

## Effect of Graft Copolymerization Conditions on Grafting Yield of AA and MA onto Polyester Fiber

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### Abstract

Polyester of linear homopolymer poly(ethylene terephthalate)(PET) was chemically modified through the formation of branched copolymer to improve the undesirable properties of fiber. Photo-induced graft copolymerization of the acrylic monomers acrylic acid (AA) and methyl acrylate (MA) in the liquid and vapor phase, respectively, onto N,N-dimethylformamide (DMF)-pretreated PET fibers was carried out. The effect of various synthesis conditions and DMF pretreatment of the PET on the graft yield was investigated. Grafting mechanism was analysed. The grafting was promoted by increasing DMF pretreatment temperature and amount of DMF retention in the fiber. The increasing biacetyl and monomer flow time, and irradiation time enhanced the grafting up to a certain amount and thereafter it decreased.

*Key words : acrylic acid, copolymerization, graft, methyl acrylate, polyester*

### I. Introduction

Polyester(PET) is very important to the fiber industry due to its desirable physical and chemical properties. It still has problems to be overcome with regard to its textile use, due to its chemical inertness, hydrophobicity and high crystallinity. These defects give problems in the areas of dyeing, comfort, and static properties. Therefore, many studies have been done to improve the undesirable properties of PET. Photo-induced graft copolymerization is one of the effective methods to modify the PET chemically. Using various monomers, the fiber properties of linear homopolymer PET can be controlled and modified through the formation of branched copolymer.

However, there are still some problems involved in obtaining deep grafting of monomers onto PET. The high crystallinity and chain orientation of PET restrict radical formation and monomer diffusion inside the fiber resulting in a grafting zone only in surface regions of the fiber. It provides only surface modification of PET fibers. Swelling of PET by solvent treatment prior to graft copolymerization was introduced as a method for deeper grafting into fibers. Depending on the solvent treatment conditions and the nature of the solvent, pretreatment can affect grafting quite differently.

In this study, the specific aim is to obtain graft copolymers of PET by the reliable procedures of photo-induced graft copolymerization of acrylic monomers onto PET using the vapor-phase or liquid phase methods and to establish

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the effects of several grafting conditions on graft yield, especially the effect of the DMF pretreatment.

## II. Theoretical Background

### I. Graft Copolymerization onto PET

Graft copolymerization techniques have been used to modify existing polymers thereby altering the surface properties of the fiber without changing the bulk polymer structure fundamentally. Graft copolymers can be tailored for specific end uses. This chemical modification technique for PET by grafting<sup>1)</sup> has been used widely compared to other methods such as corona discharge, oxidizing agent treatment, plasma polymerization and coating due to its durability. The surface properties of PET are very important in the fields of wettability, printing, antistatic and antistaining properties. Recently, studies on the depth of grafting have shown the degree of modification of bulk properties possible in PET fiber by graft copolymerization.

Solvent treatments prior to grafting have shown higher graft yields and differences in the distribution of grafts. Depending on the specific solvent-polymer interaction, grafting zones were found in the surface and subsurface region only or over the cross-section of the fiber<sup>2-4)</sup>. Therefore graft copolymerization can be used for the

modification of the bulk properties as well as the surface properties of the PET backbone. The most common technique of synthesizing graft copolymers is the use of free radical polymerization. The grafting effects can be controlled diversely by various grafting conditions, initiators, monomers and solvent pretreatment.

Graft copolymerization of PET can be initiated by normal chemical initiation, thermal decomposition, and irradiation techniques used in other conventional polymerizations<sup>5)</sup> including use of benzoyl peroxide, azobisisobutyronitrile, butyl peroxybenzoate,  $\gamma$ -radiation and photo irradiation. Addition of the metal salts such as Fe(II), Ni(II), and Cu(II) salts has been used very effectively for inhibition of homopolymer formation on the fiber surface, since homopolymer lowers the graft uptake of monomer and the complete removal of homopolymer is not guaranteed.

Avny, Rebenfeld and Weigmann<sup>6)</sup> investigated the solubility parameters of fourteen vinyl monomers and studied their uptake by PET finding a scattered bimodal distribution. The maximum and higher uptakes were observed with the monomers near the solubility parameters of PET,  $\delta=9.8$  (cal/cm<sup>3</sup>)<sup>1/2</sup> for the semirigid aromatic segment and  $\delta=12.1$  (cal/cm<sup>3</sup>)<sup>1/2</sup> for the flexible aliphatic ester. Those monomers act as additional swelling agents and restore the partially collapsed pre-swollen structure by solvent exchange between monomer

<sup>1</sup> Z. P. Yao, and B. R. Randy, "Surface Modification by Continuous Graft Copolymerization. III. Photoinitiated Graft Copolymerization onto Poly(ethylene Terephthalate) Fiber Surface", *Journal of Applied Polymer Science* 41 (1990): 1459-1467.

<sup>2</sup> I. F. Osipenco and V. I. Martinovicz, "Grafting on the Acrylic Acid on Poly(ethylene Terephthalate)", *Journal of Applied Polymer Science*, 39 (1990): 935-942.

<sup>3</sup> S. Tazuke, T. Matoba, H. Kimura, and T. Okada, "A Novel Modification of Polymer Surfaces by Photografting", ACS Symposium Series 121, Modification of Polymers, American Chemical Society, Washington, D. C. (1980): 17-241.

<sup>4</sup> J. E. Johnson, "X-Ray Diffraction Studies of the Crystallinity in Poly(ethylene Terephthalate)", *Journal of Applied Polymer Science II* (1959): 205-209.

<sup>5</sup> Y. Avny, L. Rebenfeld, and H.-D. Weigmann, "The *In Situ* Polymerization of Vinyl Monomers in Polyester Yarns", *Journal of Applied Polymer Science*, 22 (1978): 125-147.

<sup>6</sup> Y. Avny, L. Rebenfeld, and H.-D. Weigmann, *op. cit.*, p. 125.

and swelling agent.

## 2. Photo-Induced Graft Copolymerization of PET

The ultraviolet (UV) region of the spectrum contains powerful energy levels (eg. 70~90 Kcal associated with 3000~4000 Å)<sup>7</sup>. This is enough to lead to photochemical reactions, such as photopolymerization, photografting, photodegradation and photostabilization. Photo-induced graft polymerization is well known, and numerous studies have been carried out with the use of UV light for initiation under various grafting conditions using photosensitizers, monomers, solvents and fibers<sup>8,9</sup>. This process has several advantages in comparison with other chemical methods including little homopolymer formation, cheap and safe energy source for photoreaction, low-temperature reactions, and environmental advantages<sup>10</sup>.

Moreover, since PET is reasonably stable under UV irradiation, photo-induced graft copolymerization can be accomplished easily. The PET absorbs UV radiation mostly at 3130 Å and photodegradation occurs by direct chain scission of the bonds in the PET backbone. However, photografting of PET without photodegradation can be achieved by filtering out UV radiation below 3200 with a clear glass/pyrex

filter system. The impurities or additives, such as titaniumdioxide(TiO<sub>2</sub>) being used as delustrant in semi-dull polyester, can behave as photosensitizers when they are able to absorb UV light, but they do not act in the absence of oxygen and moisture in the system<sup>11</sup>.

However, free radicals are formed only on the surface of the PET fiber under moderate UV irradiation by which the depth of penetration is far less than by ionizing radiation<sup>12</sup>. Since the incident light is absorbed within a thickness of 1~3 μm, UV-initiated grafting has been limited to surface modification of a polymer, therefore suitable photosensitizers and preswelling agents are required for the penetration into the fiber. The grafting effects of photo-induced graft copolymerization can be controlled by the photografting conditions, photosensitizers and light sources as well as using preswelling agents and different monomers. Photosensitizers are added to activate the photosensitized reactions through indirect photolysis in photografting, if chemical reaction can not be initiated by UV light directly.

Kubota et al.<sup>13</sup> classified sensitizers into the four types of photo-initiation reactions in photografting depending on the function of photo-excited sensitizer: Sensitizers of aromatic ketone and quinone types such as benzophenone, biacetyl<sup>14</sup>, and anthraquinone belong to this cate-

<sup>7</sup> E. L. Lawton, and D. M. Cates, "Liquid-Induced Crystallization of Poly(ethylene Terephthalate)", *Journal of Applied Polymer Science*, 13 (1969): 899-909.

<sup>8</sup> H. Kubota and Y. Ogiwara, "Vapor Phase Photografting of Methyl Methacrylate on Polymer Films: Accelerating Effects of Solvent Mixed with Monomer", *Journal of Applied Polymer Science*, 38 (1989): 717-725

<sup>9</sup> Y. Ogiwara, M. Kanda, M. Takumi and H. Kubota, "Photosensitized Grafting on Polyolefin Films in Vapor and Liquid Phases", *Journal of Polymer Science: Polymer Letter Edition*, 19 (1981): 457-462

<sup>10</sup> J. F. Rabek, *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*, John Wiley & Sons Ltd. (1987) 240.

<sup>11</sup> M. J. Wall, G. C. Frank and J. R. Stevens, "A Study of the Spectral Distribution of Sun-Sky and Xenon-Arc Radiation in Relation to the Degradation of Some Textile Yarns, Part II: Spectral Distribution Studies", *Textile Research Journal*, 41 (1971): 38-43.

<sup>12</sup> G. Ordian, *Principles of Polymerization*, 2nd Ed. John Wiley & Sons, Inc. (1981).

<sup>13</sup> H. Kubota, K. Kobayashi, and Y. Ogiwara, "Comparative Examination of Sensitizers in Photografting on Polymer Films", *Polymer Photochemistry*, 7 (1986): 379-387.

<sup>14</sup> S. A. Siddiqui, K. McGee, W.-C. Lu, K. Alger and H. L. Needles, "Photo-induced Polymerization of Acrylic Acid on DMF-Wetted Polyester", *American Dye Staff Reporter*, 70 (1981): 20-43.

gory. They also examined the effect of 31 sensitizers on photografting of methacrylic acid, acrylic acid, and methyl methacrylic acid onto polyethylene, polypropylene, and nylon 6 films. Depending on the monomers and substrates, the effect of sensitizers varied widely with regards to photografting. Generally, aromatic ketones lead to high graft yield for the monomers used.

Vapor phase photografting technique has been studied to obtain even grafting and to limit the formation of homopolymer, which improves the aesthetic properties of the graft copolymer and enhances grafting, respectively. Vapor phase photografting of vinyl monomers onto various types of polymers have been investigated examining solvents and grafting conditions<sup>15</sup>.

### 3. Solvent Effect on Grafting

Solvent-induced preswelling and interaction have a drastic effect on grafting which is due to physical and chemical effects. First, solvents determine the depth of grafting depending on the degree of preswelling of substrates. Solvent-induced preswelling is controlled by solvent-polymer compatibility which is determined by the nature of the solvent and the polymer, the solvent treatment temperature, treatment time and tension for the constant length of polymer. Secondly, the solvent with active hydrogen atoms acts as a hydrogen donor in photografting. Solvent effects on grafting have been investigated widely under varying conditions and procedures, including solvent effects by pretreatment with solvent only, with mixed solvents, with solvent mixed with monomer, and

solvent effects in liquid phase grafting or under vapor phase photografting. Many strongly interacting solvents and solvent mixtures have been recommended for the swelling of PET before or during graft copolymerization including DMF<sup>16,17</sup> and 1,1,2,2-tetrachloroethane<sup>18</sup>.

In this review section, the effects of added solvents on grafting during the grafting process were not dealt with, but only effects of solvent pretreatment on grafting have been reviewed.

Kim<sup>19</sup> compared the effect of 13 preswelling solvents of varying solubility parameter (SP) on graft yield in formation of polyester-poly(acrylic acid) grafts (PET-g-PAA). He found the pretreatment of PET in solvents with a SP which was near that of the aromatic residue of PET promotes the graft yield extensively.

Needles and Alger<sup>20</sup> have polymerized MA vapors onto polyamide and polyester fibers pretreated with the polar solvents methanol, N,N-dimethylformamide, or dimethyl sulfoxide (neat and aqueous solution) at room temperature. Photografting was done without photosensitizers. Polyester gave highly limited PMA uptakes (0.1~1.8 %) and neat DMF as wetting solvent caused highest grafting (1.8 %) by allowing more monomer to penetrate into the fiber, but addition of water as cosolvent decreased the graft yield.

Seiber and Needles<sup>21</sup> have photografted a series of acrylic monomers of different volatilities and reactivities onto various fibrous substrates pretreated with water, methanol, n-propanol, benzene, dimethylsulfoxide, DMF or chlorinated hydrocarbon solvents at room tem-

<sup>15</sup> R. P. Seiber and H. L. Needles, "Photo-Initiated Vapor-Phase Grafting of Acrylic Monomers onto Fibrous Substrates in the Presence of Biacetyl", *Journal of Applied Polymer Science*, 19 (1975): 2187-2206.

<sup>16</sup> Y. Avny, L. Rebenfeld, and H.-D. Weigmann, *op. cit.*, p. 125.

<sup>17</sup> H. L. Needles, and K. W. Alger, "Photo-induced Polymerization of Methyl Acrylate Vapors on Pretreated Polyamide and Polyester Fibers", *Journal of Applied Polymer Science*, 22 (1978): 3405-3418.

<sup>18</sup> H. D. Kim, "Grafting of Hydrophilic Monomer onto Poly(ethylene Terephthalate) Fiber", *Journal of Engineering College of Pusan University*, 27 (1975): 349-355.

<sup>19</sup> H. D. Kim, *op. cit.*, p. 349.

<sup>20</sup> H. L. Needles, and K. W. Alger, *op. cit.*, p. 3405.

<sup>21</sup> R. P. Seiber, and H. L. Needles, *op. cit.*, p. 2187.

perature. Photo-induced polymerization occurred in the vapor phase in the presence of biacetyl as initiator. They showed the dramatic effect of wetting solvents on grafting, the degree of grafting increased with the wetting and wet-pickup on the fabric and use of a wetting solvent with an affinity for the biacetyl vapors and monomer vapors favored grafting. They obtained 1.2 % and 8.2 % uptake grafted poly(acrylic acid) (PAA) and poly(methyl acrylate) (PMA) on PET, respectively. Later, Siddiqui et al.<sup>22)</sup> established the higher graft yield (up to 5.1 %) of PAA on polyester pretreated with DMF at 120 Å. From this result it could be deduced that pretreatment of PET with DMF at high temperature would promote the grafting of AA and MA monomer onto PET through the changes in the internal morphology of PET.

Avny, Rebenfeld and Weigmann<sup>23)</sup> investigated the effect of DMF pretreatment on PET yarns prior to grafting with various vinyl monomers. The pretreatment at high temperatures (above 120 Å) led to high graft yields due to the stable swollen structure formed. However, the swollen structure at low treatment temperatures was unstable and collapsed after removal of DMF, which resulted in a low graft uptake.

Tazuke et al.<sup>24)</sup> examined the effect of solvent on grafting rate and surface photografting. Nonpolar polymers had higher affinity for nonpolar solvents, resulting in deep grafting. Using ESCA, they measured the surface concentration of the grafts on the grafted polymer treated with different solvents and proposed three different graft layer locations depending on the solvent polarity used: surface grafting, surface and subsurface grafting, and internal grafting.

Kubota et al.<sup>25)</sup> investigated solvent effects on vapor phase photografting of methyl methacrylate onto polyester films, and obtained enhancement of grafting with certain mixtures of monomer and solvent that cause substrate swelling and result in promotion of radical formation.

Osipenko and Martinovicz<sup>26)</sup> treated PET films in dichloroethane at 20°C for 1-60 minutes before grafting with acrylic acid. They found that dichloroethane preswollen PET showed higher graft yields than untreated PET. Also preswelling led to distribution of PAA throughout the film unless there was localization on the film surface. They concluded that changes in sorption-diffusion behavior of the initiator and monomer affect the graft yield and grafting zone.

Yao and Rånby<sup>27)</sup> found three ketones (acetone, methyl ethyl ketone, and methyl propyl ketone) used for pretreatment were effective, especially acetone, in higher rates of photografting of AA and acrylamide onto PET. They suggested that the role of ketone as a photo-initiator was that of a Norrish Type I. However, they could not say to what extent the excited carbonyl groups in solvents participated in grafting reaction.

### III. Experimental

#### 1. Materials

Dacron type 54 polyester fabric (catalog No. 767 from Test fabrics, Inc.) was used. It consisted of semicrystalline, oriented spun fibers.

#### 2. Chemicals

AA, MA and biacetyl were reagent grade

<sup>22</sup> S. A. Siddiqui, K. McGee, W.-C. Lu, K. Alger and H. L. Needles, *op. cit.*, p. 20.

<sup>23</sup> Y. Avny, L. Rebenfeld and H.-D. Weigmann, *op. cit.*, p. 125.

<sup>24</sup> S. Tazuke, T. Matoba, H. Kimura and T. Okada, *op. cit.*, p. 17.

<sup>25</sup> H. Kubota and Y. Ogiwara, *op. cit.*, p. 717.

<sup>26</sup> I. F. Osipenko and V. I. Martinovicz, *op. cit.*, p. 935.

<sup>27</sup> Z. P. Yao and B. R. Randy, *op. cit.*, p. 1459.

from Aldrich Chemical Co. DMF and phenol were reagent grade from Fisher. DMF was used after distillation (BP=153 °C).

### 3. Light Source

A high-pressure quartz mercury-vapor lamp (Ace-Hanovia Lamp Cat. No. 6515-32, from Ace Glass Inc.) was used as a source of ultraviolet radiation. The lamp wattage is 200W and the arc-length is 12cm.

### 4. DMF Pretreatment Procedure

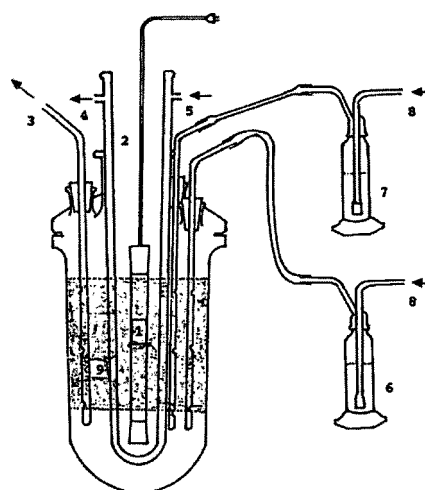
The polyester fabrics (10×20 cm<sup>2</sup>) were immersed in DMF at 60, 100, 120, and 140°C for 10 minutes without tension. After treatment, DMF-treated fabrics were air-dried or oven-dried in the vacuum oven at 60°C for 48 hours. Samples of DMF-treated at 120°C were used for evaluation.

### 5. Copolymer Synthesis Procedure

#### 1) Vapor Phase Photografting Conditions

Photo-initiated vapor-phase grafting of methyl acrylate onto PET fibers in the presence of biacetyl was carried out at room temperature and under a nitrogen atmosphere, using a simple photoreactor system as shown in (Fig. 1). Prior to the graft copolymerization, two polyester fabric samples pretreated with DMF were stapled on to a cylinder-shaped screen. The screen with attached samples was placed in a 3-liter resin reaction kettle so that they conformed to the wall. In the center of the reactor was a Pyrex cold finger containing a UV lamp.

Biacetyl was used as a photosensitizer to initiate the reaction effectively. It was placed in a gas bubbler, and biacetyl vapors carried by nitrogen gas (10 cc/sec) were allowed to flow into the reactor through the gas inlet located in the top of the reactor. Biacetyl vapor diffused onto the sample fabric, and initial flushing of biacetyl and nitrogen expel the oxygen and moisture in the system through the gas outlet and prevented inhibition of the photo reactions. After initial flushing of biacetyl for a given



(Fig. 1) Apparatus of Vapor Phase Photografting of MA onto PET.

(1) UV Lamp, (2) Pyrex Cold Finger, (3) Gas Outlet, (4) Water Outlet, (5) Water in, (6) Biacetyl, (7) Methyl Acrylate, (8) Nitrogen Gas, (9) Shaded Areas: Nylon Screen.

length of time, its flow was continued or discontinued during irradiation and monomer flow.

Graft copolymerization began when the fabric surface was irradiated with near UV region for a given length of time. The 200 W UV light was used as an energy source to initiate the radical formation. To avoid the direct photolysis of the PET, the far and mid UV region (under 3200 Å) was pyrex-filtered. The distance between the lamp and the fabric surface was 6 cm. Methyl acrylate monomer was placed in the bubbler through which nitrogen was bubbled, and monomer vapor was carried into the reactor at 10 cc/sec for a given length of time with simultaneous or subsequent irradiation.

Photografting was terminated by ceasing the irradiation, and monomer and biacetyl flow. Then samples were removed from the reactor and washed in boiling water for 3 hours, and air-dried, conditioned and weighed. Reaction conditions for the PMA photografting procedures and MA monomer uptake were examined.

### 2) Liquid Phase Photografting Conditions

Photo-initiated liquid-phase grafting of acrylic acid onto PET fibers was carried out under the same experimental conditions as vapor phase photografting mentioned previously except for dealing with the monomer. The DMF-pretreated polyester fabrics were presoaked with various amounts of AA monomer, and excess monomer was removed using a paper pad to a wet pickup of usually 50 %. Then, two sample fabrics were placed in the reactor and irradiated in the presence of biacetyl. After termination of photografting, PAA homopolymers were removed by washing with boiling water for 3 hours. The sample fabrics were air-dried, conditioned and weighed. Reaction conditions for the PAA photografting procedures and AA monomer uptake were examined.

### 3) Graft Yield Calculation

The degree of grafting was determined by weight gain according to the following equation:

$$\text{Graft yield (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

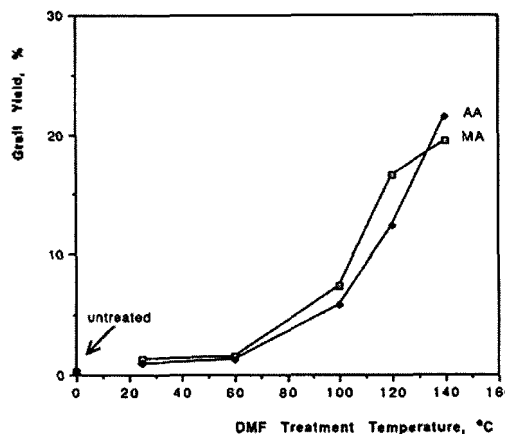
where  $W_0$  is the conditioned sample weight before grafting, and  $W_1$  is the conditioned sample weight after grafting and washing the homopolymer.

## IV. Results and Discussion

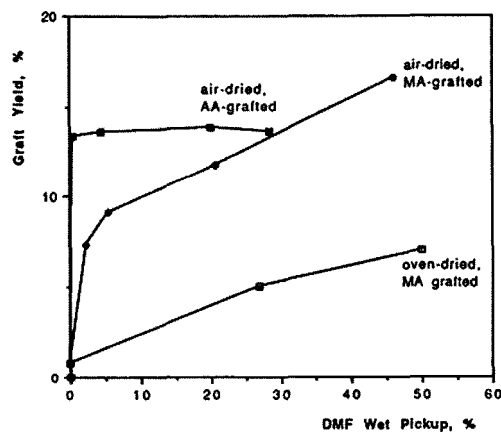
### 1. Effect of DMF Pretreatment on Graft Yields

The effect of DMF pretreatment temperature on PET prior to photografting and DMF retention in DMF-treated PET during the photografting of AA and MA were investigated. The results are represented in <Fig. 2> and <Fig. 3>, respectively. As shown in <Fig. 2>, the DMF pretreatment provides tremendous increases in graft yields with increasing DMF treatment temperature. Without DMF pretreatment, little grafting of AA and MA occurred. <Fig.

3> shows that the residual DMF in DMF-treated PET affects the grafting of AA and MA remarkably. The oven-dried PET sample, where there is no DMF residues and no DMF wet-pickup after oven drying, shows remarkably lower graft yields than air-dried PET's that has never been dried completely. DMF wet-pickup after oven drying enhances the grafting of MA onto oven-dried PET.



<Fig. 2> Effect of DMF Treatment Temperature on Photografting of MA and AA onto DMF-pretreated PET.



<Fig. 3> Effect of DMF Retention in DMF-pretreated PET on Photografting of MA and AA.

The quantity of graft yield correlates with changes in fiber diameter, longitudinal shrinkage, weight loss of the fiber after DMF treatment and some parameters of internal morphology and selective properties of DMF-treated PET fibers<sup>28)</sup>. Lateral swelling of the fiber, removal of low molecular weight oligomers, and DMF-induced recrystallization and rearrangement of PET fibers results in void formation that enhances its sorption and diffusion properties; the fast and deep diffusion of monomers into the fiber promotes high monomer uptake and spreads out the grafting zone over the cross section.

DMF retained in the DMF-treated PET has a very important role in grafting. DMF removal from the fiber by oven-drying may cause complete or partial collapse of the DMF-swollen structure, whereas the remaining DMF in samples air-dried at room temperature and exchanged with the monomers would lead to minimal collapse and support of the swollen structure to give the reaction for growing grafted chains. Weigmann et al.<sup>29,30)</sup> have suggested that after removal of DMF, the small crystallites formed during DMF treatment can not support the swollen structure and collapse consequently, which results in the partial restoration of the original state. Also residual DMF in the fiber may act as a plasticizer by interrupting the secondary forces between adjacent PET molecules and interacting with the ester groups in PET, allowing monomers to diffuse faster into the fiber to enhance grafting.

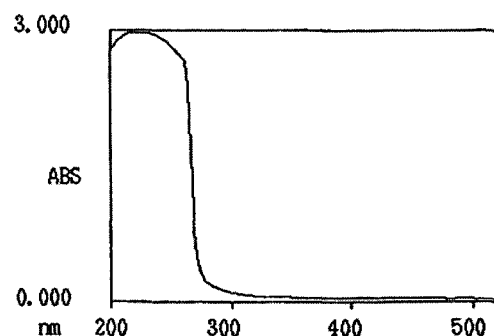
Viewing the role of DMF from the standpoint of photografting, there is no possibility that

DMF contributes to the photosensitized reaction as a photosensitizer, since DMF has no absorption band above 280nm under radiation as represented in (Fig. 4).

## 2. Effect of Irradiation Time on Graft Yields

The effect of irradiation amount on the photografting of MA and AA was examined by changing exposure time during the polymerization. The results are shown in (Fig. 5). With increasing irradiation time, there is an increase in the graft yield for both AA and MA monomers up to certain point, beyond that a decrease is noticed.

The irradiation results in the formation of radical species of both PET backbone and monomers. The amount of those free radicals formed during the irradiation presumably depend on the dose proportionally<sup>31)</sup>. The greater number of free radicals would be produced at the prolonged irradiation time, and a higher opportunity for homopolymerization might be expected with increased monomer radicals. This homopoly-



(Fig. 4) Absorption Spectrum for DMF.

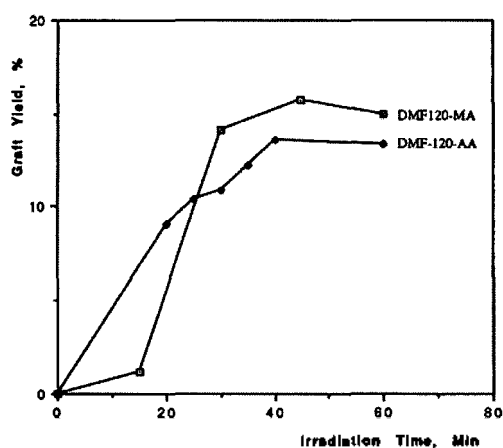
<sup>28</sup> M.-J. Park, "Dyeing Study on DMF-modified Polyesters for Morphology Characterization", *The International Journal of Costume Culture*, 5 (2002): 131-143.

<sup>29</sup> H.-D. Weigmann, M. G. Scott, A. S. Ribnick and L. Rebenfeld, "Interactions of Nonaqueous Solvents with Textile Fibers, Part VII: Dyeability of Polyester Yarns After Heat and Solvent-Induced Structural Modifications", *Textile Research Journal*, 46 (1976): 574-587.

<sup>30</sup> A. S. Ribnick, H.-D. Weigmann and L. Rebenfeld, "Interactions of Nonaqueous Solvents with Textile Fibers. Part I: Effects of Solvents on the Mechanical Properties of the Polyester Yarn", *Textile Research Journal*, 42(1972): 720-726.

<sup>31</sup> H. L. Needles, S. Holmes and M.-J. Park, "The Dyeing and Color Characteristics of Disperse-Dyed Alkali-treated Polyester", *Journal of the Society of Dyers and Colorists*, 106 (1990): 385-388.





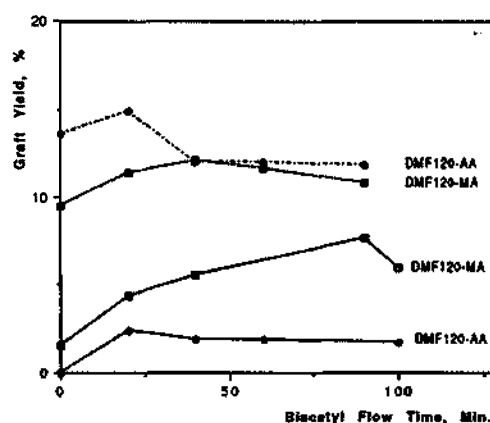
⟨Fig. 5⟩ Effect of Irradiation Time on Photo-grafting of MA and AA onto DMF-pretreated PET.

merization on the fiber surface would cause a decrease in the rate that monomers diffuse into fiber matrix. Therefore, the amount of monomer available is lower at the grafting sites on PET backbone, which results in a decrease in the grafting efficiency in the final stages of polymerization.

### 3. Effect of Biacetyl Flow Time on Graft Yields

The effect of biacetyl photosensitizer on the photografting of MA and AA was investigated by changing its amount before and during the irradiation. As shown in ⟨Fig. 6⟩, the graft yield increases up to certain amount of biacetyl and thereafter decreases with increasing biacetyl amount. Initial biacetyl flow before irradiation enhances the MA-grafting greatly but AA-grafting slightly. Biacetyl flow during the irradiation gave a tremendous improvement in both MA-, and AA-grafting in the initial polymerization reaction stages.

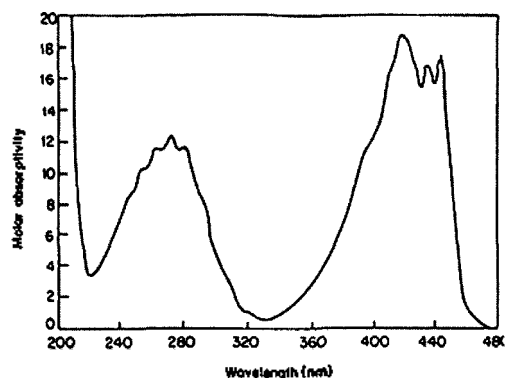
As represented in ⟨Fig. 7⟩, biacetyl has two absorption bands at 254 nm (which was filtered out in this system) and 430 nm under irradiation. As biacetyl flow time increases, the extensive amount of biacetyl absorbs UV in the near and visible, and it is excited and disso-



⟨Fig. 6⟩ Effect on Biacetyl Flow Time on Photo-grafting of MA and AA onto DMF-pretreated PET.

— Initial biacetyl flow only for each time without final flow during irradiation.

--- Initial biacetyl flow for each time with final flow for 60 min. during irradiation.



⟨Fig. 7⟩ Absorption Spectrum for Biacetyl.

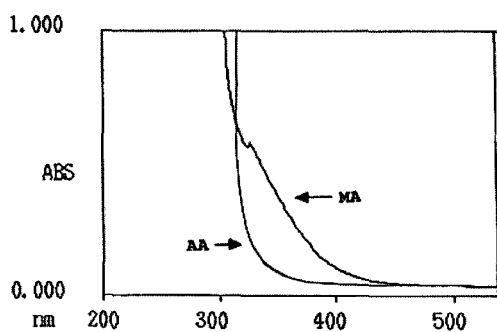
ciated to give sufficient acetyl radicals that are capable of initiating reactions and enhancing the graft yield. Moreover, initial biacetyl flow with nitrogen is assumed to eliminate the oxygen and moisture in the system that inhibit grafting through terminating the growing polymer chains. Decreases in graft yield at higher biacetyl amount might be due to (i) the reduction of radical sites by termination of growing chains with excess radicals and (ii) the formation of

homopolymer on the fiber surface which hinders the further reaction.

No initiation of PAA photografting is observed without the sensitizer biacetyl. Therefore, it is certain that DMF-pretreated PET is not responsible for initiation of polymerization through monomer vapors diffusing into the fiber in this photografting system. Even PET absorbed significant UV radiation in the region of 3130 ~3400 Å and mostly 3130 Å<sup>32,33</sup>, irradiation might not lead to bond cleavage in PET directly under the conditions in this system, which could result in free radicals in the fiber that could initiate graft polymerization. No evidence of DMF radicals to initiate graft polymerization is found. Only indirect photolysis by biacetyl activates the photografting of AA.

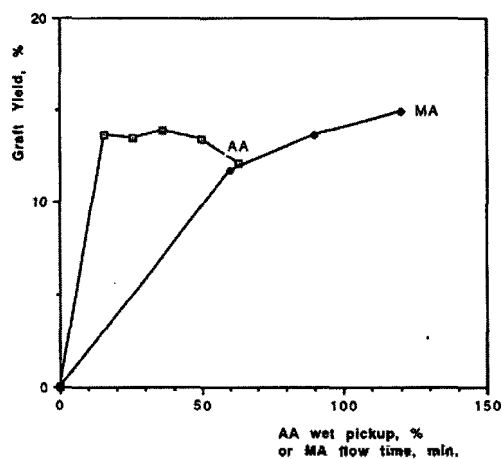
Contrasted to the result of PAA photografting, a little initiation of PMA photografting is shown in the absence of biacetyl. As shown in (Fig. 8), AA does not absorb near UV (3200 ~4000 Å), but MA absorbs small amounts of it, then the UV absorbed MA is excited and produces monomer radicals, which can act as a photosensitizer.

#### 4. Effect of Monomer Amount on Graft Yields



(Fig. 8) Absorption Spectrum for MA and AA.

The effect of monomer amount on the graft yield was investigated by varying MA flow time and AA wet pick-up. The results are shown in Fig. 9. The graft yield rises up to a certain monomer amount and thereafter it decreases. The possible reasons for the increases in graft yield include (i) PET fibers continue complexation with the monomers which enhances monomer activity and (ii) monomers may themselves behave as sufficient swelling agents that contribute to swelling the fiber and gel effects. However, polymerization with the excess AA monomer by the liquid phase system, does not give a higher graft uptake. This subsequent decrease in the graft yield might be due to the homopolymerization of PAA formed as transparent 'gel' phase on the surface through a faster rate of combination of growing radicals with the monomer, which reduces the apparent monomer amount and hinders UV penetration and biacetyl diffusion.



(Fig. 9) Effect of Monomer Amount on Photografting of MA and AA onto DMF-pretreated PET.

<sup>32</sup> M. J. Wall and G. C. Frank, "A Study of the Spectral Distribution of Sun-Sky and Xenon-Arc Radiation in Relation to the Degradation of Some Textile Yarns, Part I: Yarn Degradation", *Textile Research Journal*, 41 (1971): 32-38.

<sup>33</sup> M. J. Wall, G. C. Frank and J. R. Stevens, "A Study of the Spectral Distribution of Sun-Sky and Xenon-Arc Radiation in Relation to the Degradation of Some Textile Yarns, Part II: Spectral Distribution Studies", *Textile Research Journal*, 41 (1971): 38-43.

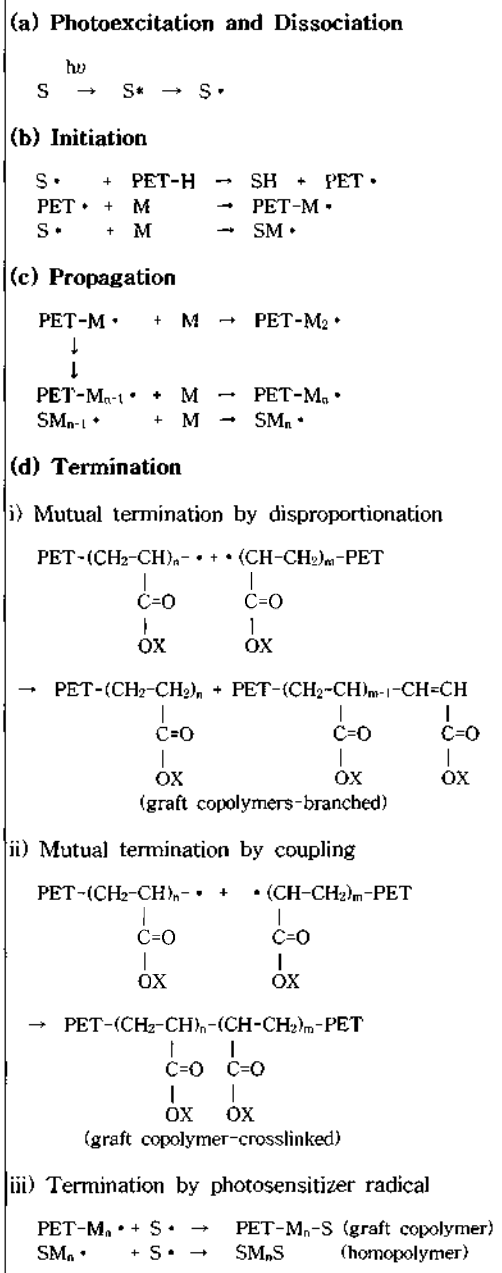
### 5. Mechanism of Photografting

The main mechanism for photografting of MA and AA onto PET in the presence of biacetyl under the conditions in this system is proposed, and represented in (Fig. 10)(a)-(d). It is as follows: biacetyl under UV is excited and photolyzed to produce acetyl radicals (Fig. 10-(a)). This photoexcited sensitizer or the free radicals directly abstract accessible hydrogen atoms from the aromatic rings and ethylene groups of PET backbone, which gives the sites for monomers to graft onto the PET fibers, and the first monomer is introduced on the substrate radical (Fig. 10-(b)). Monomers continue to attach onto the sites (Fig. 10-(c)) and growing chains are then terminated by some way (Fig. 10-(d)). As the reaction ends, PET and biacetyl radicals are deactivated to a stable form.

Titanium dioxide (TiO<sub>2</sub>) used as delustrant in semi-dull polyester, which was used in this study, can behave as a photosensitizer because it is able to absorb UV light. However, it may not affect the photografting mechanism in the absence of oxygen and moisture in this system.

### V. Conclusion

The photo-induced graft copolymerization of the two acrylic monomers (acrylic acid and methyl acrylate) onto DMF-pretreated PET fiber was carried out using liquid and vapor phase photografting technique. Graft uptake was dependent on DMF pretreatment, DMF pretreatment temperature, amount of DMF retention in the fiber and synthesis conditions; monomer concentration, irradiation time and biacetyl initiator concentration. The grafting of both AA and MA monomers was enhanced up to optimal level and thereafter it decreased. The optimal synthesis conditions were obtained. DMF-pretreatment of PET prior to graft copolymerization caused the changes in the internal morphology of the fiber that resulted in increases the diffusion properties of the monomers into the PET fiber and promote the grafting effect. Mechanism of photografting was proposed: acetyl



**(Fig. 10)** Schematic Mechanism of Photografting of MA or AA onto PET.

(where S, S\* and S· represent biacetyl, photoexcited biacetyl and fragment radicals of biacetyl, respectively. PET· is free radical formation of PET. M and M· are monomers and their radicals. m and n are number of monomer repeat units. X is H (for acrylic acid) or CH<sub>3</sub> (for methyl acrylate).

radicals produced from excited biacetyl initiator under UV abstract hydrogen atoms in PET backbone, which gave the sites for monomer growing. Then, copolymers of PET-g-PAA and PET-g-PMA were synthesized.

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