is supplied with rubber tubing for entrance and exit of cooling water.

The sample carrier is a glass rod three millimeters in diameter, 20 inches long and bent on the lower end to form a hook. The hook of
the carrier is used to attach the fiber sample and the shaft extends upward through the condenser and protrudes from the top. The top of the condenser is fitted with a number five rubber stopper having one hole six millimeters in diameter. This allows free passage of the shaft but prevents excessive horizontal oscillation.

The top of the shaft is connected by means of flexible rubber tubing to an aluminum shaft affixed eccentrically to a motor driven wheel 3/4 inch from the axis. The speed of the motor driving the eccentric is continuously variable from 0 to 400 revolutions per minute and is controlled by a voltage regulator.

**Gamma Radiation Source**

The radiation source used in this work is a 12,000 curie Cs-137 gamma radiation source located in the Radioisotopes and Bioengineering Laboratory Building on the Georgia Institute of Technology Campus. The source is owned by Georgia Institute of Technology and is operated under the supervision of Dr. James A. Knight.

The actual source material is encapsulated cesium chloride and is contained in a Notre Dame type holder (12). The energy of the gamma radiation emitted from the Cs-137 source is 0.662 Mev and the dose rate is approximately 1.1 Megarads per hour.

The tube nest holding the source is shown in Figure 5. The source is positioned in the smaller tubes and samples are inserted in the large center and smaller outside holes.

The active material is located 8.5 feet below floor level but extension of the tube nest is provided so that experiments may be run from desk top level.
Figure 5. Cesium-137 Source Tube Nest
Spectrophotometric Instruments

Ultraviolet-Visible

All measurements in the ultraviolet and visible range were made on a Beckman Model DU U.V./Vis. Spectrophotometer. Samples to be measured were placed in a matched set of fused silica cells having a 1 cm. optical pathlength. Pure absolute ethanol was used as the solvent in all U.V./Vis. measurements.

Infrared

All infrared spectra presented in this work were prepared using a Beckman Model IR-10 Infrared Spectrophotometer. Samples were prepared using the potassium bromide pellet technique. Reagent grade potassium bromide was used in preparation of the samples.
Purification of Fiber

Preliminary investigation indicated that impurities present in the fiber were detrimental to radiation grafting and optical measurements, therefore necessitating purification of the fiber. The method described below was found to be satisfactory for this work.

Extraction Procedure

Five grams of the fiber were weighed out and placed in a Soxhlet extractor charged with 200 ml. of an azeotrope of ethanol and perchloroethylene (approximately 63 per cent ethanol and 37 per cent perchloroethylene - b.p. 76.75°C.).

A sample of the virgin mixture was taken to be used later as a reference. The extraction was allowed to continue and two ml. samples were removed after 3/4, 1 1/2, 3, 6, 12, and 24 hours of extraction.

Determination of Extraction Rate

The two ml. samples of extraction mixture taken at various time intervals were diluted to 10 ml. with absolute ethanol. A two ml. aliquot of the virgin azeotrope was diluted in like manner for use as a reference. The ultraviolet spectrum of the sample taken at 3/4 hour was then determined in the Beckman DU Spectrophotometer (See Appendix Figure 10) and from this the wavelength was selected for subsequent measurements. The absorbances of the remaining samples were then measured at 350 nm. The absorbances thus obtained were plotted against
extraction time (See Figure 6).

No attempt was made to determine the actual amount of material extracted but it was assumed that according to the Beer-Lambert law (discussed later in this chapter) that the absorbance was a relative measure of the amount of material. It is evident from Figure 6 that most impurities have been removed after three hours. The declining trend of the curve is probably due to some decomposition of the extracted material.

**Purification of Dyes**

Solvent Yellow 3 was purified by recrystallization from hot saturated solutions of the commercial dye in absolute ethanol. The hot solutions were placed in an ice bath and allowed to remain for several hours in order for crystals to form. The crystals were then removed from the solution by vacuum filtration. The recrystallization was repeated three times using the recrystallized solid from the preceding step. The final recrystallized solid was dried under a vacuum of 1 mm. Hg over calcium chloride for a period of 24 hours.

The purity of the final recrystallized dye was then checked by column chromatography. A slurry of aluminum oxide in absolute ethanol was used to prepare the column. A sample of the purified dye was dissolved in absolute ethanol, placed in the column, and developed with the same solvent. Only one reddish yellow band was visible in the column after development. The infrared spectrum of this purified compound is shown in Appendix Figure 11.

Solvent Brown 1 was used as received. The infrared spectrum of this compound is shown in Appendix Figure 12.
Preparation of Dye Derivatives

Solvent Yellow 3 Derivative

Preparation. The amine group of this dye reacts with acryloyl chloride according to the equation

\[
2D\text{-}NH_2 + \text{Cl}\text{-}C=\text{CH}=\text{CH}_2 \rightarrow D\text{-}NH\text{-}C=\text{CH}=\text{CH}_2 + D\text{-}NH_3\text{Cl}
\]

to form the acrylamide derivative and the hydrochloride. D in the above equation indicates the aromatic portion of the dye molecule.

Five grams (0.022 moles) of the purified Solvent Yellow 3 was weighed out and dissolved in 150 ml. of reagent grade benzene. This solution was placed in a 200 ml. three-neck reaction vessel. The center neck of the vessel was provided with a motor-driven stirring device. One gram (0.88 ml., 0.011 moles) of acryloyl chloride was measured out and dissolved in 50 ml. of reagent grade benzene.

One of the side necks of the reaction vessel was fitted with a dropping funnel into which was introduced the acryloyl chloride-benzene solution. The third neck of the flask was fitted with a thermometer which dipped into the dye solution.

The acryloyl chloride solution was then added dropwise to the dye solution over a period of one hour. The temperature of the dye solution was approximately 20°C. at the start of this addition. During the addition, a temperature rise of about 5°C. was noted. Stirring was continued for six hours until the temperature returned to 20°C.

The products appeared as a precipitate in the reaction mixture.
and were separated from the mother liquor by vacuum filtration.

**Purification.** The reaction products were allowed to remain on the vacuum filtration funnel until the benzene had evaporated. The products were then removed from the funnel and dissolved in warm (50°C.) absolute ethanol to make a saturated solution. Enough distilled water was then poured into the solution to cause precipitation of the bulk of the material. The precipitate was allowed to settle and then was removed by vacuum filtration. By this method most of the hydrochloride portion of the product was removed. The precipitate was again allowed to dry and was redissolved in enough warm (50°C.) absolute ethanol to form a saturated solution. This solution was placed in an ice bath for several hours and crystallization allowed to take place. The recrystallization process was repeated three times using the recrystallized solid from the preceding step.

The final recrystallized derivative was then dried under 1 mm Hg. vacuum over calcium chloride for 24 hours. The infrared spectrum of this derivative is shown in Appendix Figure 13.

**Verification of Purity.** The column chromatogram of the derivative, when carried out as described in the section **Purification of Dyes,** indicated only one dark yellow band. A mixture of the Solvent Yellow 3 starting material and its derivative was made and run in the column in the same manner. In this case two bands were observed one being the reddish yellow starting material and the other the dark yellow derivative.

A sample of the derivative was sent to Galbraith Laboratories, Inc. of Knoxville, Tennessee for elemental analysis. The results of
this analysis showed the compound to contain 73.20 per cent carbon, 6.04 per cent hydrogen, and 5.86 per cent oxygen, the remainder being nitrogen. Theoretical percentages are 73.09 per cent carbon, 6.14 per cent hydrogen, 5.73 per cent oxygen, the remainder being nitrogen.

**Solvent Brown 1 Derivative**

**Preparation.** The amine groups of this dye are reacted with acryloyl chloride according to the equation

\[
\text{D}_2\text{NH}_2 + 2\text{Cl}-\text{CH} = \text{CH}_2 \rightarrow \text{D}_2\text{NH}-\text{C}-\text{CH} = \text{CH}_2
\]

where D indicates the aromatic portion of the molecule. The product in this case is probably a mixture of compounds as shown.

Five grams (0.019 moles) of Solvent Brown 1 were weighed out and dissolved in 150 ml. of reagent grade benzene.

Into 50 ml. of benzene was measured 1.72 grams (0.019 mole, 1.5 ml.) of acryloyl chloride. The reaction procedure was carried out in the same manner as for the preparation of the previous derivative.

The resulting products appeared as a precipitate which was separated from the reaction liquor by vacuum filtration.

**Purification.** No attempt was made to separate the various
possible products. One purification step was carried out to remove the dye hydrochlorides.

The derivative mixture was rendered free of benzene and dissolved in warm (50°C.) absolute ethanol to form a saturated solution. Enough distilled water was then added to precipitate the bulk of the dissolved material. The precipitate was allowed to settle and was removed by filtration. The derivative was then filtered and dried under 1 mm Hg vacuum over calcium chloride for 24 hours. The infrared spectrum of this derivative is shown in Appendix Figure 14.

Dyeing Procedure

Preparation of the Fiber Sample

After purification of the fiber, as described earlier, all traces of solvent were removed and exactly one gram was carefully weighed out for each dye and derivative to be applied. The yarn was then attached to the sample carrier of the dyeing apparatus and wound loosely around the sample carrier hook.

Preparation of the Dyebaths

Twenty milligrams of the dye or derivative were carefully weighed out and placed in a 25 ml. volumetric flask. Ten ml. of absolute ethanol were then added to dissolve the dye. A solution of Triton X-100 (Rohm and Haas Co.) in distilled water (1 g/l.) was then added to bring the volume to the 25 ml. mark. The flask was then shaken to mix the contents.

The dyeing formula described here is similar to a patented process for dyeing polyolefins in which the solvent dyes are dissolved in water-soluble polyhydric alcohols (13).
Dyeing Operation

The prepared dyebath was introduced into the dyeing vessel and the temperature control system set to keep the bath temperature at 85 ± 0.5°C. The fiber sample attached to the carrier was put in place and the apparatus properly assembled for operation.

The oil bath stirring device was started and the sample agitation mechanism set into operation. The flow of cooling water to the condensing unit was also started.

The dyeing operation was allowed to continue in this manner for a period of not less than two hours.

At the end of the dyeing period, all systems were deactivated and the sample and carrier removed. The sample was rinsed under cold running tap water for one minute and then rinsed with three 100 ml. portions of distilled water. Excess water was squeezed from the sample and it was allowed to dry.

The dyed samples were further dried under a vacuum of 1 mm. Hg over calcium chloride for 24 hours.

Samples so prepared were divided into five equal portions - four to be given radiation treatments and the remaining portion to be retained as a control.

Irradiation of Samples

Preparation of Samples

Each sample to be exposed to gamma radiation was compacted and placed in the bottom of a 1/2 X 5 inch test tube. The tubes were then heated and drawn in the center to approximately three mm. in diameter.
The tube was then fitted with a suitable one-hole rubber stopper carrying a stopcock. The assembly was then attached to a vacuum pump and evacuated to 1 mm. Hg. The stopcock was closed and the assembly removed from the vacuum system and attached to a supply of oil-free nitrogen. The nitrogen was allowed to flow into the tube to a pressure of 2.5 lb./in.². The tube assembly was again attached to the vacuum system and evacuated. This degassing process was repeated five times after which the tube was left under 1 mm. Hg of nitrogen. The tube was then heated where drawn and sealed off.

**Irradiation Procedure**

Samples prepared above were then placed in the source sample carrier and lowered into proximity to the source material.

The samples were irradiated to doses of 5, 10, 15, and 20 Mega­-rads and were allowed to remain in contact with the source for sufficient time to receive the designated radiation dose.

**Testing of Samples**

**Preparation of Samples for Testing**

After the samples were removed from the source the vials were broken open and the contents removed.

Exactly 50 milligrams of each sample was carefully weighed out and labeled according to its history.

**Extraction of Dye**

The 50 mg. of dyed fiber were placed in 25 ml. round-bottom flasks. Ten ml. of perchloroethylene dry-cleaning fluid was added to each flask. The samples were allowed to remain in contact with the solvent for 24 hours at room temperature. At the end of this time the
flask and sample were attached to a vacuum distillation apparatus. The fiber was drawn up into the head of the distillation unit so that by condensation of vapors on it, any adhering dye was washed back into the flask. Vacuum was applied from a water aspirator and the vapors were drawn off into a cold trap. In this manner all of the perchloroethylene solvent was removed at a temperature below 50°C. The flask was then removed from the distillation apparatus and the residue dried under a 1 mm. Hg vacuum over calcium chloride.

The residue was then dissolved in 10 ml. of absolute ethanol which was carefully measured out.

**Measurement of Dye Extracted**

The residue dissolved in absolute ethanol was placed in the sample silica cell and positioned in the cell compartment of the Beckman DU Spectrophotometer. The reference cell was filled with pure absolute ethanol and also placed in the cell compartment. The Absorbance of the sample was then measured at a predetermined wavelength.

**Determination of Wavelength of Measurement**

Ultraviolet-Visible spectra were prepared for both dyes and their derivatives (See Appendix Figures 15, 16, 17, 18, 19, and 20). From these spectra, the wavelength at which each was to be measured was determined.

Solvent Yellow 3 was measured at 295 nm and its derivative at 270 nm. Solvent Brown 1 was measured at 310 nm while its derivative was measured at 315 nm.
Calculation of Dye Extracted

The Beer-Lambert law of spectrophotometric absorption states, "Successive increments in the number of identical absorbing molecules in the path of a beam of monochromatic radiation absorb equal fractions of the radiant energy traversing them."

This can be expressed mathematically as:

\[ A = abc \]  \hspace{1cm} (1)

Where:

- \( A \) = Absorbance
- \( a \) = Absorptivity coefficient
- \( b \) = Pathlength of absorber
- \( c \) = Concentration of the absorber.

If the Beer-Lambert law is true for a given compound, then both \( a \) and \( b \) must be constants. If the absorbances of successive concentrations are measured and plotted against the concentration, \( b \) remaining constant and the Absorptivity coefficient calculated from the curve, \( a \) can only be constant if the curve is a straight line.

Each compound used in this work was studied in this manner and their curves plotted (See Appendix Figures 21 and 22). All compounds were found to apply to the law at the wavelengths designated.

Using the Beer-Lambert law the dye extracted from the fiber was then calculated in millimoles per kilogram of fiber from the following formula:

\[ \phi = \frac{VA}{ab(M.W.)W} \times 10^6 \]  \hspace{1cm} (2)
Where: \( \phi = \) Dye extracted in millimoles/kg. fiber
\( V = \) Volume of dissolved residue in liters
\( \text{M.W.} = \) Molecular weight of compound being measured
\( W = \) Weight of fiber sample in grams
\( a = \) Slope of plot conc (g/l.) vs. Absorbance.

Since the volume of the extract, the weight of the fiber sample
and the pathlength of the measuring cell are all extensive constants,
the formula may be reduced to

\[
\phi = \frac{2A}{a \text{ (M.W.)}} \times 10^5 \quad (3)
\]

if 0.05 grams of fiber are used and the residue is diluted to 0.01
liter with absolute ethanol.

**Calculation of Dye Retained**

The per cent dye retained by the fiber as a result of the radia-
tion treatments can therefore be calculated using the above values.

Then:

\[
R_s = \left( \frac{\phi_{ns} - \phi_{is}}{\phi_{ns}} \right) \times 100 \quad \text{and} \quad R_d = \left( \frac{\phi_{nd} - \phi_{id}}{\phi_{nd}} \right) \times 100 \quad (4)
\]

Where: \( R = \) per cent dye residue
\( n \) indicates no radiation treatment
\( i \) indicates a level of radiation treatment
\( s \) indicates a starting dye residue
\( d \) indicates a derivative residue.

**Calculation of Dye Grafted**

The per cent of grafting of the derivative may be calculated by applying a correction factor for the amount of dye which may be entrapped by crosslinking of the polymer during irradiation. The per cent grafting may then be expressed as:

\[
G = \frac{(\phi_{nd} - \phi_{id}) - \phi_{nd} \left(\frac{\phi_{ns} - \phi_{is}}{\phi_{ns}}\right)}{\phi_{nd}} \times 100
\]

Where:  
\( G \) = per cent grafting of the derivative.

This can be reduced to:

\[
G = \left(\frac{\phi_{nd} - \phi_{id} - \phi_{ns} - \phi_{is}}{\phi_{nd}}\right) \times 100
\]

Referring then to equation 4, it is evident that the per cent grafting can be expressed as:

\[
G = R_d - R_s
\]
CHAPTER IV

DISCUSSION OF RESULTS

Cross-linking of Polypropylene

The major reaction of polypropylene when exposed to ionizing radiation, in the absence of any other possible reactants, is cross-linking (14).

A possible mechanism for this reaction is shown below.

\[
\begin{align*}
\text{CH}_3 & \quad \text{gamma} \quad \rightarrow \quad \text{CH}_3 \\
-\text{CH}_2-\text{C}^- & \quad \text{H}^+ \quad \rightarrow \quad -\text{CH}_2-\text{C}^- + \text{H}^+ \quad \text{(1)} \\
\text{CH}_3 & \quad \rightarrow \quad -\text{CH}_2-\text{C}^- + \text{H}_2 \quad \text{(2)} \\
-\text{CH}_2-\text{C}^- + -\text{CH}_2-\text{C}^- & \quad \rightarrow \quad -\text{CH}_2-\text{C}^- \quad \text{(3)}
\end{align*}
\]

Throughout this work it has been assumed that no actual reaction is possible between the starting dyes and the polymer. This assumption makes it possible to apply a correction factor to the data obtained from the derivative dye experiments to allow for any dye which was mechanically held by this cross-linking reaction.
Reaction of Derivatives with Polypropylene

The theory of this work lies in the possibility that the polypropylene polymer may react with a dye having a vinyl group attached to it, and that this reaction will occur under the influence of ionizing radiation. Some possibilities for this reaction are shown below.

\[ \begin{align*}
\text{Dye-CH=CH}_2 + \cdot 
\text{CH} = \text{CH}^* & \rightarrow \text{Dye-CH}_2 \cdot \text{CH}_2 \text{ or Dye-CH-CH}_3 \\
\text{Dye-CH}_2 \cdot \text{CH}_2 + \cdot \text{CH} & \rightarrow \text{Dye-CH}_2 \cdot \text{CH}_2 \cdot \text{Dye} \\
\text{Dye-CH=CH}_2 + 2 \cdot 
\text{CH} & \rightarrow \text{Dye-CH-CH}_2 \\
\cdot \text{CH} + \text{Dye-CH}_2 \cdot \text{CH}_2 & \rightarrow \text{Dye-CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Dye}
\end{align*} \]
Determination of Grafting

The absorbances of each extract of dyed, irradiated fiber are shown in Appendix Table 2. From this data the per cent residues were calculated according to the method described under Calculation of Dye Retained. The actual values of dye extracted expressed in mmoles/kg. are shown in Table 1.

If the per cent residues for each dye and its respective derivative are plotted against radiation dosage, (See Figures 7 and 8), then according to equation 7 (Chapter III) the per cent grafting is simply the difference between the two curves. These curves as shown have been smoothed to show trends although the data points are real.

Having established these curves, the difference or amount of grafting was taken from the curves for each does level and plotted against dose level in Figure 9.

The reader must keep in mind that the per cent grafting as expressed here is not based on the weight of the fiber, but is a percentage based on the amount of dye material originally placed on the fiber.

Sources of Error

It must be pointed out that the results shown here cannot be taken as absolute. The author has only attempted to show trends in this work due to the great number of possibilities for experimental error. It was hoped that by performing each operation as similarly as possible, errors would cancel out and rational trends could be shown.

Some of the more major sources of error are listed below.

1. Unevenness in dyeing
2. Error in weighing samples

3. Error in Absorbance readings.
<table>
<thead>
<tr>
<th>Radiation Dose (Megarads)</th>
<th>Solvent Yellow 3</th>
<th>Solvent Yellow 3 Derivative</th>
<th>Solvent Brown 1</th>
<th>Solvent Brown 1 Derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.60</td>
<td>7.98</td>
<td>3.07</td>
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<tr>
<td>5</td>
<td>8.55</td>
<td>7.82</td>
<td>11.13</td>
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<td>10</td>
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<td>6.57</td>
<td>2.70</td>
<td></td>
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<td>15</td>
<td>7.61</td>
<td>6.73</td>
<td>10.15</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>7.22</td>
<td>5.80</td>
<td>9.66</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7. Per Cent Dye Residue of Solvent Yellow 3 ($R_s$) and its Acrylamide Derivative ($R_d$) Versus Radiation Dosage.
Figure 8. Per cent Dye Residue of Solvent Brown 1 ($R_s$) and its Acrylamide Derivative ($R_d$) Versus Radiation Dosage
Figure 9. Per Cent Grafted Dye Versus Radiation Dosage

○ Solvent Yellow 3 Derivative
□ Solvent Brown 1 Derivative
CHAPTER V

CONCLUSIONS

1. Acrylamide derivatives of selected solvent dyes can be prepared which react with polypropylene under the influence of ionizing radiation.

2. It is feasible that a series of reactive dyes for polypropylene could be prepared which could be reacted with the polypropylene polymer thereby enhancing the fastness properties of the colored material.

3. As the size of the derivative molecule becomes larger, the effect of entrapment by cross-linking of the polymer becomes relatively more significant than grafting.

4. The rate and extent of reaction of the derivative with the polymer relative to radiation dose level is a function of the number of possible dye reaction sites and the proximity of the dye molecule to the polypropylene chain.
CHAPTER VI

RECOMMENDATIONS

Although the dye application method was not the major concern of this work, it was indeed an integral part. No attempt was made in this work to optimize the dyeing process. The dyes were applied from as simple a system as possible to avoid complication of the main issue. This does not, however, exclude the fact that more work is needed in the area of application to determine the best conditions for application of the dyes and particularly the derivatives. Perhaps various types of carriers could be used to increase the dye uptake of the fiber. This would then necessitate a study of the effects of other compounds used, on the grafting of the dye and the polymer after irradiation.

The rate of dyeing and kinetics of diffusion of these new dye derivatives should also be investigated.

Formation of the acrylamide derivatives of the solvent dyes used here caused a slight lowering of their tinctorial value. The need exists then to investigate various types of dye structures to first determine the relation of the dye structure to the rate of reaction with the polymer and second, to determine optimum dye structure to give high color yields and high percentage of grafting.

One of the adverse effects of ionizing radiation on polypropylene is a decrease in tensile strength. Studies could be made then to determine the optimum radiation dose level to achieve maximum dye grafting with minimum loss in tensile strength.
Most polypropylene fiber produced contains a light stabilizer to prevent degradation of the polymer by ultraviolet light. These compounds may be radiation absorbers and it would be interesting to determine the effect of these compounds on the radiation grafting to polypropylene. For this work, however, pure samples of polypropylene would be required.

In addition, a study of the effects of dye concentration in the fiber on the rate of grafting would be necessary to determine optimum conditions. Also, a study of the effects of various atmospheres in which the specimens are irradiated would be of great interest.
APPENDIX
Table 2. Absorbances of Extracts of Dyed Polypropylene Fiber

<table>
<thead>
<tr>
<th>Radiation Dose (Megarads)</th>
<th>Solvent Yellow 3 A (λ=295nm)</th>
<th>Solvent Yellow 3 Derivative A (λ=270nm)</th>
<th>Solvent Brown 1 A (λ=310nm)</th>
<th>Solvent Brown 1 Derivative A (λ=315nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.156</td>
<td>0.243</td>
<td>0.113</td>
<td>0.100</td>
</tr>
<tr>
<td>5</td>
<td>0.155</td>
<td>0.238</td>
<td>0.103</td>
<td>0.088</td>
</tr>
<tr>
<td>10</td>
<td>0.140</td>
<td>0.200</td>
<td>0.103</td>
<td>0.086</td>
</tr>
<tr>
<td>15</td>
<td>0.138</td>
<td>0.205</td>
<td>0.098</td>
<td>0.084</td>
</tr>
<tr>
<td>20</td>
<td>0.131</td>
<td>0.175</td>
<td>0.097</td>
<td>0.079</td>
</tr>
</tbody>
</table>
Figure 10. Ultraviolet Spectrum of Extract of Herculon in Ethanol
Figure 12. Infrared Spectrum of Solvent Brown 1 Run in Potassium Bromide Pellet.
Figure 13. Infrared Spectrum of Solvent Yellow 3 Acrylamide Derivative
Run in Potassium Bromide Pellet.
Figure 14. Infrared Spectrum of Solvent Brown 1 Acrylamide Derivative Run in Potassium Bromide Pellet.
Figure 16. Visible Spectrum of Purified Solvent Yellow 3 (3.0 g/l.)
Figure 17. Ultraviolet Spectrum of Purified Solvent
Yellow 3 Acrylamide Derivative (5 X 10^{-3} g/l.).
Figure 21. Concentration Versus Absorbance for Solvent Yellow 3 and its Acrylamide Derivative
Figure 22. Concentration Versus Absorbance for Solvent Brown 1 and its Acrylamide Derivative
BIBLIOGRAPHY


5. German Patent 1, 129, 925 to Agency of Industry Science and Technology.


