

The *In Situ* Polymerization of Vinyl Monomers in Polyester Yarns

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Synopsis

The effects of a pretreatment of polyester (PET) yarns with a strongly interacting solvent such as dimethylformamide (DMF) on vinyl monomer incorporation were investigated. When the DMF pretreatment is carried out at high temperatures (above 120°C), the swollen PET structure is stabilized by solvent-induced secondary crystallization. This substrate is highly suitable for the incorporation of vinyl monomers. *In situ* polymerization of vinyl monomers in DMF-treated PET was investigated using chemical and γ -irradiation polymerization techniques, both in the presence and in the absence of excess monomer outside the PET fibers. When polymerization was carried out in a system in which a constant supply of free radicals was available from the outside of the PET fibers, lower initiator concentrations and smaller γ -irradiation doses were necessary. These results are attributed to a low efficiency of the initiator inside the PET fiber due to mobility restrictions. Water uptake and moisture regain of PET yarns containing poly(hydroxyethyl methacrylate) and poly(acrylic acid) were also investigated. When most of the vinyl polymer was inside the PET fiber, water absorption was limited. The changes in mechanical properties of the PET yarns resulting from the DMF pretreatment were partially reversed by *in situ* polymerization of vinyl monomers.

INTRODUCTION

Continuous filament and spun polyester (PET) yarns are becoming of increasing importance in the textile industry. Despite the highly desirable chemical and physical properties of these yarns, means are constantly being sought to improve various properties of PET. The essentially hydrophobic character of PET, as reflected in its low ($\sim 0.4\%$) standard moisture regain, is at the heart of certain problems associated with polyester textiles. Often quoted problems focus on soil retention, static properties, dyeability, and comfort.

The *in situ* bulk polymerization of vinyl monomers in PET and the graft polymerization of vinyl monomer to PET are potentially useful tools for the chemical modification of this polymer. The distinction between *in situ* polymerization and graft polymerization is a relatively minor one, and from a practical point of view may be of no significance. In graft polymerization, the newly formed polymer is covalently bonded to a site on the host polymer (PET), while the *in situ* bulk polymerization of a vinyl monomer results in a polymer that is physically entrapped in the PET. The existence of a covalent bond after graft polymerization has not always been conclusively established, and it is not known whether the lack of solubility of a newly formed polymer is due to the covalent linkage or due to physical entrapment of the polymer.

In the work described in this report, no attempt has been made to achieve a true graft polymerization, although it is possible that some grafting did take place in certain instances. The principal purpose of this work was to achieve the *in*

situ polymerization of vinyl monomers in PET and to establish the effects of several process variables on the quantity of polymer formed, particularly on the location of the polymer within the yarn and fiber structure. A special feature of this work involved the investigation of a solvent pretreatment of the polyester, which has been shown to have a major influence on the PET fine structure.

Many useful applications of vinyl monomer polymerization for the chemical modification of PET can be visualized, and many have been reported in the literature. For example, the polymerization in PET of acrylic acid,¹⁻³ hydroxyethyl methacrylate,^{4,5} and N-vinylpyrrolidone^{6,7} have been reported. These and other monomers that yield strongly hydrophilic and even water-soluble polymers should lead to an increase in the moisture regain of the PET, resulting in improved antistatic properties, soil release properties, and comfort characteristics. Dyeability of PET can also be modified by vinyl monomer polymerization. For example, if an acidic monomer such as acrylic acid is polymerized within PET, the modified PET can be dyed with basic dyes²; if a basic monomer such as vinyl pyridine is used,^{8,9} the modified PET can be dyed with acid dyes. Flame retardancy can be improved by polymerization of bromine-containing monomers in PET.¹⁰ The incorporation of suitable vinyl polymers in PET has also found medical applications. For example, PET sutures¹¹ containing poly(acrylic acid) with long-lasting germicidal properties were obtained by attaching antibiotics to the poly(acrylic acid) in the PET.

Most of the known chemical initiation and irradiation techniques of polymerization have been applied to PET. In the case of chemical initiation, the conventional free-radical polymerization initiators such as benzoyl peroxide,² hydrogen peroxide,⁷ and persulfate ion⁵ have been used. Purely thermal initiation has also been used.³ It is reasonable to expect that although unextractable polymers were incorporated in the PET, true graft polymers were not always achieved. Specific attempts to obtain true graft polymers by chemical means were reported. Even the ceric ion grafting technique, which is used for vinyl monomer graft polymerization on cellulose, was applied to PET.¹²

Radiation modification of textile fibers, including PET, has been reviewed in detail by Stannett and Hoffman¹³ and later by Hoffman.¹⁴ PET is one of the most irradiation-stable fiber-forming polymers and can withstand irradiation doses up to 2×10^7 rad before noticeable chemical degradation takes place.^{15,16} As a result, grafting and polymerization of vinyl monomers can be accomplished easily by irradiation techniques. Both γ irradiation and high-energy electron beams have been used. Irradiation can be applied in different ways. Polymerization can be accomplished either by mutual irradiation of the monomer and of the PET or by preirradiation of the PET prior to the introduction of the vinyl monomer.

The kinetics of γ irradiation-induced grafting of styrene to PET fibers has been studied by Valagin and Stannett.¹⁷ The grafting rate was found to increase with temperature but reached a maximum in the vicinity of the PET glass transition temperature. Sakuroda et al.¹⁸ investigated graft polymerization of styrene onto PET by γ irradiation using both mutual and preirradiation techniques. Although formation of true graft polymers was proven, the extent of grafting was very low even with preirradiation doses as high as 1.4×10^7 rad. When either chemical or irradiation polymerization techniques are used, considerable amounts of polymer are always formed on the surface of the PET fibers.

Removal of that polymer requires tedious and time-consuming extraction procedures, and complete removal of excess surface polymer is not always achieved. In order to limit the extent of this surface polymer, the use of certain transition metal salts has been recommended, and cupric salts were found to be the most effective.¹⁹

Severe experimental conditions are generally recommended for the polymerization of vinyl monomers in PET. In the case of γ irradiation, doses much higher than those sufficient for the polymerization of vinyl monomers in bulk or in solution are required. Extended reaction times and elevated reaction temperatures are always recommended.

Swelling of the PET host fiber is essential. In any heterogeneous reaction system, the substrate must be swollen so that the reactants may diffuse easily into the internal structure. The importance of swelling and diffusion during a graft polymerization process is well known. When grafting is carried out on a hydrophobic fiber such as PET, some vinyl monomers may themselves act as sufficient swelling agents. For example, it was reported² that a 50% aqueous acrylic acid solution was adequate both for swelling and for grafting of that monomer to PET. Normally, however, a separate swelling solvent is needed. Many solvents have been recommended as swelling agents during graft polymerization of PET, among them pyridine,²⁰ acetic acid,²¹ methanol,¹⁸ and various chlorinated hydrocarbons such as ethylene dichloride,^{22,23} trichloroethylene, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane.²⁴ Solvent mixtures have also been recommended. DMSO and water mixtures were used as swelling systems in the grafting of styrene to PET by γ irradiation.¹⁷ Mixtures of dichloroethane and water and of tetrachloroethane and water² were used in the grafting of other vinyl monomers. The vinyl polymerization in the PET is usually carried out in the presence of the swelling solvent, thereby maintaining the swollen PET structure during polymerization. The swollen structure allows the monomer to diffuse in sufficient quantities to react at the active centers that have been produced either by chemical initiation or by irradiation before termination takes place.

The use of a swelling solvent as a pretreatment prior to incorporation of the monomer and polymerization is less common but has been reported.² Successful grafting of acrylic acid and of acrylonitrile to PET was achieved after pretreatment of the PET with tetrachloroethane/water and dichloroethane/water mixtures at 90–95°C for 2 to 3 hr. Excess chlorinated hydrocarbons were removed by successive treatments with boiling alcohol and boiling water.

It was recently shown²⁵ that pretreatment of PET yarns with certain strongly interacting solvents such as DMF, tetrachloroethane, and γ -butyrolactone can lead not only to swelling but also to irreversible modifications of the fiber structure. The modified PET structure permits rapid diffusion of disperse dyes under atmospheric conditions without addition of carriers. The basis of the structural modification during the DMF treatment of PET yarns is solvent-induced crystallization which occurs while the PET structure is swollen by DMF. At low treatment temperatures, only small crystallites are formed; and after removal of the solvent, the swollen structure cannot be supported by the small crystallites and consequently collapses. When the DMF treatment is carried out at higher temperatures, formation of larger crystallites occurs. These larger and more stable crystallites are capable of supporting the solvent-swollen

structure to a greater extent so that total collapse of the swollen structure upon removal of the solvent is prevented.

The open structure left after the DMF treatment dramatically increases the rate of disperse dye diffusion and dye uptake by the PET. Encouraged by these results, an investigation of the possible use of this treatment for incorporation and polymerization of vinyl monomers in PET fibers was carried out. Though investigation was limited to the effects of a DMF pretreatment, the concept is of much broader interest. It is considered that this treatment can be used as a model for other solvent treatments that would lead to similar irreversible structural changes in a swollen PET yarn.

This report summarizes initial studies of the incorporation and subsequent polymerization of several vinyl monomers in PET that has been pretreated in DMF.

EXPERIMENTAL

Materials. PET yarns (du Pont Dacron 55, 70-34-R02) were used. The following monomers were used: butyl methacrylate (Matheson Coleman & Bell); ethyl methacrylate and butyl acrylate (Celanese); methyl methacrylate (J. T. Baker Chemical Company); ethylene dimethacrylate and 4-vinylpyridine (Chemical Procurement Laboratories Inc.); 4-bromostyrene, N-vinyl-2-pyrrolidone, methacrylic acid, divinylsulfone, and acrylic acid (Aldrich Chemical Company); and styrene, acrylonitrile, and 2-hydroxyethyl methacrylate (Eastman Kodak Company). The monomers were redistilled when used for polymerization. Initiators used were azobisisobutyronitrile and benzoyl peroxide (Eastman Kodak Company), and *tert*-butyl peroxybenzoate (Aldrich Chemical Company, Inc.).

DMF Treatment of PET Yarns. Skeins of PET yarns (60 yards, 0.42 g) were exposed to DMF at 140°C (or at any other specified temperature) for 2 min. The yarns were washed first with cold water and then with boiling water for 0.5 hr. The yarns were dried first in air and then under vacuum in the presence of Drierite.

Monomer Incorporation. DMF-treated PET skeins (60 yards, 0.42 g) were exposed to (40 ml) monomer for six days. Excess monomer was removed by centrifugation for 1 hr at ~500 g over glass beads in a closed centrifuge tube. When monomer was introduced by a solvent exchange technique, a similar procedure was followed. After the DMF treatment, excess DMF was removed by pressing the PET skeins with a paper towel. The PET skein was left in monomer which was exchanged four times during four days.

Polymerization. Polymerization by γ irradiation was carried out using a ^{60}Co source. Samples were irradiated in closed glass vials under nitrogen. Irradiation rate was 1.04 Mrad/hr. Chamber temperature was 49°C.

Water Uptake and Moisture Regain. Water uptake was determined after equilibration of the specimens for four days in water at 21°C. Weight increase was determined after centrifugation at ~500 g for 1 hr. Moisture regain was determined at 65% R.H. Yarn skeins were conditioned for 48 hr at 65% R.H. and 21°C before weight increase was determined.

Mechanical Properties. Mechanical properties were determined on the Instron tensile tester using standard methods.

Dyeing of PET Yarns Containing Poly(acrylic Acid). PET yarns containing poly(acrylic acid) were exposed to a 0.5% aqueous Methylene Blue solution at 100° for 3 hr. The yarns were washed first with cold water and then for 2 hr with boiling water and dried. DMF-treated PET was dyed similarly. Microtome cross sections were taken in order to establish the location of the polymer in the fiber cross section.

Staining of PET Yarns Containing 4-Vinylpyridine. Microtomed cross section of PET yarns containing poly(4-vinylpyridine) and DMF-treated PET yarns fixed on a microscope slide were left for 10 min in a bromine atmosphere. Excess bromine was removed by washing with methanol.

Redox Initiation of In Situ Polymerization of 4-Vinylpyridine. DMF-treated PET skein (0.42 g) was left in 4-vinylpyridine for 48 hr and was transferred to a solution of 4-vinylpyridine (4 ml) in water (8 ml). A mixture of 2% $\text{Na}_2\text{S}_2\text{O}_5$ in water (25 ml) and 0.4% $\text{K}_2\text{S}_2\text{O}_8$ in water (35 ml) was added. Polymerization was carried under nitrogen at room temperature for 20 hr. The PET yarns were extracted with pyridine for 24 hr, washed with methanol, and dried. Weight increase of 13.7% was determined.

RESULTS AND DISCUSSION

Monomer Incorporation

The vinyl monomers used in this study, with the abbreviations used in the remainder of this report, are shown in Table I. The uptake by PET pretreated with DMF of three of these monomers is shown in Figure 1 as a function of the DMF treatment temperature. The DMF was removed from the PET by boiling water; and after drying, the yarns were exposed to the monomer. After monomer diffusion was complete (four days at room temperature), excess monomer was removed by centrifugation and monomer uptake determined from weight increase measurements. It can be seen that only in the case of DMF pretreatments at elevated temperatures, when solvent-induced crystallization in the swollen state takes place, is the monomer uptake increased significantly. The data in

TABLE I
Vinyl Monomers Used

| Monomer | Abbreviation | No. |
|---------------------------|--------------|-----|
| Butyl methacrylate | BMA | 1 |
| Ethyl methacrylate | EA | 2 |
| Butyl acrylate | BA | 3 |
| Methyl methacrylate | MMA | 4 |
| Styrene | S | 5 |
| Ethylene dimethacrylate | EDMA | 6 |
| 4-Bromostyrene | 4-BrS | 7 |
| 4-Vinylpyridine | 4-VP | 8 |
| Acrylonitrile | AN | 9 |
| N-Vinylpyrrolidone | NVP | 10 |
| Hydroxyethyl methacrylate | HEMA | 11 |
| Methacrylic acid | MAA | 12 |
| Acrylic acid | AA | 13 |
| Divinylsulfone | DVS | 14 |

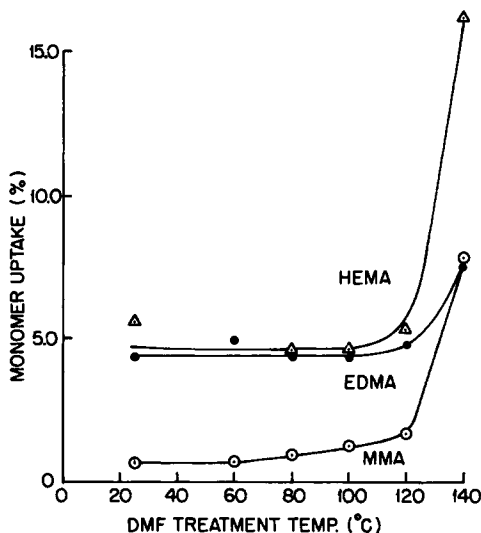


Fig. 1. Uptake of vinyl monomers by DMF-treated PET yarns as a function of DMF treatment temperature.

Table II indicate that a treatment time of 2 min at 140°C is sufficient for these structural changes to occur since prolonged treatment times do not lead to further increases but actually to slight decreases in monomer uptake. The time dependence of acrylic acid uptake by DMF-treated PET is shown in Figure 2. It can be seen that monomer incorporation in the case of acrylic acid is completed within 1 hr, although with other monomers much longer times were necessary. Accordingly, an equilibration time of four days was generally allowed.

The structural changes in the PET filaments leading to an increase in monomer uptake are known to be dependent on the dimensional constraint during the DMF treatment.²⁵ In Table III the influence of shrinkage conditions during the DMF treatment on monomer uptake is shown. When shrinkage is prevented, monomer uptake is drastically reduced. The decrease in monomer uptake is observed also when shrinkage is partially prevented by the mechanical restraints of a fabric structure. For maximum monomer uptake by PET, DMF pretreat-

TABLE II
Effects of Treatment Time on Monomer Uptake by DMF-Treated PET^a

| Monomer | DMF treatment time, min | Monomer uptake, % |
|-----------------|-------------------------|-------------------|
| Acrylic acid | 0 | 10.0 |
| Acrylic acid | 2 | 24.5 |
| Acrylic acid | 180 | 22.8 |
| 4-Vinylpyridine | 0 | 18.9 |
| 4-Vinylpyridine | 2 | 26.8 |
| 4-Vinylpyridine | 180 | 23.4 |

^a PET was treated with DMF at 140°C; DMF was removed by water and dried prior to monomer incorporation.

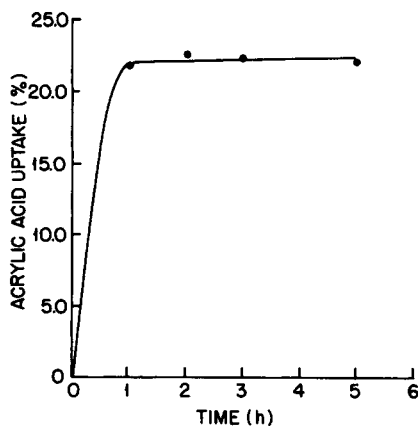


Fig. 2. Time dependence of uptake of acrylic acid by DMF-treated (140°C, 2 min) PET yarns.

ment at 140°C for 2 min under unrestrained conditions is essential, and these treatment conditions were followed throughout this study.

Vinyl monomers can be introduced into the PET by two different procedures. In one procedure, the monomer is introduced into the PET after removal of the DMF. In the other procedure, the monomer is solvent exchanged with the DMF in the PET. These two procedures are compared in Figure 3, where monomer uptake by untreated PET, DMF-pretreated PET, and DMF-treated PET (monomer exchanged) is shown for several monomers. The lowest monomer uptake is always observed with the untreated PET. Following the procedure in which DMF is removed from the PET prior to monomer incorporation, lower monomer uptake is observed as compared with results obtained by the solvent exchange technique. A partial collapse of the PET-swollen structure occurs when the DMF is removed. On the other hand, when the solvent exchange technique is used and the monomer is exchanged with the DMF in the PET, minimal collapse of the PET structure takes place and higher monomer uptake values are obtained.

It was of interest to determine whether monomer uptake is related to the solubility parameter of the monomer (Table IV and Figs. 4–6). The dependence

TABLE III
Effects of Dimensional Constraints on Monomer Uptake by DMF-Treated PET^a

| Monomer | PET | Shrink., % | Monomer uptake, % |
|---------|-----------------------|----------------|----------------------|
| EDMA | yarn—free shrinkage | 33.0 | 32.6 |
| EDMA | yarn—const. length | 0.0 | 6.9 |
| 4-BrS | yarn—free shrinkage | 33.0 | 36.1 |
| 4-BrS | fabric—free shrinkage | 12.0 F, 10.0 W | 14.2 |

^a PET was treated with DMF at 140°C for 2 min, and monomer was solvent exchanged with the DMF in the PET.

^b PET twill, 3.9 oz/yd², J. P. Stevens.

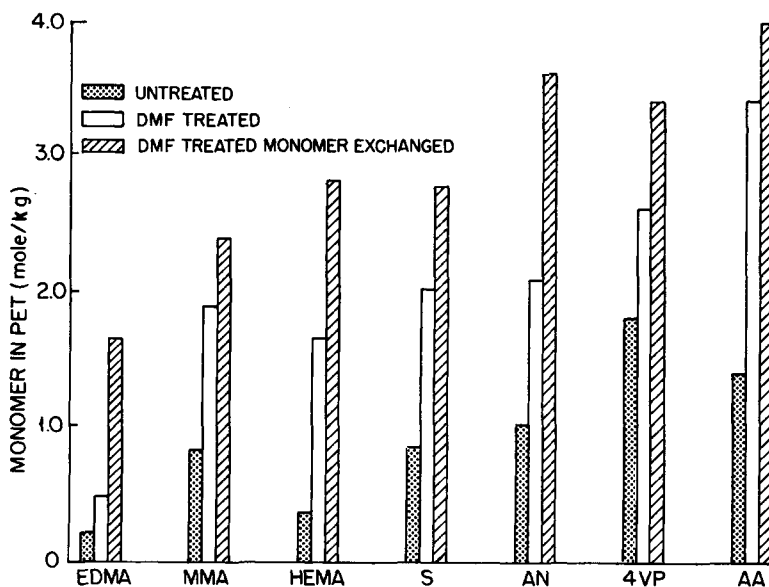


Fig. 3. Uptake of vinyl monomers by PET yarns: untreated; DMF-treated, 140°C, 2 min, dried; DMF-treated, 140°C, 2 min, monomer solvent exchanged.

on solubility parameter was examined for untreated PET, DMF-pretreated PET, and DMF-treated PET (monomer exchanged). Solubility parameters which were not available from the literature were calculated according to the method described by Hoy.²⁶ Although results are scattered, a positive relationship be-

TABLE IV
Solubility Parameters of Vinyl Monomers and Their Uptake by PET

| Monomer | Sol. Parameter δ , (cal/cm^3) ^{1/2} | Monomer uptake by PET | | |
|------------------------------|--|-----------------------|--------------------------------------|--|
| | | Untreated, mole/kg | DMF-treated, ^a mole/kg | DMF-treated ^a (monomer exchanged), mole/kg |
| Butyl methacrylate | 8.2 | 0.22 | 0.61 | 1.91 |
| Ethyl methacrylate | 8.6 | 0.77 | 1.65 | — |
| Butyl acrylate | 8.8 | 0.15 | 1.24 | 1.97 |
| Methyl methacrylate | 8.8 | 0.83 | 1.89 | 2.59 |
| Styrene | 9.3 | 0.84 | 1.99 | 2.76 |
| Ethylene dimethacrylate | 9.4 ^b | 0.21 | 0.47 | 1.64 |
| 4-Bromostyrene | 10.1 ^b | 1.47 | 2.43 | 2.76 |
| 4-Vinylpyridine | 10.1 ^b | 1.80 | 2.55 | 3.39 |
| Acrylonitrile | 10.5 | 1.15 | 2.75 | 3.61 |
| N-Vinylpyrrolidone | 10.5 ^b | 1.85 | 2.99 | 3.31 |
| Hydroxyethyl methacrylate | 11.0 ^b | 0.37 | 1.63 | 2.78 |
| Methacrylic acid | 11.2 | 0.41 | 2.09 | 3.51 |
| Acrylic acid | 12.0 | 1.39 | 3.40 | 3.96 |
| Divinylsulfone | 12.4 ^c | 0.36 | 1.73 | 2.92 |

^a Treatment conditions: 2 min, 140°C.

^b Calculated according to Hoy.²⁶

^c δ of diethylsulfone.

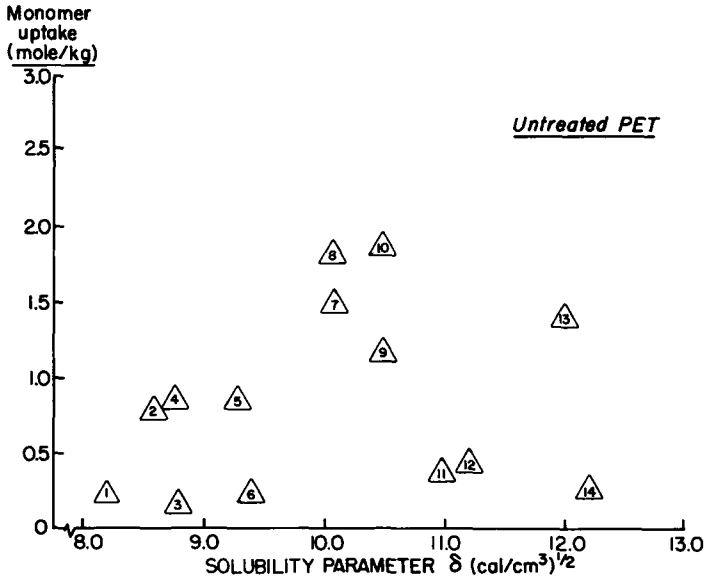


Fig. 4. Uptake of vinyl monomers by untreated PET yarns as a function of monomer solubility parameter (see Table I).

tween monomer uptake and the solubility parameter of the monomer can be observed. In the case of untreated PET (Fig. 4), a maximum near the solubility parameter of the PET ($\delta = 10.7$) is obtained, and the scatter of the data at higher δ values may reflect a bimodal distribution similar to that previously shown for solvent-induced crystallization of PET²⁷ and for other PET-solvent interactions.^{28,29}

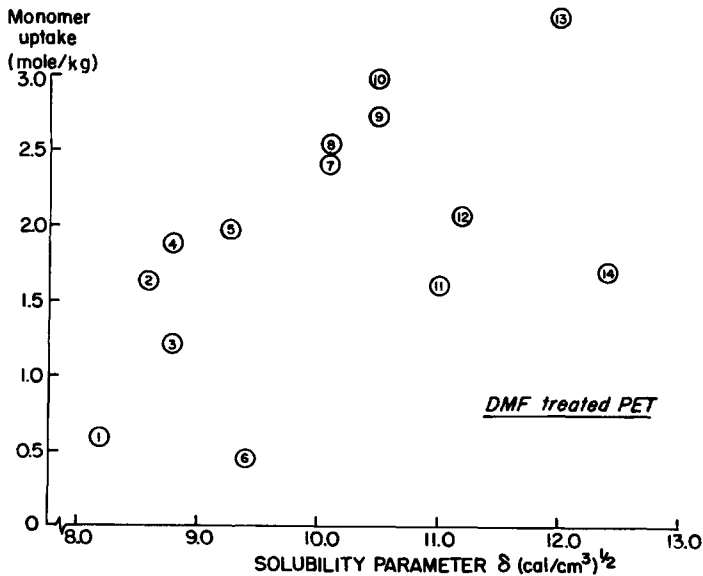


Fig. 5. Uptake of vinyl monomers by DMF-treated (140°C, 2 min) PET yarns as a function of monomer solubility parameter (see Table I).

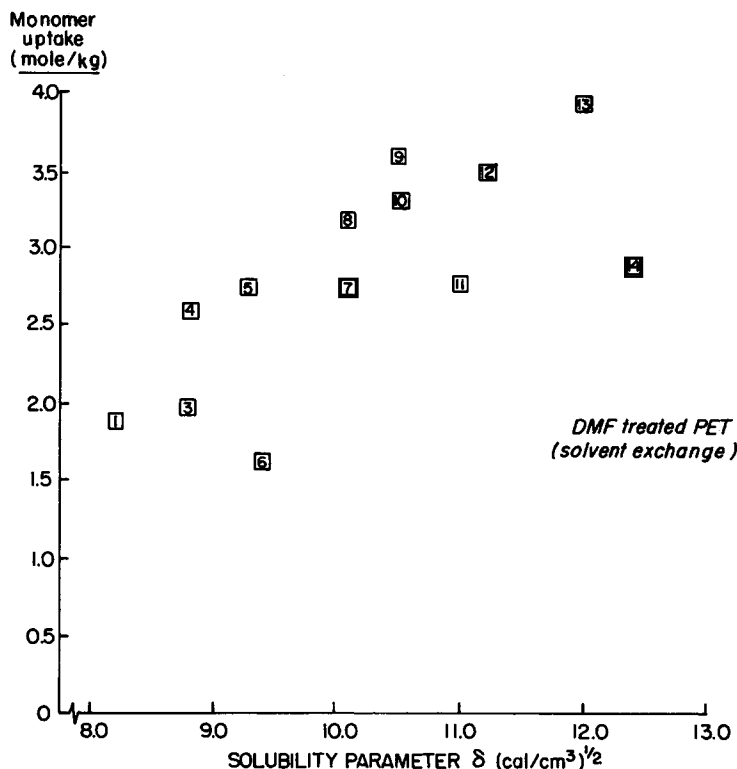


Fig. 6. Uptake of vinyl monomers by DMF-treated (140°C, 2 min) PET yarns by solvent exchange as a function of monomer solubility parameter (see Table I).

Monomer uptake in DMF-treated PET yarns is significantly higher and shows a similar dependence on solubility parameter (Fig. 5). Apparently, monomers with a solubility parameter near that of polyester itself are capable of interacting with the polyester structure leading to a reversal of the partial collapse experienced by the structure after removal of the DMF. Other monomers, especially those of lower solubility parameter, have little capability to interact with polyester, and their uptake is therefore severely limited. When the monomer is solvent exchanged with DMF after the solvent treatment (Fig. 6), a general increase in monomer uptake levels is observed, indicating that the highly swollen polyester structure is to a large extent maintained. Monomer uptake approaches values of about 3.40 moles/kg, which is identical to the value obtained for DMF itself, indicating an almost stoichiometric exchange between DMF and monomer.

In Situ Polymerization

Polymerization in the Presence of Excess Monomer

In situ polymerization of vinyl monomers in PET was investigated using both chemical and γ -irradiation initiation techniques. When *in situ* polymerization is carried out in the presence of excess monomer, a constant supply of monomer is available and high polymer uptakes by the PET may be expected. Under such

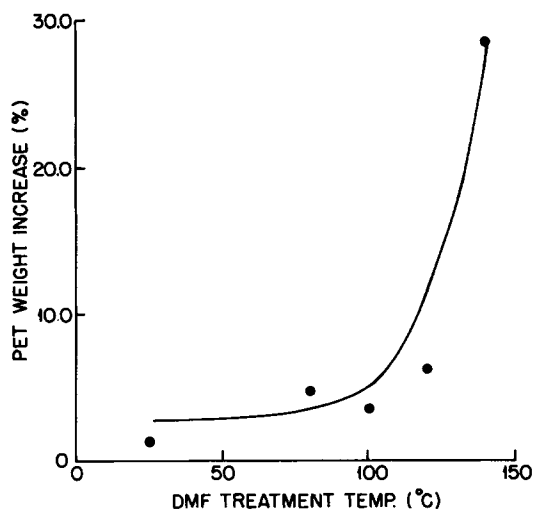


Fig. 7. Polymerization of 4-vinylpyridine in DMF-treated PET yarn as a function of DMF treatment temperature. Polymerization conditions: excess of monomer; BPO, 0.041 mole/l.; 70°C; 48 hr.

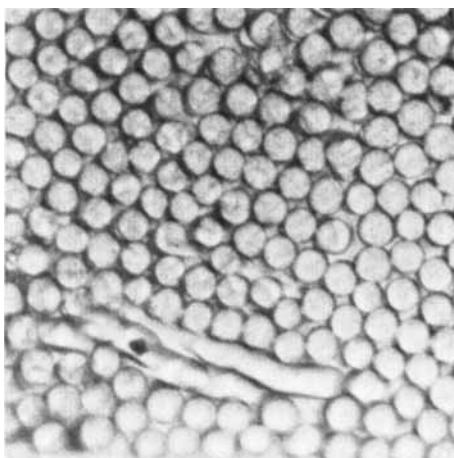
experimental conditions, the monomer present on the surface of the PET fibers and in the liquid phase polymerizes also, and rather tedious and time-consuming extraction procedures must be applied to remove that polymer. The total polymer uptake is reduced by removing excess monomer prior to polymerization, in which case the amount of polymer formed within the fiber will be limited to the quantity of monomer incorporated within the PET fiber.

The polymerization of 4-vinylpyridine in PET pretreated with DMF at different temperatures is shown in Figure 7. Polymerization was initiated by benzoyl peroxide (BPO), and enough time was allowed for complete penetration of both the monomer and the initiator. Polymerization was carried out in the

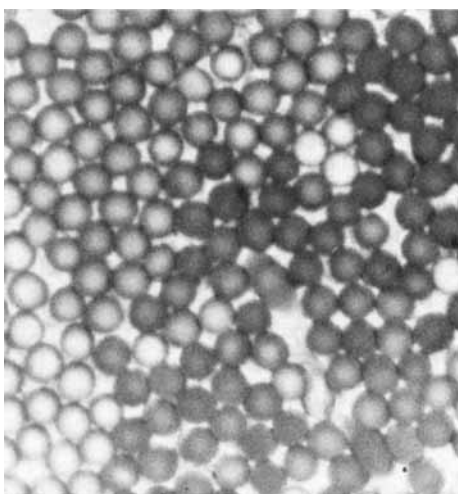
TABLE V
Polymerization of Vinyl Monomers in DMF-Treated PET Without Removal of Excess Unabsorbed Monomer

| Vinyl monomer ^a | Monomer uptake, % | Weight increase after polymerization, % |
|----------------------------|-------------------|---|
| <i>Series A</i> | | |
| Acrylonitrile | 14.6 | 19.6 |
| Styrene | 20.7 | 20.3 |
| Methyl methacrylate | 18.9 | 54.6 |
| Acrylic acid | 24.5 | 20.4 |
| <i>Series B</i> | | |
| Acrylonitrile | 14.6 | 26.4 |
| Styrene | 20.7 | 21.6 |
| Methyl methacrylate | 18.9 | 108. |
| Acrylic acid | 24.5 | 18.0 |
| 4-Vinylpyridine | 26.8 | 28.8 |

^a Series A: azobisisobutyronitrile 0.061 mole/l.; 70°C, 48 hr; series B: benzoyl peroxide 0.041 mole/l.; 70°C, 48 hr.



(a)

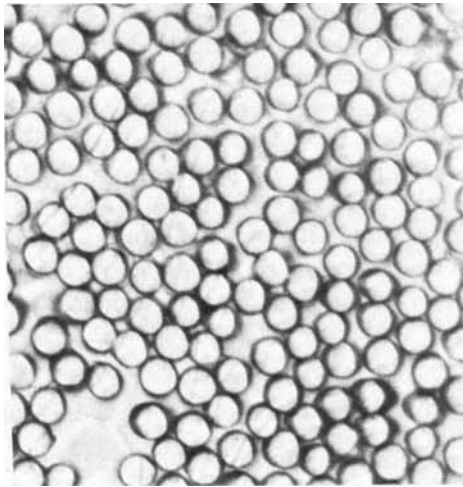


(b)

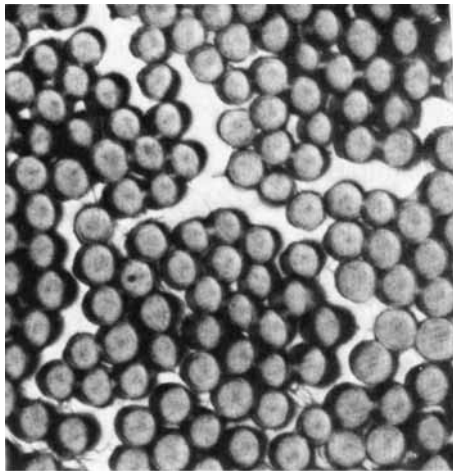
Fig. 8. Cross section of Methylene Blue-dyed PET yarns: (a) control; (b) containing 15.3% poly(acrylic acid).

presence of excess monomer, and the poly(4-vinylpyridine) formed outside the PET fibers was removed by extraction with chloroform and pyridine. When monomer uptake was increased due to the DMF treatment temperature, as shown above, the polymer uptake increased correspondingly.

The results of attempts to polymerize several different vinyl monomers in DMF-treated PET are summarized in Table V. Polymerization was initiated either by BPO or by azobisisobutyronitrile (AIBN), and excess monomer and initiator outside the PET fibers were not removed prior to polymerization. Vinyl polymers formed outside the fibers were subsequently removed by extraction. Poly(acrylic acid) and polyacrylonitrile were extracted by DMF, poly(methyl methacrylate) and polystyrene were extracted by chloroform, and poly(4-vinylpyridine) was extracted by pyridine. Even though prolonged extraction



(a)



(b)

Fig. 9. Bromine-stained cross sections of PET yarns: (a) control; (b) containing 22.4% poly(4-vinylpyridine).

times (seven days) were used to establish the final polymer uptake, surface-held polymer could not be completely removed in all cases.

Compatibility between PET and the monomer and its corresponding polymer may vary. Therefore, monomer uptake may differ from that of the corresponding polymer uptake. Nevertheless, when similar uptake values were obtained, it can be assumed that most of the polymer was formed inside the PET. When higher polymer uptake was observed, part of the polymer must be on the surface of the PET fiber. The location of some vinyl polymers in the PET fiber can be determined by selective dyeing or staining of that polymer. This was done with PET containing poly(acrylic acid) and poly(4-vinylpyridine). The poly(acrylic acid) in the PET fiber was selectively dyed with Methylene Blue (a basic dye), and the cross section was analyzed under the microscope (Fig. 8). Cross sections of PET fibers containing poly(4-vinylpyridine) were stained with

bromine vapor. The bromine formed selectively a colored N-complex with the pyridine groups of the poly(4-vinylpyridine), indicating the location of that polymer in the fiber cross section (Fig. 9). It can be seen clearly that *in situ* polymerization has taken place and that the polymer is distributed throughout the fiber cross section. Considerable nonuniformity in the extent of dye penetration is observed for the poly(acrylic acid) containing PET fibers, suggesting an unevenness either of the DMF pretreatment or of the polymerization reaction. Since the distribution of poly(4-vinylpyridine) throughout the fiber cross section is much more even, it would appear that the penetration of the acrylic acid and the subsequent polymerization reaction are responsible for the nonuniformity.

Polymerization in the Absence of Excess Monomer

In order to prevent polymer formation outside the PET fibers, polymerization was investigated in the absence of excess monomer and initiator outside the fibers. Monomers, together with suitable initiators, were allowed to diffuse into DMF-treated PET, and excess unabsorbed monomer and initiator were removed by centrifugation. Polymerization was then initiated by heating the PET fibers. The dependence of polymer uptake on the DMF treatment temperature was similar to that previously observed when excess monomer was not removed prior to polymerization (Fig. 10).

Results obtained with different vinyl monomers are summarized in Table VI. Surprisingly low polymerization yields were obtained. Good polymerization yields were obtained only with EDMA and 4-BrS, and moderate yields were obtained in the case of HEMA only when extremely high initiator concentrations were used. The lower initiator concentration (0.05% BPO) is sufficient for complete bulk polymerization of HEMA. The concentrations of initiator used with the other monomers was also much higher than that sufficient for normal complete polymerization of these monomers. Nevertheless, with acrylic acid, only a moderate polymerization yield was observed; and with styrene and methyl methacrylate, poor yields were found.

Since it was previously shown that monomer uptake by PET varies from monomer to monomer, it might be expected that initiator uptake varies also.

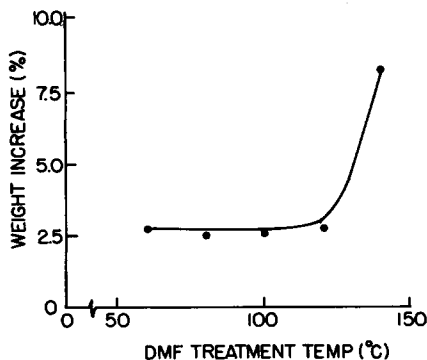


Fig. 10. Polymerization of ethylene dimethacrylate in DMF-treated PET yarns as a function of DMF treatment temperature. Polymerization conditions: no excess of monomer; BPO, 0.041 mole/l.; 70°C; 65 hr.

TABLE VI
 Polymerization of Vinyl Monomers in DMF-Treated PET with Excess Unabsorbed Monomer and Initiator Removed^a

| Monomer | BPO uptake, ^b % | Monomer uptake, % | Weight increase, % | Polymer yield, % |
|--------------------|-------------------------------|----------------------|-----------------------|---------------------|
| HEMA ^c | 0.05 | 36.2 | 0.9 | 2.5 |
| HEMA ^c | 1.00 | 36.2 | 19.5 | 53.9 |
| AA ^c | 0.60 | 28.5 | 10.4 | 36.5 |
| 4-BrS ^c | 0.38 | 39.8 | 33.1 | 83.2 |
| MMA | 0.41 | 18.9 | 0.6 | 3.2 |
| S | 0.43 | 20.7 | 0.3 | 1.4 |
| EDMA | 0.82 | 9.3 | 8.4 | 90.4 |

^a Polymerization conditions: temp., 70°C; time, 65 hr.

^b Mole percent of monomer.

^c Monomer exchanged with DMF in PET.

There is also the possibility that the distribution of initiator between PET and monomer will result in a lower effective initiator concentration in the fiber.

Accordingly, initiator uptake by DMF-treated PET was determined for three different initiators—BPO, AIBN, and *tert*-butyl peroxybenzoate (TBPB). Since high initiator concentrations were used, initiator uptake by PET was determined from acetone solutions of the initiators. PET yarns were exposed to the initiator solution until equilibrium values were achieved, and excess acetone solution was removed by centrifugation. Acetone in the PET was removed by evaporation at room temperature, and initiator uptake was determined from the weight increase of the PET. The results are shown in Figure 11. All three initiators diffused into the PET fibers, although with AIBN and BPO, uptake was limited. In the concentration range investigated, the distribution coefficient of the initiator between fiber and solution was always considerably below unity. Accordingly, it is possible that the poor polymerization yields are due to insufficient quantities of initiator being present in the PET.

In order to avoid problems associated with low initiator concentrations in the PET, it was decided to initiate polymerization by γ irradiation. Using this

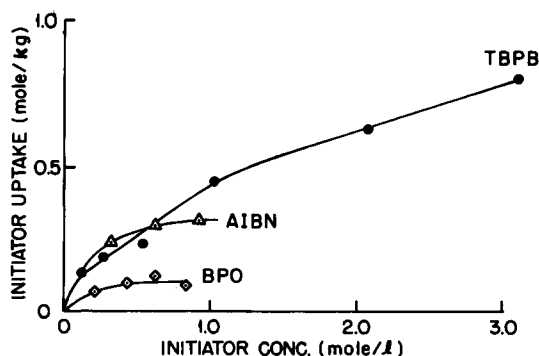


Fig. 11. Uptake of initiators by DMF-treated (140°C, 2 min) PET yarns as a function of initiator concentration.

TABLE VII
Dependence of Vinyl Polymer Uptake and Polymerization Yield on Initiator Concentration
(Excess Unabsorbed Monomer Removed)^a

| Monomer | Monomer uptake, mole/kg | Initiator uptake | | Weight increase, % | Polymer yield, % |
|---------|-------------------------|------------------|-------|--------------------|------------------|
| | | mole/kg | % | | |
| NVP | 1.63 ^c | 0.154 | 9.5 | 3.22 | 18.2 |
| HEMA | 1.34 ^c | 0.164 | 12.0 | 0.85 | 4.9 |
| | 1.67 ^d | 0.148 | 8.2 | 0.82 | 6.7 |
| | 2.05 ^d | 0.140 | 6.8 | 0.49 | 3.4 |
| | 1.80 ^d | 0.192 | 10.7 | 4.78 | 40.0 |
| AA | 1.29 ^d | 0.227 | 17.6 | 3.83 | 41.3 |
| | 1.43 ^d | 0.356 | 24.9 | 5.84 | 56.6 |
| | 1.14 ^d | 0.442 | 38.8 | 5.01 | 61.2 |
| | 1.20 ^d | 0.633 | 52.8 | 4.17 | 48.1 |
| | 0.71 ^d | 0.805 | 113.4 | 4.05 | 78.9 |

^a Polymerization conditions: temp., 70°C; time, 48 hr.

^b Percent of monomers.

^c AIBN.

^d TBPB.

technique, initiation should be easily controlled by the irradiation dosage. All monomers listed in Table I, except 4-BrS, were allowed to diffuse into DMF-treated PET, excess monomer was removed by centrifugation, and the fibers were irradiated under nitrogen with 2 Mrad. Irradiation by 2 Mrad is more than sufficient for solution or bulk polymerization of these vinyl monomers. It had been reported^{2,18} that even lower irradiation dosages in the case of acrylic acid, acrylonitrile, and styrene in PET have led to high polymer uptakes. After irradiation, unpolymerized monomer was extracted with methanol, and it was found that no polymerization had taken place. No polymerization occurred when experiments were repeated with styrene and HEMA using irradiation doses up to 10 Mrad. With an irradiation dose of 15 Mrad, which is known to lead to the formation of free radicals in PET,¹⁸ a 60% polymerization yield was observed with styrene. Low yields (3%) were still obtained with HEMA.

Increase in the irradiation dose should be equivalent to an increase in the initiator concentration, and accordingly the dependence of polymerization yield on initiator concentration was investigated (Table VII). Two initiators were used, AIBN and TBPB, and the initiator was introduced into the PET from acetone solution prior to the monomer. Excess acetone was removed, and the monomer was then introduced from a 20% water solution. The initiators are water insoluble. Excess monomer solution was removed prior to polymerization. Despite the relatively high molar concentration of AIBN, poor polymerization yields were obtained with this initiator. Good polymerization yields were found only at extremely high initiator concentrations, as shown for TBPB. The *in situ*-formed polymer is distributed throughout the fiber cross section, as shown in Figure 12.

It is evident that in order to achieve *in situ* polymerization, one must use either high irradiation doses or high initiator concentrations. Comparing results of *in situ* polymerization of vinyl monomers in the presence (Table II) and in the absence (Table VII) of excess monomer and initiator, it can be seen that in the

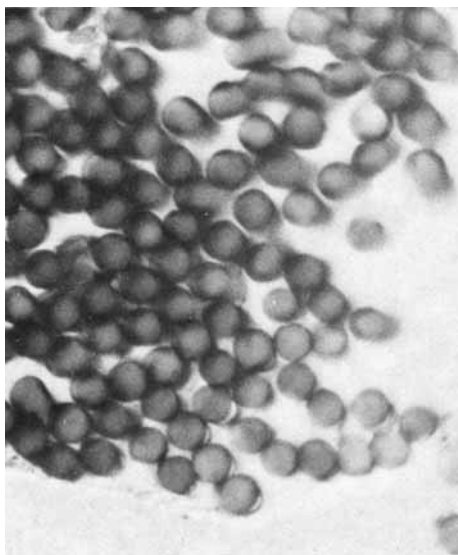


Fig. 12. Cross section of Methylene Blue-dyed PET yarns containing 5.5% poly(acrylic acid). Polymerization chemically initiated in absence of excess monomer.

absence of excess monomer and initiator, much higher initiator concentrations in the fiber are required for polymerization. It was therefore of interest to determine whether polymerization by γ irradiation is also dependent on the presence of excess monomer. When PET containing acrylic acid was irradiated with 2 Mrad in the absence of excess monomer, no polymerization occurred. The experiment was repeated using PET containing acrylic acid in the presence of a 33.3% aqueous acrylic acid solution. Under these conditions, significant *in situ* polymerization took place throughout the fiber, as shown by the Methylene Blue-dyed cross sections in Figure 13.

It appears that when polymerization is carried out using moderate irradiation doses under conditions in which free radicals can be formed outside the PET fibers, *in situ* polymerization within the fiber will occur. It seems that under these experimental conditions, free radicals formed outside the PET fiber are able to penetrate the fiber and to cause *in situ* polymerization.

It can be stated, therefore, that *in situ* polymerization of vinyl monomers in PET can be carried out successfully either by γ irradiation or by chemical initiation when monomer is present in the PET fiber and when a constant supply of free radicals is available outside the fibers.

In order to explore this point further, γ -irradiation polymerization experiments were repeated in the presence of either water or Freon E3, both of which are good sources for free radicals when irradiated (Table VIII). Irradiation was carried out in water when the monomer in the PET was water insoluble, while Freon E3 was used when the PET contained water-soluble monomers. In both cases, *in situ* polymerization took place. As previously indicated, when the same irradiation dose (2 Mrad) was used in the absence of either water or Freon E3 outside the fiber, no polymerization occurred. Lower polymer uptake values were observed in those experiments in which Freon E3 rather than water was used as the source for free radicals. This may be attributed to partial solubility of the

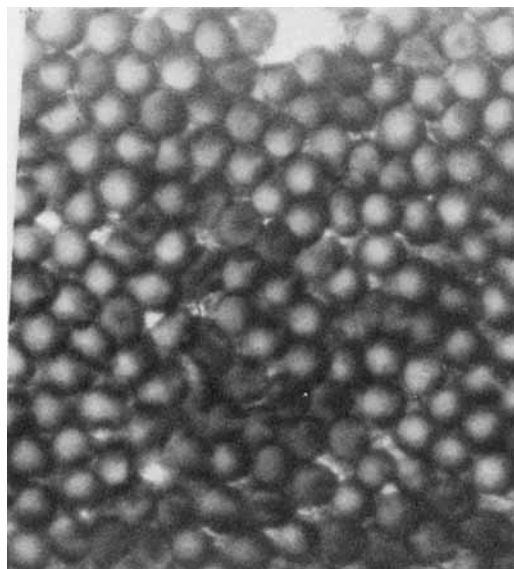


Fig. 13. Cross sections of Methylene Blue-dyed PET yarns containing poly(acrylic acid). Polymerization by γ irradiation in presence of excess monomer.

monomer in the Freon E3 solvent, which would lead to partial extraction of the monomer from the PET. In all irradiation experiments, some homopolymer was found in the external liquid phase; however, the reported polymerization yields refer only to those amounts of polymer that were formed inside the PET fibers. Table VIII again shows the important effect of the DMF pretreatment on the polymer uptake.

In situ polymerization can also be initiated by free radicals produced outside the fibers by chemical initiation. Polymerization of 4-vinylpyridine in PET was initiated by using a "redox" initiation system. PET containing incorporated 4-vinylpyridine was allowed to remain in a mixture of 4-vinylpyridine and water, and polymerization was initiated by the addition of potassium persulfate and sodium metabisulfite to the external liquid phase. In this system, polymerization

TABLE VIII
Polymerization of Vinyl Monomers in PET by γ Irradiation (Excess Unabsorbed Monomer Removed)^a

| Monomer | PET weight increase | | Polymer yield | |
|-------------------|---------------------|-------------------|-----------------|-------------------|
| | Untreated, % | DMF-treated, % | Untreated, % | DMF-treated, % |
| MMA ^b | 0.3 | 6.7 | 4.2 | 35.3 |
| EDMA ^b | 0.0 | 5.5 | 0.0 | 41.4 |
| S ^b | 4.3 | 14.5 | 48.2 | 66.4 |
| AA ^c | 2.9 | 4.2 | 20.4 | 17.1 |
| HEMA ^c | 1.1 | 11.4 | 20.6 | 50.9 |
| 4VP ^c | 2.0 | 3.2 | 11.1 | 10.7 |
| MAA ^a | 0.6 | 3.4 | 16.1 | 17.4 |

^a Polymerization conditions: irradiation dose, 2 Mrad; temp., 49°C.

^b In water.

^c In Freon E3.

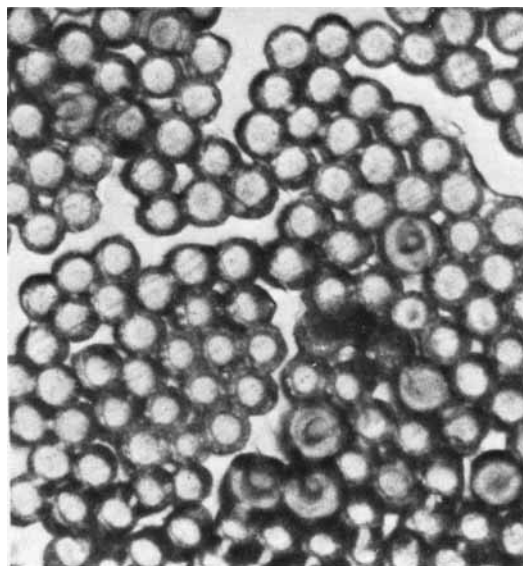
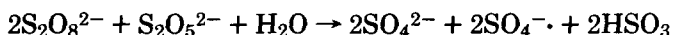
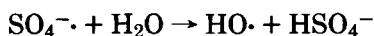


Fig. 14. Bromine-stained cross sections of PET yarns containing 13.4% poly(4-vinylpyridine). Polymerization by redox initiation.

is initiated by the free radicals formed during the oxidation-reduction reaction shown below:

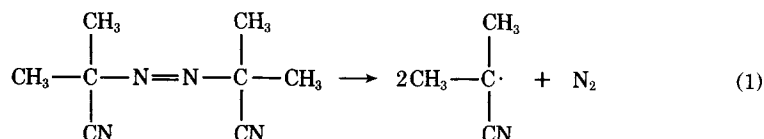


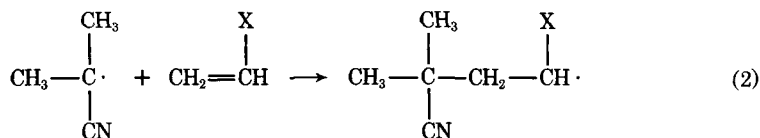
A further possible reaction for the formation of free radicals is the following:



Since free-radical formation in this case is the result of reactions between inorganic salts, it is reasonable to assume that all the free radicals were formed in the external aqueous phase outside the PET fibers. Polymerization was carried out at room temperature. After extraction of the polymer that was formed outside the fibers, a 13.4% weight increase was found. The fibers were cross-sectioned and stained by bromine, and it can be seen from Figure 14 that *in situ* polymerization has taken place. With certain fibers, polymer was distributed throughout the fiber cross section, while in the case of other fibers, the polymer was not uniformly distributed throughout the cross section, although in all cases the polymer was distributed substantially below the surface, suggesting that polymerization proceeds from the surface to the core of the fiber.

The difficulties observed in the *in situ* initiation of vinyl polymerization in PET must be attributed to differences in the initiator efficiency inside and outside the PET fibers. Initiation of vinyl monomer ($\text{CH}_2=\text{CHX}$) polymerization by AIBN proceeds by the following reactions:





Radicals formed in reaction (1) initiate polymerization as shown in reaction (2). When a low initiator efficiency is observed, it would appear that the free radicals formed in reaction (1) participate primarily in termination reactions, thereby providing fewer free radicals to initiate polymerization.

The principal difference between initiation of vinyl polymerization within the PET structure and polymerization in an external monomer solution lies in the mobility of the reacting species. Obviously, monomer mobility in the PET structure would be much lower than that in a monomer solution. Free radicals that are formed by homolytic cleavage of a covalent bond are always formed in pairs, each pair originating from the same molecule. Due to the low mobility of the free radicals formed inside the PET structure, as well as that of the monomer itself, the probability of termination reactions of the newly formed free radicals is vastly increased. Accordingly, fewer free radicals are available for the initiation reaction, resulting in a decrease in the initiation efficiency. In order to overcome the low initiation efficiency inside the PET, high initiator concentrations or high irradiation doses are required. When free radicals are formed outside the PET, initiator efficiency is much higher and more free radicals are available for polymerization. The free radicals formed outside the fibers diffuse into the PET and subsequently initiate *in situ* polymerization. When polymerization is carried out under such experimental conditions, significantly lower initiator concentrations or irradiation doses are required for adequate polymerization yields. The free radicals that diffuse into the PET structure cannot terminate as rapidly since termination requires the participation of a pair of free radicals. As polymerization progresses, the free radicals that are located at the end of a growing polymeric chain become less and less mobile, thereby suppressing the termination reaction.

Water Uptake and Moisture Regain

It was of interest to determine the water uptake and the moisture regain of PET fibers containing hydrophilic polymers such as poly(hydroxyethyl methacrylate) and poly(acrylic acid) in order to establish whether the incorporation of these polymers in the PET fibers will improve their water absorption properties. Comparison was made between fibers in which most of the water-soluble polymer was incorporated within the fiber and fibers in which most of the polymer was found crosslinked outside on the surface of the fiber. These fibers were obtained by γ irradiation with a 2-Mrad dose of 33.3% water solution of the monomer in the presence of PET. The monomer that polymerized outside the PET fibers was later crosslinked by irradiation and could not be removed by extraction.

Water uptake values of DMF-treated PET containing poly(hydroxyethyl methacrylate) and poly(acrylic acid) are shown in Table IX. The PET yarns were equilibrated in water for 48 hr at 21°C, and excess water was removed by centrifugation. Only a small increase in water uptake is observed when most

TABLE IX
Water Uptake for DMF-Treated PET Containing Polymers (Prepared by γ Irradiation)

| Polymer | Polymer content, % | Water uptake, % | Polymer water uptake, ^a % |
|---------|--------------------|-----------------|--------------------------------------|
| PHEMA | 0.0 | 0.50 | — |
| | 10.2 | 0.96 | 5.2 |
| | 75.0 | 41. | 55. |
| | 100.0 | — | 65. ^b |
| PAA | 4.0 | 0.76 | 7.7 |
| | 74.2 | 303. | 407. |

^a Water uptake of the polymer in PET.

^b Water uptake of bulk-polymerized PHEMA.

of the polymer is inside the fiber, as shown by the data for PET containing 10.2% poly(hydroxyethyl methacrylate) and 4.0% poly(acrylic acid). A much larger increase in water uptake is observed when most of the polymer is present outside the fiber, as indicated by the high polymer contents. Water uptake of the polymer itself was calculated from the water uptake of the modified PET yarns and its corresponding polymer content. It can be seen that the water uptake of the polymer inside the PET is much smaller than that of the polymer present on the outside of the fiber.

Moisture regain values at 65% R.H. of the same PET fibers are reported in Table X. Only a small improvement in the PET moisture regain is observed when most of the polymer is inside the PET fiber. When most of the polymer is present outside the fiber, rather high moisture regain values were observed. Again, moisture absorption by the polymer present within the fiber appears to be limited. Similar results were obtained with PET containing poly(hydroxyethyl methacrylate) and poly(acrylic acid) obtained by chemical initiation (Table XI). There is no apparent correlation between the polymer content and the moisture regain of either the PET yarns or the polymer itself. These results indicate that increasing the amount of polymer inside the PET does not necessarily lead to increases in moisture regain. It seems that the incorporation of these hydrophilic polymers within the PET fiber structure interferes with the

TABLE X
Moisture Regain at 65% R.H. and 21°C for DMF-Treated PET Containing Polymers (Prepared by γ Irradiation)

| Polymer | Polymer content, % | Water regain, % | Polymer regain, ^a % |
|---------|--------------------|-----------------|--------------------------------|
| PHEMA | 0.0 | 0.47 | |
| | 10.2 | 0.87 | 4.4 |
| | 75.0 | 6.8 | 8.9 |
| PAA | 4.0 | 0.69 | 5.5 |
| | 74.2 | 8.6 | 11. |

^a Water regain of the polymer in PET.

TABLE XI
Moisture Regain at 65% R.H. and 21°C for DMF-Treated PET Containing Polymers (Benzoyl Peroxide Initiation)

| Polymer | Polymer content, % | Water regain, % | Polymer regain, ^a % |
|---------|--------------------|-----------------|--------------------------------|
| PHEMA | 6.8 | 1.0 | 8.6 |
| | 9.2 | 1.3 | 10. |
| | 12.8 | 0.74 | 2.6 |
| | 15.0 | 1.3 | 6.1 |
| | 16.3 | 0.9 | 3.2 |
| PAA | 5.6 | 0.96 | 9.2 |
| | 9.4 | 1.2 | 8.1 |

^a Water regain of the polymer in PET.

absorption of water by the polymers. Since the absorption of water by poly(hydroxyethyl methacrylate) and by poly(acrylic acid) is accompanied by swelling of the polymer, the incorporation of these polymers in the rigid PET structure restricts swelling, thereby decreasing the ability of the polymer to absorb water.

Mechanical Properties

Since chemical modification of PET yarns by means of *in situ* vinyl polymerization can be used to achieve several different effects, it was of importance to determine whether the incorporation of small amounts of vinyl polymer into the PET yarns leads to changes in their mechanical properties. In Table XII are shown the mechanical properties of DMF-treated PET yarns containing three different vinyl polymers. The properties of these modified PET yarns are compared with those of DMF-treated PET and of untreated PET. During the DMF treatment of the PET under free shrinkage conditions, which is essential for the successful incorporation and polymerization of vinyl monomers, a loss in mechanical properties is observed. A decrease in modulus, yield stress, and tenacity at break accompanied by an increase in elongation was found. These changes in mechanical properties are mainly reflections of the disorientation of molecular segments in the amorphous PET regions. In the presence of the three different polymers in the PET, significant improvement in mechanical properties was observed. Evidently, the changes in mechanical properties which

TABLE XII
Mechanical Properties of DMF-Treated PET Containing Vinyl Polymers^a

| | Polymer content, % | Initial modulus, g/d | Yield stress, g/d | Break exten., % | Break tenacity, g/d |
|-------------|--------------------|----------------------|-------------------|-----------------|---------------------|
| Untreated | — | 83.1 | 1.44 | 23.2 | 4.04 |
| DMF-treated | — | 21.3 | 0.49 | 96.6 | 2.26 |
| Poly-4VP | 22.4 | 43.7 | 1.19 | 63.3 | 3.59 |
| Poly-AA | 16.9 | 43.1 | 1.08 | 55.4 | 2.58 |
| Poly-AN | 16.4 | 44.8 | 1.16 | 71.8 | 3.79 |

^a Polymers were prepared by chemical initiation.

occur during the DMF pretreatment of the PET can be at least partially reversed by *in situ* polymerization. It is expected that by suitable control of the DMF pretreatment conditions, viable methods for the chemical modification of PET yarns via *in situ* vinyl monomer polymerization can be realized.

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