Photodegradative Wavelength Dependence of Thermally Resistant Organic Polymers

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Synopsis

The wavelength dependence of photodegradation of three "high temperature" aromatic polyamide polymers has been very accurately determined by means of a fast grating spectrograph used in conjunction with a high pressure xenon arc. One of these polymers, the poly-(isophthalamide) of 4,4'-bis(p-aminophenyl)-2,2'bithiazole, was found to be degraded significantly by visible light, especially that of 4140 Å, wavelength. Both the poly-terephthalamide of 1,3-bis(3-aminobenzamido) benzene and Du Pont Nomex, also an aromatic polyamide, were damaged primarily by radiation in the near ultraviolet region. Degradation band maxima for these polymers were observed at 3700 Å and 3600 Å, respectively. All three thermally resistant polymers were thus found to be degraded by light of much longer wavelength than that which is harmful to other common polymers.

INTRODUCTION

In the past few years a number of new organic polymeric systems have been synthesized which show considerable resistance to loss of physical properties when exposed to high (>300°C) temperatures. These materials are primarily polyaromatic or aromatic/heterocyclic systems, and many can be processed into fibers with properties generally suitable for textile applications. Several fibers prepared from thermally resistant polymers are of potential commercial interest, and one (Du Pont's Nomex) is currently being marketed.

Despite their resistance to thermal degradation, many of these polymeric systems degrade severely upon exposure to either natural or simulated sunlight. This sensitivity to light has been reported for a number of these materials[1-3] but few careful experiments on this phenomenon have been published to date. The present work was undertaken to provide more quantitative information on the degradation of some selected thermally resistant polymers. It has previously been noted that color changes occur in a number of these materials on exposure in the laboratory to even the light from a fluorescent lamp.[4] This observation suggested that the wavelength dependence of degradation of these materials may be quite different from that observed for more conventional textile fibers. Wavelength dependence of degradation therefore seemed a logical point for beginning the studies on degradation.

Hirt and Searle have successfully applied an excellent method of wave-length sensitivity determination to a number of polymer systems.[5-8] Similar techniques were applied to various samples in the course of this investigation. The basic idea behind the method is to disperse light from a high pressure xenon arc through a very fast spectrograph, allowing the resulting dispersed light to fall upon a sample. The different areas of the sample are exposed to light of different wavelengths, thus producing a degradation "spectrum."

The resulting "spectrum" may be further defined and quantified in many ways depending upon exactly which manifestation of photodegradation is of prime interest. Hirt and Searle have employed samples in film form and have applied ultraviolet, infrared, and visible absorption spectro-photometric techniques as well as fluorescence emission. In our laboratory, film samples have been subjected primarily to microdensitometer readings of either transmission or reflectance while new techniques have been worked out to utilize fiber samples. Fibers are wrapped in a transverse direction around the exposure plate, thus exposing the center of each fiber to essentially monochromatic light. Breaking strength measurements are subsequently made on individual fibers, and plotted against wavelength. By studying both films and fibers of the same material it is possible to determine if the same wavelengths are responsible for both discoloration and strength loss.

EXPERIMENTAL

Materials

Three different thermally resistant polymers were selected for these studies. A brief description of each follows.

It has previously been reported[4,9] that the poly-(isophthalamide) of 4,4'-bis(p-aminophenyl)-2,2'-bithiazole has excellent short term thermal
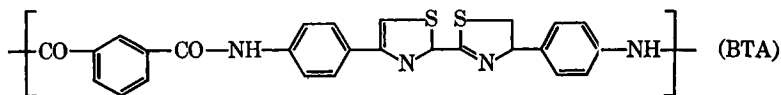
stability, but rather poor long term thermal stability and considerable sensitivity to photodegradation. It has also been reported[4,10] that this amidebithiazole ordered copolymer, hereafter referred to as BTA, undergoes a color change from light yellow-brown to dark purple upon exposure to light from various sources. This discoloration has been shown to be the result of a photo-oxidation process.[4] Since some of the exposure conditions described were such that only very small amounts of ultraviolet radiation could reach the sample, it appeared that this polymer had been significantly degraded by visible light. This phenomenon made the polymer especially interesting for the current study.

The second polymer selected for study was the poly-terephthalamide of 1,3-bis(3-aminobenzamido)benzene, hereafter referred to as M3P.

$$\left[NH-\bigcirc-CO-NH-\bigcirc-NH-CO-\bigcirc-NH-CO-\bigcirc-CO\right]$$

(M3P)
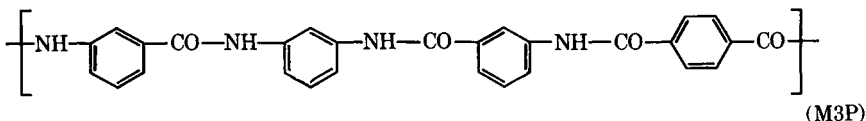
The preparation and properties of this polymer and its fibers have previously been reported.[1,11,12] Photodegradation of this material manifests itself by two effects; yellow discoloration, and loss of physical properties such as tensile strength. Relatively short xenon arc or sunlight exposure produces fairly extensive damage.

The third material studied was a commercial sample of Du Pont's Nomex, also an aromatic polyamide. The properties of this polymer have been described elsewhere.[13,14] Two studies of radiative degradation of polymers have included experiments on Nomex,[2,3] but no photodegradative wavelength dependence studies have been reported. This polymer was of interest for the current investigation because of its resemblance to M3P, and also because it is currently commercially available.

All samples of the three polymers used in this study were free of "finish," dyes, or other extraneous materials.

Equipment

A Jarrell Ash F 16.3 Plane Grating 0.75 Meter Spectrograph was adapted for photodegradation studies in conjunction with a Hanovia 900 w high pressure xenon arc.

This spectrograph is equipped for photographic recording of spectra, and the camera is readily adaptable for use as a sample holder. The holder is designed for 5 × 7 in. plates or film, so all samples were wound upon or taped to 5 × 7 in. glass photographic plates from which the emulsion had been stripped. The spectrograph wavelength settings were calibrated by use of a low pressure mercury arc line source and standard photographic procedures. Several calibrations showed that, when care was taken to eliminate "backlash," these settings were reproducible to within 10 Å. The spectrum dispersion at the sample plate was found to be 20 Å per mm.

The energy distribution of the light source and the wavelength interval of the experiments were such that second order diffraction effects could not affect the data. This possibility, however, must always be borne in mind during the design of similar experiments with grating instruments and subsequent interpretation of data.

The xenon arc was placed about three feet from the entrance slit of the spectrograph, and two quartz lenses (the first one cooled by distilled water) were used to focus the beam so that maximum energy reached the sample plate. A 400 μ entrance slit width was employed for the BTA experiments and a 3-mm slit was used during exposure of the less sensitive M3P and Nomex.

A BTA film was exposed to the dispersed radiation from the xenon source for 4 hr. After this exposure, a noticeable color change had taken place within a certain region of the sample. In order to better define and quantify this degradation band, it was necessary to make physical measurements related to the discoloration of the film as a function of position on the sample plate. Sample plate position could in turn be related to wavelength of incident light. A Joyce, Loebl, and Company Recording Microdensitometer Model Mark III B was employed for these measurements. Since the film used was reasonably opaque, the microdensitometer was
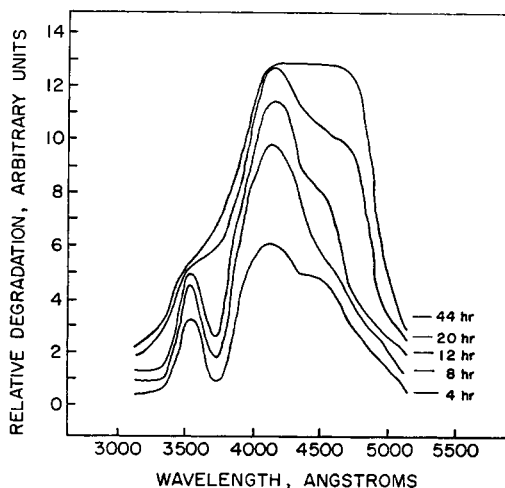
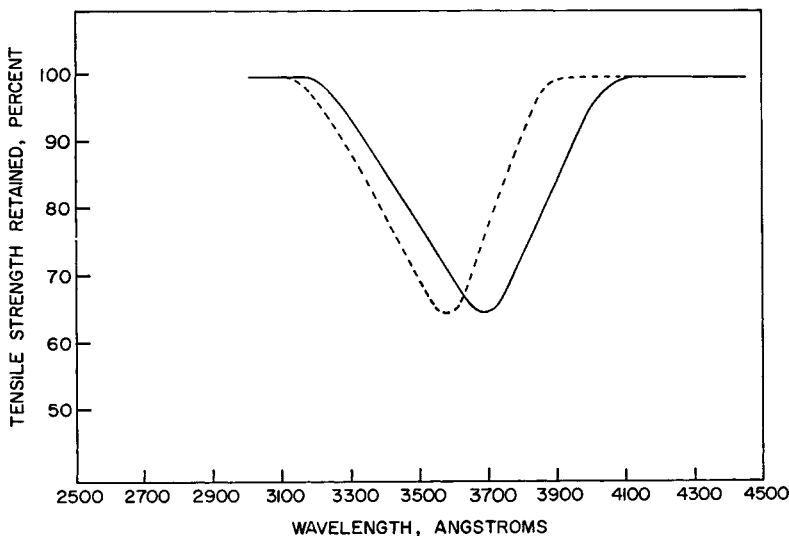Fig. 1. Photodegradation spectrum of BTA.

Fig. 2. Photodegradation spectra of M3P and Nomex; (—), M3P; (---), Nomex.

operated in the reflectance mode.   Conditions of highest sensitivity were
employed at all times.   Measurements were made immediately after re-
moval of the sample from the exposure unit and again after about 18 hr in
the dark.   The reason for this, of course, was to observe the effect of any
"dark reactions" that might occur.

The sample was returned to the exposure unit and irradiated for an addi-
tional 4 hr.   The entire process of irradiation and measurements was
carried out for total exposure times of 4, 8, 12, 20, and 24 hr.   In all cases,
no further discoloration developed upon standing in the dark.   It may thus
be concluded that any "dark reactions" which might have occurred had
little effect on discoloration.   The data obtained from this series of ex-
posures are shown in Figure 1.

Fiber samples rather than films were employed for the experiments on
M3P and Nomex.   Samples were mechanically wound around the glass
plates.   The mounted samples were exposed with the fibers perpendicular
to the dispersed spectrum, thus exposing a section in the center of each
fiber to essentially monochromatic light of known wavelength.   Each
sample was exposed continuously for 96 hr.   After this time, one hundred of
the exposed fibers were cut from each sample and individual tensile strengths
were determined with an Instron tensile testing instrument.   Figure 2
illustrates the results of the experiments on M3P and Nomex.

The relative energy distribution of the dispersed light at the sample
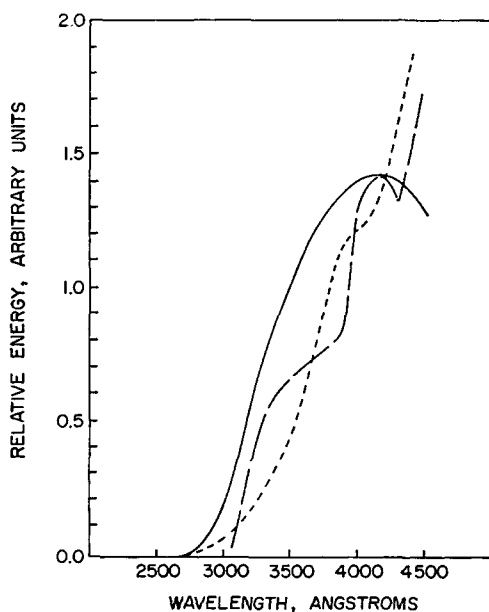plate was first measured photographically.   Several neutral density filters

Fig. 3. Comparison of incident radiation to sunlight; (———), photographic calibra-
tion; (- - -), photomultiplier calibration; (— —), average sunlight, Judd 1964.

placed in the beam and short exposure times permitted direct photography of the light incident upon the plate. Kodak Type 103-0 Spectroscopic Plates, which have a very flat response curve over the area of interest, were employed. The "neutrality" of the neutral density filters was checked with a Cary Model 14 Spectrophotometer and found to be excellent. Transmission measurements of the developed photographic plates by means of the microdensitometer described earlier permitted quantification of the results. The resultant curve is shown in Figure 3.

Relative energy distribution at the sample plate was also determined by use of a 1P28 photomultiplier and a special housing available from Jarrell Ash. All readings were corrected for nonlinear photomultiplier response and plotted in Figure 3.

RESULTS AND DISCUSSION

It may readily be seen from Figure 1 that BTA is indeed discolored by visible light. The most damaging radiation lies in a band between 3700 and 5000 Å. The primary discoloration sensitivity occurs at 4140 Å. A second important inflection occurs in the curves in the region between about 4400 and 4700 Å. The wavelength of appearance of this inflection seems much more dependent upon exposure time and other experimental variables than that of the primary peak. In an earlier experiment with a much wider entrance slit, this inflection actually became a relative maximum and was located at 4850 Å.

It may also readily be observed that it is a simple matter to extract kinetics data from these curves at any wavelength of interest. The possibility of accomplishing this has been mentioned by Hirt and Searle.[7] It is also possible to obtain kinetics data in this manner from similar multiple fiber exposure experiments.

Figure 2 shows the similarity of photodegradative behavior between M3P and Nomex, and at the same time illustrates their basic difference from most other synthetic polymers. Although, their respective degradation bands at 3700 and 3600 Å are of considerably lower wavelength than that of the BTA previously discussed, they are still of much higher wavelength than those of other common polymers.[5-8] Since average sunlight,[15] as shown in Figure 3, contains considerably more radiation in the visible and near ultraviolet than in the farther regions of the ultraviolet; there is, in effect, an increased exposure for polymers whose photodegradative sensitivity occurs at higher wavelengths.

Discoloration of M3P and Nomex was observed visually to occur at the same wavelengths as strength loss. This is a strong indication that the same initiating species is involved in both effects, but does not conclusively prove that the two effects are necessarily produced by the same mechanism.

The energy distribution of the dispersed light at the sample plate is illustrated in Figure 3. It is this incident light distribution which is im-

portant to the experiment, and not just the distribution of the original source. This original energy distribution will of course be perturbed to one degree or another by passage through the various lenses, mirrors, and the diffraction grating. It may be observed from Figure 3 that the relative energy distribution of radiation actually incident upon the sample does, indeed, resemble average sunlight[15] very closely in the spectral region below 4000 Å. Even better agreement in the 3000 Å region could easily be accomplished by use of an appropriate filter at the xenon source, but this was not considered critical for the present work. Disagreement between the two calibration methods is evident above 4000 Å. The lower intensity above this wavelength recorded by the photographic technique is due to decreased efficiency of exposure near the extreme ends of the photographic plate. This well known effect is inherent in the design of the spectrograph, and will not be discussed in detail at present. All intensity measurements made with the photomultiplier were necessarily restricted to the center of the sample plate, and therefore were not subject to this effect. Since the sample was exposed in exactly the same manner as the photographic plates, the photographic calibration is definitely most representative of experimental conditions. Due to this decreased efficiency of exposure near the edge of the sample plate, slightly less BTA degradation was probably produced at the higher wavelengths than would have been caused by sunlight. Degradation of the other two polymers should have been unaffected by this phenomenon.

It is possible to present photodegradation "spectra" of this sort in several forms by performing various experimental and mathematical manipulations. First of all, the "spectra" may be "energy corrected" by simply dividing the degradation units by the relative energy at each wavelength. This produces a plot of degradation per unit energy vs. wavelength for a given time interval and set experimental conditions. Although this type of curve is perhaps more fundamental than Figures 1 and 2, it distorts the results very badly since the time factor is neglected. If the increase in degradation with time were linear, or even perhaps some reasonably well behaved function, it should be possible to produce a plot of degradation per unit energy per unit time. This curve would definitely be more fundamental than Figures 1 and 2. It should also be possible to determine quantum yields for the degradation as a function of wavelength by suitable experimental modifications. This too, would produce very fundamental data. However, after working with data in all these forms for some time, the firm conviction has been reached that the uncorrected spectra such as Figures 1 and 2 are preferable for one who is primarily interested in photodegradation by a single energy source, such as sunlight. The one condition which must be fulfilled is that the relative energy distribution of the incident light must closely approximate that of the energy source of interest.

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