AN INVESTIGATION OF RADIATION GRAFTING

METHODS TO IMPROVE THE DYEABILITY OF POLYESTER FIBERS

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SUMMARY

One of the most dramatic developments within the United States textile industry during the past five years has been the introduction of Dacron and other polyester fiber blends with cotton into such basic fabric constructions as the batiste, broadcloth, voile, and poplin. The "ease of care" properties imparted to the fabric by the polyester elements are responsible for the great popularity of these blends. However, a very serious dyeing problem is encountered when dealing with the polyester fibers. The ester groups, which account for 46 per cent of the polymer weight, provide good dyeing sites for certain selected disperse dyes. However, the fiber is so compact that the dyes have great difficulty in penetrating the polymer and reacting with those ester groups. Thus, a considerable kinetic dyeing problem exists with polyester fibers in that it takes a relatively long time to reach a given depth of shade.

There are essentially two methods that are being used to overcome these kinetic dyeing problems. The first involves the use of costly pressure equipment necessary to conduct dyeings at a temperature near 250° F., and involves the addition to the dyebath of expensive carriers or agents that promote the rate of dye diffusion into the fiber. The second method, known as the Thermosol Process, requires special continuous dyeing equipment capable of bringing the fabric temperature up to 400° F. at the disperse dyeing step of the process.

In this investigation, an attempt was made to chemically modify the polyester fiber in such a manner as to render it dyeable by conventional, less costly, methods. This modification was achieved by grafting vinyl monomers to the fiber to make a copolymer. It was hoped that the monomers selected, methyl acrylate and acrylic acid, would accommodate at least one of the following dye classes: basic, disperse, and acid.

The grafting was attempted by three radiation chemical techniques:

1. Direct Radiation Grafting

    In this method, the polyester fiber, Dacron, and the monomers, diluted with methanol, were irradiated together.

2. Peroxidized Polymer Grafting

    The Dacron fiber was first irradiated in the presence of pure oxygen until sufficient peroxide groups had formed on the polymer chains. The peroxidized polymer was then heated in the presence of the vinyl monomers.

3. Trapped Radical Grafting

    The Dacron fiber was first irradiated in a vacuum. Instead of peroxide groups forming within the polymer, radical sites were produced; these sites were thought to be entrapped within the polymer. The trapped-radical polymers were subsequently reacted with the vinyl monomers.

It was found that all three methods could be used to make Dacron copolymers with either monomer. The direct radiation method was clearly the most efficient, while methyl acrylate was more readily grafted than was acrylic acid on a mole as well as on a weight basis.

The breaking strength, elongation at break, and toughness of the copolymers were investigated to make sure these properties were not im-

paired by the nuclear radiation and/or subsequent graft reactions. It was found that these properties were not impaired; in most cases they were enhanced.

The copolymers containing the most grafted monomer were dyed using conventional techniques with one dye of each of the following classes: acid; basic; and disperse. It was found that there was a considerable increase in the dye absorption by the graft copolymer compared to the absorption exhibited by the pure Dacron. The Dacron-methyl acrylate copolymers were dyed best with disperse dyes. Heavy depths of shade were obtained in only one hour of dyeing at the boil. No carrier was required. The Dacron-acrylic acid copolymers were dyed best with the basic dye. In one hour of dyeing at the boil, heavy depths of shade were obtained.

One advantage of using nuclear radiation, as opposed to certain catalyst techniques for example, to initiate graft copolymerization reactions, is that the copolymers produced are relatively void of impurities. Add to this advantage the fact that the only way to make copolymers of condensation polymers such as Dacron or nylon is to graft vinyl monomers to the condensation polymer, and it appears that radiation-induced graft copolymerization may have great industrial potential.

CHAPTER I

INTRODUCTION

Historical

Man's first attempts at dyeing his crudely woven cloths probably consisted of staining them with the colored juices obtained from flowers, fruits, and tree bark. The variety of shades was limited, and for the most part did not survive exposure to sunlight and washing. The same problems were confronted as the so-called natural dyes were discovered. Very few natural dyes formed fast combinations with textile materials. But eventually it was found that this lack of affinity could be overcome by using mordants, substances which caused the natural dyes to adhere strongly to the fabric. It was not until this discovery was made, probably in India before 2000 B.C., that dyeing made any appreciable progress.

The discovery of the first synthetic dye, Mauve, was made by Perkin in 1856. This discovery opened up an entirely new era in the chemical industry as a whole and especially in the field of textile coloring. An equally important reaction in dye synthesis was discovered in 1864 by Griess — the coupling of diazotized amines with other amines and phenols to give colored azo compounds. Following these discoveries came an avalanche of synthetic dyes for the natural fibers of cotton, silk, and wool. The majority of them included direct, acid, basic, naphthol, vat and sulfur dyes, and as they were being discovered, tech-

niques were developed for their application which insured far superior fastness properties than could be obtained with the natural dyes. But just as important, an extensive range of shades was made available to the dyer.

In 1883, the first regenerated fibers were introduced. These regenerated fibers, including viscose rayon, cuprammonium, alginate, Ardil, Vicara, etc., have the same chemical composition as the parent natural fiber, and were dyed in the same manner with the same dyes. Cellulose acetate, whose chemical composition was different from that of cotton, was an exception and could not be satisfactorily dyed with any of the existing dyes.

The method developed for dyeing the acetate fibers consisted of treating the fibers with a dispersion of a water insoluble anthra-quinoid type dye at a high enough temperature to cause the fine dye particles to actually dissolve in the acetate fiber. It has since been confirmed that the process does, in fact, consist of a solid solution of dyestuff in the fiber and the development of these disperse dyes for cellulose acetate is the counterpart for synthetic fibers to Perkin's development of a coal tar dye for natural fibers.

In 1938, nylon, a true synthetic fiber, was introduced. There followed a variety of synthetic fibers including polyesters, vinyl polymers and copolymers, polyethylenes, polyflouroethylenes, poly-propylenes, glass and even metallic fibers. Many of these fibers could at first be colored only with disperse dyes resembling those developed for cellulose acetate, and each different chemical class of fibers exhibited its own peculiar dyeing problems.

One of the most interesting of the above classes of fibers, from the standpoint of problems introduced to the dyer, is the polyester class. The groundwork for the development of polyester fibers was laid by the late Dr. W. H. Carothers, duPont research chemist, in his work on high polymers. Polyesters were among the first condensation polymers investigated by Carothers; however, instead of continuing with an exhaustive study of polyesters, Carothers elected to devote the major portion of his research to polyamides, a course which resulted in the development of nylon (1).

British research chemists of the Calico Printers Association Ltd., after studying the published works of Carothers, initiated a further study of polyesters. Their work led to the development of a polyester fiber now known in England as Terylene. In 1946, the duPont Company purchased the patent rights to this fiber under the provisional title of "Fiber V" and since that time an intensive development program has been in effect. The first commercial production of "Fiber V", now called Dacron, took place in 1953 at the duPont plant located in Kinston, North Carolina (1), (2).

The Dacron Polymer

The chemical name for Dacron is polyethylene terephthalate, a linear polymeric fiber obtained by the condensation of terephthalic acid with ethylene glycol. Dimethyl terephthalate, a flaky white powder made from nitric acid, xylene, and methanol, is the principal raw material. Commercial preparation involves the following steps:

1. Direct esterification of terephthalic acid.

$$COOH-\langle\bigcirc\rangle-COOH \ + \ 2CH_3OH \longrightarrow CH_3O-\overset{O}{\overset{\|}{C}}-\langle\bigcirc\rangle-\overset{O}{\overset{\|}{C}}-OCH_3 \ + \ 2H_2O$$

2. Catalyzed ester interchange between the dimethyl terephthalate and excess ethylene glycol (3).

$$CH_3O-\overset{O}{\overset{\|}{C}}-\langle\bigcirc\rangle-\overset{O}{\overset{\|}{C}}-OCH_3 \ + \ 2\overset{OH}{\overset{|}{C}H_2}-\overset{OH}{\overset{|}{C}H_2} \longrightarrow$$

$$O=\overset{O-CH_2-CH_2-OH}{\overset{|}{\underset{|}{C}}}-\langle\bigcirc\rangle-\overset{}{\underset{O-CH_2-CH_2-OH}{\overset{|}{C}=O}} \ + \ 2CH_3OH$$
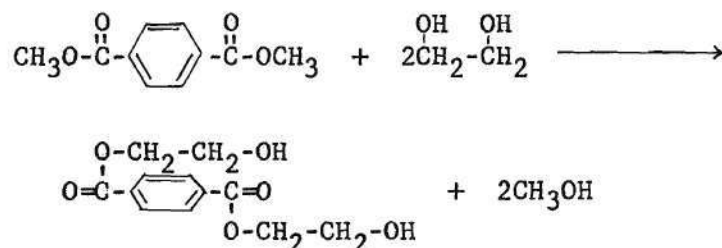
The above reaction is carried out in an autoclave at a high temperature. The bis-hydroxyethyl terephthalate continues to react with the dimethyl terephthalate and ethylene glycol monomers to yield the following polymer:

$$OH[-\overset{O}{\overset{\|}{C}}-\langle\bigcirc\rangle-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-]_nH \ + \ (2n-1)CH_3OH \qquad (4)$$

Polyethylene Terephthalate
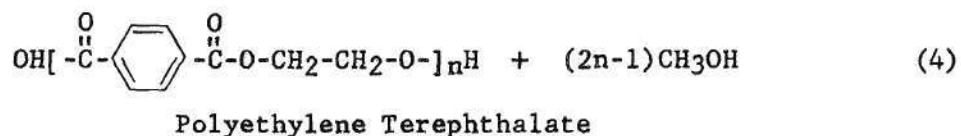
The polymer is extruded in the form of a ribbon from the auto-clave on to a casting wheel. The ribbon of polymer solidifies on the wheel after which the ribbon is cut into chips for easy handling. The polymer chips are dried to remove residual moisture and are put into hopper reservoirs ready for melting. The fiber is spun from the molten

polymer through a spinneret and the individual filaments solidify almost instantaneously; they are wound together as undrawn yarn onto cylinders.

In the attempt to make the fibers possess outstanding tensile strength, dimensional stability, and chemical resistance, the Dacron filaments are subjected to stretching and heat setting treatments. These treatments yield dense, oriented, and very strong fibers into which dye particles have great difficulty in penetrating (5). Due to the inertness of the fiber and its compact structure, Dacron was said to be undyeable when it was first introduced.

The first attempts to dye Dacron were with the disperse acetate dyes. The chemical similarity between Dacron and cellulose acetate is clearly shown by the fact that ester groups constitute 41 per cent by weight of acetate and 46 per cent by weight of Dacron (6). Dacron does have an affinity for these dyes but it is much more resistant to dyeing than is acetate. Since the disperse acetate dyes show poor penetration and exhaustion, even at the boil, on Dacron, experiments were carried out to determine whether this was due to the chemical inability of the fiber to absorb disperse dyes, or due to the physical difficulty of the dye particle to diffuse into the fiber (7). The results of the experiments showed that the capacity of Dacron to absorb disperse dyes was as great as that of acetate and greater than that of nylon; however, at 185° F., these dyes diffuse 500 times faster into cellulose acetate and 700 times faster into nylon than they do into Dacron.

Further experiments were conducted in which Dacron was allowed to dissolve slowly in caustic soda and it was observed that, as the filaments slowly decreased in diameter, the rate of diffusion was just

as slow. These experiments indicate, then, that the problems associated with dyeing Dacron are not thermodynamic because there are plenty of ester sites that can react with the disperse dyes (8). Rather, the problem is purely kinetic; that is, the sites are not readily available to the disperse dyes. Thus, there was a great need for new methods to increase the rate of diffusion of dyes into Dacron.

Methods Used for Dyeing Dacron

One method for dyeing Dacron involves proper dye selection. By proper selection of small molecular weight disperse dyes, light to medium shades may be obtained on Dacron by dyeing for 90 minutes at the boil.

At temperatures as high as the boil, or 100° C., Dacron molecules are freer to move and the dyestuff molecules can penetrate faster such that pale shades may be obtained in a reasonable time; even so, penetration is poor and most of the dye is located on the surface of the fibers (9). If, however, the temperature is taken still higher, say to 120° C., the chain molecules are much freer to move and the dyestuff can penetrate the fibers well. As a result, medium and heavy shades can be obtained within a reasonable dyeing time of say one hour. This method, of course, involves the use of costly pressure equipment and a careful selection of dyes must be made that do not decompose or sublime at 120° C.

Another method other than high temperatures to move the chain molecules apart is to use a swelling agent, or "carrier". A relatively small quantity of carrier in the dyebath enables the chain molecules to

move about more easily until the distances between them are increased
(10). However, the carriers are rather costly and the dyed fabrics are
inclined to retain the carrier odor. Moreover, the light fastness of
the dyeing is badly impaired since most of the effective carriers are
degraded by ultraviolet light.

Purpose of this Investigation

The purpose of this study was to investigate an altogether dif-
ferent method that might render Dacron more dyeable. The three methods
previously discussed did not chemically change the polymer molecules
themselves; rather, they changed the position of the polymer chains
relative to each other in such a manner as to allow dye molecules and
aggregates to diffuse into the fiber. These methods have not been al-
together satisfactory for reasons previously mentioned, the most impor-
tant of which being that it takes too long to reach a given depth of
shade. In this study an attempt was made to actually change the chemi-
cal structure of the Dacron molecule itself, especially the structure
of those chain molecules at and near the surface of the fiber where the
initial dyeing takes place. It was hoped that this chemical modifica-
tion would accommodate dyes other than the disperse dyes normally used
on Dacron. But at the same time, this modification should not serious-
ly alter the polymer's desirable physical properties such as its high
tenacity and extension at break.

The Dacron polymers were modified by grafting selected mono-
meric units onto them to form copolymers. A copolymer is by definition
(11) a polymer consisting of two or more chemically different monomer

units. In an ordinary or random copolymer, the monomer units are dis-
tributed at random along the chain: -A-A-B-A-B-B-B-A-A-B-B-A-A-A-B-

A graft copolymer (11) is a molecule composed of two or more
chemically different polymeric parts. According to this definition,
a graft copolymer can be considered to result from the bonding together
of two chemically different macromolecules, the resulting molecule re-
sembling a feather:

```
                    B
                    B
                    B
        -A-A-A-A-A-A-A-A-
          B           B
          B           B
          B           B
```
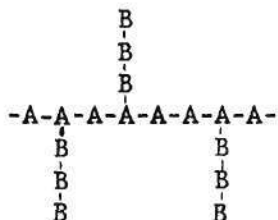
The fact that copolymers contain long sequences of two different
monomer units confers some unique properties on this type of macromole-
cule. Thus, a graft copolymer $A_p B_q$ may combine some of the character-
istic properties of both polymers A_p and B_q, while random copolymers
usually exhibit properties which are intermediate between those of the
two basic homopolymers A_p and B_q (12). Since the proper combination of
the polymeric parts A and B theoretically could yield any desired set
of properties, graft copolymers play a role in polymer science similar
to that of alloys in metallurgy. Indeed, it is conceivable that a de-
tailed understanding of grafting reactions may permit the polymer
scientist to synthesize polymers that are "tailor-made".

Numerous methods have been suggested and used for the prepara-
tion of graft copolymers by conventional chemical techniques. A feature

common to most of these methods is the production of an active site on
the existing polymer and reacting this activated polymer with selected
monomers. Some of the techniques used to activate the polymer and
initiate the copolymerization have been the peroxidation of the polymer,
the use of ultraviolet radiation, initiation by chemical catalysts, and
mastication (13).

The active site created on the reference polymer may be either a
free radical or a chemical group which may become involved in an ionic
polymerization or in a condensation process. A graft copolymer is then
obtained from the activated polymer by four different chemical proc-
esses:

(1) the addition polymerization of a vinyl monomer B initiated by the
activated polymer A_p;

(2) the polycondensation of a monomer B on a reactive group of polymer
A_p;

(3) the combination of two polymeric free radicals $A_p\cdot$ and $B_q\cdot$;

(4) the condensation of two macromolecules A_p and B_q both containing
appropriate reactive groups.

Various radiation-chemical methods have been developed in the
last few years for the preparation of graft copolymers, the most
abundant of which being those based on methods (1) and (3). These in-
vestigations have stimulated considerable interest and activity among
polymer chemists because it was found that radiation-chemical methods
for the preparation of graft copolymers are often easier to handle than
most conventional chemical techniques, and that both types of processes

are comparable as far as their costs are concerned (14). Moreover, radiation-chemical grafting techniques are very general due to the unselective absorption of radiation by matter, and can, theoretically, be used to prepare any desired combination of polymers.

When subjecting polymers to ionizing radiation, however, there is always the danger of degrading the polymer or cross-linking the molecular chains. Cross-linking may not be dangerous if it is desirable to increase the modulus of elasticity, i.e., the load at break divided by the extension at break. However, too much cross-linking reduces the extensibility of polymers and leaves them brittle.

Investigators are not in agreement about the cross-linking characteristics of Dacron. Charlesby (15) found that the Dacron polymer does cross-link, but to a very small extent. However, Bopp and Sisman (16) irradiated Dacron films with a dose of approximately 500 megarads and concluded that degradation, not cross-linking, occurred. Teszler and Rutherford (17) distinguished between drawn, oriented Dacron fibers and unoriented polyethylene terephthalate polymers. With the unoriented polymer, cross-linking occurs, but to a small extent. The drawn fibers, on the other hand, degrade considerably with high dosages, reducing the tenacity of the fiber by 20 per cent. Both of these effects were studied as a function of the radiation dose.

In this investigation, polyester copolymers were made using the above-mentioned radiation-chemical techniques. As was stated, almost any monomer-polymer system could be treated with the proper radiation method to form a copolymer. The monomers in this investigation were selected based on the concept that certain chemical sites produced on

the Dacron fiber would react with certain particular classes of dyes. For example, it was attempted to produce acid sites on the Dacron fiber by making a Dacron-acrylic acid copolymer. It was thought that if sufficient acrylic acid monomer were grafted to Dacron, the fiber would readily be dyed by basic, cationic dyes.

Since the success of these experiments depended on an efficient graft reaction, a reaction made possible by the irradiation of the different systems employed, this investigation is essentially a study of radiation chemistry. Before looking at the specific mechanisms of the reacting systems in this report, then, it would seem logical to first gain an overall picture of radiation chemistry.

CHAPTER II

GENERAL ASPECTS OF RADIATION CHEMISTRY AND GRAFT COPOLYMERIZATION

I. Radiation Chemistry[a]

Radiation chemistry is that area of chemistry pertaining to nuclear radiations that produce ionization in their passage through matter. Of particular importance to the radiation chemist are the chemical reactions that are sometimes induced by the primary process of ionization. Equally as important, as far as inducing subsequent chemical reactions are concerned, are the products, such as free radicals, arising from secondary reactions of the initial ions. Thus, in radiation chemistry studies, it is important to consider both primary and secondary processes.

The commonest sources of ionizing radiation are certain radio-isotopes that emit gamma rays, such as $Cobalt^{60}$ and $Cesium^{137}$. However, a wide variety of radiation sources can be employed. They include: alpha particles from nuclear decay; ions from particle accelerators; beta particles from nuclear decay; electrons from accelerators; x-rays from x-ray machines; and gamma rays from radio-active isotopes and from nuclear reactors.

(a) The following information pertaining to radiation chemistry is in part a re-statement of a summary previously written by Professor H. M. Neumann of the Georgia Institute of Technology and presented as part of Chemistry 657.

Reaction Mechanisms

The following processes are thought to occur in systems under-going irradiation. Furthermore, the sequence of presentation is thought to correspond to the sequence of events that occur immediately as the ionizing particle penetrates the system.

A. Formation of Positive Ions

(1) Direct ionization

$A \longrightarrow\!\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\longrightarrow A^+ + e^-$, where the symbol $\longrightarrow\!\!\!\wedge\!\!\wedge\!\!\wedge\longrightarrow$ indicates the absorption of energy from some radiation. In many cases the electrons formed in this primary process will have kinetic energies on the order of a few hundred electron volts. This amount of energy is sufficient to cause further ionization near the original ion. Indeed, it is these secondary electrons that cause most of the ionization in a system.

(2) Spontaneous decomposition of ions

$$A^+ \longrightarrow B^+ + C,$$

where the unstable ion A^+ has rearranged to form the stable ion B^+ and the neutral fragment C, which in many cases is a radical.

(3) Reactions between ions and neutral molecules

$$A^+ + A \longrightarrow D^+ + E$$

B. Formation of Negative Ions

Slowly moving electrons may become attached to molecules which

have sufficient electron affinity, such as water or oxygen.

$$A + e^- \longrightarrow A^-$$

Sometimes the negative ion formed is in an excited enough state to dissociate into fragments:

$$A + e^- \longrightarrow (A^-)^* \longrightarrow F^- + G$$
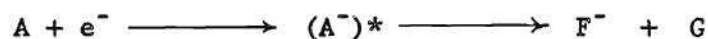
C. Formation of Radicals

The positive and negative ions and the electrons originally formed, as illustrated above, have considerable kinetic energies. After undergoing enough collisions, they will return to thermal energies and will be neutralized by an ion of opposite charge. As illustrated by the following reaction, this combination may contain sufficient excess energy to effect a dissociation into radicals.

(1) $\quad X^+ + Y^- \longrightarrow (XY)^* \longrightarrow X\cdot + Y\cdot$

or, $\quad X^+ + e^- \longrightarrow (X)^* \longrightarrow B\cdot + C\cdot$
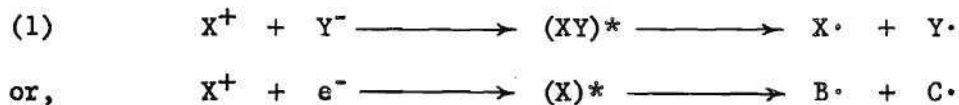
This entire process, from the instant the nuclear radiation strikes the molecule and ionizes it, until the ions return to thermal energies and become neutralized, takes only 10^{-6} seconds.

There are essentially three other methods which are thought to yield free radicals.

(2) Primary excitation of molecules, followed by dissociation

$$A \longrightarrow\!\!\!\!\!\wedge\!\!\wedge\!\!\wedge\longrightarrow A* \longrightarrow B\cdot \ + \ C\cdot$$

(3) Spontaneous decomposition of ions

$$X^+ \longrightarrow B^+ \ + \ C\cdot$$

(4) Reactions between ions and neutral molecules

$$X^+ \ + \ A \longrightarrow D^+ \ + \ E\cdot$$

For each proposed mechanism, the radicals formed will be left in the system long after the ions have disappeared by neutralization. At this point the system loses its uniqueness as a radiation chemistry system and behaves like any other chemical system containing the same distribution of radicals.

Irradiation of Organic Compounds

Consider the irradiation of a simple organic compound such as propane, $CH_3CH_2CH_3$. The energy of radiation is greater than any of the bond energies; therefore we can expect each bond to be broken at some time. Assuming that the probability of a bond breaking is the same for all bonds, a number of different radicals could exist simultaneously. They include: $H\cdot$; $CH_3\cdot$; $C_2H_5\cdot$; $C_3H_7\cdot$, either $CH_3\overset{|}{C}HCH_3$ or $CH_3CH_2\overset{|}{C}H_2$. These radicals are free to react in a number of ways. For example, two of the $CH_3CH_2\overset{|}{C}H_2$ radicals could react to form n-hexane, or one of these

radicals could react with one or more of the other radicals. It appears, then, that the irradiation of an organic system even as simple as propane is too complex to elucidate reaction mechanisms.

In most cases the irradiation of organic systems produces considerable gaseous products, notably hydrogen. If the irradiated molecules contain oxygen, gases such as CO and CO_2 are also observed. Also -in most cases, products both larger and smaller than the irradiated molecules are found, and in a number of instances, polymerization products are found.

However unpredictable and complex these radiation chemistry systems appear, the following statements can be made with confidence (18). First, at least 50 per cent of the main product, hydrogen, when it appears, comes from processes that do not involve the reactions of free hydrogen radicals. Secondly, most of the organic products are formed by the reactions of free radicals. Thirdly, some of the organic products which are formed do not depend on any free radical mechanism.

It should also be noted that free radicals do not always combine to form products. The following reactions could conceivably occur:

(1) Spontaneous decomposition of a radical

$$C_3H_7\cdot \longrightarrow \cdot CH_3 + C_2H_4$$

(2) Hydrogen abstraction reactions

$$CH_3CH_2CH_3 + \cdot CH_3 \longrightarrow CH_3\overset{|}{C}HCH_3 + CH_4$$

Of particular interest with regard to the irradiation of organic substances are the aromatic compounds. They are found to resist fragmentation that would otherwise be caused by the ionizing radiation. This stability to dissociation may be explained by the resonance stabilization properties of aromatics; the radiation energy cannot be localized at any one bond in the molecule. Even in mixtures, the aromatic compounds exert a protective effect on the entire system.

Radiation Chemistry of Unsaturated Compounds

The radiation chemistry of unsaturated organic molecules is of extreme importance to the polymer chemist. The yields of products formed on irradiation differ from those of the saturated hydrocarbons in three ways: the yield of hydrogen and other gaseous products is less; the yield of materials of higher molecular weight, particularly polymers, is much greater; and the overall yield is greater.

Of particular interest to the polymer chemist, with regard to the unsaturated molecules, are the vinyl compounds. These molecules polymerize by a free-radical chain reaction upon exposure to high energy radiation (19). For example, consider the polymerization of the vinyl monomer acrylic acid. It is thought that this type of polymerization involves three steps:

1. Initiation

The polymerization can be initiated by any reaction which forms a radical R· . Possible initiation reactions are:

$$CH_2=\underset{\underset{COOH}{|}}{\overset{\overset{H}{|}}{C}} \xrightarrow{\hspace{1cm}} CH_2=\overset{\overset{H}{|}}{C}\text{-}COO\cdot \; + \; \cdot H$$

$$CH_2 = \overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}} \quad \text{~~~~} \longrightarrow \quad CH_2=\overset{\overset{\text{H}}{|}}{C}-\overset{\cdot}{C}=O \quad + \quad \cdot OH$$

$$\text{and } CH_2 = \overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}} \quad \text{~~~~} \longrightarrow \quad \overset{\cdot}{C}H_2-\overset{\cdot}{C}HCOOH$$
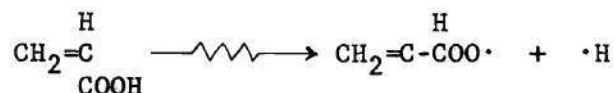
The radicals formed then react with the monomers to form larger

radicals:

$$R\cdot \quad + \quad CH_2{=}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}} \quad \longrightarrow \quad R\text{-}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\cdot$$

It is these radicals that are thought to initiate the subsequent

propagation reaction.

2. Propagation

$$R\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{CH}}\text{-}C\cdot \quad + \quad nCH_2{=}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}} \quad \longrightarrow \quad R\text{-}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-}(CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{CH}}\text{-})_{n-1}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\cdot$$

3. Termination

$$2R\text{-}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-}(CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-})_{n-1}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\cdot \quad \longrightarrow \quad R\text{-}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-}(CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{CH}}\text{-})_{2n}CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-}R$$

Besides the coupling of two growing radicals, as illustrated in

the above reaction, two other termination methods are feasible (20):

1. Disproportionation

$$R\text{-}(CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-})_nCH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\cdot \quad \longrightarrow \quad R\text{-}(CH_2\text{-}\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{COOH}}{|}}{C}}\text{-})_nCH{=}\overset{\overset{}{}}{\underset{\underset{\text{COOH}}{|}}{CH}} \quad + \quad H\cdot$$

$$H\cdot \ + \ R\text{-}(CH_2\text{-}\underset{COOH}{\overset{H}{C}}\text{-})_nCH_2\text{-}\underset{COOH}{\overset{H}{C}}\cdot \ \longrightarrow \ R\text{-}(CH_2\text{-}\underset{COOH}{\overset{H}{C}}\text{-})_nCH_2\text{-}\underset{COOH}{\overset{H}{CH}}$$
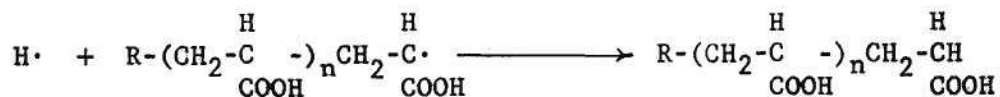
2. Chain Transfer

This method involves the addition of a chain transfer agent, or telomerizing agent, which is capable of ending one chain and starting another. If $R'\text{-}S\text{-}H$ is the telomerizing agent employed, the reaction is as follows:

$$R\text{-}(CH_2\text{-}\underset{COOH}{\overset{H}{C}}\text{-})_nCH_2\text{-}\underset{COOH}{\overset{H}{C}} \ + \ R'SH \ \longrightarrow$$

$$R\text{-}(CH_2\text{-}\underset{COOH}{\overset{H}{C}}\text{-})_nCH_2\text{-}\underset{COOH}{\overset{H}{C}}\text{-}H \ + \ R'S\cdot$$

The radical fragment, $R'S\cdot$, is free to initiate another chain reaction of the monomers $CH_2{=}CH\text{-}COOH$.

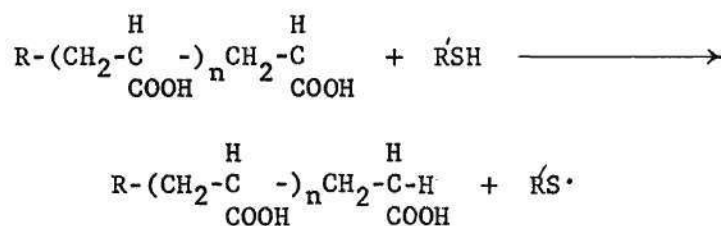The above equations illustrate the mechanism of the polymerization of acrylic acid where the polymerization is initiated by ionizing radiations. These radiations serve only to produce free radicals in sufficient quantity for use in the initiation step. Once these radicals have been produced, the system behaves as any other system with the same distribution of radicals. Therefore, other initiators such as chemical catalysts could be used to initiate vinyl polymerizations. However, there are distinct advantages in using radiation chemical techniques.

Advantages of Using Radiation Methods to Induce Polymerization

Radiation methods have several general advantages to offset their main disadvantage, which is that radiation is expensive. One advantage is good penetration which enables a uniform treatment to be given. A uniform treatment is not always easy when using heat to initiate a reaction, as in the cross-linking of thick objects.

A second general advantage is flexibility. For example, radiation introduces a new variable, and may permit the temperature and pressure to be adjusted to give optimum conditions for propagation reactions, with radiation being used to provide initiation.

Thirdly, radiation-induced reactions can be easily controlled by varying the dose or dose-rate, and can often be stopped simply by switching off the source of radiation. Also, radiation methods are particularly adaptable to flow methods of production.

However, the most important advantage of using radiation to initiate reactions, especially to the polymer chemist, is that other initiators, such as chemical catalysts, leave impurities in the treated materials. These impurities can lead to many difficulties; for example, in the case of certain polymers, poor electrical characteristics and subsequent degradation of the polymer are observed. Also, many of the chemical catalysts are expensive, although none is as expensive as radiation.

The preceding information pertaining to radiation chemistry should serve as sufficient background material prior to examining graft copolymerization reactions induced by radiation. All the types of reactions made possible when nuclear particles penetrate matter should be

considered when examining any radiation chemistry system. It is hoped, therefore, that the types of reactions chosen for illustration are appropriate and sufficient for an understanding of the graft copolymerization phenomenon.
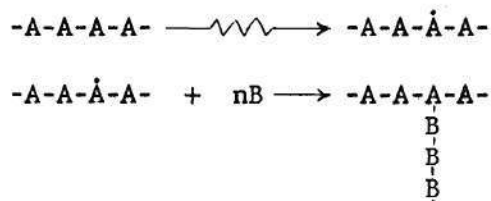
II. Graft Copolymerization

Since graft copolymers result from the chemical combination of two macromolecules of different chemical nature, and since radiations are known to create active sites in polymers, it appears that numerous radiation-chemical processes involving macromolecules could, in principle, lead to the production of graft copolymers. Among the various methods that could conceivably be used, four have received special attention:

(1) a direct radiation grafting in which the polymer is irradiated in the presence of a vinyl monomer;

(2) initial irradiation of the polymer in such a manner as to produce a peroxidized polymer, followed by the graft reaction with a vinyl monomer;

(3) grafting initiated by first producing trapped radicals within the polymer by means of radiations;

(4) the intercross-linking of two different polymers.

The common feature of these four methods of radiation grafting is that, in all cases, the initial radiation event leads to the formation of polymeric free radicals in the reference polymer (21). These radicals are thereafter used in different ways to achieve grafting.

Direct Radiation Grafting

The simplest radiation-chemical method for producing graft copolymers is derived directly from the study of radiation polymerizations. In these polymerizations, a homopolymer grows according to free-radical combinations, the free-radicals being produced by the radiolysis of the monomer. The resulting polymer can be considered to be a "graft homopolymer" (22). On the other hand, since the action of ionizing radiations on matter is unselective, any substance which is added to the monomer is also irradiated and consequently contributes to the initiation of polymerization. Therefore, if instead of irradiating a system containing a monomer and its own polymer, one irradiates a polymer A_p in the presence of a vinyl monomer B, the resulting substance is a graft copolymer. This reaction can be written schematically as follows:

$$-A-A-A-A- \xrightarrow{\text{\tiny\textasciitilde}} -A-A-\dot{A}-A-$$

$$-A-A-\dot{A}-A- + nB \longrightarrow -A-A-\underset{\underset{\underset{\dot{B}}{\overset{|}{B}}}{\overset{|}{\underset{\dot{B}}{\overset{|}{B}}}}}{\overset{|}{A}}-A-$$

In addition, the monomer B can be radiolysed in the process to form the undesirable homopolymer,

$$B \xrightarrow{\text{\tiny\textasciitilde}} B\cdot \xrightarrow{nB} B_q \;.$$

The feasibility of a given graft copolymerization, then, will depend upon the relative ability of a polymer $\underline{A}$ and a monomer $\underline{B}$ to form free

radicals when subjected to ionizing radiation (23). For example, if
the rate of free radical production is larger in the monomer to be
grafted than in the polymer, the quantity of homopolymer formed will
be large compared to the amount grafted, making the process wasteful.
It has also been found that the grafting yield is greater if the con-
centration of the monomer is low. In this respect, fairly large yields
of grafting can be obtained even if the free radical yield of the mon-
omer is higher than that of the polymer, provided the polymer is only
slightly swollen with the monomer.

A very significant discovery was made by Odian and co-workers
in their graft copolymerization studies. It was observed that the
rates of various radiation-induced graft polymerizations would be sub-
stantially increased by dilution of the monomers with certain solvents
(24). An analysis of the kinetics of this phenomenon was made in
order to elucidate the mechanism of the solvent acceleration. These
accelerations were demonstrated to be due to two mechanisms.

The first mechanism is the enhancement in the degree of acces-
sibility of the monomer to the grafting sites within the polymer brought
about by the greater ability of the solvent additive to swell the base
polymer. However, this mechanism must be discarded if it is known that
the base polymer cannot be swelled by the solvent used. For example,
it is known that essentially no solvent will swell highly compact poly-
mers such as polyethylene terepthalate unless this swelling is done at
very high temperatures with selected solvents.

The other mechanism is the incursion of a Trommsdorff effect due
to the insolubilization of the growing graft polymer chains in the

solvent-monomer medium. This Trommsdorff effect is a phenomenon well known in homopolymerization and refers to the increased rate of polymerization that occurs during the later stages of the process when either the polymer precipitates or there is a large increase in viscosity. This accelerative effect has been ascribed to the fact that the large, growing polymer chains become immobilized and their rate of collision and hence termination becomes sharply decreased. However, the reactions of the monomer remain unaffected since it is a small entity and does not lose its mobility. This decrease in termination rate due to the Trommsdorff effect of the solvent, with no change in initiation rate, leads to a higher steady state concentration of radicals and hence to a higher over-all rate of graft polymerization (25).

The specific grafting systems investigated by Odian in which solvent acceleration was observed were:

1. polyethylene-styrene, with methanol as the solvent.

2. polyethylene-methyl acrylate, with methanol solvent.

3. polyethylene-t-butylaminoethyl methacrylate with hexame solvent.

4. polypropylene-styrene, with methanol solvent.

5. polypropylene-methyl acrylate, with methanol solvent.

6. nylon-styrene, with methanol solvent.

7. nylon-methyl acrylate, with methanol solvent.

8. Teflon-methyl acrylate, with methanol solvent.

For any grafting system, although both the Trommsdorff and the solvent swelling effect can be operative in leading to acceleration in the rate of graft polymerization, usually only one of these effects predominates (26). The Trommsdorff effect was found to predominate in

the grafting of styrene, methyl acrylate, and t-butylaminoethyl metha-
crylate to polyethylene, polypropylene, polyvinyl chloride and Teflon
in the experiments indicated above. Solvent swelling was found to be
the effect mainly responsible for the acceleration in the grafting of
styrene and methyl acrylate to nylon.

Grafting on Peroxidized Polymers

In chemical methods of making polymers and copolymers it is
necessary to initiate a free-radical chain reaction of the monomers.
This initiation is sometimes prompted by the thermal decomposition of
peroxide catalysts into peroxide radicals. A much cleaner method of
introducing peroxide groups into the system is to produce these groups
directly on the reference polymer prior to the grafting reaction. It
has been found that the irradiation of polymers in oxygen atmospheres
is a convenient method for producing these peroxide groups. A reason-
able mechanism (27) for their formation postulates that the initially
formed macroradicals attack an oxygen molecule:

```
    R H R                      R H R
   -C-C-C-    ~~~~~~>         -C-C-C-
    H H H                      H · H
                                macroradical


    R H R                      R H R
   -C-C-C-  +  ·O-O·  ------>  -C-C-C-
    H · H                       H O H
                                  O
                                  ·

    R H R                                R H R
   -C-C-C-                               -C-C-C-
    H O H                                 H O H
    H O H                                   O
   -C-C-C-                                  O
    R H R                                   H

Diperoxidic Crosslink                  Hydroperoxide
```
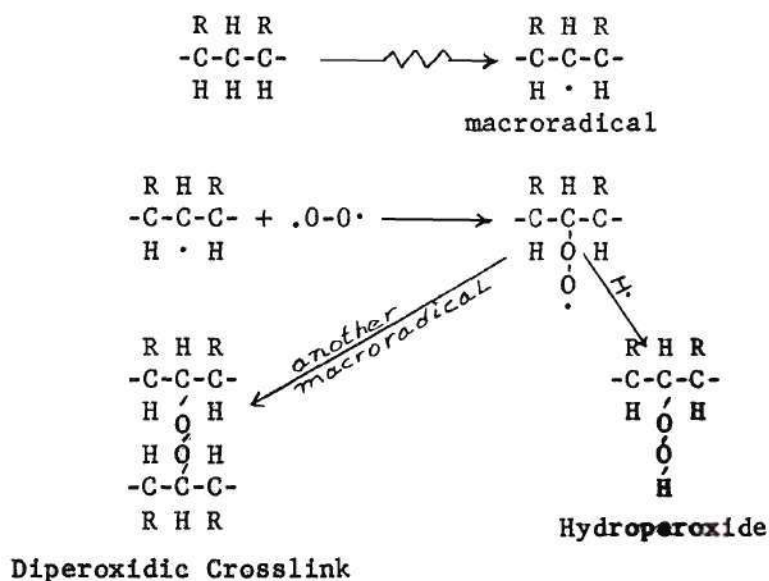
One of the major questions raised by this reaction is whether diperoxides or hydroperoxides are formed upon irradiation of each particular polymer. From the available data it appears that, at room temperature, chain peroxidation, leading to hydroperoxides, occurs only in polymers containing a labile hydrogen atom, such as in polypropylene. In most other cases, the peroxidation process is observed.

Regardless of whether diperoxides or hydroperoxides are formed, their thermal stability is essentially the same as that of their low molecular weight homologs; in other words, decomposition to free radicals takes place at elevated temperature. Thus the sites left on the polymer initiate the graft reaction when the peroxidized polymer is heated in the presence of vinyl monomers. For example,
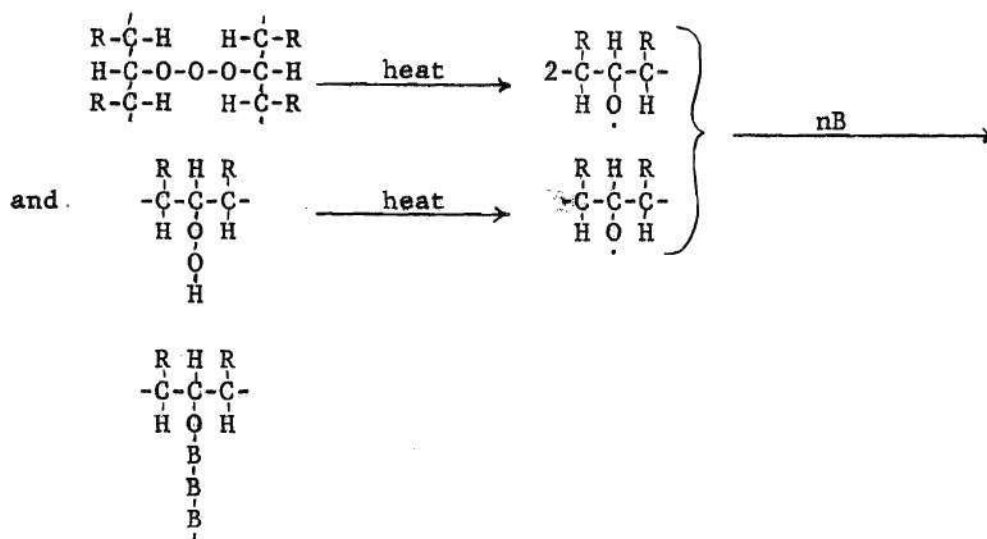
A number of substances, even when present in small amounts, can strongly affect the radiation peroxidation. Most antioxidants reduce the yield of peroxidation, but certain compounds can also be expected

to promote the reaction. This promotion is particularly true in the case of "indirect peroxidation" which occurs if the polymer is irradiated in the presence of a substance which generates active free radicals (e.g., OH·, Cl·, etc.) capable of abstracting hydrogens from the polymer (28).

The problem of making a homopolymer, B_q, is not a serious one as was the case when the polymer and monomer were irradiated together. Homopolymer reactions can occur, however, if the peroxidized polymer contains low molecular weight peroxides, such as ROOR, ROOH, or H_2O_2, adsorbed on its surface. These free peroxide molecules are usually formed during the irradiation. In such an event, the extraction of the irradiated polymer in a proper solvent, prior to the grafting operation, can prove helpful.

Grafting Initiated by Trapped Radicals

It has been well established that the reactivity of free radicals is drastically reduced if these radicals are embedded in a viscous medium. In some cases, radicals can remain trapped for extremely long periods, of the order of several days or even several months (29). The presence of trapped radicals has been detected in irradiated polymers. They are trapped, of course, because the polymer medium is extremely viscous, and if the polymer is partially crystalline, as most of the shaped polymers are, the radicals are even more firmly entrapped. They are more firmly entrapped because the mobility of polymeric segments is very low when involved in an organized structure such as a crystal.

It has been found that the free radicals which are formed in the amorphous regions of the polymer can be utilized readily in a number of
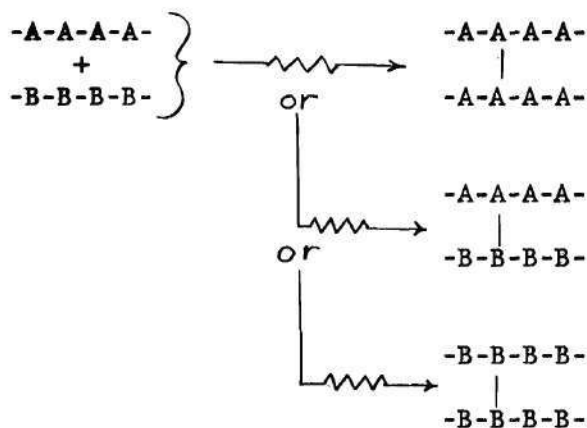
chemical processes, such as cross-linking or grafting, whereas those radicals which are located within the crystalline areas react only at elevated temperatures when most of the crystallites have melted. However, small molecules such as oxygen can diffuse into even the crystalline regions and react with the trapped radicals (30).

The most important points, as far as the grafting process is concerned, are the yields of the trapped radicals formed in the various polymers and the efficiency of these radicals for initiating the grafting reaction. These factors, in turn, depend on the physical state and nature of the polymer, both during the irradiation and during the grafting process, the physical and chemical nature of the trapped radicals, and the chemical nature of the monomer to be grafted. It therefore follows that there is an optimum dose of ionizing radiation for each particular system and this dose must be determined experimentally.

Oxygen is known to destroy trapped radicals, presumably because it converts radicals P· into peroxidic radicals PO_2· which can abstract hydrogen atoms from surrounding polymer molecules, thus favoring the diffusion of radical sites. Much higher radical yields are indeed found if the irradiation is carried out in a vacuum. At the same time, an homogenous product, free from homopolymer, is obtained upon grafting because no residual small molecular weight peroxides groups can be formed (31). It will be recalled that these residual peroxides can initiate a free-radical chain reaction among the vinyl monomers themselves, resulting in the undesirable homopolymer. Also for this reason, the subsequent grafting reaction must be conducted in an oxygen-free system.

The Intercross-Linking of Two Different Polymers

A very simple method of radiation grafting is based on the cross-linking of an intimate mixture of two polymers A_p and B_q. If both polymers, by themselves, cross-link upon irradiation, the following reactions are expected to occur:

$$
\left.\begin{array}{c}
\text{-A-A-A-A-} \\
+ \\
\text{-B-B-B-B-}
\end{array}\right\}
\quad
\text{or} \quad
\begin{array}{c}
\text{-A-A-A-A-} \\
| \\
\text{-A-A-A-A-}
\end{array}
$$

$$
\text{or} \quad
\begin{array}{c}
\text{-A-A-A-A-} \\
| \\
\text{-B-B-B-B-}
\end{array}
$$

$$
\text{or} \quad
\begin{array}{c}
\text{-B-B-B-B-} \\
| \\
\text{-B-B-B-B-}
\end{array}
$$

If one of the polymers degrades upon irradiation, say polymer B_q, one can still expect the formation of grafted structures such as:

$$
\begin{array}{c}
\text{-A-A-A-A-} \\
| \\
\text{-B-B-B-B-}
\end{array}
$$
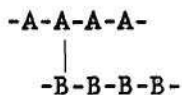
If both polymers are of the degrading type, the yield of graft copolymer should in principle be low (32). Very little experimental work is available in this field.

Since cross-linking yields are usually low when polymers, by themselves, are irradiated, the intercross-linking of two polymers is a very inefficient method of grafting. In addition, large amounts of

cross-linked homopolymers are necessarily formed in this reaction. Another problem connected with this method is that most polymers are incompatible; consequently, it may be difficult to prepare the intimate mixture of polymers required for this graft reaction. However narrow in scope this method appears to be, it can lead to useful products in certain specific cases (33).

In preparing the graft copolymers of this investigation, the first three methods were used, i.e., direct radiation grafting, peroxidized grafting, and trapped-radical grafting. The intercross-linking method was not used for two reasons: it was indicated from the above discussion that the grafting yields would be very low; and the units which were to be grafted to the existing reference polymer were not available in polymer form.

It was decided to investigate all three of the grafting methods indicated above, instead of selecting one method known to be an efficient one. It was not known beforehand which method would be more efficient. This is because very little work has been done with regard to the grafting of monomers to Dacron. Ballantine, et al., (34) grafted styrene to Dacron using the direct radiation method. The per cent grafts obtained were on the order of only 1 to 2 per cent. He did not use an accelerative solvent, such as methanol, which, as has been explained previously, increases the efficiency of the graft reaction considerably.

Bevington (35) succeeded in grafting acrylonitrile to Dacron using the trapped radical method. Chapiro (36) grafted the same monomer, but used the peroxidation method. The peroxidation method was

also used by Houlton and Thomas (37) with 4-vinyl pyridine as the mono-
mer. Grafts as high as 17 per cent were obtained and it was found that
the vinyl pyridine copolymers absorbed a considerable quantity of acid
wool dyes.

CHAPTER III

MATERIALS AND INSTRUMENTATION

The polymer under investigation, polyethylene terephthalate,
known commercially as Dacron, was obtained from the duPont company.
It had been shaped into filament form and had the following speci-
fications:

1. Yarn Count (Denier)   250

2. Filaments per End   50

3. Filament Count (Denier)   5

4. Luster Characteristics   Bright

The sample holders used in the irradiation step consisted of
glass-blown tubes provided with a constriction such that the tubes
could be sealed with an oxygen torch.

Irradiation and Related Equipment

The irradiator, provided by the Radioisotopes Laboratory of the
Georgia Institute of Technology, was a 12,000 curie Cesium-137 source,
a gamma ray emitter. The source was constructed in such a manner that
12 capsule tubes, each holding 1,000 curies of Cesium-137 pellets, were
positioned in a circle. Within this circle there is a sample space
that receives a constant dose of approximately 1.4×10^6 rads per hour,
if the sample is positioned correctly. There are 12 other sample tubes
located in a circle around the 12 capsule tubes. If the samples in
these tubes are positioned correctly, a constant dose of approximately

9.5×10^5 rads per hour is obtained. The 12 outer holes, each of which could hold standard six-inch test tubes, were the ones employed in this investigation.

Other equipment used in the Radioisotopes Laboratory included a vacuum pump, an acetone-dry ice trap, a mercury manometer, a cylinder of pure oxygen, and other related equipment used in conjunction with the evacuation of vessels, oxygen-bleeding into those vessels, and the sealing of those vessels.

Monomers and Solvents

The monomers used for the grafting reactions were glacial acrylic acid, $CH_2=CH-COOH$, and "practical grade" methyl acrylate, $CH_2=CH-COOCH_3$. The monomer solvent in each case was reagent grade methanol, CH_3OH, while pre-purified nitrogen gas was used to purge the monomer-solvent systems, or polymer-monomer-solvent systems, depending on which grafting technique was used.

Various other solvents, including ethyl acetate and methanol, were used to wash impurities and homopolymer from the graft copolymers. Benzene, in a Soxhlet Extractor, was used to clear the polymer samples of coning oils and other labile impurities prior to the irradiation step.

Dyes and Dyeing Equipment

Three different classes of dyes, from an application standpoint, were used. They were:

1. an acid dye, C.I. Acid Red 1. (duPont "Pontacyl" Carmine 2G, 2/5/62, Lot 40.)
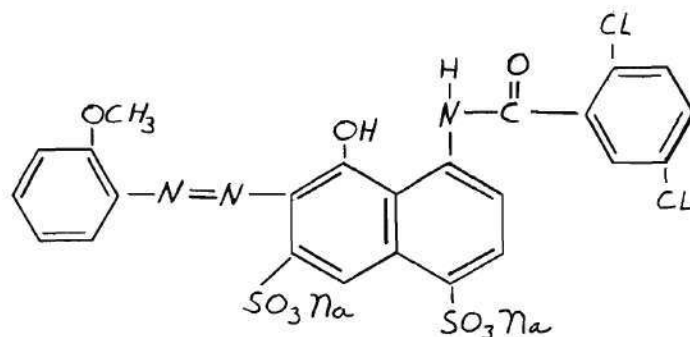
2. a basic dye, C.I. Basic Blue 26. (duPont Victoria Blue B, 4/12/62, Lot 497.)
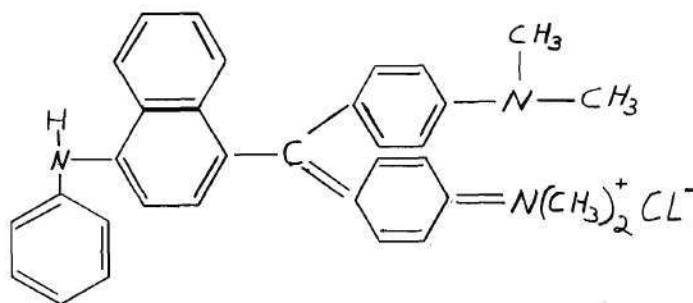
3. a disperse dye, C.I. Disperse Blue 61. (duPont "Latyl" Brilliant Blue 2G, 3/25/60, Lot 45.)

(Formula not available; this dye is believed to be a derivative of either an anthraquinone or disperse azo dye.)

Chemical auxiliaries normally employed in conjunction with each dyeing technique were used. In particular, a formic acid-ammonium sulfate buffer solution was introduced into all the disperse dye dyebaths to keep the pH below 7.

All dyeings were carried out on electrically heated metal plates provided with a variable resistor; the temperature of each plate could be controlled independently. Each dyeing was made in a 125 ml. Erlenmeyer flask equipped with a 16-inch, water-jacketed, reflux condenser.

Instrumentation

A Bausch and Lomb Spectronic 500 Recording Spectrophotometer, provided by the School of Chemistry of the Georgia Institute of Technology, was used to obtain absorbance curves for each dye. Once these curves had been examined to determine which wavelength would give the maximum precision and sensitivity on subsequent absorbance measurements, the Beckman DU Spectrophotometer was used.

The Beckman Model H-2 pH Meter was used to measure the pH of all solutions. This instrument was equipped with a glass electrode and a standard calomel electrode; it could be used in a temperature range from 15° C. to 100° C.

The Instron Electronic Tensile Testing Instrument was used to determine the various physical characteristics of the Dacron polymer and copolymers. The instrument was equipped with a 2-50 gram load cell, an automatic chart and pen, and an integrator. This instrument, together with the two Beckman instruments previously described, was supplied by the A. French Textile School, Georgia Institute of Technology.

CHAPTER IV

PROCEDURE

I. Sample Preparation

Dacron skeins weighing approximately three grams were reeled off and placed in a Soxhlet Extractor. The skeins were extracted 24 hours in benzene to remove impurities such as coning oils or sizing compounds, materials usually found on synthetic fibers to facilitate processing. All samples were oven-dried for two hours at 300° F. and conditioned for at least six hours at 70° F. and 65 per cent relative humidity.

After the skeins had conditioned, they were cut into various sample sizes, depending upon the grafting technique to be used, and weighed to the nearest tenth of a milligram. These weighed samples were placed in five-inch standard test tubes if the direct radiation grafting procedure was to be used. If the trapped-radical grafting technique, or the peroxidized polymer method was to be used, the samples were placed in specially made glass tubes.

After the weighed samples had been placed in these tubes, the glass-blower fashioned a constriction at one end so the tube could be sealed. A round glass projection was fitted above the constriction that could be inserted into pressure tubing. The finished sample holder resembled the following:
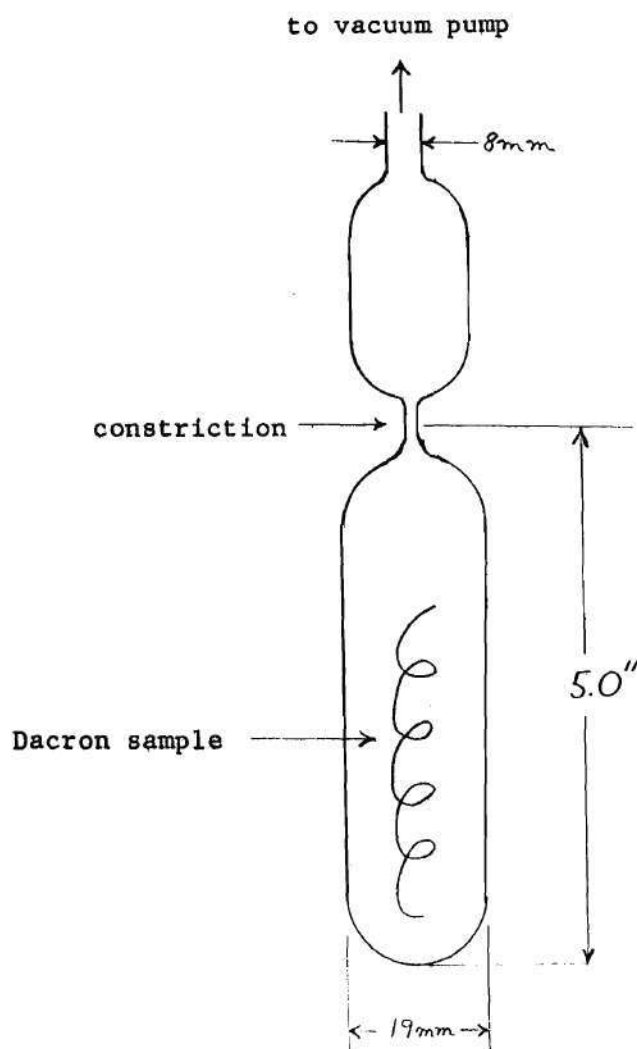
to vacuum pump

Figure 1. Diagram of Sample Holder

II. Irradiation Procedure

A. Direct Radiation Grafting

In the direct radiation procedure, the **weighed polymer** samples were placed in standard five-inch test tubes. Twenty per cent by volume solutions were made of the monomers, acrylic acid and methyl

acrylate, in methanol. These solutions were purged 15 minutes with pre-purified nitrogen gas in the attempt to make them oxygen-free. The purged solutions were added to the sample tubes until the fibers had been covered. The exact volume added was not critical as long as an excess (but not a large excess) of monomer was present. At this point the entire monomer-solvent-polymer system was purged with nitrogen, stoppered, and allowed to equilibrate at room temperature (about six hours). During this interval, it was hoped that a portion of the monomer would diffuse into and swell the Dacron polymer.

Prior to the irradiation step, a small slit was cut into each stopper to allow gases that might be formed during the irradiation to escape. The samples were immediately lowered into the gamma ray source and irradiated for two hours. This time of irradiation amounted to approximately 1.9×10^6 rads, or 7.60×10^{19} electron volts per gram.

B. Irradiating to Produce a Peroxidized Polymer

The sample holders containing the weighed polymer samples (see Figure 1, page 37) were evacuated on a vacuum line. When the pressure inside the sample holder was as low as possible, which was approximately 24 ml. of Hg for the system being used, a three-way stop-cock was positioned in such a manner as to hold this pressure constant and open a line from the sample holder to an Hg manometer. Another three-way stop-cock was opened and oxygen was bled carefully into the sample holder. When the manometer indicated an oxygen pressure of approximately 760 ml. Hg, the system was again evacuated and filled with fresh oxygen.

With the three-way stop-cocks positioned to cut off the line to the vacuum pump, and the line to the oxygen cylinder opened and dis-

connected from the cylinder, the constriction was sealed, leaving only Dacron and oxygen in the sample holder. The line from the sample holder to the oxygen cylinder was disconnected to allow small amounts of oxygen to escape as the constriction was heated and sealed. If this were not done, the increased oxygen pressure upon heating would make bubbles in the molten glass at the constriction.

The sealed sample holders were lowered into the gamma ray source and irradiated for two hours, receiving a dose of approximately 7.60×10^{19} electron volts per gram.

C. Irradiating to Produce Trapped Radicals

The sample containers were again evacuated, but this time no other gases were bled into the system. When the pressure gauge on the vacuum pump indicated 24 ml. of Hg pressure, the evacuation was continued for 15 minutes. It was hoped that this prolonged evacuation would remove gases adsorbed on the surface of the Dacron. After the 15-minute evacuation, the samples were sealed with the vacuum line open and the pump running.

Again, the sample holders were irradiated for two hours, receiving a dose of approximately 7.60×10^{19} electron volts per gram.

III. Grafting Procedure

A. Direct Radiation Grafting

In the direct radiation grafting procedure, all the grafting that took place occurred during the two hours that the monomer-polymer-solvent systems were in the irradiator. All that was necessary to do was to remove the samples and wash away impurities and homopolymer.

For the methyl acrylate grafts, ethyl acetate, a known solvent for methyl acrylate and its homopolymer, was used to purify the graft copolymer. The copolymer was refluxed in boiling ethyl acetate for four hours, dried to constant weight in an oven at 300° F., conditioned for at least six hours at 70° F. and 65 per cent relative humidity, and weighed. The per cent graft was calculated as follows:

$$\text{Per cent graft} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100$$

The acrylic acid copolymers were purified by a ten-minute rinse in running water, a three-hour reflux in methanol, a fifteen-minute wash in 10 per cent sodium hydroxide (room temperature), and a one-minute rinse in dilute acetic acid. The copolymers were dried to constant weight in an oven, conditioned at 70° F. and 65 per cent relative humidity for at least six hours and weighed. The per cent grafts were calculated using the above formula.

B. Peroxidized Polymer Grafting

The peroxidized Dacron polymers, sealed in their respective sample tubes, were not broken open until the grafting equipment was set up and the monomer solutions were prepared. In the graft reaction, it is necessary for all substances to be very pure; impurities in this reaction medium inhibit the desired grafting reaction and accelerate homopolymerization. For this reason, reagent grade glacial acrylic acid was used. The purest methyl acrylate available was "practical grade". It was washed with 5 per cent sodium hydroxide, 10 per cent

sodium chloride, and water. These washings were followed by a thorough drying with anhydrous sodium sulfate, and the monomer was stored under nitrogen.

The grafting apparatus consisted of a water bath, an electric stirrer, a gas burner, and reaction flasks. Thirty per cent by volume solutions of the pure monomer in reagent grade dry methanol were purged for at least 15 minutes with pre-purified nitrogen. One hundred milliliter portions of these monomer solutions were added to the reaction flasks. At this point, the sealed tubes containing the peroxidized polymer were broken open. The polymers were added to their respective monomer solutions, each system was again purged with nitrogen (about two minutes), and the reaction flasks were partially submerged in the water bath. As the temperature of this bath was raised to 60° C., stoppers were held loosely over the flasks. However, when the temperature 60° C. was reached, and the vapor pressure above the monomer-methanol solutions remained constant, the flasks were tightly stoppered.

The reaction flasks were held in the 60° C. water-baths for two hours. At this time, the graft copolymers were removed and purified as described previously. The per cent grafts were calculated using the preceding formula.

C. Trapped-Radical Grafting

The grafting reactions induced by the trapped radicals within the Dacron polymer were carried out in a manner similar to the peroxidized polymer graft reactions. The main difference was the fact that the trapped radicals were stable; as a result, there could be a considerable time lag from the breaking open of the sealed sample tubes

to the carrying out of the graft reaction. Also, since some of the trapped radicals were thought to be more stable than some of the others, particularly those radicals entrapped in the more ordered regions of the polymer, another set of experiments was carried out varying the grafting time.

In the first set of experiments the vacuum-irradiated Dacron samples and the respective monomer-methanol solutions were added to the reaction flasks. The flasks were purged with nitrogen for 15 minutes and partially submerged in the water bath. After the temperature of the bath reached 60° C., the flasks were stoppered tightly and the reaction was carried out for two hours.

In the second set of experiments, the vacuum-irradiated polymers and monomer solutions were again purged with nitrogen. The flasks were stoppered immediately and placed in an oven. The oven temperature was held at 45° C. and the reactions were carried out for 6, 12, 24, 48, and 72 hours.

The copolymers were purified by the methods described previously. They were dried to constant weight in an oven, conditioned for six hours at 70° F. and 65 per cent relative humidity, and weighed. The per cent grafts were determined using the preceding formula.

IV. Determination of Physical Properties

It was necessary to compare some of the physical properties of the various copolymers with the properties of Dacron to make sure that these properties were not seriously altered by the irradiation and graft reaction. To be consistent, for the sake of the Analysis of

Variance calculations that were to be made when interpreting the data, the Dacron skeins were first treated with the two monomers. However, these skeins were not irradiated. Single filaments were separated from them and ruptured on the Instron Electronic Tensile Testing Instrument. By making simple calculations from the stress-strain curves obtained, and by making appropriate calculations of the area under those curves with the help of the automatic integrator, the Dacron filaments were characterized as follows:

1. Breaking strength, grams per denier;

2. Elongation at break, expressed as a percentage of the original sample length;

3. Energy required to rupture, or toughness, gram-inches per denier.

Since the last property, toughness, was a function of both the breaking strength and elongation, it was used in the Analysis of Variance calculations (see Appendix).

The acrylic acid and methyl acrylate copolymers, obtained from all three grafting techniques, were also tested on the Instron. The radiation dose for each combination was 1.9×10^6 rads; if this amount of radiation did not significantly reduce the toughness values obtained, the grafting procedures would not have to be adjusted.

The results were calculated using the following formulae:

1. Breaking strength $= \dfrac{\text{gms at break, indicated on chart}}{\text{filament denier}}$

$= \dfrac{\text{gms at break}}{5}$

2. Per Cent Elongation $= \dfrac{\text{jaw speed} \times \text{no. of divisions on chart} \times \frac{\text{inches}}{\text{div.}}}{\text{chart speed} \times \text{sample length}}$ (100)

$= \dfrac{6\text{in.}/\text{min.} \times \text{no. of div.} \times 1/10\text{in.}/\text{div.} \times 100}{10 \text{ in.}/\text{min.} \times 3 \text{ inches}}$

$= 2$ (no. of divisions on chart)

3. Toughness

$= (k)$ Integrator reading/denier, where $\underline{k}$ is a constant depending on the load cell used.

$= (.006)$(Integrator reading)$/5$ gram-inches/denier.

V. Dyeing Procedure

Since polyester fibers are normally dyed with selected disperse dyes, it was decided to apply one of these dyes to all three polymers—Dacron, Dacron-acrylic acid copolymer, and Dacron-methyl acrylate copolymer—and to compare the results. Also, since the Dacron-acrylic copolymers contained acidic -COOH groups, it was thought that these groups would serve as dye sites for a basic dye. One was selected and used to dye all combinations. To confirm any results that might be obtained with the basic dye, an acid dye was selected; it was thought that this dye would behave oppositely.

It was decided that quantitative results could be interpreted with more accuracy than could qualitative ones. Therefore, instead of making a visual examination of each dyeing and comparing the results, an actual calculation was made—milligrams of dye absorbed per gram of fiber. The best way to make such a calculation is to compare light absorbance measurements on the dyebaths before and after the dyeing. However, these calculations are not accurate unless the absorbing

species, in this case the dye molecules, obey the Beer-Lambert Law:

$A_\lambda = a_\lambda bc$ where $\underline{A}$ = absorbance at wave length λ .

a = the extinction coefficient at wave length λ, a coefficient depending on the nature of the absorbing species.

$\underline{b}$ = length of the light-path through the absorbing medium.

and $\underline{c}$ = the concentration of the absorbing species.

It is extremely important to operate at a wave length that will give the maximum change in $\underline{A}$ for a given change in $\underline{c}$. Such a wave length may be determined by constructing a wave length vs. absorbance curve. The optimum wave length at which to conduct future measurements is the wave length where a sharp peak in the curve occurs. Four or five dyes in each class—acid, basic, and disperse—were characterized by constructing these absorbance curves. They were made on an automatic recording spectrophotometer, the Bausch and Lomb Spectronic 500, where $\underline{A}$ was plotted against λ in the visible region of the spectrum, 400 to 700 mu. The wave lengths for future measurements were selected

and the dyes were diluted to see if, in fact, A = abc. The dyes investigated were the ones that best obeyed this law.

Even so, the absorbance measurements could be compared accurately only in very narrow concentration regions, and the optimum region had to be selected for each dye. When this region had been selected, the milligrams of dye absorbed into each gram of fiber could be calculated in the following manner. Assume that a stock solution of dye contained .2000 grams dye per liter. A 50 ml. portion of this solution was pipetted into a dyebath and a skein of yarn weighing 1.2000 grams was added. It had been determined that the best concentration for duplicating the absorbance readings was a 16:1 dilution of the bath with water, and the optimum wave length was 560 mu. Assume the absorbance of that diluted portion was .450, before any dye had been absorbed. After the dyebath had been raised to the boil and the skein dyed for one hour, suppose the absorbance of a portion of the bath, diluted 16:1, was .250. With this data, the milligrams of dye absorbed per gram of fiber may be calculated:

$$A_1 = abc_1$$

$$\text{and } A_2 = abc_2.$$

Therefore, $\dfrac{A_1}{A_2} = \dfrac{c_1}{c_2}$ and since $\underline{c}$ = grams/unit volume, and since the dilution is the same in every determination,

$$\frac{A_1}{A_2} = \frac{\text{mgms in bath before dyeing}}{\text{mgms of dye in bath after dyeing}}.$$

Therefore,

$$\text{mgms dye in bath after dyeing} = (\text{mgms in bath before dyeing}) \frac{(A_2)}{(A_1)}$$

$$= \frac{(50)(.2000)(.250)}{.450} = 5.56.$$

$$\text{mgms dye in fiber} = \text{mgms dye in bath before dyeing} -$$

$$\text{mgms in bath after dyeing}$$

$$= 50(.2000) - 5.56 = 4.44.$$

Therefore, mgms dye absorbed per gram of fiber $= \dfrac{4.44}{1.2000} = 3.70.$

Other complications arise when dealing with complex species such as dye molecules. For example, small pH changes in some dye solutions markedly affect absorbance values. In other dyes, the thermal history of the bath is important. For these reasons, some of the baths were buffered. In all cases, the "blank" dyebath, from which was obtained the original absorbance measurement to be compared with the measurement obtained after dyeing, was prepared simultaneously with the actual dyebath and given the same thermal treatment. For example, the "before dyeing" absorbance value used in the disperse dye series was obtained in the following manner:

(1) pipette 60 ml. of stock dye solution into dyeing flask.

(2) add five ml. of formic acid-ammonium sulfate buffer solution; stir.

(3) bring bath to boil over a period of 30 minutes.

(4) boil one hour; cool slowly.

(5) dilute dyebath 3:1 with acetone and measure absorbance.

The absorbance value obtained was compared to the value deter-
mined from a dyebath containing the same chemicals and having the same
thermal history, the only difference being that the latter dyebath
contained a skein of yarn. Thus, differences in concentration of the
two baths could be attributed to dye exhaustion only. Otherwise,
differences attributed to dye exhaustion might have been caused by a
difference in the degree of dye hydrolysis and/or reduction.

Before any of the dyeing experiments were conducted, it was de-
cided which copolymers should be further investigated. The copolymers
that had the maximum grafts were chosen and dyed with each class of
dyes. Thus each dyeing series consisted of dyeing at least four pure
polymer specimens and two specimens containing the highest per cent by
weight of graft from each of the following combinations:

1. Dacron-methyl acrylate, direct grafting method;

2. Dacron-acrylic acid, direct grafting method;

3. Dacron-methyl acrylate, peroxidized polymer grafting method;

4. Dacron-acrylic acid, peroxidized polymer grafting method;

5. Dacron-methyl acrylate, trapped-radical grafting method;

6. Dacron-acrylic acid, trapped-radical grafting method.

Note that replicate dyeings were made on the same copolymers,
the only difference being the method in which they were produced. It
was thought that the amount of dye absorbed in each case might indicate
where the grafting had occurred. For example, consider two acrylic
acid copolymers, both one per cent grafts on Dacron. If the copolymers
were made by different methods, a higher basic dye absorption by one of

the copolymers would indicate that the method employed to make this co-
polymer had deposited most of the grafted acrylic acid on the surface
of the Dacron, where dyeing takes place. Dyeing takes place on the
surface because the Dacron chains are so closely packed. Likewise, the
other grafting method produced just as much graft (one per cent), but
the grafting probably occurred within the polymer and the acrylic acid
sites were not available to the basic dye. Similar explanations can be
proposed for the other monomer, grafting method, and dye combinations.

A. Acid Dye Series

For the acid dye series of experiments, C.I. Acid Red 1 was se-
lected for several reasons. It was available in relatively crystal-
line form, it almost obeyed the Beer-Lambert Law in the proper concen-
tration region, it exhibited a fairly sharp absorbance peak, it was
soluble in cold water, and it could be used in a conventional manner.

To obtain an absorbance value on which to base future calcula-
tions, the following procedure was used:

(1) pipette 50 ml. of the stock acid dye solution into a 125 ml.
    Erlenmeyer flask; add a boiling chip.

(2) add 4 ml. of a 5 gpl sodium sulfate solution slowly, while
    stirring.

(3) add 2 ml. of a 2 per cent sulfuric acid solution; stir.

(4) bring dyebath to boil over a period of 30 minutes.

(5) boil solution for one hour.

(6) cool the bath slowly and dilute a portion 8:1 with water.

(7) obtain absorbance readings for these diluted portions with the
    Beckman DU Spectrophotometer, λ =530 mu.

This exact procedure was followed when dyeing the various Dacron and Dacron copolymer skeins, except that the accurately weighed skeins were added to the bath prior to step number 4.

B. Basic Dye Series

Few of the basic dyes studied remotely obeyed the Beer-Lambert Law. Furthermore, it was found that upon standing in a beam of mono-chromatic light, the light-absorbing capacities of many of these dyes declined. However, one dye, C.I. Basic Blue 26, retained its light ab-sorbing capacity long enough to duplicate the measurements if that absorbance was near 1.00. It is not normal to operate at this high a concentration, the maximum accuracy of a spectrophotometer being near .435. However, measurements made at A = .435 could not be reproduced within one minute of each other since the absorbing nature of the dye declined while standing in the monochromatic light. C.I. Basic Blue 26 was used, nevertheless, and absorbance measurements were made near 1.00.

The following procedure was followed to obtain the initial ab-sorbance value of the basic dye:

(1) pipette 15 ml. of the stock dye solution into a 125 ml. flask; add a boiling chip.

(2) add 35 ml. of deionized water; stir.

(3) add 2 ml. of a 1 per cent sodium chloride solution; stir.

(4) add 2 ml. of a 1 per cent solution of 28 per cent acetic acid; stir.

(5) adjust the pH to 3.5, if necessary, with additional acetic acid.

(6) raise the dyebath temperature to the boil over a period of 30 minutes.

(7) boil dyebath one hour.

(8) dilute a portion of the bath 1:4 with water.

(9) obtain absorbance readings of this diluted portion at λ = 620 mu.

The above procedure was repeated exactly, except that weighed skeins of Dacron and Dacron copolymers were added to the bath prior to step number six.

C. Disperse Dye Series

It was necessary to make clear solutions of the dye dispersions before suitable disperse dyes could be selected on the basis of their absorbance characteristics. It was found that a dilution of these dispersions by at least three to one with acetone solubilized the dye particles. It was also found that, in many cases, this solubilization caused the dye molecules to absorb light in regions of the spectrum that would not ordinarily be predicted, considering the dye's color. C.I. Disperse Blue 61 was chosen because its absorbance peak, when the dye was diluted with acetone, was unusually sharp. All measurements could be reproduced and the absorbing molecules obeyed the Beer-Lambert Law in the experimental region chosen.

The following procedure was used to obtain the initial absorbance value. Note that the baths had to be buffered below pH 7. It had been noticed that boiling the deionized water, used in all these dyeing experiments, caused a change in pH from 5.2 to 9.0. It is known that such a change in pH causes both hydrolysis and reduction of certain disperse dyes.

(1) pipette 60 ml. of the stock dye solution into a 125 ml. flask; add a boiling chip.

(2)   add 5 ml. of a **formic** acid-ammonium sulfate **buffer** solution; stir.

(3)   bring bath to **boil over a** period of 30 minutes.

(4)   boil one hour; **cool slow**ly.

(5)   dilute a portion **of the** bath 3:1 with acetone.

(6)   obtain absor**bance value**s for this portion of the dyebath, λ = 668 mu.

This **exact proce**dure was followed when dyeing the Dacron and Dacron copoly**mers, exce**pt that the weighed samples were added to their respective **baths prior** to step number 3.

In **every case**, the milligrams of dye absorbed per gram of Dacron, or Dacron **copolymer**, was calculated. Comparisons were made between the dyes, the **copolymers**, and the grafting techniques with respect to this dye absorpt**ion. These** comparisons were made utilizing the Analysis of Variance proc**edure** (38) (see Appendix) and the numbers used to make these calculat**ions were** obtained as follows:

Number in **analysis** calculation = mgms dye per gram of copolymer -

mgms dye per gram of Dacron.

CHAPTER V

RESULTS AND DISCUSSION

A. Grafting Yields

The per cent grafts obtained, in each of the three grafting methods with both monomers, ranged widely. (See Appendix 1, Tables 1-3.) For example, in the grafting of methyl acrylate to Dacron by the direct radiation method, the per cent grafts ranged from approximately 2.75 to 5.13. The same copolymer made by the trapped radical method had a per cent graft range from zero to 1.418. Similar results were obtained with the Dacron-acrylic acid copolymers.

It is thought that small impurities in the grafting systems are responsible for these large variations. It will be recalled that traces of oxygen are particularly notable for decreasing the efficiency of grafting and promoting homopolymerization. Therefore, for a given grafting method and monomer, the per cent graft is probably a function of the oxygen concentration. If the systems had not been purged with nitrogen, the variation of the grafting yield would be low, but so would the yield itself. Even though the systems were all purged for the same time with nitrogen, those systems which retained the most oxygen, say oxygen trapped within the polymer, underwent the least grafting.

Even so, an average of the per cent grafts for each grafting method and each monomer should give a visual indication of which methods

were the most efficient and which monomer was most readily grafted
(see Figure 2). A more precise analysis of the grafting data appears
in Appendix 2.

Direct Radiation Method

In Figure 2, it may be seen that the most efficient grafting
technique was the direct radiation method. Recall that in this method,
the polymer and a monomer, dissolved in a selected solvent, are irradi-
ated together. Due to the Trommsdorff effect of the solvent, methanol,
an effect that has been explained previously, the rate of polymerization
in the latter stages of the reaction is though to have increased.

Another reason the direct method is more efficient is that the
growing polymers, or macroradicals, are present in high concentration
at the same time radicals are being produced on the reference polymer
Dacron. The radical sites and the macroradicals produced from the vinyl
monomer are present simultaneously due to the fact that radiation is un-
selective with regard to the ionization, and hence free-radical produc-
tion, of matter.

Therefore, two reasons are proposed for the direct method's
superiority with respect to high grafting yields. The first is that
solvent acceleration, due to the Trommsdorff effect, occurs in the
direct radiation method. The second is that there is a higher proba-
bility for a macroradical to react with a radical on the reference
polymer when both have been produced simultaneously. One reason for
this higher probability is that the small fragments, such as hydrogen
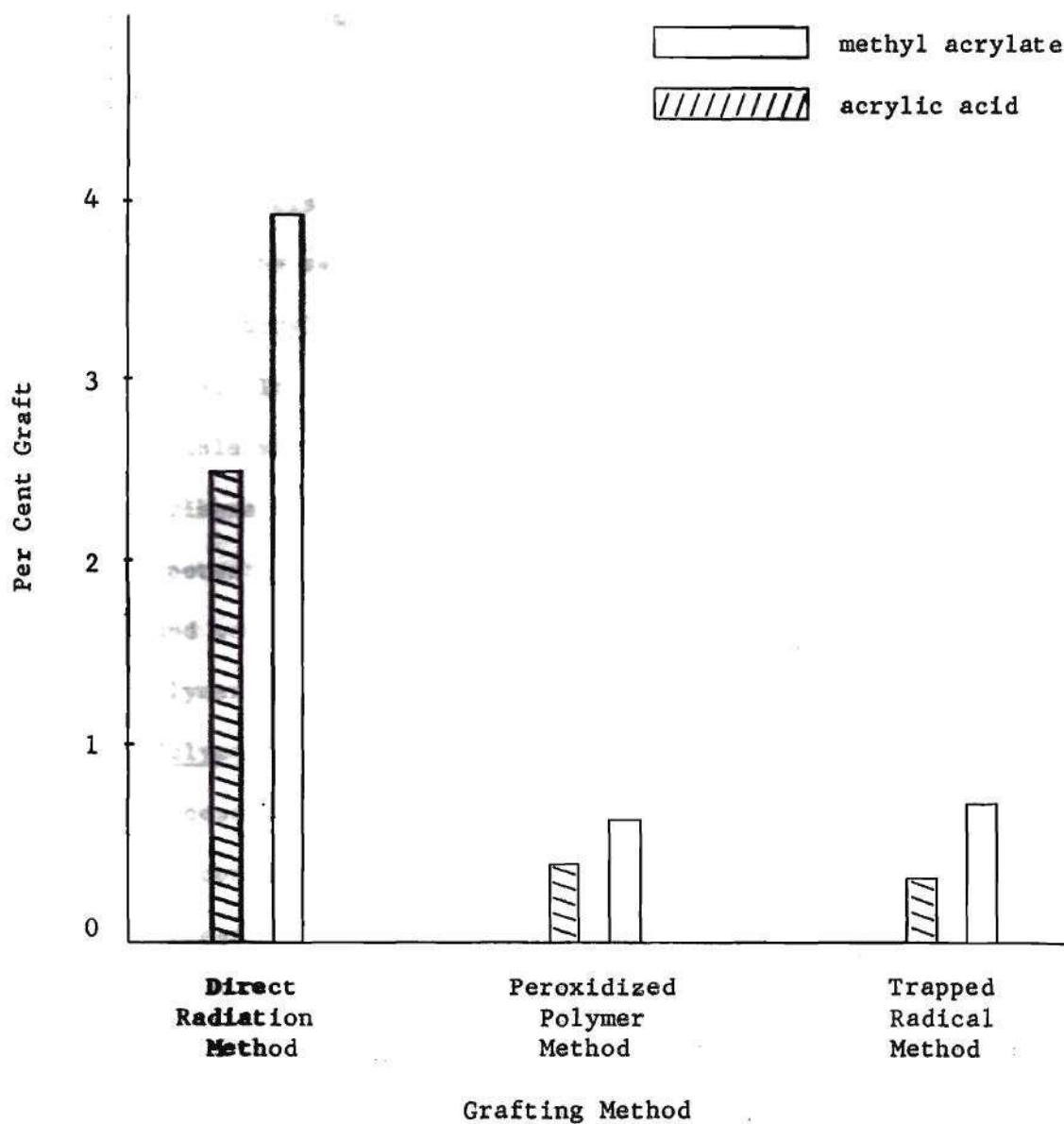radicals, that have been ruptured from the main molecules, exist

Figure 2. Effect of Grafting Method and Monomer on the Grafting Yield
(Values Are Based on the Mean of Five Grafts.)

simultaneously. These small radicals react with each other very readily to form molecules such as H_2 or CH_4. Thus, the reactions of the macro-radicals can terminate only by being grafted to the reference polymer, if the smaller radicals have been consumed.

It also can be seen that methyl acrylate is more readily grafted to Dacron than is acrylic acid. This observation was made in all three grafting methods. It is thought that methyl acrylate, being as ester, is more compatible with a polyester such as Dacron than is acrylic acid. Also, Dacron fibers, like most textile fibers, have a considerable negative surface potential. The negative acrylic acid ions would therefore be repelled and would have a higher probability to homopolymerize than to graft copolymerize to Dacron.

Peroxidized Polymer Method

The success of the graft reaction of a peroxidized polymer depends upon the concentration of peroxide groups on the polymer, the stability of these groups, and their location. If they decompose too readily, they may disappear in the time that elapses between the radiation step and the grafting reaction. If they are too stable, they may not decompose to initiate the free-radical chain reaction of the monomer at the temperature being used. If they are not too stable, but are located within the polymer, they may decompose but the radical sites left on the polymer may not be available to the polymerizing monomers.

However, it is thought that the low grafting yields can be attributed chiefly to the fact that not enough peroxide groups were formed on the polymer in the irradiation step. The optimum radiation dose was not determined in any of the grafting experiments. Such a determination

would prove very interesting and perhaps a larger radiation dose would provide enough peroxide groups to give large grafting yields. But there is a limit to the dose that can be used; this limit is necessarily determined by how much the polymer itself can tolerate before it loses its high tensile strength, resilience, and extensibility. However, it was determined in this investigation that as much as 1.9×10^6 rads does not affect these properties and this much irradiation was used in every case.

Perhaps a different radiation medium would have produced more peroxide groups. Recall that the radiation medium in this investigation was pure oxygen at atmospheric pressure. It may be that two or more atmospheres of oxygen in the enclosed reaction vessel would provide more peroxide groups. On the other hand, if the polymer were irradiated in the presence of liquid H_2O_2 or other peroxides, a higher peroxide might have been obtained. The optimum medium was not determined.

With regard to the graft reaction itself, the peroxidized polymers were treated with a monomer solution for two hours at 60° C. No attempt was made to determine the optimum monomer solvent (methanol was used), the solvent-monomer ratio (7:3 was used), the time of reaction, or the optimum reaction temperature. All of these determinations would be interesting, but they were beyond the scope of this investigation.

Trapped Radical Method

The grafting yields of the trapped radical grafting method were also considerably lower than the yields of the direct radiation method. It is likely that the polymers, which were irradiated for two hours in a vacuum prior to the grafting step, were not irradiated long enough.

It is also possible that the graft reaction temperature was not high enough (or too high), but the optimum temperature was not determined.

However, a study was made of the time of grafting. (See Appendix 1, Table 4.) Of all the three methods investigated, the trapped radical technique was the only method where the time of grafting was studied. It was thought that this method was particularly peculiar in that some of the grafting sites would be trapped within the amorphous regions of the polymer, and some would be more firmly trapped within the crystalline regions. Perhaps the radicals in the crystalline regions would react with the monomers if given enough time. The following graphs indicate that the time of grafting is indeed important.
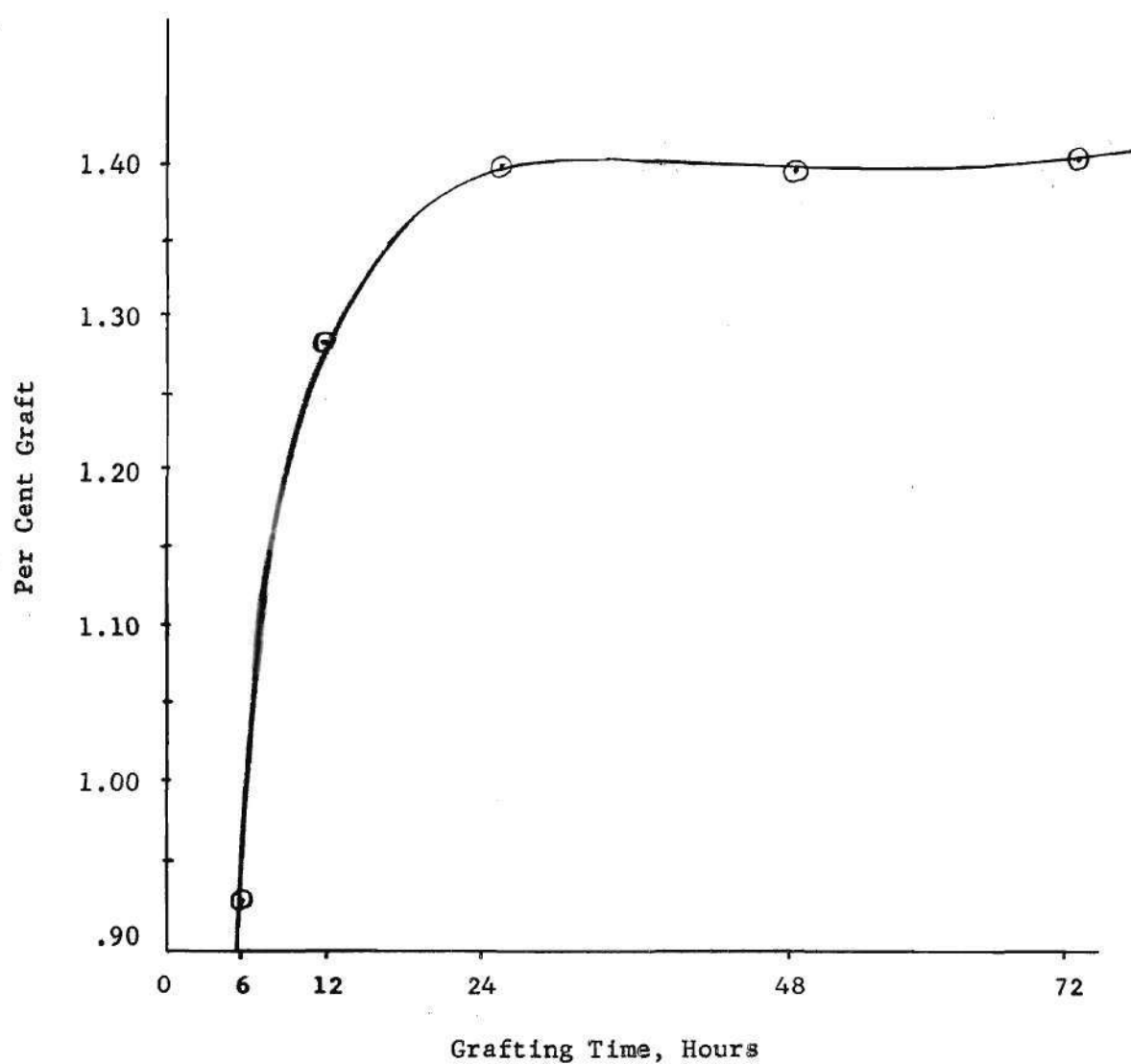
Figure 3. Grafting Yields as a Function of **Grafting** Time; Methyl Acrylate Grafted to Dacron **by the** Trapped Radical Method (Values Based on **the Mean** of Two Grafts)
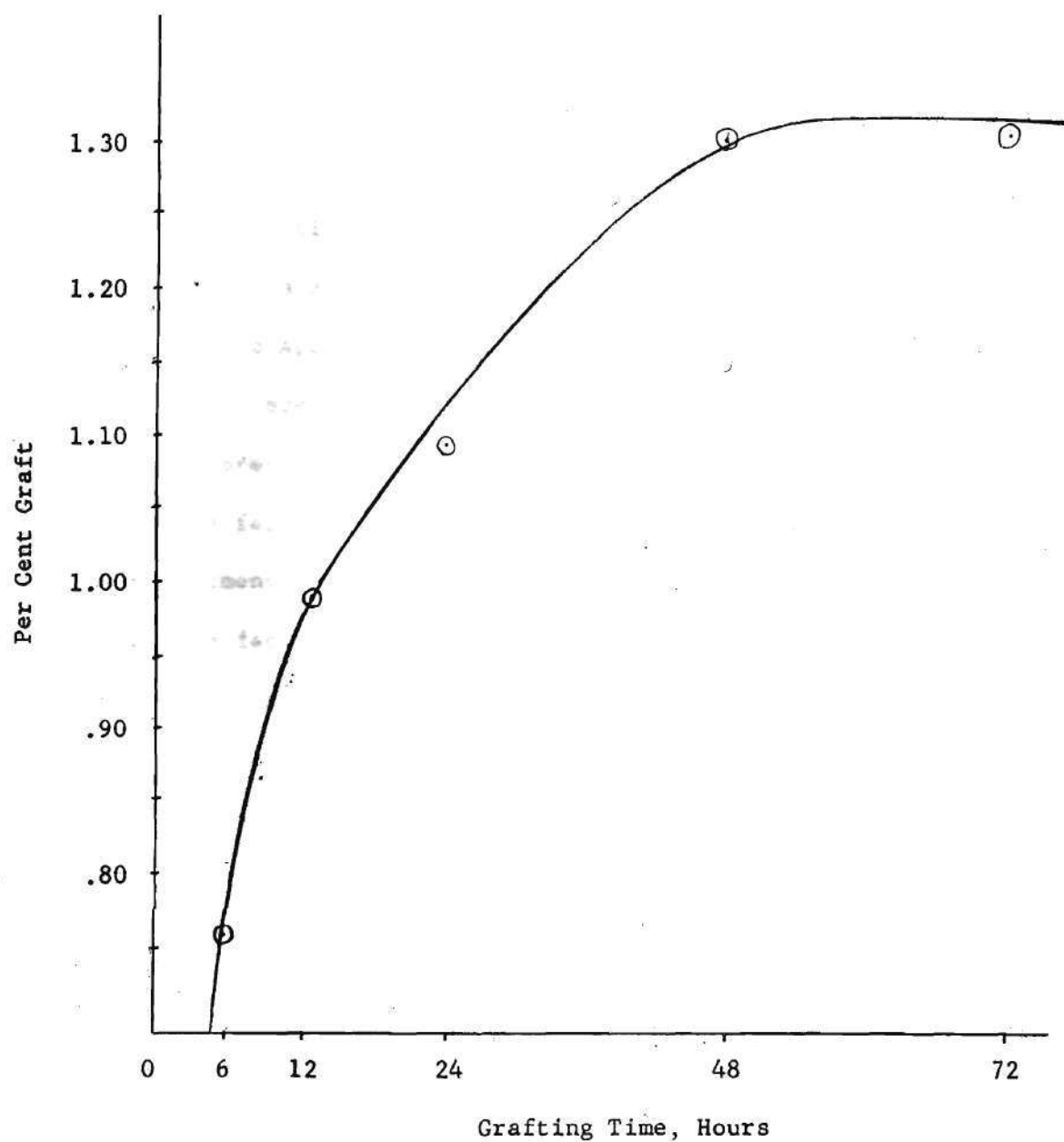
Figure 4. Grafting Yields as a Function of Grafting Time; Acrylic Acid Grafted to Dacron by the Trapped Radical Method (Values Based on the Mean of Two Grafts)

B. Effect of Irradiation Grafting on the Physical Properties of Dacron

The radiation dose, 1.90×10^6 rads, was the same for each graft-
ing method. To determine if the radiation and/or the chemical treat-
ments used in the graft reaction had a deleterious effect on some of
the physical properties of the Dacron polymer and its copolymers,
physical tests were carried out on unirradiated Dacron and on the Dacron
copolymers. (See Appendix 1, Tables 5-8.) These tests included a
determination of breaking strength, elongation at break, and toughness.
A formal interpretation of the results of these tests appears in Appen-
dix 2, but the following graphs should indicate that the radiation and
grafting treatments did not harmfully alter the above characteristics
of Dacron. In fact, in many cases these properties were enhanced.

It should be pointed out that the unirradiated Dacron was treated
with the monomers, methyl acrylate and acrylic acid, prior to testing
its physical properties. These treatments were given so that the data
would be consistent; in the Analysis of Variance procedure, not only
could radiation effects be studied, but the monomer effect could be
determined as well.

In Figure 5, note that the breaking strengths of the copolymers
were less than that of the Dacron in only one instance, the acrylic
acid copolymer produced by the peroxidized polymer method, and this
difference is almost negligible. The breaking strengths were consid-
erably enhanced in most of the other cases.

It is interesting to observe that the two copolymers made by
the direct radiation method suffered a slight decrease in elongation
at break (Figure 6). It has been established that a more efficient
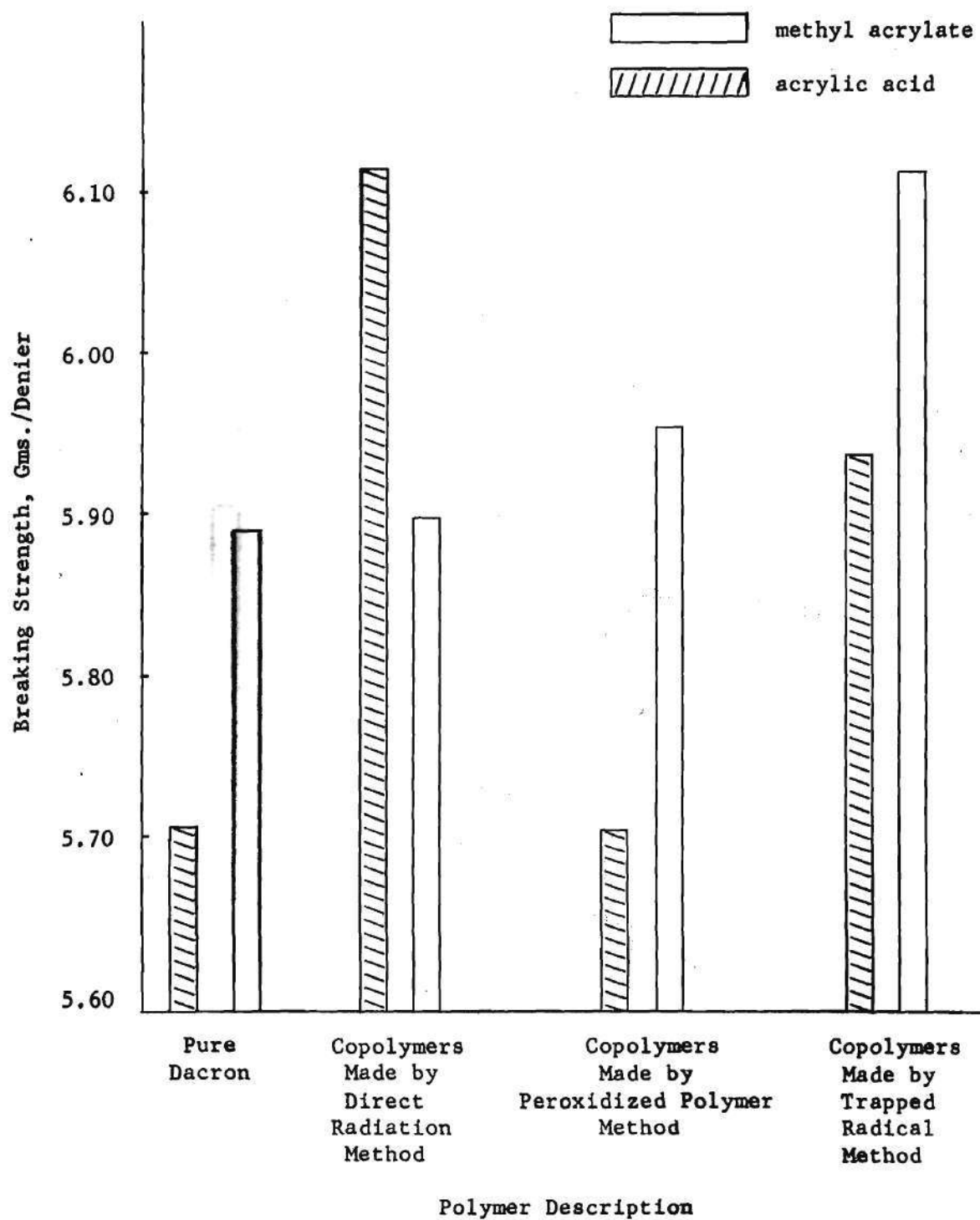
Figure 5. Breaking Strengths of the Dacron Polymer and Copolymers
(Values Based on the Mean of Five Determinations)
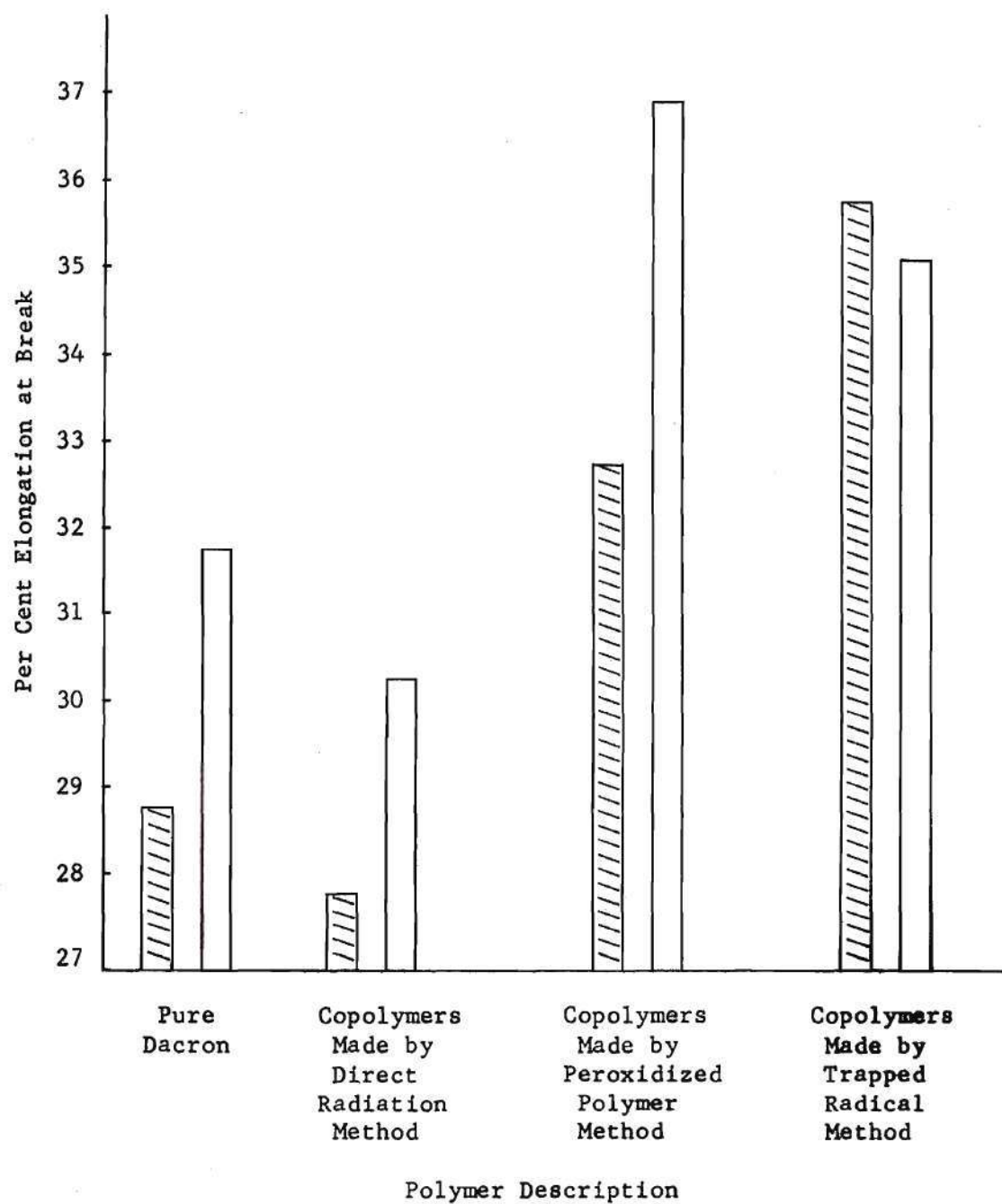
Figure 6.   Elongation at Break of the Dacron Polymer and Copolymers
            (Values Based on the Mean of Five Determinations)

graft reaction is obtained with the direct radiation method; apparently increased grafting is obtained at the expense of high elongation. One explanation is that the molecular segments in the amorphous region of the polymer that normally would slip by each other under tension, and thus make the polymer highly extensible, are now bonded to another macromolecule, the polymerized monomer; hence, these molecules have greater difficulty in slipping, the polymer has been rendered "brittle", and the extensibility is less.

If the above explanation were entirely accurate, it would be difficult to explain why the elongation in all other cases increased. Even in these instances, some grafting occurred, and according to the above explanation, an appropriate decrease in extensibility should result.

The third physical property investigated, toughness, is a function of the breaking strength and elongation. In fact the toughness is calculated by integrating the area under the load-elongation curve. For this reason, the toughness data was the data chosen for precise analysis; this analysis appears in Appendix 2.

C. Dye Absorption

Disperse Dye Series

The selected disperse dye used in all the dyeing experiments was designed and synthesized specifically for polyester fibers such as Dacron. Apparently, this dye has certain chemical groups that react with the ester sites within the Dacron polymer. In Figure 7, it can be seen that the increased uptake of the disperse dye for the methyl acrylate copolymer is considerable. (Also see Appendix 1, Tables 9-11.)

When grafted to the **Dacron, me**thyl acrylate, an **ester** in its own right, made additional dye **sites for** the disperse dye. If these sites were positioned on the **surface of** the polymer, as they were thought to be, this would not only **explain** the increased uptake of dye, but it would explain the rate **at which** the dye was absorbed. It would take several hours to reach **a given** depth of shade on pure Dacron; it takes only one hour to reach **that depth** with the Dacron-methyl acrylate copolymers.

As **would be ex**pected, the more methyl acrylate grafted, the more dye was **absorbed in** the dyeing time employed, one hour. Remember that the direct **radiation** grafts were on the order of 5 per cent while the other **methods yiel**ded graft copolymers on the order of only one per cent. **Hence, the** direct radiation copolymers were superior as far as dye uptake **is concer**ned.

It can **also be** observed that a slight increase in dye absorption was obtained **for the** acrylic acid grafts, although this increase was not proportional **to** the amount of acrylic acid grafted. Perhaps the grafted acrylic **acid** will accommodate only so much additional disperse dye, and no **more, re**gardless of how much acrylic acid has **been** grafted. However, the **Dacron-**acrylic acid copolymer made by the **peroxidized** polymer method absorbed slightly less disperse dye than did **the** Dacron. Results of this type can probably be attributed to either experimental errors, or non-homogenous grafts. If the grafts **were** non-homogenous, and if the dyeing sample were cut from a region **of the copolym**er that had little or no grafted acrylic acid, a **correspondingly** low dye uptake would be expected.

Figure 7. Absorption of Disperse Dye by Dacron and Its Copolymers
(Values Based on the Mean of Four Dyeings for the Pure
Dacron; Two Dyeings for All Copolymers)

Basic Dye Series

Polyester fibers are very resistant to all dyes except disperse dyes. It was therefore very interesting to observe (Figure 8) the high basic-dye absorption of the Dacron-acrylic acid copolymer. Basic dyes have always presented the dyer with an extensive range of clear, bright shades. Their main disadvantage was poor light-fastness. Recently, however, basic dyes have become very popular for dyeing the acrylic fibers. Dye chemists, as a result, have developed extensive shade ranges of light-fast basic dyes. These dyes are easy to apply; the dyeing temperature must never be above the boil and dyeing times are relatively short. Compare these characteristics with those of the disperse dye class; dyeing times are long, temperatures sometimes must be as high as $250°$ F., which requires expensive pressure equipment, and "carriers", expensive chemical agents, must be added to the dye-baths to assist the dye-absorption. These agents also impair the light-fastness of the otherwise fast-to-light disperse dyes.

As was to be expected, the direct radiation graft copolymers, with grafts on the order of 3 per cent for acrylic acid, absorbed more dye than did the other graft copolymer. Notice also that the methyl acrylate copolymers absorbed some basic dye, although this increased absorption was hardly significant for the peroxidized polymer and trapped-radical graft copolymers. But the basic dye absorption of the Dacron-methyl acrylate copolymer made by the direct radiation technique absorbed a considerable quantity of basic dye. However, if one were to choose between which copolymer to make as far as enhancing Dacron's

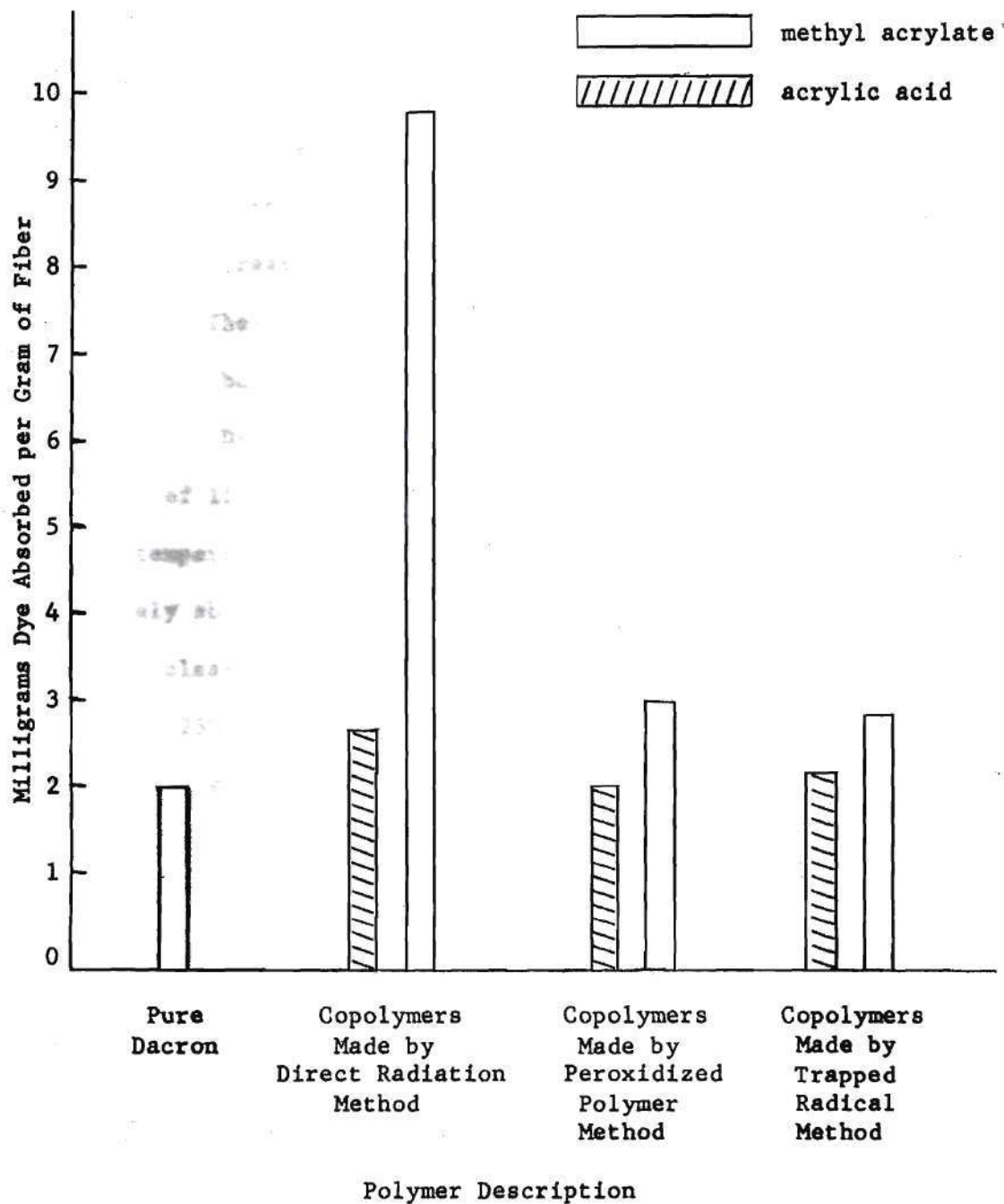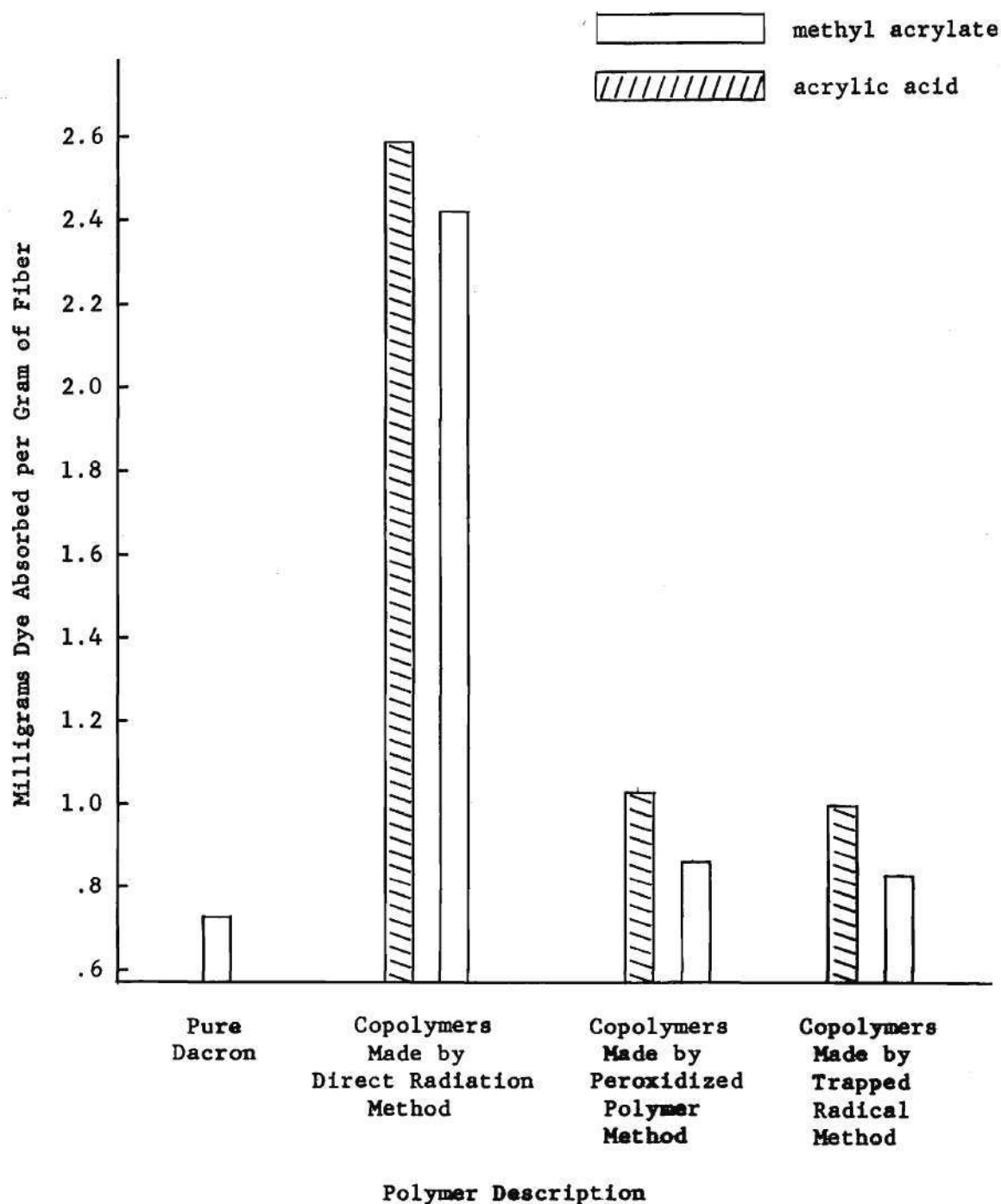Figure 8. Absorption of Basic Dye by Dacron and its Copolymers
(Values Based on the Mean of Four Dyeings for the Pure
Dacron; Two Dyeings for all Copolymers)

dyeability with basic dyes, the choice would be the acrylic acid co-polymer. It took only a 3 per cent acrylic acid graft, compared with the 5 per cent methyl acrylate graft, to obtain the very high basic dye absorption. In fact, the absorption was higher with the acrylic acid copolymer, even though the per cent graft was considerably lower.

It should be pointed out that the "color yields" of basic dyes are much higher than those of disperse dyes. For example, a good depth of shade was obtained in one of the disperse dye dyeings where approximately 9.35 milligrams of disperse dye was absorbed per gram of methyl acrylate copolymer. This same depth of shade was obtained when only 2.61 milligrams of basic dye was absorbed per gram of acrylic acid copolymer. It becomes obvious, then, that another advantage of using basic dyes is that less dye is required for a given depth of shade.

Acid Dye Series

It was known that an anionic dye, such as the acid dye selected in this investigation, would do little more than stain Dacron. An acid dye was selected to help confirm the results obtained with the basic dye. In other words, it was hoped that the acid dye would behave oppositely. Observe that it did (Figure 9). In fact, the acid dye molecules were so repelled by the acid groups on the acrylic acid co-polymer that absolutely no dye was detected within that fiber. Sur-prisingly, the methyl acrylate copolymers absorbed some acid dye. But the "color yield" of the dye was so small that, essentially, it can be said that none of the copolymers were dyed with the acid dye.
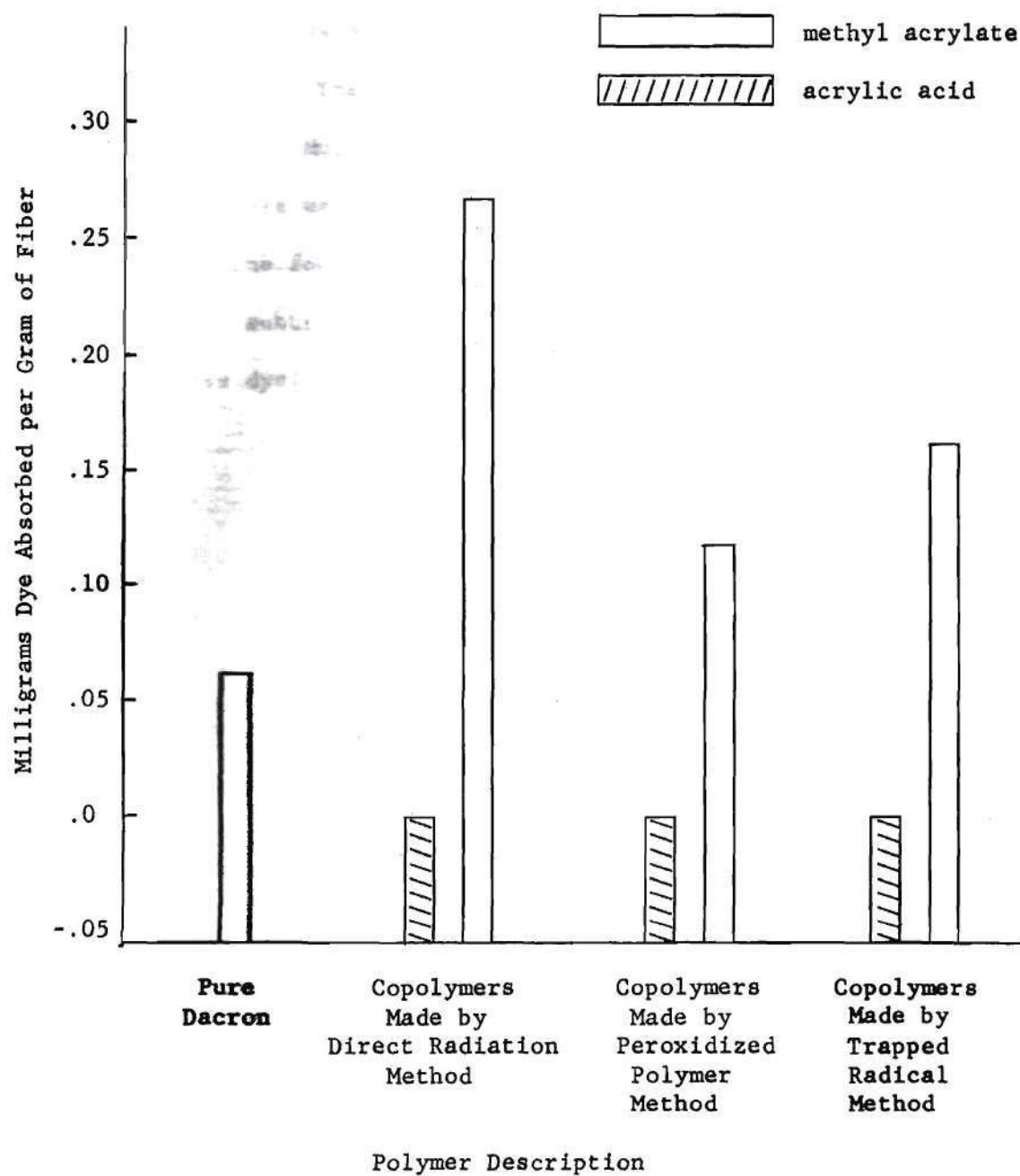
Figure 9. Absorption of Acid Dye by Dacron and its Copolymers (Values Based on the Mean of Four Dyeings for the Pure Dacron; Two Dyeings for all Copolymers)

A precise analysis of the acid, basic, and disperse dyeings appears in Appendix 2. The Analysis of Variance procedure (38), in conjunction with the Multiple Range Test (39), was employed. The quantitative numbers used to make these calculations were obtained by first averaging the four dye absorption values of the pure Dacron, for a given dye, and subtracting that number from the absorption values of each of those dyeings.

CHAPTER VI

CONCLUSIONS

Methyl acrylate and acrylic acid can be grafted to Dacron by each of three grafting techniques: direct radiation grafting; peroxidized polymer grafting; and trapped radical grafting.

At the 5 per cent level of significance, the direct radiation method is more efficient than both the trapped radical and peroxidized polymer methods. The term "more efficient" means that a higher per cent graft can be obtained with the same amount of radiation.

The peroxidized polymer method of grafting and the trapped radical technique are not significantly different with respect to grafting efficiency.

In all three methods, methyl acrylate is grafted to Dacron more readily than is acrylic acid.

With the radiation dose used, 1.90×10^6 rads, none of the physical properties of Dacron that were tested—breaking strength, elongation at break, and toughness—were impaired. In fact, these properties were enhanced in many instances. The following statements pertaining to toughness can be made. These statements are based on an Analysis of Variance (38) and a Multiple Range Test (39) at the 5 per cent level of significance:

(1) The type monomer used in the graft reaction does
not affect the toughness.

(2) The grafting technique does affect toughness.

(3) There is no significant difference in toughness between the pure Dacron polymer, the copolymers made by the peroxidized polymer method, or the copolymers made by the trapped radical method.

(4) There is a difference in toughness between the trapped radical copolymer and the direct radiation copolymer; the toughness of the trapped radical copolymer is greater.

Radiation grafting of methyl acrylate or acrylic acid to Dacron greatly enhances the dyeability of Dacron. The methyl acrylate-Dacron copolymers are best dyed with disperse dyes. The acrylic acid-Dacron copolymers are best dyed with basic dyes. The following specific statements can be made about the dyeability of the copolymers based on an Analysis of Variance calculation (38) and a Multiple Range Test (39), both at the 5 per cent level of significance:

1. The dye used—acid, basic or disperse—makes a large difference with respect to dye absorption.

2. The monomer grafted—methyl acrylate, or acrylic acid—makes a large difference.

3. No statement can be made concerning the best dye to use unless the grafted monomer is specified. If the grafted monomer is methyl acrylate, disperse dyes are best. If the grafted monomer is acrylic acid, basic dyes are best.

4. The technique employed—direct radiation method, peroxidized polymer

method, or trapped radical method—makes a large difference. For both copolymers, the direct radiation method is best for improving the dyeability of Dacron. There is no significant difference between the other two methods.

CHAPTER VII

RECOMMENDATIONS

It has been stated that one advantage of making copolymers by
irradiation methods is the fact that the copolymers are relatively
void of impurities. Add to this advantage the fact that there is
essentially only one way to make a copolymer out of a condensation
polymer such as Dacron or nylon, and that way is to graft vinyl
monomers to the condensation polymer, and it appears that graft co-
polymerization induced by radiation has great industrial potential.
It follows that a number of monomers should be investigated with
respect to their grafting efficiency on condensation polymers. In
this investigation, the monomers were grafted to Dacron to improve
Dacron's dyeability. There is no reason why monomers should not be
selected that would improve certain physical properties of Dacron
(or nylon).

If radiation-induced graft copolymerization is the technique
selected to produce copolymers of condensation polymers, as opposed
to catalyst or mastication techniques for example, it follows that
the optimum grafting conditions should be determined. In this in-
vestigation it was demonstrated that the direct radiation grafting
procedure was the most efficient. It would be interesting to deter-
mine, for the direct radiation method, the optimum dose, the optimum
monomer-solvent combination, the optimum concentration of monomer in

that solvent, and the optimum temperature (if possible) of irradiation. These optimum conditions, of course, would have to be determined for each monomer-polymer combination and they would have to be consistent with maintaining the prevailing physical characteristics of the polymer in question, if those characteristics are desirable.

If it is decided that a method besides radiation-induced graft polymerization is better to make graft copolymers from condensation polymers, the radiation method is nevertheless a very important and convenient research tool. A dye chemist, for example, could select a neutral substrate such as Dacron that is relatively undyeable with ionic dyes. To that substrate could be grafted many different monomers and a study could be made that would determine exactly which chemical dyeing sites react with which ionic dyes. As a matter of fact, the disperse dyes could be studied in this respect.

If it is decided that what was actually attempted in this investigation warrants further study, i.e., improving the dyeability of a specific fiber, Dacron, by grafting monomers to it, there are many monomers that could prove interesting. For example, in this investigation an acidic monomer, acrylic acid, was grafted to Dacron in the attempts to make Dacron dyeable with basic dyes. In like manner, basic monomers, such as 4-vinyl-pyridine, acrylamide, etc., could conceivably be grafted to Dacron and the resulting copolymers dyed with acid dyes or other anionic dyestuffs. Also, monomers could be chosen for grafting to other "undyeable" fibers such as polyethylene, polypropylene, and polytetrafluoroethylene yarns.

APPENDIX 1

TABULATION OF DATA

Table 1. Grafting Yields
Direct Radiation Method

Monomer	Skein Weight Before Irradiation (gm)	Skein Weight After Irradiation (gm)	Per Cent Graft
Methyl Acrylate			
1.	1.0922	1.1442	4.760
2.	0.9969	1.0404	4.372
3.	1.0632	1.1177	5.125
4.	1.0248	1.0558	3.022
5.	1.0513	1.0802	2.748
Acrylic Acid			
1.	1.0830	1.1151	2.970
2.	1.1115	1.1360	2.205
3.	1.1551	1.1936	3.335
4.	1.0236	1.0643	3.975
5.	1.1023	1.1201	1.612

(1) The skeins were immersed in a 1:4 monomer-methanol solution.

(2) The systems were irradiated for two hours.

(3) Per Cent Graft $= \dfrac{\text{wt. after irradiation - wt. before irradiation}}{\text{wt. before irradiation}} \times 100$

Table 2. Grafting Yields
Peroxidized Polymer Method

Monomer	Skein Weight Before Irradiation (gm)	Skein Weight After Grafting (gm)	Per Cent Graft
Methyl Acrylate			
1.	3.0632	3.0887	.833
2.	3.0659	3.0930	.884
3.	3.0702	3.0994	.951
4.	3.1028	3.1220	.618
5.	2.9716	2.9810	.316
Acrylic Acid			
1.	3.0757	3.0995	.775
2.	3.0456	3.0527	.233
3.	3.0680	3.0680	.000
4.	3.0693	3.0923	.749
5.	2.9749	2.9811	.208

(1) The skeins were irradiated two hours in the presence of pure oxygen.

(2) The skeins were grafted in a 7:3 methanol-monomer solution for two hours at 60° C.

Table 3. Grafting Yields
Trapped Radical Method

Monomer	Skein Weight Before Irradiation (gm)	Skein Weight After Grafting (gm)	Per Cent Graft
Methyl Acrylate			
1.	2.9757	2.9938	.609
2.	3.0804	3.1241	1.418
3.	3.0761	3.0962	.654
4.	3.1141	3.1142	0
5.	3.0927	3.1322	1.278
Acrylic Acid			
1.	3.0443	3.0510	.220
2.	3.0897	3.1047	.485
3.	2.9743	2.9835	.309
4.	3.1104	3.1236	.424
5.	3.0620	3.0622	0

(1) The skeins were irradiated for two hours in a vacuum.

(2) The skeins were grafted in a 7:3 methanol-monomer solution for two hours at 60° C.

Table 4. Per Cent Graft as a Function of Time:
Trapped Radical Method

Monomer	Skein Weight Before Irradiation (gm)	Skein Weight After Graft (gm)	Per Cent Graft
Methyl Acrylate			
6 Hours	1.5703	1.5853	.955
	1.5421	1.5559	.895
12 Hours	1.5058	1.5250	1.275
	1.5560	1.5763	1.305
24 Hours	1.5582	1.5803	1.420
	1.5266	1.5476	1.376
48 Hours	1.5150	1.5347	1.300
	1.5326	1.5543	1.414
72 Hours	1.5476	1.5685	1.351
	1.5173	1.5391	1.437
Acrylic Acid			
6 Hours	1.5142	1.5262	.793
	1.5631	1.5749	.754
12 Hours	1.4840	1.4986	.984
	1.5260	1.5411	.990
24 Hours	1.5619	1.5792	1.107
	1.5004	1.5172	1.119
48 Hours	1.4978	1.5171	1.289
	1.5179	1.5379	1.319
72 Hours	1.5385	1.5591	1.341
	1.5109	1.5307	1.310

(1) The skeins were irradiated for two hours in a vacuum.

(2) The skeins were grafted in a 7:3 methanol-monomer solution for the hours indicated at 45° C.

Table 5. Physical Characteristics of the Dacron Polymer

Monomer Used	Breaking Strength (gms per Denier)	Per Cent Elongation	Toughness or Energy (gm Inches/Denier)
Methyl Acrylate			
1.	5.96	28.4	.445
2.	5.66	24.6	.248
3.	5.90	38.6	.425
4.	6.04	38.8	.418
5.	5.86	29.4	.343
Acrylic Acid			
1.	5.84	20.4	.230
2.	5.84	38.4	.404
3.	6.14	34.6	.364
4.	5.08	27.0	.279
5.	5.64	23.0	.257

(1) The polymers were soaked in the indicated monomers, but not irradiated.

(2) Single filaments were ruptured on the Instron.

Table 6.   Physical Characteristics of the Copolymers
Prepared by the Direct Radiation Method

Grafted Monomer	Breaking Strength (gms per Denier)	Per Cent Elongation	Toughness or Energy (gms Inches/Denier)
Methyl Acrylate			
1.	6.00	26.6	.330
2.	5.66	26.8	.261
3.	6.28	41.8	.474
4.	5.48	25.6	.186
5.	6.04	31.2	.227
Acrylic Acid			
1.	5.64	29.6	.337
2.	6.06	35.0	.369
3.	5.72	25.0	.258
4.	6.04	22.6	.260
5.	7.10	27.0	.420

(1)   After irradiation, the copolymers were purified in various
solvents.

(2)   Single filaments were ruptured on the Instron.

Table 7. Physical Characteristics of the Copolymers
Prepared by the Peroxidized Polymer Method

Grafted Monomer	Breaking Strength (gms per Denier)	Per Cent Elongation	Toughness or Energy (gm Inches/Denier)
Methyl Acrylate			
1.	5.74	35.8	.372
2.	5.86	40.6	.443
3.	6.20	38.8	.440
4.	6.00	34.8	.377
5.	5.96	34.8	.377
Acrylic Acid			
1.	5.87	21.2	.241
2.	5.77	38.1	.396
3.	6.03	33.2	.328
4.	5.12	34.7	.310
5.	5.70	37.2	.398

(1) After irradiation, the copolymers were purified in various solvents.

(2) Single filaments were ruptured on the Instron.

Table 8. Physical Characteristics of the Copolymers
Prepared by the Trapped Radical Method

Grafted Monomer	Breaking Strength (gms per Denier)	Per Cent Elongation	Toughness or Energy (gm Inches/Denier)
Methyl Acrylate			
1.	6.16	36.0	.384
2.	5.80	40.4	.422
3.	5.84	33.8	.336
4.	6.60	27.2	.355
5.	6.08	38.2	.438
Acrylic Acid			
1.	5.76	35.2	.369
2.	5.90	39.1	.432
3.	6.13	37.2	.427
4.	6.02	32.3	.368
5.	5.91	34.7	.370

(1) After irradiation, the copolymers were purified in various solvents.

(2) Single filaments were ruptured on the Instron.

Table 9. Dye Absorption
Acid Dye Series

Polymer Description	Dyebath Absorbance Before Dyeing	Dyebath Absorbance After Dyeing	Mg. dye/ gm. Fiber
Pure Dacron			
1.	.597	.594	.0517
2.	.597	.593	.0824
3.	.597	.593	.0732
4.	.597	.595	.0416
Direct Radiation Method			
a. Methyl Acrylate			
1.	.597	.579	.288
2.	.597	.583	.240
b. Acrylic Acid			
1.	.597	.600	0
2.	.597	.598	0
Peroxidized Polymer Method			
a. Methyl Acrylate			
1.	.597	.591	.112
2.	.597	.589	.130
b. Acrylic Acid			
1.	.597	.598	0
2.	.597	.598	0
Trapped Radical Method			
a. Methyl Acrylate			
1.	.597	.589	.132
2.	.597	.587	.169
b. Acrylic Acid			
1.	.597	.600	0
2.	.597	.598	0

(1) The above values are based on three readings for each dyebath.

(2) Mg dye per gm of fiber $= \dfrac{\text{mg dye added to bath} - \dfrac{\left[\text{mg dye added to bath}\right]\left[\text{dyebath absorbance after dyeing}\right]}{\text{dyebath absorbance before dyeing}}}{\text{skein weight}}$

Table 10.   Dye Absorption
Basic Dye Series

Polymer Description	Dyebath Absorbance Before Dyeing	Dyebath Absorbance After Dyeing	Mg Dye per Gm. Fiber
Pure Dacron			
1.	.935	.691	.787
2.	.935	.726	.706
3.	.935	.723	.690
4.	.935	.704	.760
Direct Radiation Method			
a. Methyl Acrylate			
1.	2.00	.198	2.470
2.	2.00	.201	2.421
b. Acrylic Acid			
1.	2.00	.166	2.630
2.	2.00	.168	2.597
Peroxidized Polymer Method			
a. Methyl Acrylate			
1.	.898	.649	.845
2.	.898	.655	.825
b. Acrylic Acid			
1.	.898	.574	1.103
2.	.898	.570	1.114
Trapped Radical Method			
a. Methyl Acrylate			
1.	.898	.658	.817
2.	.898	.653	.831
b. Acrylic Acid			
1.	.898	.579	1.089
2.	.898	.582	1.077

Table 11. Dye Absorption
Disperse Dye Series

Polymer Description	Dyebath Absorbance Before Dyeing	Dyebath Absorbance After Dyeing	Mg Dye per Gm. Fiber
Pure Dacron			
1.	.331	.280	1.917
2.	.331	.268	2.260
3.	.331	.275	2.098
4.	.331	.282	1.851
Direct Radiation Method			
a. Methyl Acrylate			
1.	.331	.062	9.382
2.	.331	.068	9.310
b. Acrylic Acid			
1.	.331	.270	2.337
2.	.331	.267	2.371
Peroxidized Polymer Method			
a. Methyl Acrylate			
1.	.331	.262	2.746
2.	.331	.259	2.712
b. Acrylic Acid			
1.	.331	.278	1.994
2.	.331	.273	2.036
Trapped Radical Method			
a. Methyl Acrylate			
1.	.331	.258	2.712
2.	.331	.259	2.723
b. Acrylic Acid			
1.	.331	.272	2.187
2.	.331	.275	2.164

APPENDIX 2

INTERPRETATION OF DATA—ANALYSIS OF VARIANCE METHOD (38)

I. GRAFTING YIELDS

A. Data

Grafting Technique	Methyl Acrylate (% Grafted)	Acrylic Acid (% Grafted)	$\sum$ Rows
	4.760	2.970	
	4.372	2.205	
Direct Radiation	5.125	2.335	33.124
Grafting	3.022	3.975	
	2.748	1.612	
	20.027	13.097	
	.833	.775	
	.884	.233	
Peroxidized Polymer	.951	0	5.567
Grafting	.618	.749	
	.316	.208	
	3.602	1.965	
	.609	.220	
	1.418	.485	
Trapped Radical	.654	.309	5.397
Grafting	0	.424	
	1.278	0	
	3.959	1.438	
$\sum$ Columns	27.588	16.500	44.088

1. Correction factor, CF, $= \dfrac{44.088^2}{30} = 64.791$

2. Monomer sum of squares $= \dfrac{27.588^2 + 16.500^2}{15} - CF = 4.115$

3. SS(Technique) $= \dfrac{33.124^2 + 5.567^2 + 5.397^2}{10} - CF = 50.941$

4. Crude SS $= 4.760^2 + 4.372^2 + \cdots + .424^2 + 0^2 = 131.380$

5. $SS(\text{Residual}) = \text{Crude SS} - \dfrac{20.027^2 + \cdots + 1.438^2}{5} = 9.942$

6. $SS(\text{Total}) = \text{Crude SS} - CF = 66.589$

B. Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees Freedom	Mean Square		F	$F_{.05}$
Monomer (M)	4.115	1	4.115	$\sigma_0^2 + n\sigma_{MT}^2 + nt\sigma_M^2$	9.268	4.23
Technique (T)	50.941	2	25.471	$\sigma_0^2 + n\sigma_{MT}^2 + nm\sigma_T^2$	57.367	3.37
Interaction (M)(T)	1.591	2	.796	$\sigma_0^2 + n\sigma_{MT}^2$	1.923	3.40
Residual (Error Term)	9.942	24	.414	σ_0^2		
Total	66.589	29				

(1) At the 5 per cent level of significance, the monomer effect is significant.

(2) The technique effect is highly significant.

(3) The effect of interaction between the grafting technique and the monomer employed is not significant.

C. Multiple Range Test (39)

Since there are only two monomers, and since the monomer effect is significant, a simple calculation of the mean grafting yield for each monomer will indicate which monomer is better as far as high grafting yields are concerned:

$$\overline{X}_{\text{methyl ac.}} = 27.588/15 = 1.838.$$

$$\overline{X}_{\text{acrylic a.}} = 16.500/15 = 1.100.$$

Therefore the monomer, methyl acrylate, is better for making graft co-polymers of Dacron.

Since there are three techniques, it is necessary to use the Multiple Range Test to determine which of these techniques is best, and which are significantly different:

(1) Standard error of the mean, $s_{\overline{x}}$, $= \sqrt{\dfrac{MS(\text{Residual})}{\text{Degrees F.}}} = \sqrt{\dfrac{.414}{5}} = .288$

df of $s_{\overline{x}}$ = 24.

(2) The significant ranges, found in the Multiple Range Tables (41), are 2.92 and 3.07, at the 5 per cent level.

(3) The least significant ranges are $(s_{\overline{x}})(2.92)$ and $(s_{\overline{x}})(3.07)$ = .841 and .884.

(4) Number of means in range: 2   3

   Least significant range: .841   .884

(5) Results of Test

	Trapped Radical Method	Peroxidized Polymer Method	Direct Radiation Method
mean	.5397	.5567	3.3124

   a. $3.3124 - .5397 = 2.7727 > .884$.
   Therefore, the direct method is better than the trapped radical method.

   b. $3.3124 - .5567 = 2.7557 > .841$.
   Therefore, the direct radiation method is better than the peroxidized polymer method.

   c. $.5567 - .5397 = .0170 < .841$.
   Therefore, the peroxidized polymer method and the trapped radical method are not significantly different.

II. PHYSICAL CHARACTERISTICS OF THE DACRON POLYMER AND CO-POLYMERS—AN ANALYSIS OF THE ENERGY TO RUPTURE, OR TOUGHNESS

A. Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees Freedom	Mean Square	Expected Mean Square	F	$F_{.05}$
Monomer (M)	.0064	1	.0064	$\sigma_0^2 + n\sigma_{MT}^2 + nt\sigma_M^2$	1.280	4.12
Technique (T)	.0356	3	.0187	$\sigma_0^2 + n\sigma_{MT}^2 + nm\sigma_T^2$	3.740	2.88
Interaction (M)(T)	.0195	3	.0065	$\sigma_0^2 + n\sigma_{MT}^2$	1.327	2.90
Residual (Error)	.1551	32	.0049	σ_0^2		
Total	.2166	39				

(1) At the 5 per cent level of significance, the monomer effect is not significant.

(2) The technique effect is significant.

(3) The effect of interaction between the grafting technique and the monomer employed is not significant.

B. Results of the Multiple Range Test

(1) There is no significant difference in toughness between the co-polymers made by the trapped radical method, the copolymers made by the peroxidized polymer method, or the pure Dacron polymer.

(2) There is a **significant** difference between **the trapped** radical co-
polymer and **the direct** radiation copolymer; **the toughness of the**
trapped **radical copolym**er is greater.

(3) However, **the toughness** of the copolymers made by the peroxidized
method **and the toughness** of the pure Dacron polymer are not
significantly greater than that of the direct radiation copolymer.

III. DYE ABSORPTION

A. Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees Freedom	Mean Square	Expected Mean Square	F	$F_{.05}$
Technique (T)	69.5554	2	34.777	$\sqrt{}o^2 + mdr\sqrt{}_T 2$	6.96×10^4	**3.55**
Monomer (M)	7.2618	1	7.262	$\sqrt{}o^2 + tdr\sqrt{}_M 2$	1.45×10^4	**4.41**
Dye (D)	13.4720	2	6.736	$\sqrt{}o^2 + tmr\sqrt{}_D 2$	1.35×10^4	**3.55**
Interaction (T)(M)	-37.0288	2	-18.514	$\sqrt{}o^2 + rd\sqrt{}_{TM} 2$	-3.7×10^4	**3.55**
Interaction (T)(D)	-31.4192	4	-7.855	$\sqrt{}o^2 + mr\sqrt{}_{TD} 2$	-1.57×10^4	**2.93**
Interaction (M)(D)	15.6739	2	7.834	$\sqrt{}o^2 + tr\sqrt{}_{MD} 2$	1.56×10^4	**3.55**
Interaction (T)(M)(D)	64.0660	4	16.017	$\sqrt{}o^2 + r\sqrt{}_{TMD} 2$	3.20×10^4	2.93
Residual (Error)	.0090	18	.0005	$\sqrt{}o^2$		
Total	101.5901					

(1) At the 5 per cent level of significance, the technique effect is highly significant.

(2)   The monomer **effect is** highly significant.

(3)   The dye **effect is** highly significant.

(4)   The **technique-mon**omer interaction is not significant.

(5)   The **technique**-dye interaction is not significant.

(6)   **The monomer**-dye interaction is highly significant.

(7)   **The** technique-monomer-dye interaction is highly significant, **presuma**bly because of the monomer-dye interaction.

(8)   Since the monomer-dye interaction is so large, it is necessary to **make** a separate analysis for each dye. From this analysis, the **best** grafting technique and monomer combination can be determined, **but** that combination applies only to the dye under consideration. **The** following statements are the results of the separate analyses:

   1. Acid Dye

      (a)   The technique and monomer effects are both sig-
            nificant. The Multiple Range Test indicates
            that the best technique is the direct radiation
            method and the best monomer is methyl acrylate.

   2. Basic Dye

      (a)   The technique and monomer effects are both sig-
            nificant. The Multiple Range Test indicates that
            the best technique is the direct radiation method
            and the best monomer is acrylic acid.

   3. Disperse Dye

      (a)   The technique and monomer effects are both sig-
            nificant. The Multiple Range Test indicates
            that the best technique is the direct radiation
            method and the best monomer is methyl acrylate.

B.   Results of the **Multiple Range Test**

(1)   The direct radiation method **copolymers absorb more dye.**

(2)   There is no significant **difference between the peroxidi**zed co-
polymers and the trapped-**radical copolymers.**

(3)   Since the **monomer-dye interaction is** so **large, Mu**ltiple Range
Tests on these items **have no meaning.**

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