

# Formation of Cracks on Photodegraded Nylon 6 Filaments

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## Synopsis

Cracks were found on the surface of drawn nylon 6 filaments irradiated with ultraviolet (UV) light from a mercury lamp under various humidities at room temperature. The cracks were formed perpendicular to the fiber axis and were of varying sizes. No cracks were observed on undrawn filaments or drawn filaments exposed to UV light in a dry atmosphere. Considerable shrinkage was found in drawn samples by thermomechanical analysis indicating the presence of residual stress in the material. The cracking is explained in terms of the residual stress and plasticization by moisture.

## INTRODUCTION

We have studied previously changes induced in the surface of polyamide fibers or filaments by exposure to ultraviolet (UV) light or by  $\gamma$ -ray irradiation. Cavities and/or cracks were observed on sample surfaces either with outdoor exposure, which included rainy days,<sup>1,2</sup> or with UV irradiation from a xenon arc lamp combined with intermittent water spraying of the samples.<sup>3,4</sup> However, nylon 6 filaments enclosed in a quartz tube to provide protection from environmental moisture and then exposed to sunlight did not show any surface morphological changes, although significant deterioration occurred due to phototendering.<sup>5,6</sup> When nylon 6 fibers were irradiated with  $\gamma$ -rays and the dose exceeded 30 Mrad, cracks developed on their surfaces after treatment with hot water.<sup>7</sup> Thus the presence of water appears to play an important role in the formation of cracks on nylon fibers which have been subjected either to UV light or to  $\gamma$ -ray irradiation.

The objective of this study was to establish the effect of changes in the humidity of the ambient atmosphere on the surface morphology of nylon 6 filaments exposed to UV light from a mercury lamp. The exposure caused photooxidative as well as photolytic degradation. Undrawn, laboratory drawn, and commercially drawn nylon 6 samples were examined. The analytical techniques employed were thermal analysis and scanning electron microscopy.

## EXPERIMENTAL

### Materials

The samples used in this study were undrawn (UD) (907 denier/24 filaments) and 4.4× commercially drawn (CD) (207 denier/24 filaments) nylon 6 obtained from Toyobo Company, Japan. They were free of additives and delustrant. UD and CD nylon 6 filaments extracted with hot methanol also were employed (UDE and CDE, respectively). The extraction removed low molecular weight oligomers from the nylon.<sup>8</sup> Also this treatment allowed stress relaxation to occur in strained chain segments of the drawn materials. Extracted UD nylon was drawn 2.7× in the laboratory at room temperature on a tensile tester at a rate of 50 mm/min (LD filaments). 2.7× was the optimum drawing under the conditions used.

### Ultraviolet Light Exposures

The light source was a high pressure mercury lamp (Toshiba SHL-100UV) which emits a spectrum composed of wavelengths longer than 250 nm. The nylon samples, in a tensionless state, were placed in quartz tubes which were then sealed. Silica gel was placed in the bottom of the tubes when a dry atmosphere was required. For a humid atmosphere, water or saturated solutions of magnesium acetate or of barium chloride were used. These liquids provide a relative humidity (RH) of 100%, 90%, and 65%, respectively, at the temperature at which the samples were irradiated. The quartz tubes were placed at 18 cm distance from the lamp and the samples exposed to the UV radiation at 20°C for predetermined lengths of time.

### Analyses

**Scanning electron microscopy.** An Akashi-Hitachi MSM-2, was used in the secondary mode at 15 kV acceleration voltage. Samples were coated with gold (30 nm).

**Thermal analysis.** Differential thermal analysis (DTA) was performed on a Shimadzu DTA-20 analyzer in an air atmosphere at a heating rate of 10°C/min. Thermomechanical analysis (TMA) was carried out with a Shimadzu TMA-20 instrument with a load of 100 mg/filament in an air atmosphere at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Effect of Humidity on Photodegradation

A large exothermic peak appeared in the region of 200°C in the thermograms run in the air of the unexposed CDE nylon (Fig. 1). This exotherm is attributed to thermal oxidation of the sample.<sup>2</sup> The size of the exothermic peak was smaller after the CDE samples had been exposed to UV light for 150 h in a dry atmosphere or when the samples were exposed in a humid atmosphere (90% or 100% RH). It is suggested that this change in the thermograms is indicative of photooxidative damage in the samples.

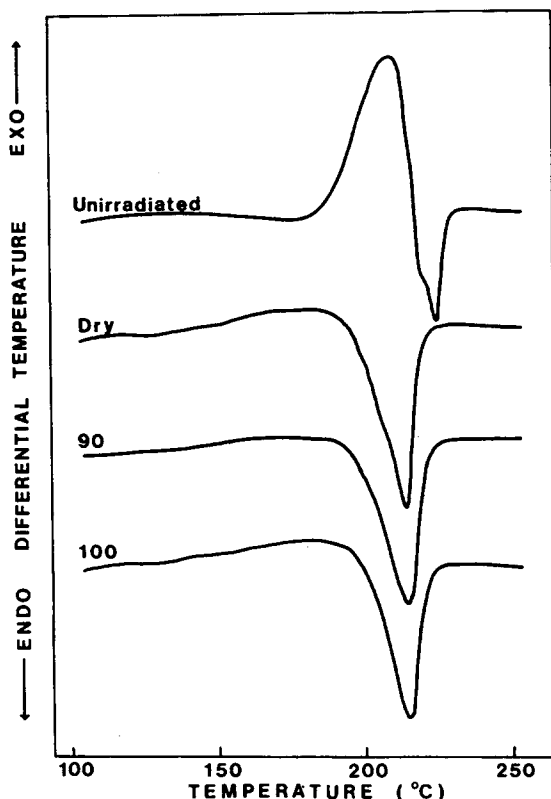
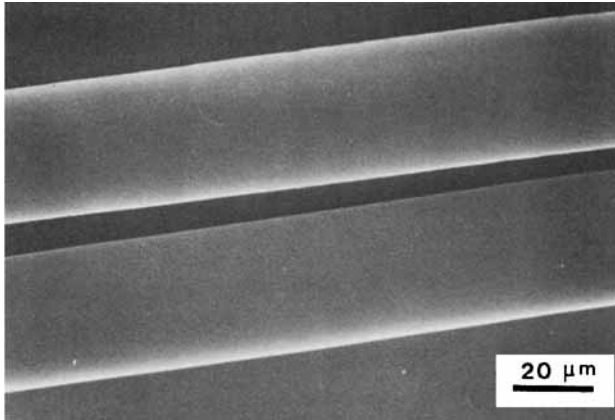


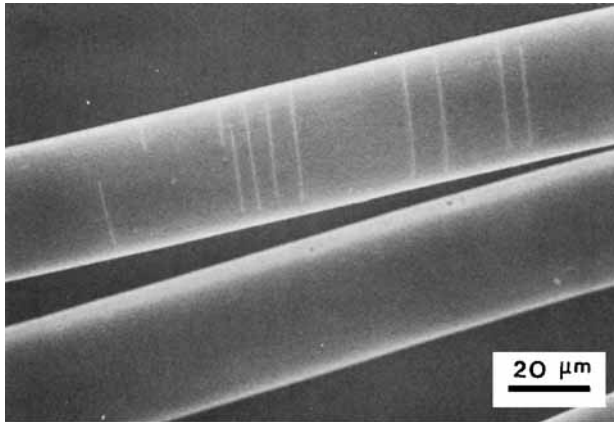
Fig. 1. DTA curves for commercially drawn and methanol extracted (CDE) nylon 6 filaments unirradiated or exposed to UV light for 150 h in an atmosphere with the following relative humidity; 0%, 90%, or 100%.

Crack formation on UV-exposed CDE filaments was affected by the humidity of the ambient atmosphere during irradiation. In a dry atmosphere, no cracking of their surfaces was observed [Fig. 2(a)]. At 65% and 90% RH, cracks were rarely observed on some filaments [Fig. 2(b)]. However, at 100% RH, many small cracks developed over the whole surface of the filaments [Fig. 2(c)]. The irradiation time for all these samples was 600 h. It is noteworthy that the cracks were formed perpendicular to the fiber axis. The presence of moisture has been found to cause little additional effect on the tensile properties of UV-exposed bright nylon 66 yarn especially when the exposures are made below 60°C.<sup>9,10</sup> It appears, therefore, that in this instance scanning electron microscopy gives a better indication of physical damage than tensile measurements. It is possible, however, that nylon 66 may differ from nylon 6 in its reaction to water in the presence of UV light.

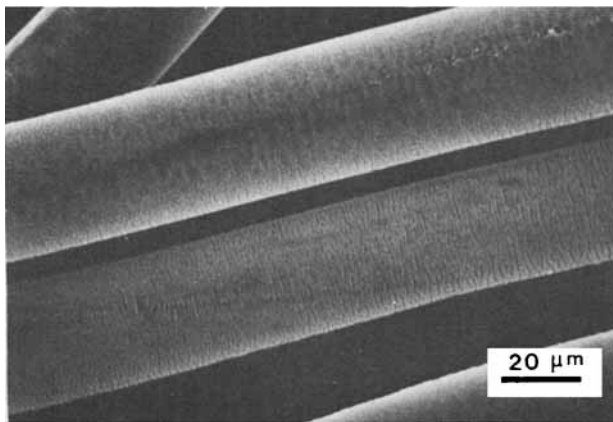
Water vapor might contribute to the photodegradation process through the formation of hydroperoxides, or it might act as a plasticizer and enhance photooxidation by increasing the mobility of polymer chains and permitting the rate of diffusion of oxygen into the filaments to increase. The second postulation is similar to one suggested for the influence of water vapor in photooxidation of polymers having acyl-oxyimino groups.<sup>11</sup> While water might be contributing to the photodegradation process, it is possible that it is a participating mainly



(a)



(b)



(c)

Fig. 2. Scanning electron micrographs of the effect of the relative humidity of the UV exposure atmosphere on surface cracking of commercially drawn and methanol-extracted (CDE) nylon 6 filaments: (a) 0%; (b) 90%; (c) 100%. Irradiation time = 600 h.

in the formation of cracks by acting as a plasticizer in a stress-relaxation process as discussed later.

### Effect of Irradiation Time on Photodegradation

The size of the exothermic peak at about 200°C, which appeared on the thermogram of nonexposed CDE nylon, decreased sharply when the sample was first exposed to UV light in an atmosphere of 100% RH (Fig. 3). Changes in the size of this peak became smaller as the time of UV irradiation was increased above 100 h. It appears that there is a progressive increase in the degree of photodegradation.

The endotherm present in the thermograms is caused by the melting of the samples. As the endotherms follow large exothermic peaks, it is difficult to estimate the melting temperature range precisely. However, when thermograms of these samples were run in nitrogen to eliminate the exothermic peaks, the endotherms were essentially similar to those shown in Figure 3 for the UV-exposed samples. The starting and peak temperature of the endotherms shifted to lower temperatures as the UV-exposure time was increased. The products of photodegradation formed in the amorphous regions of the filaments may be preventing recrystallization as the sample is heated in the DTA. Any changes

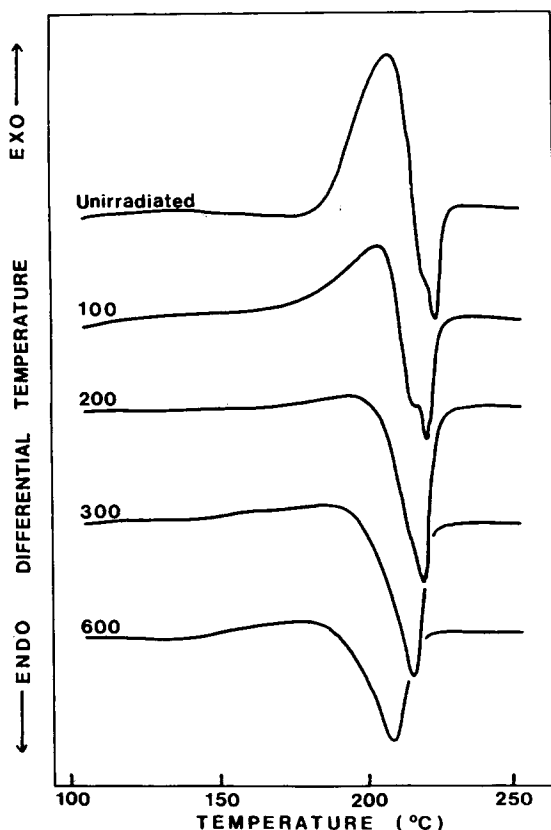


Fig. 3. DTA curves for commercially drawn and methanol extracted (CDE) nylon 6 filaments unirradiated or exposed to UV light at 100% RH for 100, 200, 300, or 600 h.

in the crystalline regions caused by the UV exposures would be expected to affect the melting temperature region also. Further discussion of the effect of photodegradation on the melting of nylon 6 can be found elsewhere.<sup>5</sup>

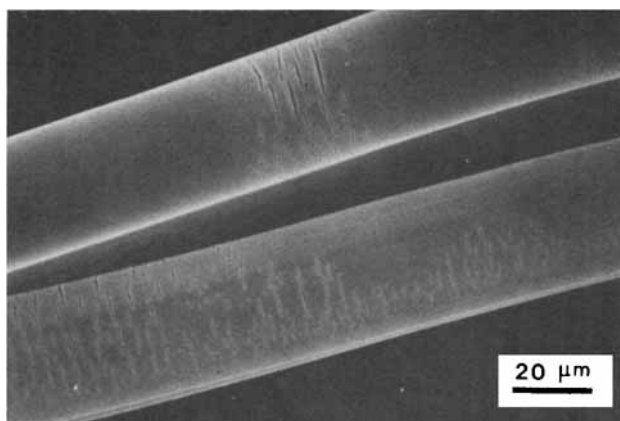
It should also be noted that the shoulder present on the endotherm of the nonexposed CDE sample was eliminated as the UV-exposure time was increased above 100 h. The effect of exposure to light from a xenon arc lamp on double endothermic peaks found in the DTA curves of nylon 66 has been discussed previously.<sup>4</sup> It has been suggested that there are two parts in the crystalline component of a semicrystalline polymer. One part (form I) can recrystallize when melted at a given heating rate, and the second part (form II) will not recrystallize on melting at a given heating rate.<sup>12</sup> The high temperature endotherm (form I) is thought to result from the melting of crystals produced by recrystallization of material melting at a lower temperature in the DTA. We have suggested that photodegradation can prevent recrystallization in nylon 6; thus it appears that on exposure to UV light the amount of form I crystalline material in nylon 6 decreases. Our results with nylon 66 indicated the opposite, i.e., a loss of form II material.<sup>4</sup> The discrepancy could be due to a number of factors including the difference in type of polymer, the presence of delustrant in the nylon 66, the difference in types of UV exposure, and differences in the processing history of the fibers (e.g., previous heat treatment received by the fibers).

No surface cracks were observed on the CDE nylon exposed to UV light for 100 h in an atmosphere of 100% RH. As the exposure time increased above 100 h, cracks appeared on filament surfaces. Some filaments at lower exposure times showed only partial crack formations [Fig. 4(a)]. However, when samples had been irradiated for 600 h, deep cracks could be observed on their surfaces as well as much finer cracks [Fig. 4(b)].

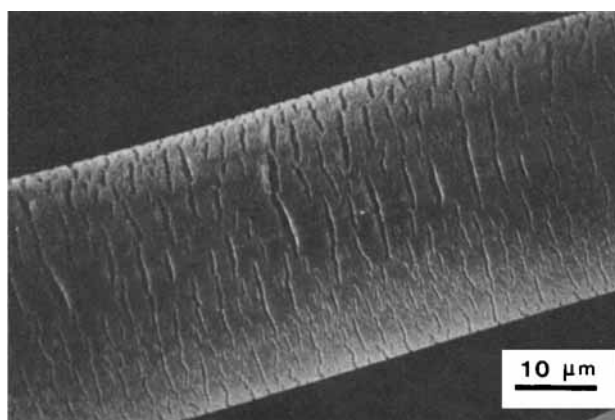
### Relation between Surface Cracks and Residual Stress in Filaments

Evidence for the presence of residual stress in drawn nylon 6 filaments was found by using the TMA (Fig. 5). On heating, shrinkage of the CD filaments started at about 50°C and then progressively increased until just below their melting point. The great contraction in length of the CD nylon indicated that a large amount of stress remained oriented parallel to the fiber axis. CDE samples showed 50% less shrinkage than the CD nylon. Thus, the hot methanol extraction which had been given to the CDE sample not only extracted monomer and oligomers but also had a relaxation effect on the CD filaments.

The difference in residual stress in the CD and CDE nylon is reflected in the surface cracking phenomenon. After 300-h UV exposure, more uniform and therefore, in totality, a larger number of cracks were formed on the surface of the CD filaments (Fig. 6) than on the CDE samples [Fig. 4(a)]. However, dense stress cracking developed all over the surfaces for both CD and CDE filaments after 600-h exposure. Additional evidence which relates residual stress to the surface cracking phenomenon was obtained by studying UD and LD nylon. The large differences in residual stress of these samples can be estimated from their TMA curves (Fig. 5). On heating, UD filaments did not shrink at all, but progressively elongated until melting occurred. In contrast, LD samples showed shrinkage comparable to that of CD filaments. The shrinkage of the LD filaments was larger than that of CD nylon at temperatures less than 200°C, indicating the instability of the LD samples in that temperature range.



(a)



(b)

Fig. 4. Scanning electron micrographs of the effect of UV exposure time in an atmosphere of 100% RH on cracking of commercially drawn and methanol-extracted (CDE) nylon 6 filaments: (a) 300 h; (b) 600 h.

The difference in behavior of the LD and CD nylon as indicated by TMA is due to differences between commercial drawing and the drawing technique used in our laboratory. No cracks were observed on UD filaments after 600-h exposure to UV light at 100% RH [Fig. 7(a)], although the nylon was highly degraded and easily broken when the samples were touched. In contrast, severe cracking was observed on the whole surface of similarly exposed LD filaments [Fig. 7(b)]. It is suggested that the amorphous regions of the CD nylon 6 filaments contain tie molecules in which strain caused by the drawing process has been frozen. Application of thermal energy causes relaxation of the strained tie molecules and can result in shrinkage as indicated by TMA. It is also suggested that photodegradation occurs primarily in the amorphous regions of the nylon 6 filaments. Photodegradation results in chain scission.<sup>13</sup> Thus it is speculated that, as chain scission occurs in the amorphous regions, it will permit movement of polymer chains and allow relaxation of strain in the tie molecules. Therefore, there will be a tendency for retraction to occur, and, after sufficient chain scission has oc-

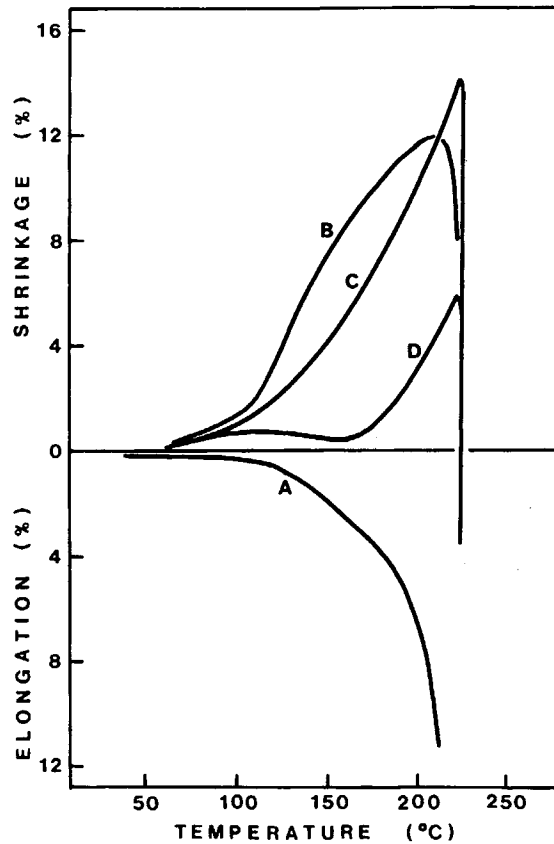


Fig. 5. Effect of drawing on the TMA curve of nylon 6 filaments: Undrawn (A); laboratory drawn (B); commercially drawn (C); commercially drawn and extracted with hot methanol (D).

curred, cracks will form. As indicated earlier, no cracks were observed until samples had been exposed to UV light for at least 100 h. Since the strain in the filaments was oriented parallel to the fiber axis, retraction will be parallel to it also, and the cracks will be oriented perpendicular to this axis, as shown by our

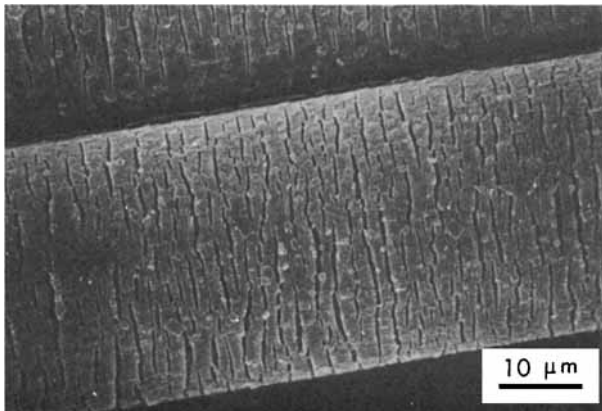
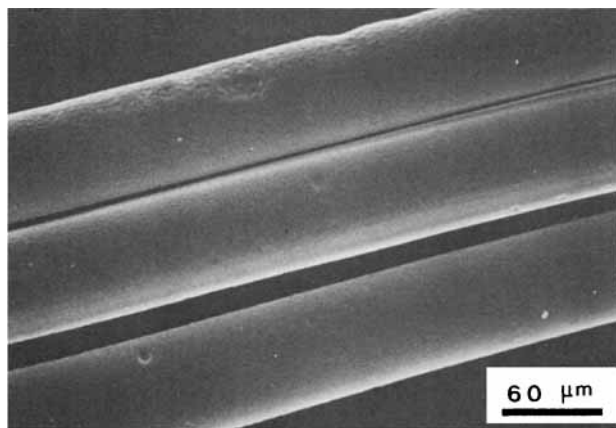
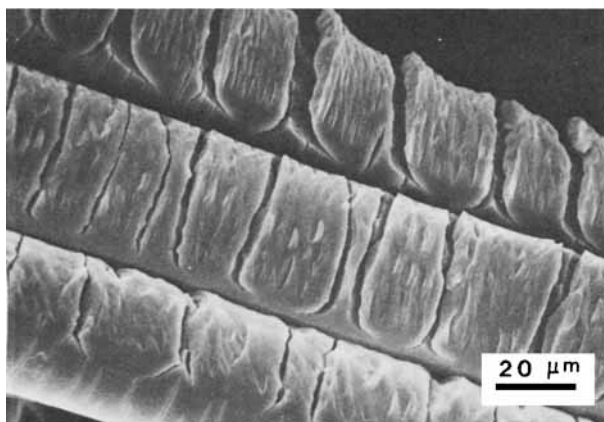


Fig. 6. Crack formation on the surface of commercially drawn (CD) nylon 6 filaments after UV exposure for 300 h at 100% RH.





(a)



(b)

Fig. 7. Effect of drawing on crack formation on nylon 6 filaments exposed to UV light for 600 h at 100% RH: (a) undrawn (UD); (b) laboratory drawn (LD).

scanning electron micrographs. It appears that water, acting as a plasticizer, promotes movement of polymer chains and, consequently, assists in crack formation. It will be remembered that when CDE nylon was exposed to UV light for 600 h, no cracks were observed when the atmosphere was dry [Fig. 2(a)].

The effect of UV exposure on the maximum shrinkage of CD nylon 6 filaments was measured by TMA. It was found that in contrast to a shrinkage of 15% for the unexposed CD sample, shrinkage fell to 9% after 100-h UV exposure and 3% after 300-h exposure. It is possible that at least part of this decrease is caused by the relaxation of stress in the filaments caused by scission of tie molecules and by fracture formation. It is likely that crosslinking caused by the photodegradation<sup>13</sup> is also contributing to the reduction of shrinkage.

Photodegradation proceeds from the surface to the core of fibers; thus the cracks are essentially a surface phenomenon.<sup>14</sup> No cracks were observed on undrawn filaments. Thus it appears that residual stress created by the drawing process is necessary together with moisture for cracks to form during the photodegradation of nylon 6 filaments.

### References

1. Y. Fujiwara and T. Yasuda, *Sen-I Gakkaishi*, **29**, T-274 (1973).
2. Y. Fujiwara, S. Kobayashi, and T. Yasuda, *Sen-I Gakkaishi*, **30**, T-434 (1974).
3. S. H. Zeronian, *Text. Res. J.*, **41**, 184 (1971).
4. S. H. Zeronian, K. W. Alger, and S. T. Omaye, *Text. Res. J.*, **43**, 228 (1973).
5. Y. Fujiwara and S. H. Zeronian, *J. Appl. Polym. Sci.*, **26**, 3729 (1981).
6. M. S. Ellison, Y. Fujiwara, and S. H. Zeronian, to appear.
7. Y. Fujiwara and S. Kobayashi, *Kobunshi Ronbunshu*, **33**, 711 (1976).
8. Y. Fujiwara and S. H. Zeronian, *J. Appl. Polym. Sci.*, **23**, 3601 (1979).
9. R. F. Moore, *Polymer*, **4**, 493 (1963).
10. G. S. Egerton and K. M. Shah, *Text. Res. J.*, **38**, 130 (1968).
11. M. Tsunooka, private communication.
12. G. E. Sweet and J. P. Bell, *J. Polym. Sci., Part A-2*, **10**, 1273 (1972).
13. B. S. Stowe, R. E. Fornes, and R. D. Gilbert, "UV Degradation of Nylon 66," in *Polymer-Plastics Technology and Engineering*, L. Naturman, Ed., Marcel Dekker, New York, 1974, Vol. 3, pp. 159-197.
14. S. H. Zeronian, "Effect of Photochemical and Environmental Degradation on the Surface Properties of Textile Fibers," in *Surface Characteristics of Fibers and Textiles*, M. J. Schick, Ed., Marcel Dekker, New York, Part I, 1975, pp. 365-386.

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