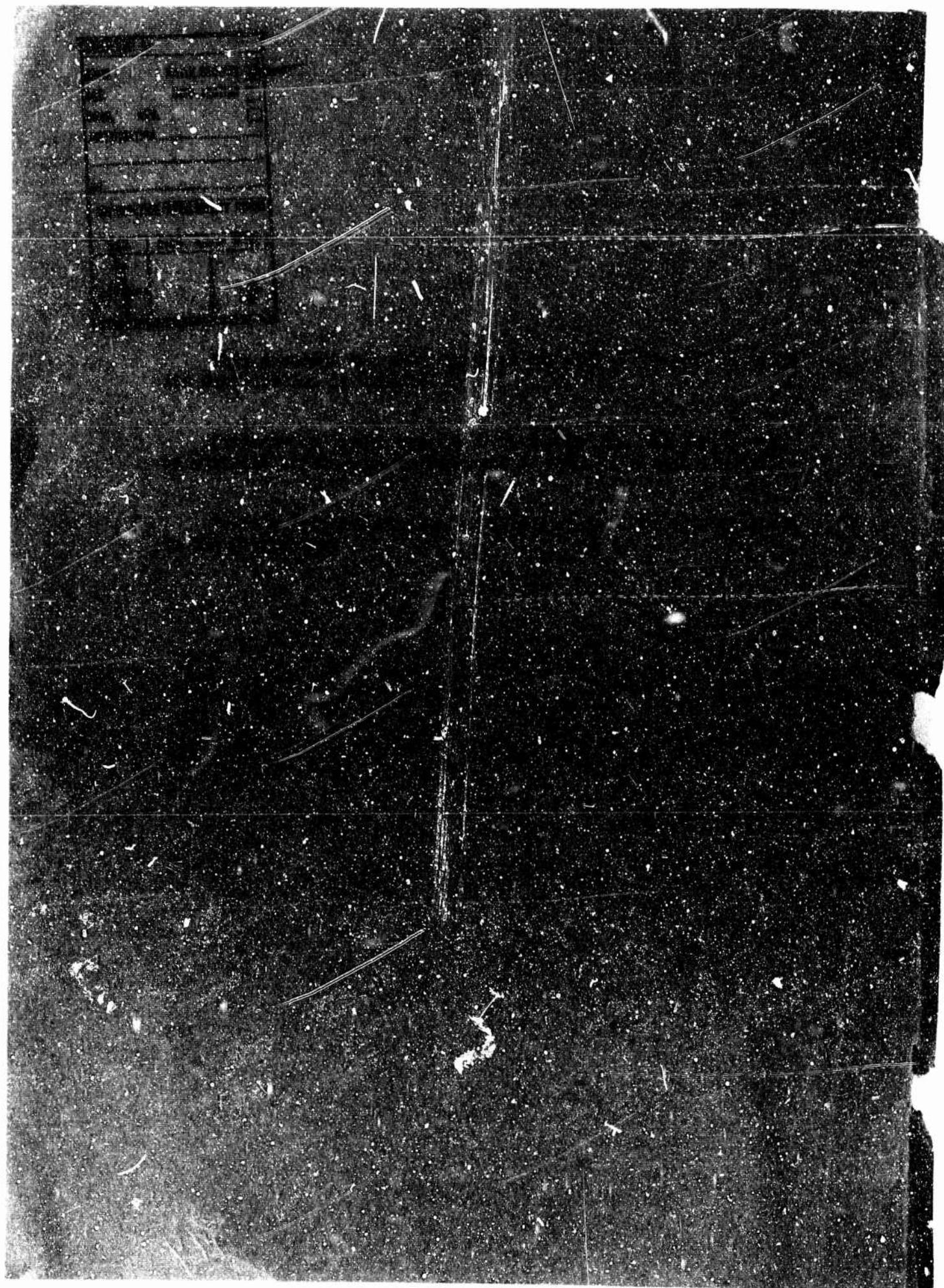
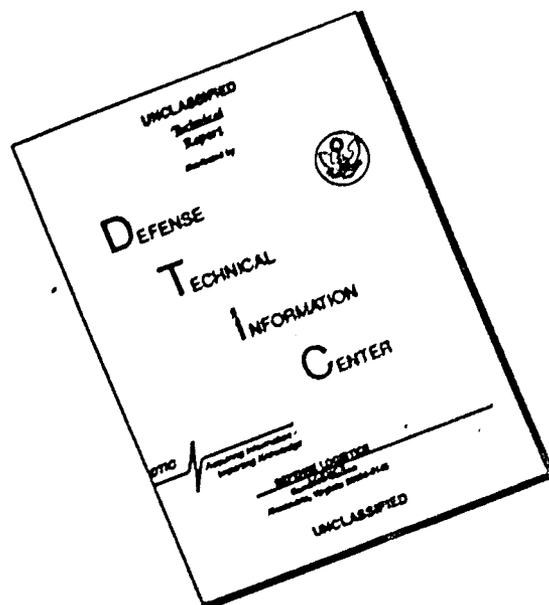


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Isolation of the reacted product from within the fabric was accomplished by the removal of unreacted PAA with water followed by the removal of unreacted nylon 66 with 2,2,2 trifluoro ethanol. The PAA nylon 66 product was characterized by thermal analysis (differential scanning calorimetry) and infrared spectrophotometry. Thermal analysis showed a complete loss of the nylon 66 melting point endotherm and instead showed a strong endotherm at 337°C. and a moderate endotherm at 230°C. The melting point of the product was found to exceed 337°C. The infrared analysis showed that the basic nylon 66 spectrum was modified by the addition of a carbonyl band at 1730 cm^{-1} .

Blocking of nylon 66 terminal amine groups by acetylation or formation of a sulfamic acid derivative decreased the amount of PAA reacted. Thus, a reaction between the terminal amine groups of nylon 66 and carboxyl groups of PAA forming an amide linkage was concluded to be partially responsible for the fixation. This suggested that a block copolymer and perhaps a graft copolymer were obtained.

In the cured fabric form with 6 percent fixed PAA, and when converted to the sodium and potassium salts, this material showed moisture regain values comparable to that of cotton. The calcium salt form increased the melting temperature of the nylon to over 385°C.

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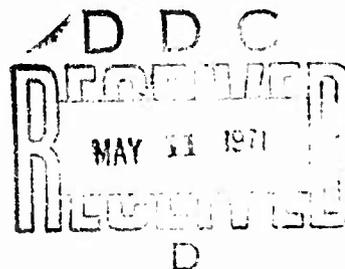
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TECHNICAL REPORT
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DIFFUSION AND COPOLYMERIZATION OF POLYACRYLIC ACID IN NYLON 66
FIBERS TO ACHIEVE IMPROVED THERMAL PROTECTION AND HIGHER MOISTURE REGAIN

by

Gilbert N. Arons
and
Richard N. Macnair



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Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY NATICK LABORATORIES
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FOREWORD

This report prepared by Gilbert N. Arons and Dr. Richard N. Macnair, Clothing and Personal Life Support Equipment Laboratory, summarizes recent successful progress in the copolymerization of polyacrylic acid prepolymer with nylon 66 polymer fiber in fabric form by means of a heat curing reaction. A unique accomplishment was the diffusion of a polymer solution inside a polymer fiber. This was contrary to the previous experience of other investigators.

The principal author performed the laboratory work described with two objectives. Efforts were part of an existing work unit for the modification of textiles assigned the Chemical Mechanisms Section of O&PLSEL. It also fulfilled the thesis requirements for an M.S. degree in Textile Chemistry at Lowell Technological Institute. The work was guided by Prof. Robert J. Feirent of Lowell Technological Institute, Lowell, Mass.

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ABSTRACT

An increase in the moisture absorption and melting temperature of nylon 66 is desirable for improving garment comfort and thermal resistance of nylon textile material. Grafting of acrylic acid monomer to nylon by various techniques has been intensively investigated for these purposes and also for potential protection against toxic agents. However, the possibility of copolymerizing polyacrylic acid (PAA) homopolymer to nylon appears to have been by-passed or considered unfeasible by other workers.

This report describes the copolymerization or fixation of a relatively low molecular weight PAA to nylon by a heat cure reaction. PAA homopolymer with a molecular weight of 15,000 to 20,000 was selected and applied to a spun nylon 66 fabric from an aqueous solution containing 28 percent polyacrylic acid by weight. The fabric was heated in the solution under pressure at 121°C. for two hours before extracting through two nips of a laboratory pad. The resulting fabric was dried at 100°C., heat cured at 177°C. for ten minutes, and scoured with 95°C. water to remove unfixed polyacrylic acid. In this manner PAA solutions in the pH range of 1.6 to 3.5 were found to fix from six to one percent PAA, respectively, onto the fabric. Penetration of PAA into the fiber prior to fixation was conclusively established by studying fiber cross sections stained by means of a cationic dye.

Isolation of the reacted product from within the fabric was accomplished by the removal of unreacted PAA with water followed by the removal of unreacted nylon 66 with 2,2,2 trifluoroethanol. The PAA nylon 66 product was characterized by thermal analysis (differential scanning calorimetry) and infrared spectrophotometry. Thermal analysis showed a complete loss of the nylon 66 melting point endotherm and instead showed a strong endotherm at 337°C. and a moderate endotherm at 230°C. The melting point of the product was found to exceed 337°C. The infrared analysis showed that the basic nylon 66 spectrum was modified by the addition of a carbonyl band at 1730 cm.^{-1} .

Blocking of nylon 66 terminal amine groups by acetylation or formation of a sulfamic acid derivative decreased the amount of PAA reacted. Thus, a reaction between the terminal amine groups of nylon 66 and carboxyl groups of PAA forming an amide linkage was concluded to be partially responsible for the fixation. This suggested that a block copolymer and perhaps a graft copolymer were obtained.

In the cured fabric form with 6 percent fixed PAA, and when converted to the sodium and potassium salts, this material showed moisture regain values comparable to that of cotton. The calcium salt form increased the melting temperature of the nylon to over 385°C.

DIFFUSION AND COPOLYMERIZATION OF POLYACRYLIC ACID IN NYLON 66
FIBERS TO ACHIEVE IMPROVED THERMAL PROTECTION AND HIGHER MOISTURE REGAIN.

1. Introduction

Nylon 66 has many excellent properties which have resulted in its clothing applications. These properties include high levels of tenacity, wet strength, elongation, elasticity, flexibility, abrasion resistance and resistance to microbiological deterioration.

However, nylon 66 has three properties which can make it undesirable for use in some military garments. One of these is a moisture adsorption capacity of only 4.2 percent under standard conditions of 70°F. and 65 percent relative humidity. This low adsorption negates comfort in hot, humid climates. Another property is the low melting point of 258°C. which results in fabrics that can cause severe skin burns during a conflagration. Also, it is inert to toxic agents unless modified. Modification of nylon 66 by copolymerization with PAA offers a means of eliminating all of these deficiencies. This was suggested by the work of Magat *et al* (1) which showed that sodium or calcium salts of acrylic acid monomer grafts were significantly hydrophilic and/or melted at a temperature higher than unreacted nylon.

The present study was encouraged by the possibility that alkali salts of other types of acrylic acid copolymers of nylon, in graft or block form, would produce moisture regain and thermal properties similar to those achieved by Magat *et al*(1). Consequently, known methods available for achieving a copolymer of polyacrylic acid with nylon 66 were sought and considered. Although a variety of techniques have been described for grafting acrylic acid monomer on nylon 66 and similar polyamides, few methods were found for copolymerizing polyacrylic acid homopolymer. Reports of both these techniques became prominent in the literature during the past several years:

Korshak *et al* (2) heated fibers from poly- ϵ -caproamide in air at 80-120°C. and then reacted the fibers by immersing them in peroxide free and dry acrylic acid or methacrylic acid. The grafted fibers showed a loss in tensile strength.

Cline and Tanner (3) were granted a patent covering the grafting of unsaturated acids on nitrogen containing polymers with the help of ultraviolet radiation. The use of acrylic acid with a polyamide was described by this patent. The use of photo-initiators was optional. Improved static resistance and hole melting properties were included in the claims made.

Horowitz (4) devised a method of grafting monomers, such as acrylic acid, to polyamide fibers in the presence of ceric ammonium nitrate, cerous acetate, or copper sulfate. The grafted material exhibited good wetting properties after several machine launderings with soap. He also described grafting acrylic acid to nylon 66 using ceric sulfate-sulfuric acid as an initiator. Improvements in wettability, handling, and wicking properties of nylon textile materials were claimed (5).

Hattori and Okira (6) achieved grafting by a pretreatment of nylon 6 with ammonium persulfate aqueous solution followed by a vapor phase treatment with acrylic acid and water. A nickel salt was prepared and was reported to have good heat and light resistance.

Haworth and Holker (7) reported the grafting of acrylic acid onto nylon 66 using ceric ammonium sulphate and ceric ammonium nitrate as initiators. Treated fibers stained with Methylene Blue were cross-sectioned and showed sharply defined deep blue peripheral layers of grafted polymer. This evidence of peripheral grafting was attributed to superficial penetration of the cerium salt into the fibers. Curing of the grafted product at a higher temperature resulted in a new product with reduced solubility in 90 percent formic acid. It was suggested that the insolubility could be accounted for by the cross-linking of fiber polymers with grafted polymers.

In an application for a patent, Imperial Chemical Industries Ltd. (8) described a catalyst system, containing a mixture of a transition-metal carbonyl derivative and an N-halogenated organic compound, used to graft acrylic acid on synthetic polymers, like nylon, which carry-NH groups on the main polymer chain.

Traumann (9) obtained grafting of acrylic acid to nylon 66 by means of an ammonium persulfate initiator. The acid form of the graft was converted to sodium and calcium salts. A fiber melting point temperature of 455°C. was claimed.

Tanner (10) found acrylic acid could be grafted to nylon 66 fabric by employing heat as the sole graft initiator. The grafting to a fabric produced an 18 percent gain in dry weight. The sodium salt of the grafted product showed improvement in nylon antistatic properties, resistance to hole melting, wet crease recovery and wickability.

Odor and Geleji (11) obtained acrylic acid grafts of a nylon using an organic initiator, dilauryl peroxide.

Faessinger and Conte (12) developed a peroxide initiated graft polymerization process using thioated nylon as a substrate. This compound was prepared by reaction of nylon with aqueous alkali and carbon disulfide, carbonyl disulfide, or a salt thereof. Vinyl monomers,

such as acrylic acid, were then graft-polymerized on the substrate.

Magat et al. (1) described the grafting of acrylic acid on a nylon 66 polymer by means of ionizing radiation. The graft copolymer was prepared by impregnating nylon 66 with aqueous acrylic acid monomer solution, allowing sorption of the acid, and then achieving a graft with radiation from a Van de Graaff generator. These grafts were readily converted to the corresponding sodium or calcium salts by treatment with sodium carbonate or calcium acetate. The sodium salts were highly hydrophilic as indicated by the moisture regain values which were similar to those for cotton. Calcium salts were more hydrophilic than the sodium salts. Greater electrical conductivity and antistatic properties accompanied this higher regain. The sodium salts also produced a high wet crease recovery of the fabric forms. The calcium salts resulted in an increase of the fiber melt temperature from 250°C. to above 400°C. In addition the excellent tensile properties of the nylon were retained. It thus appeared to Magat that grafting occurred mainly in the amorphous areas of the nylon substrate.

Nuessle et al. (13-15) investigated a reaction of polyacrylic acid homopolymer with nylon 66 in an attempt to determine why some textile producers had difficulty in removing polyacrylic acid sizing from the nylon. It was subsequently observed that the heat setting of the nylon 66 before the removal of the size insolubilized some of the polyacrylic acid. In this work Nuessle showed that when a commercial polyacrylic acid (M.W. 50,000) was heat set on nylon 66, a very durable crisp finish was produced. The polymer was applied by padding a solution of 5 percent or 10 percent solids, drying, and finally heating to temperatures from 149°C. to 218°C. The durability of the finish, as indicated by stiffness retention after laundering, varied directly with the severity of cure. Higher temperature and longer heating time were the two factors which increased the extent of fixation.

Nuessle's latest publication (15) did not reference the earlier work of Ronzoni et al. (16) in which similar heat fixation results were reported. The latter authors used three percent solutions of high molecular weight polyacrylic acids in the 250,000 to 400,000 range to achieve two percent dried residual polymer on fibers of nylons 6, 66, and 11. Heating for one hr. at 150°C. and 170°C., followed by ten minutes of water scouring at 80°C. and repeated water rinsing, showed a fixation of most of the applied polyacrylic acid. The amount of fixation was evaluated indirectly by titrating scour solutions with sodium hydroxide.

The brief study of Nuessle did not fully explore the theoretical and practical aspects of the reaction. Chemical combination of the polyacrylic acid on the surface of the nylon 66 fiber was suggested by the fact that a gossamer-like residue remained after the nylon was

extracted with boiling benzyl alcohol. This residue contained both nitrogen and unreacted carboxyl groups. Rupture of the nylon 66 amide group and formation of a new amide group with the polyacrylic acid was then considered to be the most plausible reaction. This reaction would give a type of block copolymer. However, imide formation by a nylon 66 amide linkage condensing with a polyacrylic acid carboxyl group or amide formation by a nylon 66 amine end group reacting with a polyacrylic acid carboxyl group were also considered possible and would give graft and block copolymers, respectively.

Regarding penetration, Nuessle (15) stated that "Polymer containing more than a very few monomer units cannot penetrate textile fibers - not even hydrophilic fibers such as cotton - and are thus restricted to the fiber surface, where they tend to bind fibre-to-fibre and yarn-to-yarn". This statement appears to reflect the current consensus of textile finishing experts.

The preceding literature indicates that intensive research and development on acrylic acid monomer grafting, has been carried out, but that the potential of copolymerizing polyacrylic acid on nylon has not been recognized. This may be because researchers question the ability of polyacrylic acid to diffuse into fibers and to form a block or a graft copolymer. Thus, it was decided to investigate further the reaction of polyacrylic acid with nylon 66 by heat curing. If copolymerization could be obtained by this method, the process would be more compatible with textile wet-finishing plant equipment, i.e., pad-dry-cure and dyeing equipment, than are acrylic acid monomer grafting systems.

In this investigation, polyacrylic acid having a relatively low molecular weight of 15,000 to 20,000 was applied from solution at a 121°C. temperature to promote diffusion into the fibers. This was done prior to the heat curing step. The extent of reaction was studied by determining the amount of unremovable polyacrylic acid. The location of the grafted polyacrylic acid was studied by cross-sectional staining of the fibers with a cationic dye. In addition, the copolymerized product was isolated from the unreacted nylon polymer by solvent extraction. The isolated product was characterized by thermal analysis using a differential scanning calorimeter and by infrared absorption. Finally, acetylated and sulfamated nylons were reacted with polyacrylic acid to assess the role of terminal amine groups in the reaction and thus attempt to elucidate the reaction mechanism.

2. Experimental

a. Materials

A plain weave nylon 66 fabric weighing 6.74 oz./sq. yd. and containing 38 ends and 36 picks of spun staple yarn was used throughout the study. Before use, the fabric was purified by intensive scouring in a jig with an alkaline non-ionic surfactant solution for two hours at 70°C. The solution contained 0.05 percent Triton X-100* by weight and sufficient sodium carbonate to obtain a pH of 11. This scour was followed by repeated rinsing to a neutral pH, hydroextraction and drying. Microscopic cross-sections of the scoured material showed that the yarns contained fibers of different diameters and also some pigment delustered fibers. The pigment was a titanium compound as indicated by emission spectroscopy. Details of this scouring are given in Procedure I, Appendix A.

Acetylated nylon 66 fabric was prepared by modifying the procedure of Peters (17) to further insure complete acetylation and thorough removal of the acid anhydride solution after acetylation**. Quadruplicate 2 x 12-inch samples of nylon 66 fabric, each weighing approximately 14g., were dried at 105°C. for two hours. After drying, the samples were placed in a one-liter reaction flask equipped with a reflux condenser vented with a drying tube. The samples were boiled at 86°C. for 112 hours in a solution of 140 ml. of acetic anhydride in 450 ml. of benzene. Removal of unreacted acetic anhydride was accomplished by boiling for one hour and rinsing twice in anhydrous ether. This procedure was followed by two cold water rinses and a 30 minute boiling water rinse with overnight cooling.

A PAA solution*** having 28% aqueous solids, an amber color, a density of 1.09 g./ml., and a pH of 1.6 was used throughout this study. According to the manufacturer, the molecular weight of this PAA was 15,000 to 20,000 and contained sulfuric acid.

b. Fixation Procedure

A 2 x 12-inch sample of fabric was heated to constant weight at 105°C. The dried and weighed sample was immersed in 50 ml. of the 28% PAA solution at a specific pH in an unsealed eight inch long test tube. Caustic soda flake was used to adjust the pH as required. Blank or control solutions were prepared in the same manner, substituting distilled water or dilute sulfuric acid for the PAA solutions.

* Product of Rohm and Haas Co.

** In initial work several samples gave comparable results when acetylated as in Procedure II, Appendix A.

*** An experimental solution furnished by American Cyanamid Company.

Several tubes were heated simultaneously at 121°C. for two hours in an autoclave with approximately 25 minutes additional time allowed for slow exhaustion of the autoclave chamber. The fabric samples were taken from the tubes and the surface solution was removed from each sample by passing it through two nips of a laboratory pad. Drying was accomplished for 20 minutes at 100°C. Finally, the samples were cured at 177°C. for ten minutes.

c. Removal of Unfixed PAA

Unfixed PAA was removed from each sample individually by extracting with hot water in a glass extraction thimble in a beaker. Extraction thimbles (Pyrex, Size B) were used to assure retention of loose yarn fragments. Each sample was rolled inside a weighed thimble and two thimbles were placed together in a 400 ml. beaker containing 275 ml. of water so that the samples were completely immersed. The water was heated to 95°C. on a steam bath, held at this temperature for 15 minutes, and then drained off. Each sample was subsequently rinsed with distilled water. This initial scouring and rinsing procedure was repeated twice more and was followed by three 1-hour scour cycles at the same temperature* before drying to constant weight at 105°C. Weight gain was determined by difference and the percent grafting was calculated based on the original sample weight. The samples produced in this manner were tan in color.

d. Removal of Unreacted Nylon 66

Both unreacted nylon 66 and accompanying titanium pigment were removed from the water-extracted samples by 2,2,2-trifluoroethanol extraction in a Soxhlet apparatus equipped with a cellulose extraction thimble (size 33 mm. x 80 mm., Whatman No. 2, double thickness) and a drying tube. As the nylon 66 dissolved during extraction, the titanium pigment contained was released and carried away by the trifluoroethanol solvent. Since the pigment had a small particle size, it passed through the cellulose extraction thimble and slowly settled to the bottom of the extraction flask. The extraction was continued for 6 hours (24 extractions) with a solvent temperature of 65° in the thimble. At this time the product was free of nylon 66. This was indicated first when no precipitate formed on diluting the last trifluoroethanol extract with water and second when the differential scanning calorimeter plot of the dried residue was found to be completely free of a characteristic nylon 66 endotherm at 259°C. The dark tan residues were rinsed with 75 ml. of absolute ethanol before

* A preliminary study showed that the third one-hour scour gave a minimum weight loss. Additional scourings gave small erratic weight losses which were apparently due to degradation resulting from extended heating to dryness at 105°C.

removal from the thimbles for analysis and the ethanol evaporated on a steam bath. These samples were identified as PAAN-3 and 4. In preliminary experiments, two samples identified as PAAN-1 and 2 were isolated in the more elaborate procedure shown in Procedure III, Appendix A. The Soxhlet procedure was preferred because of simplicity.

e. Thermal Analysis Procedure for Isolated Reaction Product

A Perkin-Elmer DSC-1 differential scanning calorimeter described by Watson et al.(18) and equipped with a Honeywell Electronic¹⁹ recorder was used for thermal analysis. The instrument was operated with nitrogen as the purging gas. Dried PAA control samples were placed in open platinum cups to insure that no reaction took place with residual H₂SO₄ from the pH 1.6 PAA solution. To verify whether any melting occurred with the nylon 66 control, one sample was examined in an uncovered aluminum cup. Closed aluminum cups were used as usual with other samples.

f. Cross-Sectioning and Staining Procedure

Seven yarns of each fabric sample were cross-sectioned in a Schwarz Fiber Microtome* after being imbedded in Mico Lac* mounting media. Six cross-sections each 20 microns thick were cut from each sample and were stained at room temperature by immersion for four hours in a 30 ml. bath of 0.0010% aqueous Malachite Green (91% pure) buffered at pH 7.0. They were then rinsed in water and dried. Cross-sections of the untreated nylon were also prepared unstained to serve as a standard for assessing the degree of staining.

The resulting cross-sections were examined under a microscope at 440X using mineral oil as a supplemental mounting media. Photomicrographs of selected significant slides were made at 680X using 5-second exposure times with Polaroid type 58 color film.

g. Characterization of Treated Fabric

Nylon 66 was treated as described above to achieve about six percent added weight of PAA after scouring. The material was converted to the sodium and calcium salts by boiling for one hour with one percent solutions of sodium carbonate and calcium acetate, respectively, at 25 to 1 bath ratios. This was followed by rinsing until the wash water was neutral to litmus and then drying. Moisture regain values were determined on the original free acid form and the sodium and calcium salt forms at 70°F. and 50 percent relative humidity. The melting point of the calcium form was measured in the differential scanning calorimeter. An aluminum cup with a special lid having a small

* Manufactured by Mico Instrument Company.

viewing hole was used to hold the sample. This cup was inserted in the sample chamber which also contained a viewing port. The chamber was purged with nitrogen while the temperature was elevated.

3. Discussion and Results

The relatively low molecular weight polyacrylic acid (PAA) selected for this grafting study was chosen to obtain maximum penetration into nylon fibers and minimum fabric stiffening as compared to the higher molecular weight polyacrylic acids. This was observed in a series of fabric samples treated with varying molecular weights of PAA. The color of the fabric changed from white to light tan in the treatment process, but this discoloration was not considered a serious matter at this stage of the research although it is recognized that some dyed shades cannot be achieved with a tan substrate. Moisture regain values measured on the treated material after converting it to the sodium and calcium salt were 5.5 and 4.8 percent, respectively. These values, measured at 70°F. and 50 percent relative humidity, were higher than the 4.5 percent regain value usually measured for cotton under identical conditions. The regain value of the free acid form of the grafted material was 2.5 percent, almost unchanged from that of the ungrafted nylon. A noticeable improvement in thermal properties was shown by the calcium salt of the material which maintained a fabric structure at temperatures much higher than the normal melting point of nylon, 259°C. Slight fabric darkening occurred at 340°C., increasing gradually as the temperature was raised. At 375°C. the fabric structure was still intact, but traces of melted material, assumed to be unmodified nylon, were evident; the fabric was nearly black at 385°C.

The amount of PAA fixed to the nylon substrate by this elevated pressure and temperature method varied (zero to six percent*) inversely with the pH of the grafting solution. Specifically, less than one percent fixation was obtained above pH 3.5 while the fixation increased rapidly below this pH. Table I shows these data where the pH varied from 5.5 to 1.6. The low pH of the treatment solution was due partly to PAA and partly to sulfuric acid originating in the PAA preparation. For this reason controls at different pH's were studied to determine the effect of acidity on the nylon under identical conditions of temperature and pressure. As shown in Table I, there was a small loss in weight of 0.7 to 0.8 percent in the samples under these conditions. The magnitude of this loss was only slightly higher than that for the PAA solution at higher pH. It was therefore concluded that the effect was relatively small and constant. No attempt was made, however, to use the control as a correction factor, although it indicated that the amount of PAA reacted might be somewhat higher than observed.

* Approximately three times this amount of unfixed PAA was retained by the nylon before scouring.

The inverse relationship between the amount of PAA fixed to the fabric and the pH of the PAA solution initially applied appears to depend on the extent of PAA diffusion into the nylon 66 fibers prior to reaction in situ. This diffusion is possibly a function of several factors, all of which are influenced by pH: (a) reduced hydrogen bonding between adjacent nylon 66 molecules could increase their intermolecular distances and thereby generate larger diffusion channels; (b) reduced hydrogen bonding between adjacent PAA molecules may give a narrower configuration for diffusion; (c) reduced hydrogen bonding between adjacent PAA and nylon 66 molecules might eliminate an obstacle to diffusion; and (d) PAA in solution at pH values greater than four exists as the ionized free acid in the uncoiled molecular configuration. At lower pH values where the ionization is suppressed, the coiled molecular configuration predominates, but may have an overall geometry which is more compatible with diffusion. For example, as a conceivable analogy, the wire of a coil spring can thread its way into a fiber mass as the spring rotates.

TABLE I
RELATIONSHIP OF pH TO FIXATION OF POLYACRYLIC ACID
ON NYLON 66

<u>Treatment Solution</u>	<u>pH</u>	<u>Average PAA Fixation (%)*</u>
PAA	5.5	-0.6
PAA	5.2	-0.3
PAA	4.5	-0.4
PAA	4.0	0.5
PAA	3.5	0.7
PAA	3.0	2.1
PAA	2.5	3.8
PAA	2.0	5.9
PAA	1.6	5.4
Water (Control)	5.2	-0.8
H ₂ SO ₄ (Control)	3.0	-0.7
H ₂ SO ₄ (Control)	1.6	-0.7

* Average increase in weight of sample after repeated scouring in boiling water.

Diffusion of PAA was shown to occur in the reacted materials by examining stained microscopic cross-sections of an untreated nylon control, a sulfuric acid treated nylon control, two PAA treated nylon samples (pH 1.6 and 3.0) and two PAA treated nylon samples previously

acetylated with acetic anhydride (Table II). The carboxyl groups of the PAA grafts presumably provided a site for dye fixation and an intense staining of the reacted fiber occurred. The unreacted nylon control did not stain significantly nor did the sulfuric acid treated nylon control. Both of these had a faint green tint as shown in Figures 2 and 3, respectively, with the latter somewhat darker. Unstained and untreated nylon is shown for comparison in Figure 1. The slightly greater staining after H₂SO₄ treatment can probably be explained by the formation of a sulfamic acid derivative of the nylon which provided additional sites for cationic dye reaction. Sulfamic acid formation might be expected under the relatively drastic conditions used, i.e. autoclaving in pH 1.6 H₂SO₄ at 121°C. and curing at 177°C. with residual H₂SO₄ present. All of these cross-sections show that the fibers varied in diameter and the unstained control shows that some fibers were pigment delustered. The pigment, as shown by emission spectroscopy, was a titanium compound and was assumed to be TiO₂, the delusterant normally used for textile fibers. However, these factors did not seem to prevent PAA reaction or penetration. Figure 4 shows the stained PAA-treated cross-section where staining deep into the center has taken place indicating PAA penetration. As expected, the smaller diameter fibers are more completely penetrated, but none of the fibers are merely stained at the periphery. This is the first reported observance of a penetration phenomenon of this type. Obviously, the optimum penetration conditions are yet to be achieved since all the fibers were not stained completely. However, the authors feel that this can be improved not only by changing the heat and pressure conditions, but also by using PAA of still lower molecular weights.

TABLE II
STAINING RESULTS FOR NYLON 66 SAMPLES

<u>Treatment</u>	<u>% PAA Grafted</u>	<u>Degree of Staining</u>	<u>Figure No.</u>
None (Control)	0	None (Unstained)	1
None (Control)	0	Trace	2
pH 1.6 H ₂ SO ₄ (Control)	0	Very slight	3
pH 1.6 PAA	5.5	Very heavy	4
Acetylation and pH 1.6 PAA	3.9	Very heavy	-
pH 3.0 PAA	2.1	Very heavy	-
Acetylation and pH 3.0 PAA	0.9	Very heavy	-

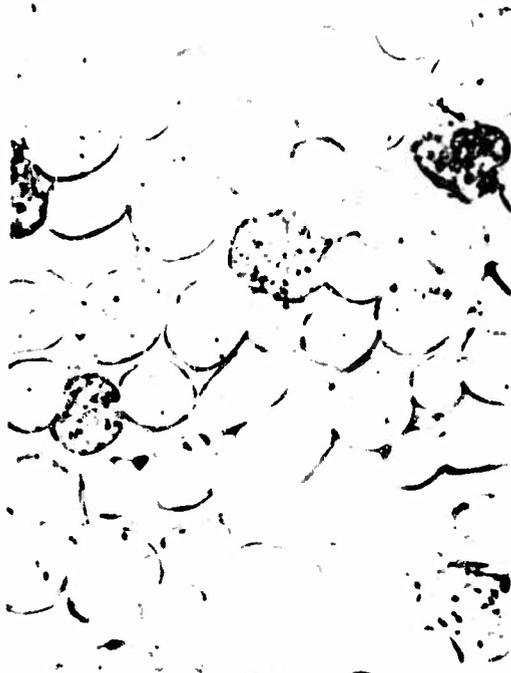


Fig. 1. Unstained untreated nylon 66 control.

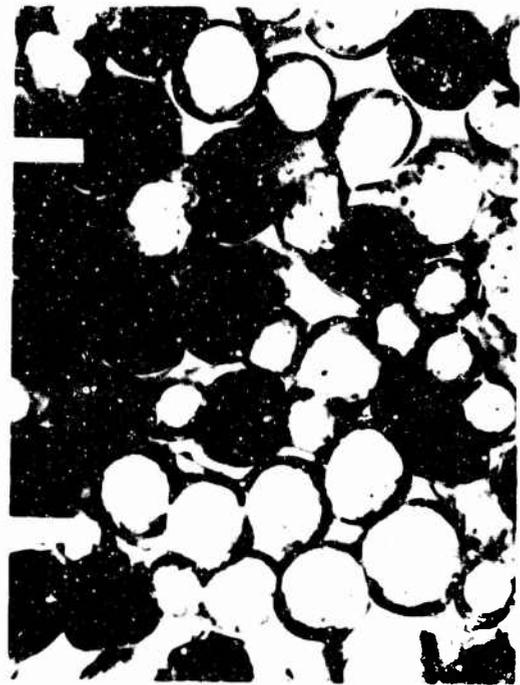


Fig. 2. Stained untreated nylon 66 control.

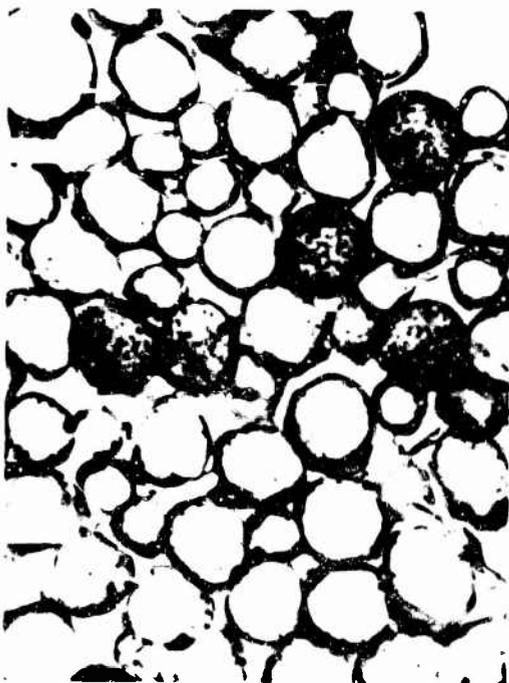


Fig. 3. Stained acid-treated nylon 66 control.



Fig. 4. Stained PAA-treated nylon 66.

An attempt was made to determine the mechanism of the fixation reaction by acetylating the amine end groups of the nylon fabric before treatment with PAA. Acetylation was carried out under stronger than normal conditions in an attempt to mask all of the amine groups. The results show a significant reduction in the amount of PAA fixed. In a similar experiment the nylon was treated with sulfuric acid to effect sulfamation of at least part of the amine end groups. When this material was treated with PAA in the usual manner at pH 3.0, a reduction in the amount of fixation was also obtained. These data are shown in Table III. It thus appears that the mechanism of the PAA reaction involves the amine end groups of nylon, presumably by amide formation with a carboxyl group of the PAA.

TABLE III

FIXATION OF PAA ON ACETYLATED AND SULFAMATED NYLON 66

<u>Treatment</u>	<u>pH</u>	<u>Average PAA Fixation (%)*</u>		
		<u>Nylon 66</u>	<u>Sulfamated Nylon 66</u>	<u>Acetylated Nylon 66</u>
PAA	1.6	5.7	--	4.4
PAA	1.6	4.1	--	2.8
PAA	3.0	2.2	1.4	0.8
H ₂ SO ₄ (Control)	3.0	-0.7	--	-1.2

* Average increase in weight of sample after repeated scouring in water at 95°C. Negative values are indicative of fiber loss during scouring.

This mechanism is not considered exclusive at this time as only a partial reduction in PAA fixation was achieved. Other mechanisms such as transamidation or imide formation are also possible as suggested by Nuessle (13-15).

Isolation of the PAA-nylon reaction product was accomplished by removal of unreacted nylon with 2,2,2-trifluoroethanol. Preliminary attempts at extracting the nylon, using boiling benzyl alcohol as described by Nuessle, were unsuccessful since PAA fixed material completely dissolved in this solvent. This solubility difference was attributed to the low molecular weight of the PAA used in this work. Other solvents, o-chlorophenol and m-cresol, were also satisfactory for extracting the nylon but were not used because of their toxicity.

The product obtained by this hot water scouring and 2,2,2-trifluoroethanol extraction procedure behaved differently from the unreacted nylon and PAA as expected. It was insoluble both in water, a PAA solvent, and trifluoroethanol, a nylon 66 solvent. Its differential scanning calorimeter curve had a moderate endotherm peak at 230°C. and a strong endotherm peak at 337°C., but it did not melt at these temperatures (See Figures 3B-6B of Appendix B). Also, there was no endotherm peak at 259°C. characteristic of unreacted nylon 66 (See Figure 1B of Appendix B). This indicated not only that the material had changed composition in the PAA fixation process, but also that the product was free of unreacted nylon. Similarly, there was no unreacted PAA present since the broad endotherm characteristic of PAA above 130°C. was also absent (See Figure 2B of Appendix B).

The infrared spectrum* of the isolated product showed a carbonyl peak at 1730 cm^{-1} indicating the presence of carboxyl groups along with the normal nylon 66 amide absorption peaks at 1650 cm^{-1} and 1550 cm^{-1} (See Figures 7B-10B of Appendix B).

The preceding has shown the following facts relating to copolymerization of a 15,000 to 20,000 MW polyacrylic acid prepolymer on nylon 66 by use of a heat cure mechanism.

- a. A five to six percent fixation of polyacrylic acid on nylon 66 fabric was obtained. The polyacrylic acid resisted removal by repeated scourings with water in which the polyacrylic acid homopolymer is highly soluble.
- b. The copolymerized product was isolated free of nylon 66 by extraction with 2,2,2-trifluoroethanol, a nylon solvent. The product was thus insoluble in both a nylon and a polyacrylic acid solvent.
- c. Thermal analysis of the isolated reaction product with a differential scanning calorimeter produced graphs with endotherm peaks at 230°C. and 337°C. which were not present in the plot of nylon 66. In addition, the nylon 66 melting point endotherm peak at 259°C. and the rapidly rising specific heat of polyacrylic acid above 130°C. were absent.

* Spectra were obtained in a Beckman Model IR 9 Spectrophotometer using KBr pellets.

d. Infrared spectra of the isolated reaction product showed a basic nylon 66 spectrum with a new carbonyl band added at the 1730 cm.^{-1} region. This carbonyl band is attributed to a polyacrylic acid copolymer.

The amount of polyacrylic acid copolymerization varied inversely with the pH of the polyacrylic acid solution used. It was necessary for the pH to be less than 3.5 to achieve adequate fixation. Fixation of from 2 to 6 percent was obtained at pH values between 3.0 and 1.6.

Diffusion and penetration of polyacrylic acid into the nylon 66 fibers prior to curing in situ were conclusively established by staining cross-sections of copolymerized fibers with a cationic dye. This diffusion of a polymer solution inside the fiber polymer is contrary to the experience and claims of previous researchers in the textile field.

A suggested mechanism for the copolymerization reaction is the formation of amide linkages (block copolymer) through a reaction of the terminal amine groups of nylon 66 with carboxyl groups of polyacrylic acid. This was indicated by the appreciable decrease of polyacrylic acid reaction with the nylon after the terminal amine groups of nylon 66 were blocked by either acetylation or probable formation of a sulfamic acid derivative. However, the fact that the reaction was not prevented entirely suggests that other copolymers were also produced.

A significant increase in the moisture regain of nylon was obtained as well as an increase in its thermal properties. For example, the sodium salt of a polyacrylic acid reacted nylon 66 fabric having six percent fixation resulted in a fiber having 5.5 percent moisture regain at 70°F. and 50 percent relative humidity. This product compares favorably with cotton which has a 4.5 percent moisture regain under the same conditions. The calcium salt of this same material was shown to be a high temperature resistant fabric which did not show significant melting tendencies up to 385°C.

4. Conclusions

Diffusion and copolymerization of polyacrylic acid (PAA) prepolymer in nylon 66 fibers has been attained as indicated by examination of stained fiber cross-sections and isolation of reacted material. The mechanism of the reaction appears to involve not only the amine end groups of the nylon by formation of a block copolymer, but also additional sites on the nylon backbone by formation of a graft copolymer. Of particular significance is the fact that penetration of the PAA into the nylon fiber can be achieved.

This diffusion and copolymerization process is advantageous as it can be accomplished in conventional textile wet-processing equipment. It

has the further advantage that the molecular weight of the copolymers can be controlled up to a point by the molecular weight of the PAA prepolymer used. Also, it yields a fabric with increased moisture sorption capacity and thermal radiation resistance.

One disadvantage of the process at present is its relatively low efficiency. The degree of fixation varies up to six percent after scouring. Since the weight increase before scouring is considerably higher, much of the PAA originally padded is unreacted. This unreacted PAA could presumably be recovered and recycled to prevent losses and increase the process efficiency. A better approach to this problem would be to obtain further penetration into the fibers and thus further fixation by lowering the PAA molecular weight and varying the process conditions.

5. Recommendations

It is recommended that further studies be conducted in the area of polyacrylic acid - nylon copolymerization including the use of other polyacrylic acids and less drastic PAA diffusion conditions to minimize damage to the nylon fiber.

The approaches would include:

- a. Eliminating H_2SO_4 from low pH polyacrylic acid solutions by either replacing it with a strong acid which can be vaporized after polyacrylic acid diffusion and prior to heat curing or by neutralizing the H_2SO_4 after diffusion.
- b. Using lower molecular weight polyacrylic acids with or without nylon 66 swelling agents to reduce the time and temperature required for polyacrylic acid solution diffusion.
- c. Determining the optimum time, temperature, pH and molecular weight conditions required for polyacrylic acid solution diffusion.
- d. Examining chemical protection properties and additional physical properties of grafted nylon 66 fabrics.
- e. Further elucidating the reaction mechanism and also investigating possible molecular weight changes caused by hydrolysis in the low pH environment of PAA.

6. Acknowledgments

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Appendix A - Procedures for Fabric Processing

PROCEDURE I

SCOURING OF NYLON 66 FABRIC

The entire 100 yard roll of nylon 66 fabric was scoured in a jig with an alkaline-detergent solution. The scouring solution consisted of 600 pounds (72 gallons) of softened water, 0.3 pounds of Triton X-100 (0.05 percent solution of nonionic surfactant), and 12.0 pounds of technical grade Na_2CO_3 which was used to achieve pH 11. Scouring was conducted at 79°C. for two hours at a rate of one minute and 50 seconds per end. Seven yards of self leader were used at each end.

The fabric was rinsed six times on the jig with softened water. This processing consisted of one 20 minute rinse at 57°C., one nine minute rinse at 46°C., and four ten minute rinses at 41°C. The fabric was then passed through squeeze rolls with a water spray rinse preceding the hydro-extraction. Drying was completed at 121°C. for two minutes in a Kenyon Pin Tenter.

PROCEDURE II

INITIAL ACETYLATION PROCEDURE
FOR NYLON 66 FABRIC

Two 2-inch by 12-inch samples of nylon 66 fabric were heated to a constant weight at 105°C. in an air circulating oven equipped with an analytical balance. These two samples with a combined weight of 7.1 g. were placed together in 300 ml. of acetic anhydride contained in a 500 ml. flask equipped with an immersion thermometer, electric heating mantle, and reflux condenser vented with a drying tube. Then the samples were reacted at approximately 110°C. for three hours and allowed to cool for 16 hours. Removal of the acetic anhydride was accomplished by boiling twice for 30 minutes in 300 ml. of anhydrous ether, washing at 50°C. for 30 minutes in 300 ml. of water, boiling twice for one hour in 300 ml. of water, and rinsing three times in 500 ml. of water. Finally, the samples were dried at 100°C. and stored in a desiccator.

PROCEDURE III

PRELIMINARY EXTRACTION PROCEDURE FOR ISOLATION OF POLYACRYLIC ACID REACTED NYLON 66 FROM UNREACTED NYLON 66

Samples of polyacrylic acid reacted nylon 66 fabric weighing about 4 g. each were dried at 105°C. for two hours in an air circulating oven. Each sample was placed in sufficient trifluoroethanol to make a 2.0 percent solution if completely dissolved and then allowed to remain undisturbed for 20 hours in a 250 ml. stoppered flask. The intent was to swell fibers and remove some nylon 66. The fabric was then disintegrated within 30 minutes by the spin bar of a magnetic agitator. A very opaque tan solution with gossamer-like fragments resulted. Next, the liquid was centrifuged for one hour in 50 ml. tubes to achieve removal of white sediment (presumably TiO_2) and a floating, agglomerated, light brown gossamer residue. Residues were separated on Whatman No. 2 filter paper along with some turbid brown liquid. The above extraction procedure was repeated three additional times with 100 ml. of trifluoroethanol and once with 50 ml. of trifluoroethanol. In these cases agitation was not required to disintegrate any fabric. When two ml. of each filtrate was diluted with five ml. of water, a turbidity from precipitated nylon 66 resulted. The gradual decrease of dissolved nylon 66 was indicated by the decreased turbidity in each of the successive filtrates. Separation of nylon 66 at room temperature after the fifth extraction appeared to be essentially complete. Each residue was dispersed in 100 ml. of water with one hour agitation and allowed to remain undisturbed for 40 hours. The intent of this water wash was to remove any trace of unreacted polyacrylic acid which may possibly have remained trapped in the fibers.

Appendix B - DSC Plots and IR Spectra of Reactants and Products

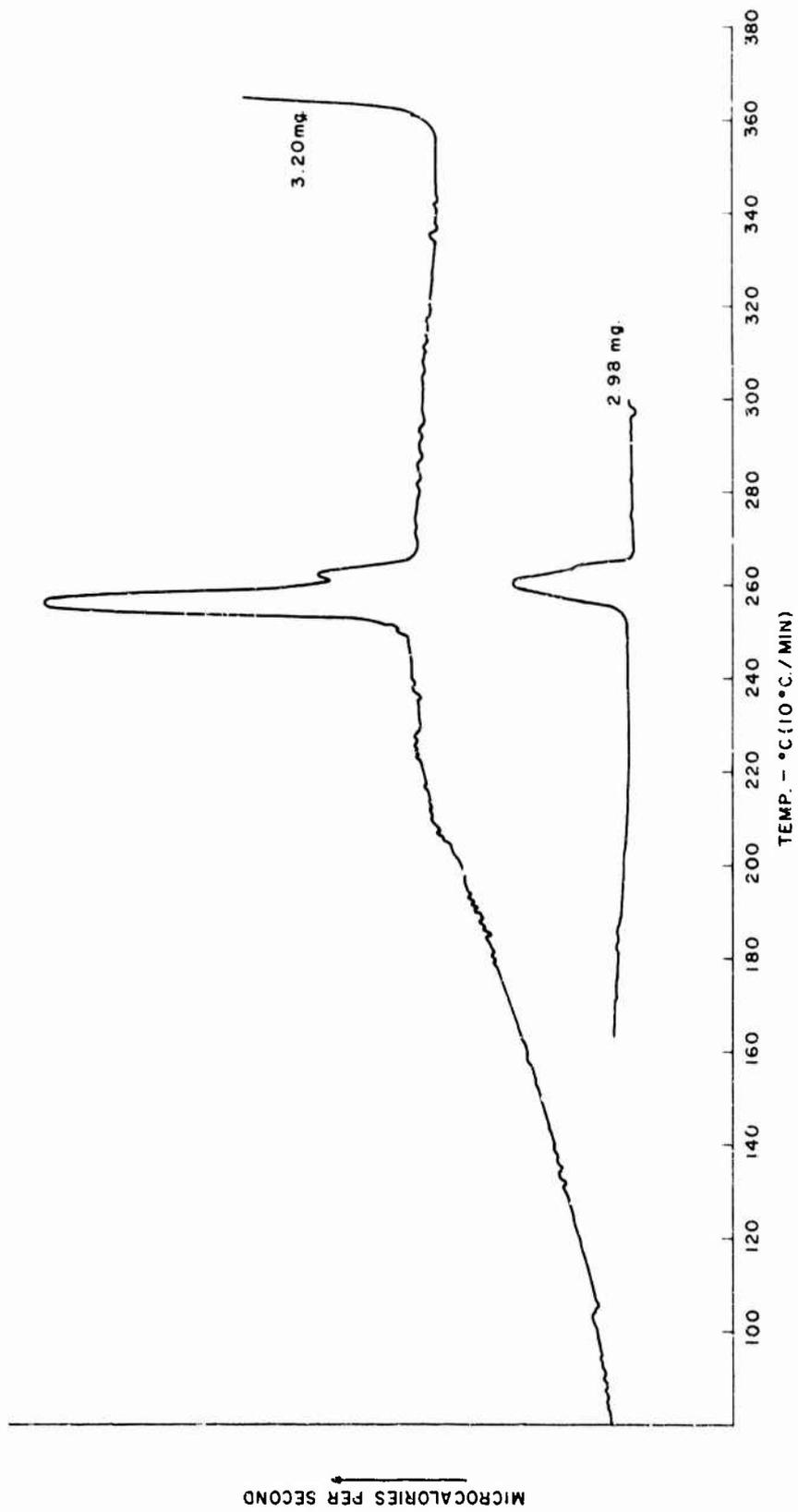


Figure 1B. DSC Plots of Nylon 66 Control

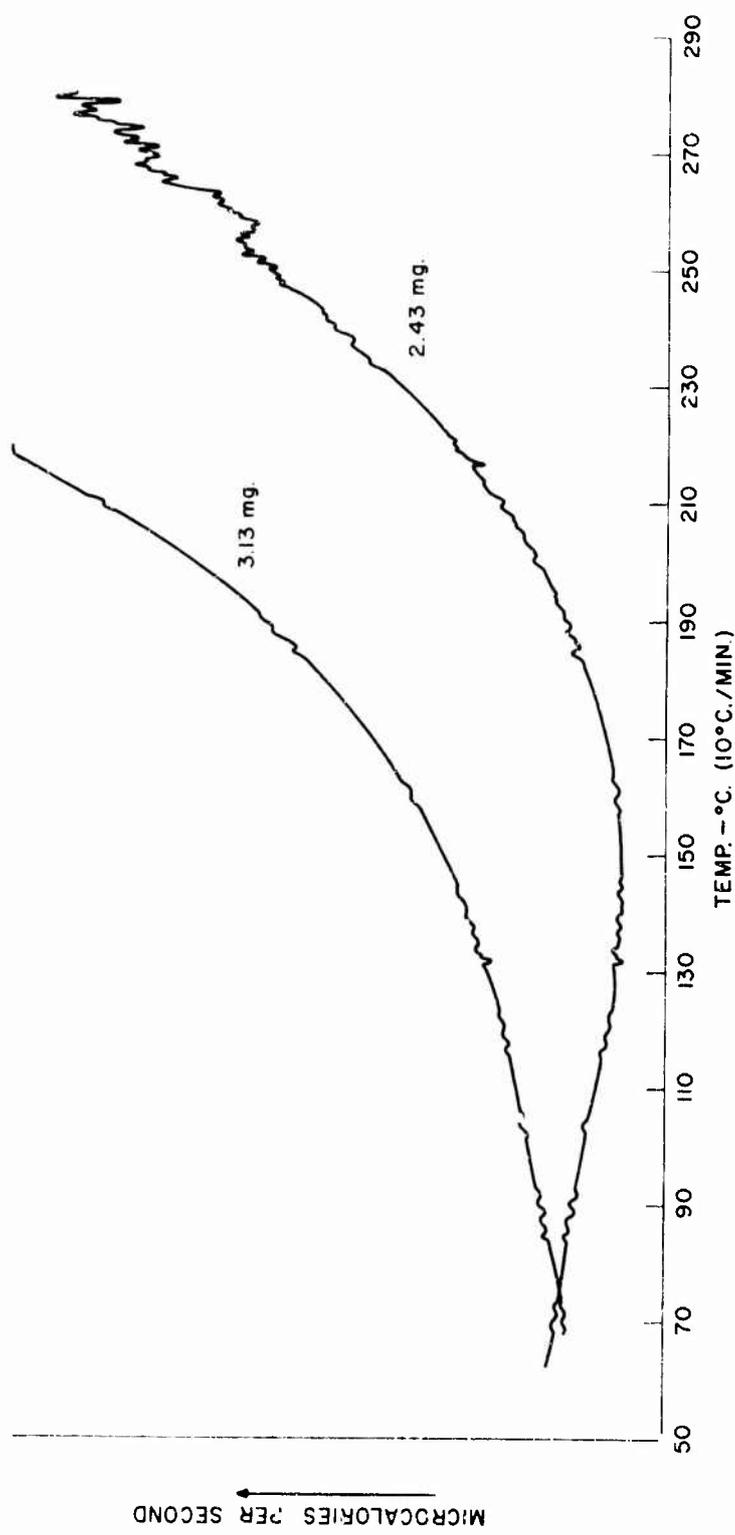


Figure 2B. DSC Plots of PAA Control

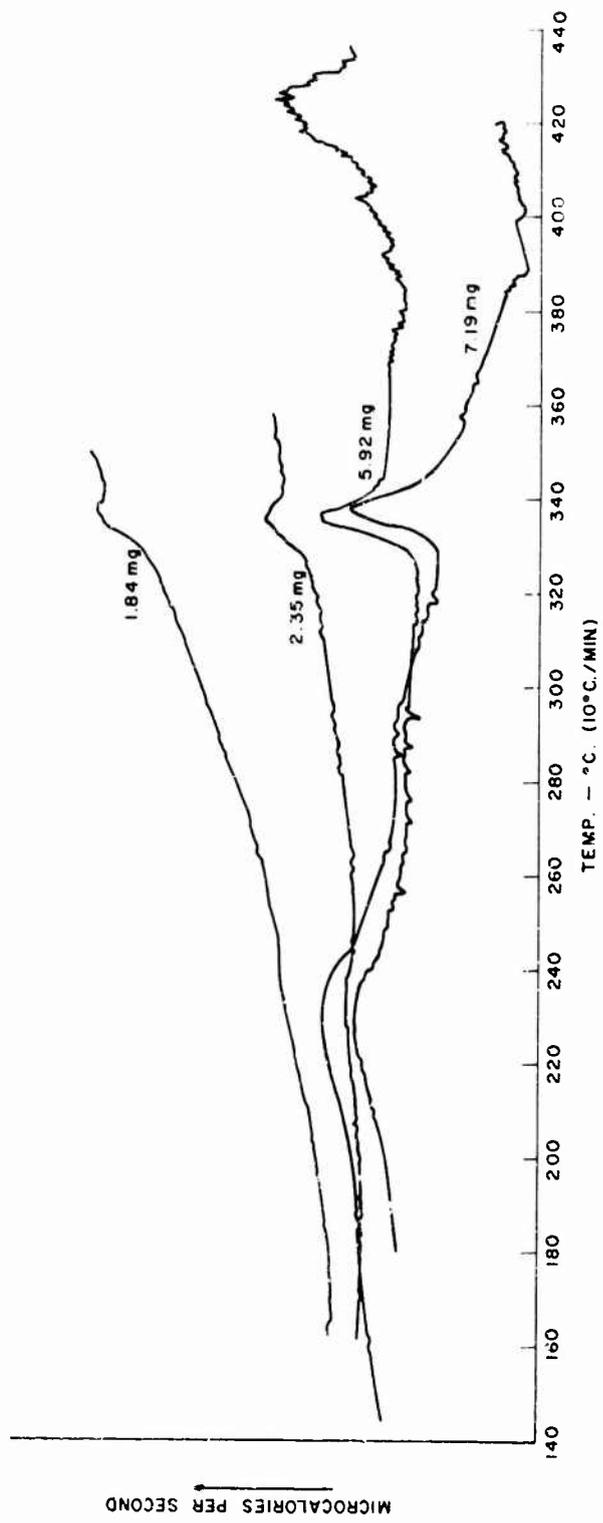


Figure 3B. DSC Plots of Copolymerized Product Isolated from Polyacrylic Acid Reacted with Nylon 66 Sample No. PAAN-1

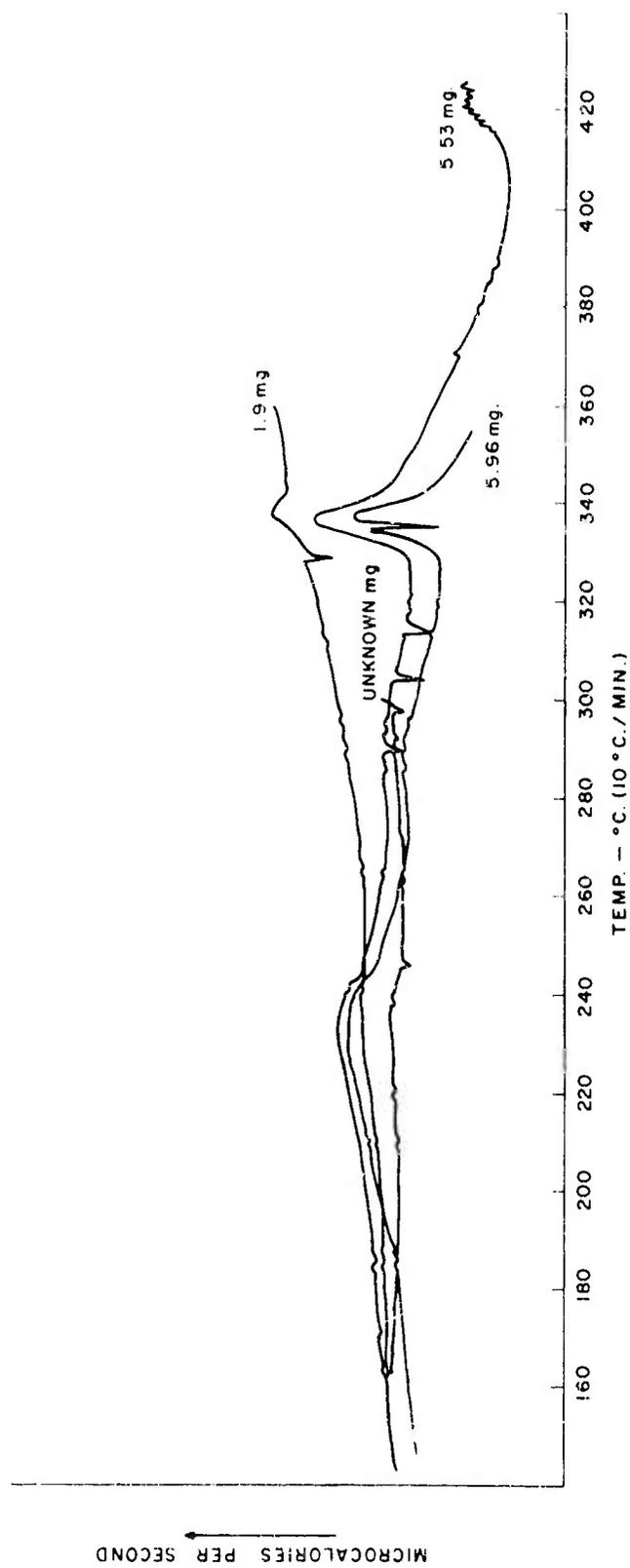


Figure 4B. DSC Plots of Copolymerized Product Isolated from Polyacrylic Acid Reacted Nylon 66
Sample No. PAAN-2

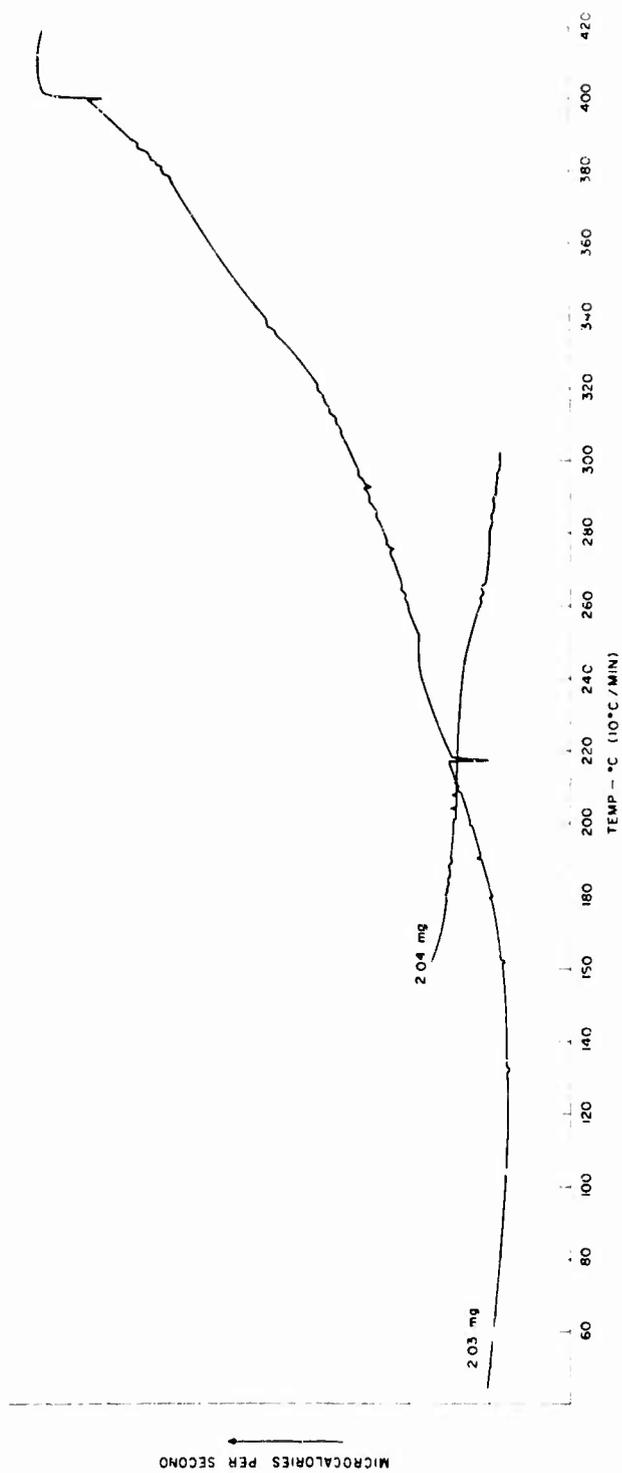


Figure 5B. DSC Plots of Copolymerized Product Isolated from Polyacrylic Acid Reacted Nylon 66 Sample No. PAAN-3

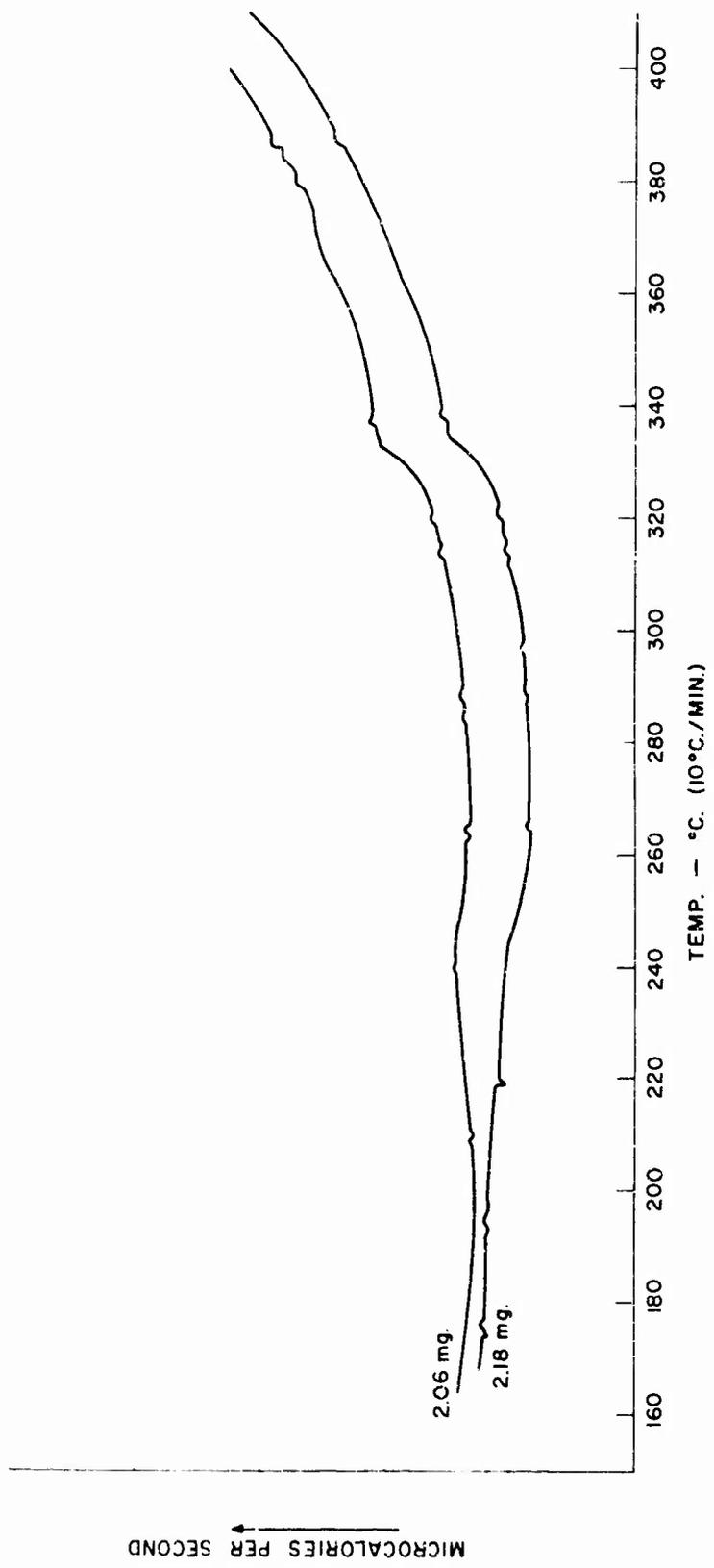


Figure 6B. DSC Plots of Copolymerized Product Isolated from Polyacrylic Acid Reacted Nylon 66
 Sample No. PAAN-4

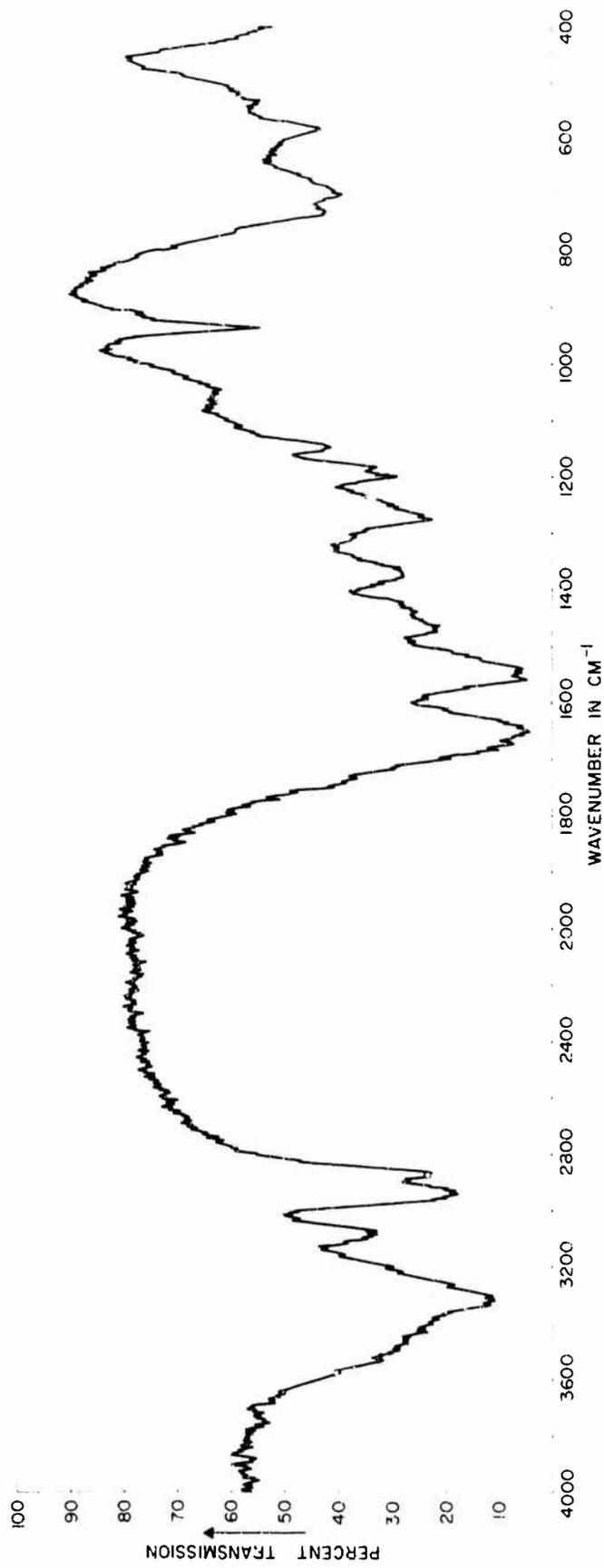


Figure 7B. IR Spectrum of Nylon 66 Control

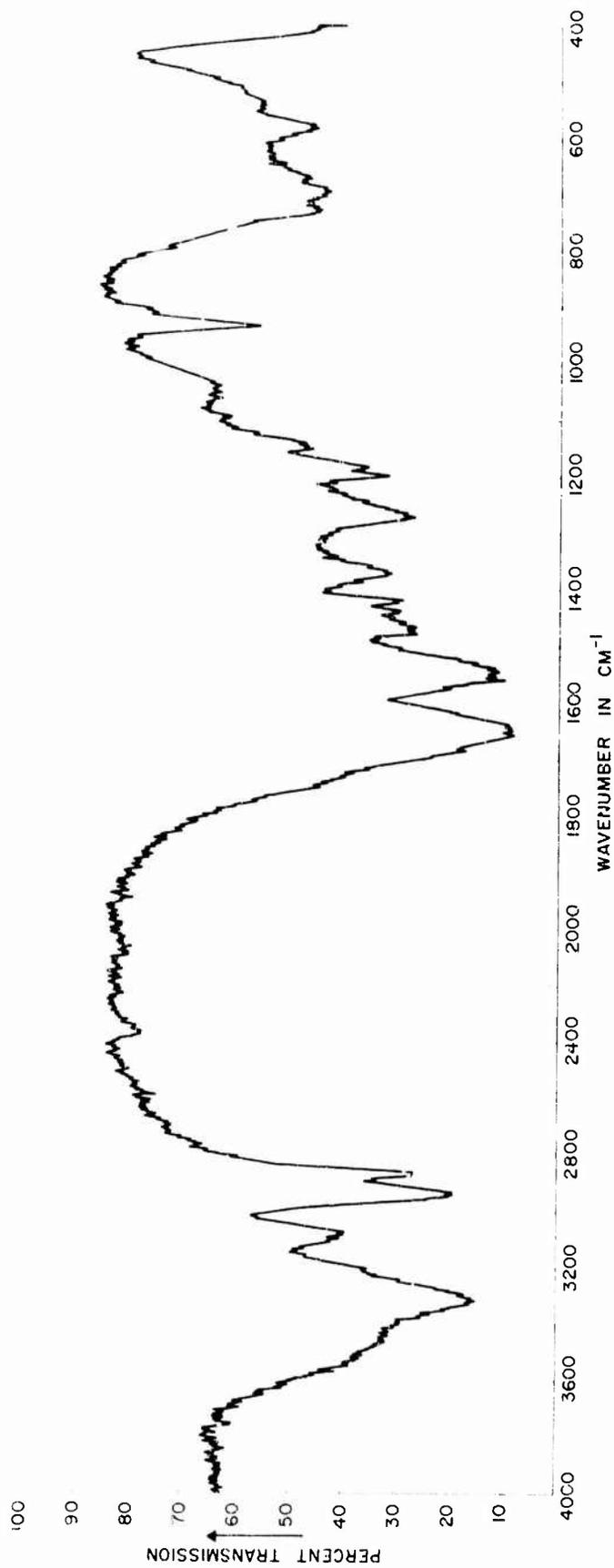


Figure 8B. IR Spectrum of Nylon 66 Control treated with H₂SO₄ at pH of 1.6
Sample No. 3-8

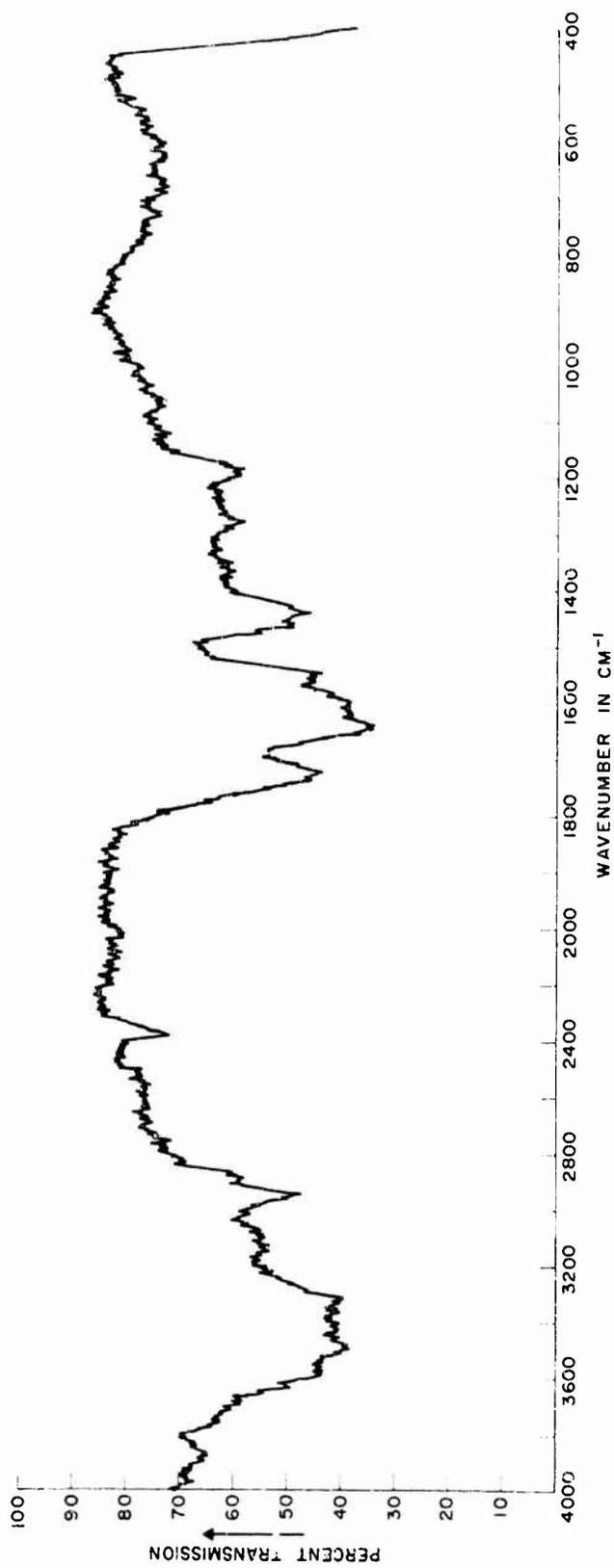


Figure 9B. IR Spectrum of Grafted Product Isolated from Polyacrylic Acid Reacted Nylon 66
Sample No. PAAN-3

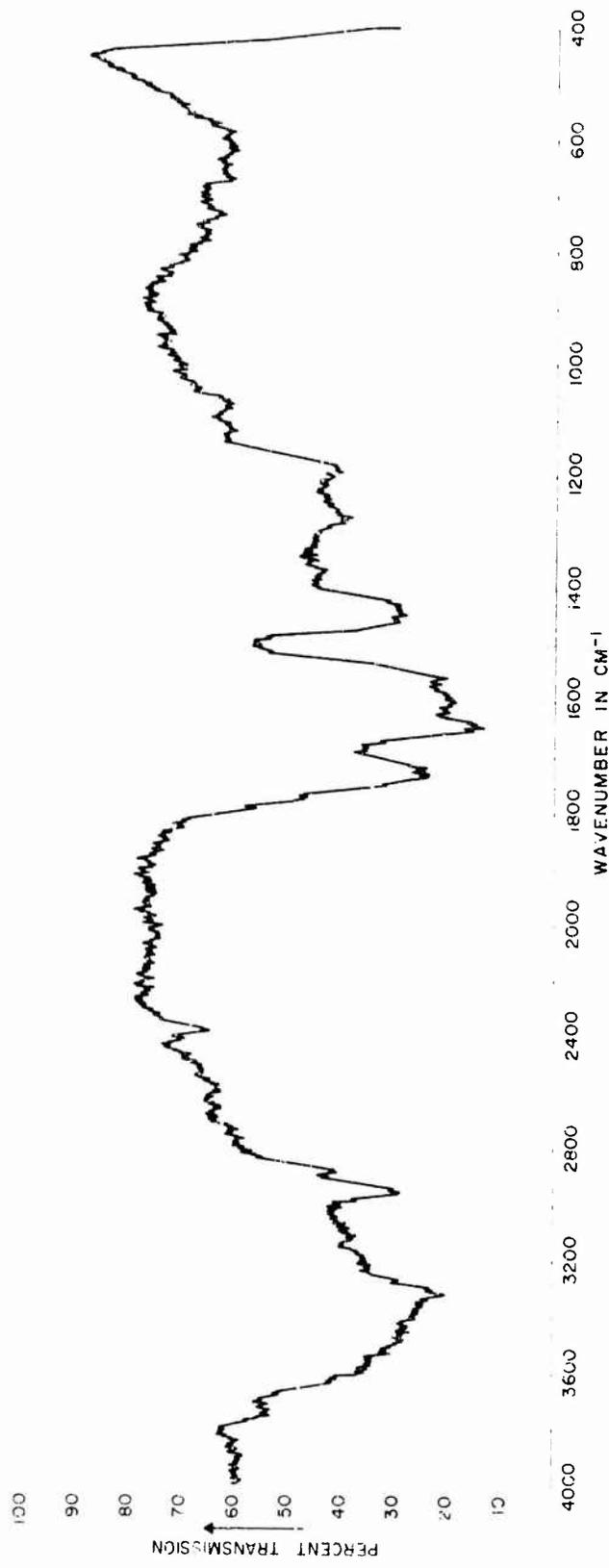


Figure 10B. IR Spectrum of Grafted Product Isolated from Polyacrylic Acid Reacted Nylon 66
Sample No. PAAN-4