

# Fibers from Polyurethanes Based on Halogen-Substituted Bisphenols\*

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## Synopsis

Fibers were prepared on an experimental scale by wet and dry spinning from eight, nonelastomeric polyurethanes based on halogen-substituted bisphenols. The fibers had properties suited to clothing textile uses. They were examined primarily for their potential in wash and wear fabrics. The fibers had moderate water absorption, low shrinkage in hot water, modest lowering of tensile properties under wet conditions, high tensile and work recoveries, and good stability to ultraviolet light. The polyurethanes from piperazines and 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane bischloroformate had unusually high thermal transitions and good solubility combined with ease of orientation and crystallization in fiber form. Fibers from the 2-methylpiperazine and homopiperazine urethanes were converted to fabrics. These fabrics exhibited a silklike handle, good wash wrinkle recovery, resistance to soil and bleach, stability to ironing at 200°C, and very low flammability.

## INTRODUCTION

There are few reports in the literature on fibers from linear, nonelastomeric polyurethanes.<sup>1-7</sup> In the 1940s German chemists developed to commercial production an aliphatic polyurethane from hexamethylene diisocyanate and 1,4-butanediol for use in fibers, bristles, and plastics under the name Perlon U.<sup>1,2</sup> Lyman<sup>3,4</sup> described fibers from polyurethanes based on aromatic diamines and bischloroformates of ethylene glycol and cyclohexane-diols. Wittbecker and co-workers<sup>5</sup> reported on a fiber from the polyurethane, poly(ethylene piperazine-1,4-dicarboxylate), with properties somewhat resembling poly(ethylene terephthalate) but with a dry hand akin to that of cotton. Fibers from an alternating polyurethane-ester from piperazine, ethylene glycol, and terephthalic acid were also described. Part of the present work has been described in patents.<sup>6,7</sup>

The apparent lack of interest in fibers from polyurethanes may be due to their general poor thermal stability for melt processing when the melting temperature is much above 200°C. The relation of chemical structure to the thermal degradation of polyurethanes and the mechanism of degradation has been extensively studied by Foti and co-workers and others.<sup>8-12</sup>

## RESULTS AND DISCUSSION

This report describes the preparation and characterization of fibers from a group of polyurethanes based on diamines and the bischloroformates of halogen-

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substituted bisphenols such as 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane and 2,2-bis(4-hydroxyphenyl)hexafluoropropane. The polymers used in this study are described in the preceding paper.<sup>13</sup>

### Fiber Preparation

Fibers were prepared by wet and dry spinning from solutions in organic solvents on small-scale, experimental equipment (Table I). Spinning procedures are subject to a large number of variables and the configuration and peculiarities of specific equipment. Detailed descriptions of such processes are given in reviews and monographs (for example, Refs. 14–17).

Tetrahydrofuran was a preferred solvent because of its volatility, water solubility, and easy removal from the fibers. Wet spinning was done by coagulation of the polymer solution in a water bath at or below ambient temperature. Dry spinning was done by extrusion of the solution into a heated column with a counter current flow of dry nitrogen. No large differences in fibers from the two spinning methods was found. Examples 7 and 8 show the effect of increased windup rate on ultimate crystallinity, tensile properties, and denier.

The fibers were drawn over heated plates and pins at the temperatures given in Table I. Although double drawing was effective (examples 9 and 11), this was not necessary as shown by the other examples. Examples 1–5 show the effect of drawing temperature on crystallinity, tensile strength, and denier.

MePip–TeCIDPPU and HomoPip–TeCIDPPU fibers crystallized readily and had tensile properties suitable for textile uses (Table I; polymer codes, footnote a). The remaining polymers spun easily; yet they responded less well to drawing. This is reflected in the lower degrees of crystallization and orientation and lower tensile strengths (examples 12–17).

### Fabric Preparation

Taffeta and twill fabrics were woven from fibers of MePip–TeCIDPPU (example 8) and HomoPip–TeCIDPPU (example 9) as well as from other similar spins. The fabrics were scoured and heat set with controlled shrinkage (tentered) at 210°C. These fabrics were used, along with fiber samples, in some of the following tests.

### Recovery Properties

The ability to recover from deformation is an important quality of textile fibers, both for processing characteristics and for end uses such as “wash and wear” fabrics. Since preparation and variation of fiber samples is far easier and less time consuming than fabric preparation, chemists have sought tests which might predict the behavior of fibers in fabrics.<sup>18–22</sup> Work and tensile recoveries (Tables II and III) and wash set recovery angles are several such tests which have been used as indicators of wrinkle resistance and wrinkle recovery in fabrics.

Fabrics from polypivalolactone,<sup>23</sup> poly[bis(4-cyclohexyl)methane azeleamide],<sup>24</sup> and poly[2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane isophthalate]<sup>25</sup> are known to have excellent wrinkle recovery after washing. The fibers show high tensile and work recoveries, dry and wet. HomoPip–TeCIDPPU and

TABLE I  
Fiber Preparation and Properties

| No. | Polymer                                    | Spinning          |                        |                   |                      |                  | Tensile properties <sup>f</sup>           |                 |   |              |          |                           |        |
|-----|--|-------------------|------------------------|-------------------|----------------------|------------------|---|-----------------|---|--------------|----------|---------------------------|--------|
|     |  | Code <sup>a</sup> | $\eta_{inh}$<br>(dL/g) | Type <sup>b</sup> | Solvent <sup>c</sup> | Solids<br>(wt %) | Spin stretch/<br>windup rate <sup>d</sup> | Drawing<br>(°C) | Crystallinity <sup>e</sup><br>(amt/perf/orient) | T<br>(g/den) | E<br>(%) | M <sub>i</sub><br>(g/den) | Denier |
| 1   | MePip-TeCIDPPU                             |                   | 0.82                   | Wet               | THF                  | 20               | 1.1/32.5                                  | 3.0X, 250       | 1/1—  | 2.89         | 11.6     | 47                        | 3.16   |
| 2   |  |                   |                        |                   |                      |                  |   | 3.2X, 250       | m/m/h   | 3.33         | 14.1     | 47                        | 3.1    |
| 3   |  |                   |                        |                   |                      |                  |   | 3.2X, 260       | m/m/h   | 3.72         | 19.1     | 45                        | 3.09   |
| 4   |  |                   |                        |                   |                      |                  |   | 2.1X, 272       | m/m/h   | 3.66         | 15.3     | 51                        | 2.49   |
| 5   |  |                   | 1.14                   | Wet               | THF                  | 20               | 1.1/32.5                                  | 3.2X, 272       | m/m/h   | 3.81         | 15.3     | 53                        | 2.36   |
| 6   |  |                   | 0.85                   | Dry               | THF                  | 24               | 4/175                                     | 3.0X, 240       | m/m/h   | 3.37         | 25.2     | 42                        | 2.52   |
| 7   |  |                   | 1.04                   | Dry               | THF <sup>s</sup>     | 25               | 2.8/111                                   | 3.2X, 250       | m/h/h   | 3.57         | 19.4     | 38                        | 3.41   |
| 8   |  |                   |                        |                   |                      |                  | 5/200                                     | 3.2X, 250       | b/h/h   | 3.63         | 17.4     | 46                        | 1.74   |
| 9   | HomoPip-TeCIDPPU                           |                   | 1.1                    | Wet               | THF-TrCE<br>(90-10)  | 18               | 1.1/33                                    | 3.8X, 205       | m/m/m   | 2.75         | 14.1     | 46                        | 1.82   |
| 10  |  |                   | 0.76                   | Dry               | THF                  | 29               | 2.2/115                                   | 1.4X, 230       | b/h/h   | 3.11         | 16.6     | 44                        | 3.70   |
| 11  |  |                   | 0.82                   | Dry               | THF                  | 27               | 2.2/115                                   | 4X, 198         | b/h/h   | 2.40         | 14.8     | 46                        | 2.77   |
| 12  | Pip-TeCIDPPU                               |                   | 1.01                   | Dry               | TrCE                 | 18               | 2.0/92                                    | 3.0X, 280       | m/l/m   | 1.75         | 13.5     | 33                        | 4.02   |
| 13  | 6-TeCIDPPU                                 |                   | 0.9                    | Dry               | THF-TrCE<br>(95-5)   | 28               | 3.5/105                                   | 1.2X, 225       | 1/1   | 0.91         | 95       | 23                        | 4.42   |
| 14  | PACM-TeCIDPPU<br>(70% <i>trans-trans</i> ) |                   | 1.11                   | Dry               | THF-TrCE<br>(95-5)   | 21               | 2.8/133                                   | 2.3X, 210       | 0/0/m   | 1.98         | 12.6     | 38                        | 3.3    |
| 15  | MePip-DCIDPPU                              |                   | 0.82                   | Dry               | TrCE-TFA<br>(70-30)  | 25               | 4/152                                     | 3.75X, 240      | 1/1   | 1.54         | 27.4     | 34                        | 2.44   |
| 16  | MePip-HFDPPU                               |                   | 1.0                    | Dry               | THF-TrCE<br>(88-12)  | 20               | —/104                                     | 1.6X, 165       |   | 1.55         | 30.8     | 23                        | 6.49   |
| 17  | DMePip-HFDPPU                              |                   | 0.93                   | Dry               | THF-TrCE<br>(97-3)   | 25               | 3/116                                     | 1.5X, 220       |   | 2.01         | 34.0     | 31                        | 8.2    |

<sup>a</sup> Polymer codes: 6 = hexamethylenediamine; Pip = piperazine; MePip = 2-methylpiperazine; DMePip = *trans*-2,5-dimethylpiperazine; HomoPip = homopiperazine; PACM = bis(4-aminocyclohexyl)methane; TeCIDPPU = urethane from 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane; DCIDPPU = urethane from 2,2-bis(4-hydroxy-3-chlorophenyl)propane; HFDPPU = urethane from 2,2-bis(4-hydroxyphenyl)hexafluoropropane.

<sup>b</sup> Wet spinning into water bath at room temperature; dry spinning by solvent evaporation in counter current flow of nitrogen.

<sup>c</sup> THF = tetrahydrofuran; TrCE = 1,1,2-trichloroethane; TFA = trifluoroacetic acid.

<sup>d</sup> Spin stretch is the ratio windup rate in yards/minute to the linear extrusion rate.

<sup>e</sup> Amount/perfection/degree of orientation: 0 = none; l = low; m = medium; h = high.

<sup>f</sup> T = tenacity; E = elongation to break; M<sub>i</sub> = initial modulus. Determined on filaments after yarn boiloff and conditioning at 21 °C and 65% relative humidity.

<sup>g</sup> Dope made by direct polymerization.

TABLE II  
Comparison of Recovery Properties of Several Fibers<sup>a</sup>

| Fiber   | Fiber <sup>b</sup><br>spin<br>no. | Tensile recovery |    |     | Work recovery |    |     | WSRA <sup>c</sup> |
|---|-----------------------------------|------------------|----|-----|---------------|----|-----|-------------------|
|   |                                   | 3%               | 5% | 10% | 3%            | 5% | 10% |                   |
| Poly(hexamethylene adipamide)                               |                                   | 93               | 89 |     | 60            | 61 | —   | 90-155            |
| Poly(ethylene terephthalate)                                |                                   | 81               | 69 |     | 42            | 33 | —   | 210-255           |
| Polypivalolactone   |                                   | 99               | 96 | 91  | 94            | 88 | 74  | 320               |
| Poly[bis(1,4-cyclohexyl)methane<br>azeleamide] <sup>d</sup> |                                   | 98               | 94 |     | 83            | 71 | —   | 315               |
| TeCIDPP-I <sup>e</sup>                                      |                                   | 86               | 85 |     | 69            | 60 | —   | 350               |
| 6-TeCIDDP   | 13                                | 86               | 75 | —   | 61            | 43 | —   | 325               |
| PACM-TeCIDPPU <sup>d</sup>                                  | 14                                | 87               | 79 | —   | 66            | 50 | —   | 310               |
| Pip-TeCIDDP   | 12                                | 89               | 78 | —   | 74            | 51 | —   | 305               |
| MePip-DCIDDP  | 15                                | 80               | 75 | —   | 63            | 49 | —   | 280               |
| MePip-TeCIDPPU  | 8                                 | 95               | 85 | 72  | 86            | 67 | 43  | 310               |
|   | 6                                 | 94               | 86 | 67  | 84            | 64 | 38  |                   |
| HomoPip-TeCIDPPU  |                                   | 96               | 88 | 64  | 87            | 67 | 34  | 325               |
|   | 11                                | 92               | 86 | 67  | 82            | 62 | 36  | 315               |

<sup>a</sup> Definitions and methods in the Experimental section. For polymer codes see Table I, footnote a.

<sup>b</sup> From Table I.

<sup>c</sup> Wash set recovery angle.

<sup>d</sup> Diamine was 70% *trans-trans* isomer.

<sup>e</sup> Isophthalate of 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane.

MePip-TeCIDPPU fibers have nearly equal recoveries under most of the conditions recorded. This good omen was borne out by the good wash wrinkle recovery of the fabrics.

TABLE III  
Shrinkage and Wet Recovery Properties of Fibers<sup>a</sup>

| Test                       | HomoPip-<br>TeCIDPPU | MePip-<br>TeCIDPPU | Poly[bis(1,4-cyclohexyl)methane<br>azeleamide] |
|----------------------------|----------------------|--------------------|--|
| Shrinkage in hot water (%) | 0.0                  | 1.4                | 2.9  |
| Wash set recovery angle    | 315°                 | 310°               | 315°   |
| Tensile recovery, 3/5/10%  |                      |                    |  |
| 21°C, dry                  | 92/86/67             | 95/85/72           | 98/94/—  |
| 21°C, wet                  |                      | 92/87/70           |  |
| 40°C, wet                  | 89/77/66             |                    | 94/91/—  |
| 60°C, wet                  | 82/75/66             | 79/75/72           | 87/81/—  |
| 90°C, wet                  | 75/73/72             |                    |  |
| Work recovery, 3/5/10%     |                      |                    |  |
| 21°C, dry                  | 82/62/36             | 86/67/43           | 83/71/—  |
| 21°C, wet                  |                      | 83/66/41           |  |
| 40°C, wet                  | 76/52/38             |                    | 76/59/—  |
| 60°C, wet                  | 64/52/35             | 60/51/43           | 68/52/—  |
| 90°C, wet                  | 58/52/45             |                    |  |

<sup>a</sup> Test methods described in the Experimental section. Polymer codes in footnote a of Table I.

Wash set recovery angles (WSRA) on a large number of fibers had shown that values above 300° could indicate good wash wrinkle recovery. However, lower values were not necessarily indicators of poor performance. All of the fibers of Table II, except poly(hexamethylene adipamide) and poly(ethylene terephthalate), recovered 300° or more.

This and other experience in the correlation of fabric behavior with fiber properties leads to the conclusion that high work and tensile recoveries in fibers are useful indicators of potential good wrinkle resistance in fabrics. However, there are numerous other factors which may enhance or detract from the desired fabric properties and behavior. Some of these are fiber denier, cross section, and surface; molecular orientation and crystallinity; yarn count and twist; fabric construction, heat-setting, and laundering. The end result is that, having screened fiber compositions for good potential, one still must prepare and process fabrics to demonstrate the final performance.

### Thermal Tests

Table IV gives the glass transition temperature, fiber stick temperature, and zero strength temperature for several polyurethane fibers and other fibers for comparison. The two urethanes from piperazines and 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane have glass transitions above 200°C, fiber stick temperatures above 300°C, and zero strength temperatures a few degrees higher.

Fibers from these two polymers became yellow when heated at 200°C in air for 2 h but showed no change in tensile properties. At 20 h the fibers had disintegrated.

Scoured taffeta fabrics from these two polymers could be ironed dry or moist at a cotton setting (200°C determined by surface pyrometer) and any wash wrinkles were removed. The fabrics were not scorched or stiffened by standing

TABLE IV  
Fiber Thermal Tests

| Polymer <sup>a</sup>                      | $T_g$ (°C) | Fiber stick <sup>b</sup><br>temperature<br>(°C) | Zero<br>strength <sup>b</sup><br>temperature<br>(°C) |
|---|------------|---|--|
| Poly(ethylene terephthalate)              | 65         |   | 238  |
| Polypivalolactone                         | 15         |   | 195  |
| Poly( <i>m</i> -phenylene isophthalamide) | 265-270    | 300   | 420  |
| DDM-2U <sup>c</sup>                       | 90         | 216   |  |
| DDP-2U <sup>c</sup>                       |            | 177   |  |
| Pip-DPPU                                  | 175        | 268   |  |
| HomoPip-TeCIDPPU                          | 210        | 317   | 335  |
| MePip-TeCIDPPU                            | ca. 220    | 352   | 360  |

<sup>a</sup> Polymer codes: DDM = bis(4-aminophenyl)methane; DDP = 2,2-bis(4-aminophenyl)propane; Pip = piperazine; MePip = 2-methylpiperazine; HomoPip = homopiperazine; 2U = urethane from ethylene glycol; DPPU = urethane from 2,2-bis(4-hydroxyphenyl)propane; TeCIDPPU = urethane from 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane.

<sup>b</sup> Test methods and definitions given in the Experimental section.

<sup>c</sup> Reference 3.

for 1 min under the hot iron. Removal of heat-set wrinkles required a slightly higher temperature. Scoured fibers from Pip-TeCIDPPU were likewise stable to hot ironing.

### Flammability

The fabrics from the chlorine substituted polyurethanes char while in a flame. There is no drip of melted polymer and burning stops as soon as the igniting source is removed. Their flame resistance exceeds any flammability rating for commercial clothing.

### Chemical Resistance

Fibers from HomoPip-TeCIDPPU wound on stainless steel bobbins and soaked in 20% aqueous sulfuric acid or sodium hydroxide showed no change in appearance. The acid treated fiber decreased some in tenacity and elongation (Table V). The changes in denier could represent some surface etching, extraction of low molecular weight polymer, or only a difference in samples. Fabric from HomoPip-TeCIDPPU was heated at the boil for 2 h in these solutions and showed no color, shrinkage, or weight loss.

Fibers from HomoPip-TeCIDPPU and a fabric from MePip-TeCIDPPU withstood 20 h in undiluted aqueous bleach (4.75% NaOCl; pH 10.9) without coloration or loss in tensile properties. These bleached and washed samples could be ironed at 200°C without damage. Pip-DPPU [polyurethane from piperazine and 2,2-bis(4-hydroxyphenyl)propane] fabric in bleach, as above, did not discolor or change. The washed, damp sample was stiffened and shrank some under a 200° iron. It also showed color upon heating for 1 min. However, the same ironing behavior resulted with an unbleached control. The glass transition temperature of this polymer is 175°C (Table III).

### Solvent Sensitivity

Treatment of boiled-off, heat-set fibers of HomoPip-TeCIDPPU and MePip-TeCIDPPU, wound loosely on a bobbin, with perchloroethylene at 60°C produced about 1% shrinkage. All samples were disintegrated in 1,1,2-trichloroethylene at 60°C. The fibers were not harmed by 2B ethanol at room temperature.

### Light Stability

Fibers of Pip-, MePip-, and HomoPip-TeCIDPPU were uncolored by exposure in the Fade-Ometer for 1000 h.<sup>13</sup> The loss in tenacity upon light exposure

TABLE V  
Treatment of HomoPip-TeCIDPPU Fibers with Aqueous Acid and Alkali

| Fiber sample                        | <i>T</i> (g/den) | <i>E</i> (%) | <i>M<sub>i</sub></i> | Denier |
|-------------------------------------|------------------|--------------|----------------------|--------|
| Untreated                           | 2.73             | 16.5         | 44                   | 1.90   |
| 20% sulfuric acid, 100 h at 25°C    | 2.32             | 14.2         | 43                   | 1.54   |
| 20% sodium hydroxide, 100 h at 25°C | 2.56             | 17.0         | 44                   | 1.51   |

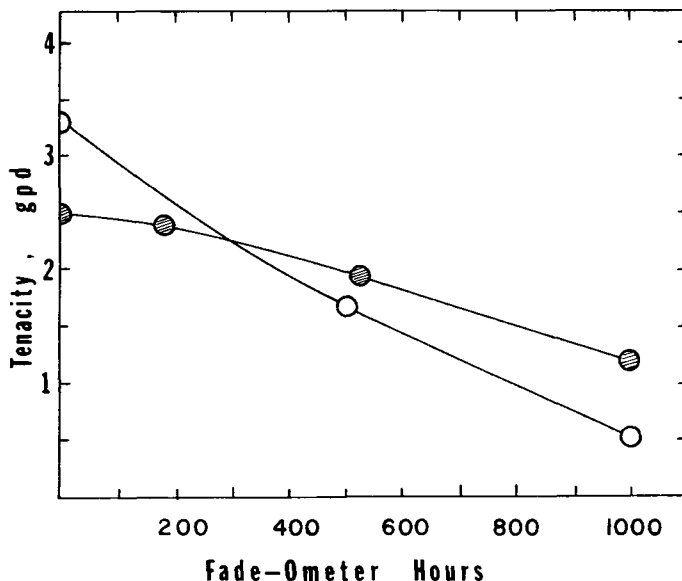


Fig. 1. Tenacity of fibers of MePip-TeCIDPPU (O) and HomoPip-TeCIDPPU (Θ) vs. hours of exposure in the Fade-Ometer.

for MePip- and HomoPip-TeCIDPPU fibers is plotted in Figure 1 and shows half-lives of 500 and 1000 h, respectively. The elongation half-lives were 300 and 650 h.

### Gamma Radiation Exposure

Yarns from HomoPip-TeCIDPPU in the form of a fabric were exposed to a Van der Graf generator with the results shown in Table VI. There was a rapid loss in inherent viscosity but the fibers did not become too brittle to test. The final sample was yellow.

TABLE VI  
Exposure of HomoPip-TeCIDPPU Fabric to Gamma-Radiation<sup>a</sup>

| Test <sup>c</sup> | Number of passes in the Van der Graf generator <sup>b</sup> |      |      |      |      |
|-------------------|---|------|------|------|------|
|                   | 0   | 25   | 50   | 100  | 200  |
| $\eta_{inh}$      | 1.03  | 0.48 | 0.31 | 0.24 | 0.19 |
| Tenacity (g/den)  | 2.26  | 1.78 | 1.46 | 1.10 | 0.20 |
| Elongation (%)    | 24  | 17.6 | 11.3 | 4.5  | 1.5  |
| Modulus (g/den)   | 40  | 34   | 32   | 32   | 16   |

<sup>a</sup> The fiber was medium in crystallization and high in orientation; 2.2 denier per filament; fabric from 30 filament yarn.

<sup>b</sup> Radiation intensity, 10 W/cm<sup>2</sup>; exposure/pass, 12.5 W s/cm<sup>2</sup>.

<sup>c</sup> Physical tests are defined in the Experimental section.

### Fabric Qualities

The taffeta fabrics, in particular, had silklike hand, luster, and liveliness. They had a high degree of resistance to wrinkling after various washing and drying procedures. They dyed well with disperse dyes and had other desirable qualities indicated by tests discussed under thermal tests, bleaching, light stability, solvent resistance and flammability. The fibers of the polymers derived from 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane had high densities when crystallized and oriented (Table VII). This is a disadvantage in terms of the weight of fiber needed to yield a given fabric structure compared to fabrics from lower density materials.

## EXPERIMENTAL

### Characterization Tests

**Dilute Solution Viscosity.** Inherent viscosity,  $\eta_{inh} = \ln(\eta_{rel})/c$ , values were determined in *m*-cresol at 30°C and a concentration *c* of 0.5 g of polymer per 100 mL of solution, unless otherwise specified.

**Polymer Melt Temperature.** Polymer melting was determined on dry powdered polymer on a chrome-plated gradient temperature bar and is noted as the temperature at which the polymer under moderate sliding pressure leaves a molten or waxy trail adhering to the bar.

**Fiber Stick Temperature.** The temperature at which fibers stick for 2 s to a brass block upon release of a light pressure is the sticking temperature. The tension on the fibers was 0.1 g/den.

**Fiber Zero Strength Temperature.** The zero strength temperature was determined as the breaking temperature of a fiber or film passing over a small heated rod under a load of 0.1 g/den.

**Density.** Density was determined in a density gradient tube containing heptane-carbon tetrachloride at 25°C.

TABLE VII  
Densities of Oriented, Crystalline Fibers

| Fiber composition  | Density<br>(g/cm <sup>3</sup> ) |
|--|---------------------------------|
| Poly(ethylene terephthalate)   | 1.39                            |
| Polypivalolactone  | 1.19                            |
| Poly(hexamethylene adipamide)  | 1.15                            |
| Poly[bis(1,4-cyclohexyl)methane azeleamide]<br>(70% <i>trans-trans</i> diamine isomer) | 1.06                            |
| Poly(ethylene piperazine-1,4-dicarboxylate)  | 1.35                            |
| Polyurethane from homopiperazine and 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane      | 1.44                            |
| Polyurethane from 2-methylpiperazine and 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane  | 1.36                            |



**X-Ray Orientation Angle.** Wide-angle X-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips generating unit Model 12045 having a copper fine-focus diffraction tube and a nickel beta filter. The distance from sample to the film was 50 mm. The arc length in degrees between the half-maximum intensity points of a principal equatorial diffraction spot is reported as the orientation angle of the sample.

The degree of crystallinity, amount, and perfection were judged by visual inspection.

**Fiber Tensile Properties.** Tensile strength ( $T$ ) (g/den), percent elongation at break ( $E$ ), and the initial modulus ( $M_i$ ) (g/den) were determined on an Instron tensile tester (Instron Engineering Corp., Canton, MA). The fibers were scoured in a 0.1% solution of sodium lauryl sulfate, rinsed well, air-dried, and conditioned for at least 16 h at 21°C and 65% relative humidity. Single filaments were broken with 1-in. initial jaw separation. Results are reported as the average of at least three breaks. Denier (the weight in grams of 9000 m of filament) was determined for each filament by a resonance method described in ASTM D1577-66, Part 25, 1968.

**Work and Tensile Recovery.** These tests were performed on single filaments scoured and then conditioned at 21°C and 65% relative humidity. The equipment used was an Instron tensile tester equipped with an automatic integrator. Alternatively, data from the tensile plots can be obtained with a planimeter.

The initial fiber clamp separation was one inch and the rate of elongation was 10%/min. The fiber was first exercised by elongation to 1%, held 30 s, and unloaded. The fiber was rested at least 90 s and any slack in the specimen was taken up by clamp adjustment. The fiber was next elongated 3%, held 30 s, and allowed to retract at the original rate. The percent work recovery is the ratio of the area under the unloading curve to the area under the loading curve times 100. The percent tensile recovery is the ratio of the retraction over the initial elongation times 100.

The procedure is repeated for 5 and 10% elongations. The average of three or more determinations is reported. For testing under wet conditions special chambers were installed on the tensile tester and the fibers were conditioned in the water 3 min before testing.

**Wash Set Recovery Angle (WSRA).** The wash set recovery angle is best determined on fibers that have been heat-set or at least treated taut in boiling 0.5% detergent solution for 30 min, rinsed, and dried. The fibers are then similarly treated relaxed, rinsed, and dried. Four-inch fiber or yarn samples (with about three turns per inch) are mounted vertically, bent 360° around a horizontal, 25-mil wire mandrel, and held in place by a weight of 0.05 g/den. The fiber assembly is immersed in a 0.15% sodium lauryl sulfate solution at 60°C for 2 min. The detergent solution is replaced with cold distilled water for about half a minute. This bath is removed and excess water is gently blotted from the fibers. The assembly is dried at 21°C and 15% RH for 1–2 h. The fibers are cut about 0.25 in. below the mandrel and then cut in the same way above the mandrel. The curled fibers are placed in a Petri dish and allowed to recover at 15% RH overnight or longer. The angle of recovery is the number of circular degrees of recovery from the 360° bend. This is conveniently measured by

placing the sample between microscope slides and projecting an image with an overhead projector. The values are read to the nearest 5° and reported as the average of at least five examples.

**Light Stability.** The light stability of fibers and films was tested by exposing them in a Model FDA-R Fade-Ometer (Atlas Electric Devices Co., Chicago, IL) equipped with a xenon arc. The equipment was operated in accordance with the standard procedure for dyed textiles except that the samples were mounted on 91-lb white Bristol Index board and clipped, top and bottom, in the usual position. Fibers were wound on the cardboard in the longer, vertical direction for physical testing. For observing development of color, fibers were wound in a mat in the shorter direction and strips of film were stapled to the cardboard face. For the color test a portion of the film or fiber was shielded by a strip of cardboard which could be lifted for observations. The machine gave a light exposure equivalent to 53 standard sunlight hours in 20 h of operating time, as determined by the use of U.S. Bureau of Standards colored papers.

## HEALTH AND SAFETY CONSIDERATIONS

For the most part fiber preparation and evaluation require no unusual precautions. Tetrahydrofuran and some halogenated solvents are toxic and conditions of use should be such as to keep skin and breathing exposure well below mandated safe limits.

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