

## Spectra of Irradiated Polyamides

JOSEPH ZIMMERMAN

*Carothers Research Laboratory, Textile Fibers Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware*

### INTRODUCTION

Many organic solids and semicrystalline as well as amorphous polymers develop characteristic colors when subjected to large doses of high energy radiation, and a number of workers have studied the behavior of these colors. In polystyrene and polymethyl methacrylate, the colors produced by x-irradiation were found to result from the long wavelength tails of ultraviolet absorption bands.<sup>1</sup> The increase in optical density was linear with dose up to a dose of  $2 \times 10^7$  r. The color disappeared as a result of thermal decay and reaction with oxygen. The reaction with oxygen appeared to be governed entirely by oxygen diffusion. Irradiation of polyvinyl chloride films with  $\gamma$  rays<sup>2</sup> gave colors which were attributed to both frozen free radicals and conjugated double bonds. When caproamide was irradiated with 2-m.e.v. electrons<sup>3</sup> it became yellow. At the same time the electron paramagnetic resonance (E.P.R.) spectrum indicated the presence of a single type of free radical formed by removal of a hydrogen atom from the carbon atom next to the carbonyl group. Disappearance of the yellow color coincided with decay of the E.P.R. absorption. In the presence of oxygen, the accelerated decay of the E.P.R. spectrum was accompanied by the appearance of a weak, single, broad electron resonance.

In the work reported here, polyamide films were irradiated and their electronic spectra observed. In addition, an approximate  $G$  yield for radical production in one polyamide (nylon 66) was obtained.

### EXPERIMENTAL PROCEDURE

A number of representative polyamide structures were selected for study. Films having thicknesses in the range of 0.05-0.2 mm. were generally used. The films were irradiated with 2-m.e.v. electrons from a Van de Graaff generator. In most of the work described here, the films were irradiated

on Dry Ice and stored at  $-78^\circ\text{C}$ . until they were examined in a Cary Model 11 spectrophotometer. The rate of decay of the transient absorption was very slow at this temperature and not significant for the storage times used (generally less than 4 hr.). The films were precut to fit a holder which could be mounted in the cell compartment of the spectrophotometer which was blanketed with nitrogen. In all cases, an unirradiated control film was placed in the reference beam to permit observation only of the changes resulting from irradiation. In addition, the spectra of solutions of a number of monomeric amides were obtained.

An approximate value of the  $G$  yield for radical production in one polyamide (nylon 66) was obtained by soaking finely powdered polymer in a boiling saturated solution of  $\text{I}_2$  in chloroform, evaporating off the chloroform, irradiating the polymer at  $-78^\circ\text{C}$ ., and determining the decrease in  $\text{I}_2$  concentration from the optical density at  $490\text{ m}\mu$  of a 0.4% solution of this polymer in *m*-cresol. Before the irradiated polymers were dissolved, they were stored at  $25^\circ\text{C}$ . under nitrogen for 4 hr.

The polymers used included the simple aliphatic polyamides nylon 66 and 610, a 75/25 copolymer of nylons 66 and 610 to observe the effect of reduced crystallinity, the polyamide (A) from hexahydro-*p*-xylylenediamine and adipic acid containing a saturated ring in the chain, the polyamide (B) from *p*-xylylenediamine and azelaic acid containing a benzene ring in the chain in the diamine portion of the molecule, the polyamide (C) from 2-methylhexamethylenediamine and terephthalic acid containing a benzene ring in the chain in the acid portion of the molecule, the polyamide (D) from *p*-bis-(2-aminoethyl)benzene and azelaic acid in which the benzene ring is attached to the carbon  $\beta$  to the amide nitrogen, and the polyamide (E) from a 2-methylhexamethylenediamine and oxalic acid as an example of an oxamide.

The monomeric amides included *N*-amylcapro-

amide, *N,N'*-dimethyladipamide,  $\epsilon$ -caprolactam, and caproamide.

### RESULTS AND DISCUSSION

Irradiation of a nylon 66 or 610 film with a 75-Mrad dose produced the differential spectrum shown in Figure 1. A transient absorption was observed with a maximum at 355  $m\mu$ . This band is responsible for the yellow color produced by irradiation. There was another band produced which peaked at 243  $m\mu$ . This intense band is shown better with a thinner film at a lower radiation dose which is also shown in Figure 1. As the 355- $m\mu$  band decreased in intensity with time, another band became increasingly evident at ca. 287  $m\mu$ . The 243- $m\mu$  absorption also decreased somewhat (ca. 25%), but it is evident that the group mainly responsible for this absorption is a molecular product of irradiation and not a free radical. This is also demonstrated by the spectra of irradiated low molecular weight amides (*N*-amylcaproamide, caproamide, *N,N'*-dimethyl adipamide, and  $\epsilon$ -caprolactam). These compounds turn yellow on irradiation. However, there is some difference in the quality of the color of caproamide. When the irradiated compounds are dissolved in cyclohexane, the colors disappear instantly and colorless solids may be recovered by evaporating the solvent. There is a band with a maximum at ca. 230–240  $m\mu$  present in the differential spectra of the solutions of the secondary amides, but it is very markedly

reduced in the caproamide spectrum (Fig. 2). Since the secondary amides develop a strong absorption in the 240- $m\mu$  region while a primary amide does not, it would appear that the group responsible for this absorption is formed on the amine portion of the molecule rather than on the acid portion. No chemical identification has been made, but it is possible that the band in the irradiated secondary amides is due to the  $-\text{CON}=\text{CH}-$  group which has also been invoked in work on the irradiation of proteins,<sup>4</sup> while the faint band in caproamide may be due to the  $-\text{C}=\text{C}-\text{CONH}_2$  group.

The spectrum of an irradiated film of polymer A is shown in Figure 3 and is essentially the same as those for nylon 66 and nylon 610, having a transient absorption peaking at 355  $m\mu$ . Polymer B (Fig. 3) also turns yellow upon irradiation, but the transient band now shows three maxima: at 443, 467, and 483  $m\mu$ . If the radicals on these polyamides were on the carbon  $\alpha$  to the amide nitrogen, it appears reasonable that the benzene ring attached to the  $\alpha$ -carbon in Polymer B would result in a shift to longer wavelengths. In Polymer D, where the benzene ring is attached to the carbon  $\beta$  to the amide nitrogen, the transient yellow color which appears on irradiation results from a band with three maxima at 305 (approx.), 315, and 328  $m\mu$  (Fig. 3). The small absorption peaks appearing in the 400–500- $m\mu$  region are, we believe, evidence of some *p*-xylylenediamine impurity in the *p*-amino-

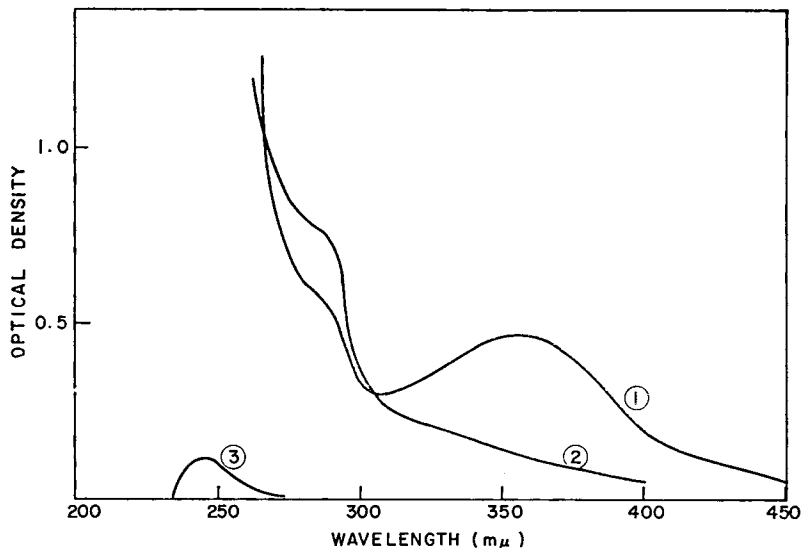


Fig. 1. Spectrum of irradiated nylon 610 film: (1) 0.2-mm. film (75 Mrad) after 12 min.; (2) same as (1) after 16 hr.; (3) 0.013 mm. film (30 Mrad) after 16 hr.

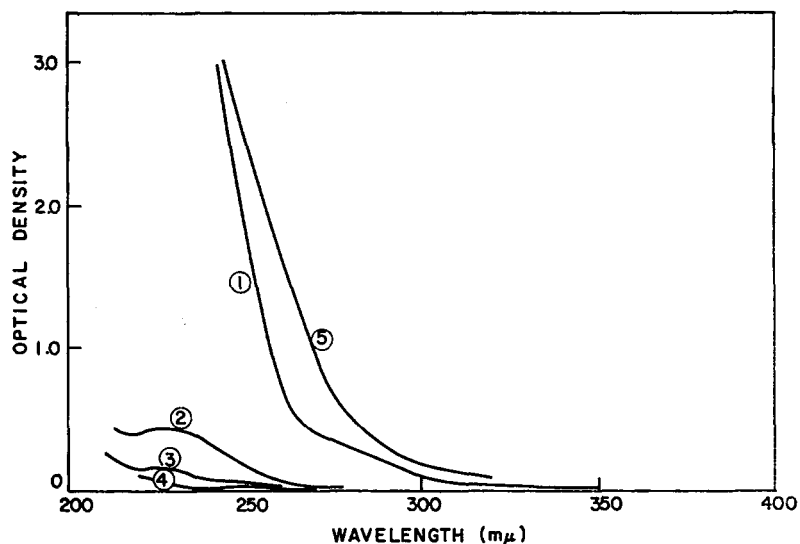


Fig. 2. Spectra of cyclohexane solutions of irradiated amides (200 Mrad): (1) *N*-amylocaproamide (0.4%); (2) *N*-amylocaproamide (0.04%); (3) *N,N'*-dimethyladipamide (0.02%); (4) caproamide (0.5%); (5)  $\epsilon$ -caprolactam (0.8%).

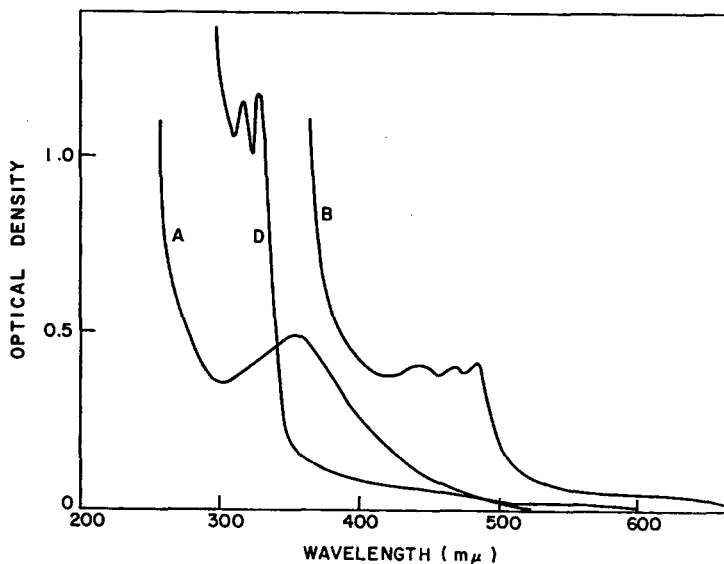


Fig. 3. Spectra of irradiated polyamides (30 Mrad): polymers from: (A) hexahydro-*p*-xylylenediamine + adipic acid; (B) *p*-xylylenediamine + azelaic acid; (C) *p*-bis(2-aminoethyl)benzene + azelaic acid.

ethylbenzene from which the polymer was prepared.

Films from the polyterephthalamide, polymer C, develop a blue color on irradiation, and two absorption bands are observed, one maximum being at 365  $m\mu$  and a second at 560  $m\mu$  (Fig. 4). This may indicate the presence of two sites of radical formation, one on the carbon  $\alpha$  to the nitrogen (365  $m\mu$ ) and the second somewhere in the acid portion of the molecule. The polyoxamide, poly-

mer E, becomes red on irradiation, a single absorption maximum at 508  $m\mu$  being observed (Fig. 4).

In the absence of oxygen, the rates of disappearance of the colors appear to be diffusion-controlled, being most rapid in polymers of lower crystallinity such as the mixed nylon 66/nylon 610 (75/25) polymer and least rapid in polymers having higher crystallinity or a greater proportion of stiff segments. Second-order plots for color disappearance in various irradiated polyamides are shown in

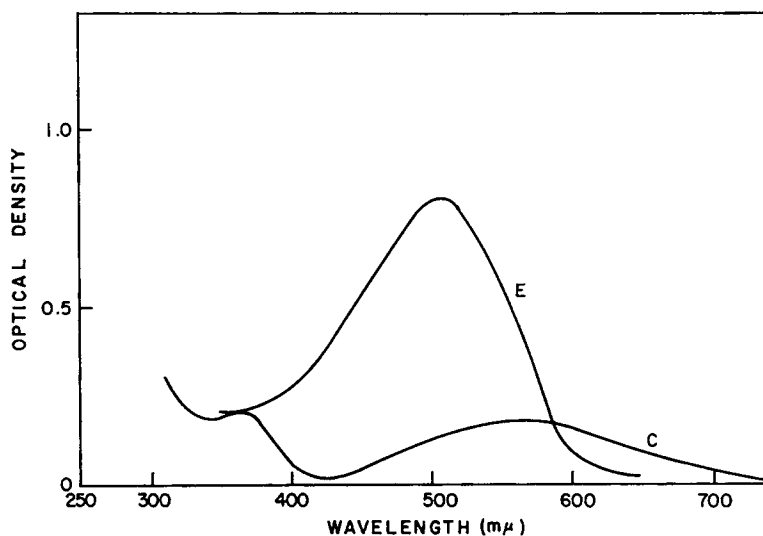


Fig. 4. Spectra of irradiated polyamides (30 Mrad): polymers from: (C) 2-methylhexamethylenediamine + terephthalic acid; (E) 2-methylhexamethylenediamine + oxalic acid.

Fig. 5. It should be noted that most of the plots show downward curvature. We attribute this mainly to the semicrystalline nature of the polymers, in which radicals in the crystalline regions terminate much more slowly than those in the amorphous regions. We might expect that true diffusion does not occur at all in the crystalline regions when the radicals are in the polymer backbone. Instead it is more likely that "diffusion" occurs by a series of hydrogen abstraction reactions

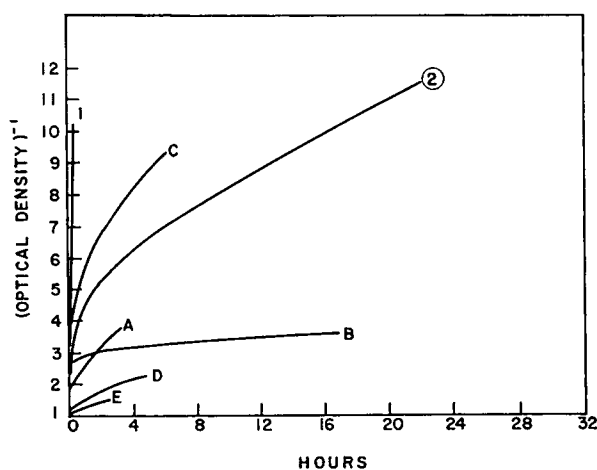


Fig. 5. Decay of transient colors at 25°C. in irradiated polyamide films (0.1 mm.): (1) nylon 66/610 (75/25) copolymer, 350  $\mu$ ; (2) 610, 350  $\mu$ ; polymer A, 355  $\mu$ ; polymer B, 483  $\mu$ ; polymer C, 365  $\mu$ ; polymer D, 328  $\mu$ ; polymer E, 508  $\mu$ .

which permit the unpaired electron to pass from one chain to the next.

If very thin, irradiated filaments are exposed to an atmosphere of oxygen, the colors disappear relatively quickly. In view of the fact that the initial optical density at 355  $\mu$  for the more amorphous nylon 66/nylon 610 copolymer differs relatively little from that for the nylon 66 homopolymer, one would tend to conclude that the radicals responsible for the color are produced in both the crystalline and amorphous regions. Thus, the complete bleaching by oxygen shows that oxygen can penetrate into the crystalline regions of these polyamides just as they do in caproamide.<sup>3</sup> On the other hand, the yellow color in irradiated  $\epsilon$ -caprolactam is not bleached rapidly in air, thus indicating that caprolactam crystals are relatively impermeable to oxygen.

Irradiation of nylon 66 polymer containing  $I_2$  (as described above) with 2-m.e.v. electrons at doses of 5, 10, 15, 20, and 30 Mrad gave an average radical concentration of  $3.0 \times 10^{-6}$  mole/g.Mrad. From the density (1.14) we calculate that the polymer is 50% crystalline.<sup>5</sup> If we assume that the radicals produced in the crystalline regions do not react with  $I_2$ , then the total radical concentration per gram of amorphous polymer is  $6.0 \times 10^{-6}$  moles/g.-Mrad. This is equivalent to a  $G$  yield of 5.8. The initial transient optical density at 355  $\mu$  of an irradiated nylon 66 film ( $1.015 \times 10^{-2}$  cm. thick) is 0.048 for a dose of 1 Mrad where the radical con-

centration is ca.  $6.0 \times 10^{-6}$  mole/g. or  $6.85 \times 10^{-6}$  mole/cm.<sup>3</sup> (density = 1.14). From this we obtain an approximate value for the molar extinction coefficient at 355 m $\mu$  of 690.

In one high-spot experiment, a film of polymer E was irradiated under N<sub>2</sub> for 2 hr. with the unfiltered radiation from an AH-6 ultraviolet lamp. A transient red color developed, just as in electron irradiation. However, upon thermal bleaching, a permanent yellowing was observed in the film, in contrast with the results of electron irradiation where the bleached films are colorless.

The conclusions one might draw from the results discussed above are: (1) that the colored products of irradiation of these polyamides are free radicals, since they terminate in a diffusion-controlled reaction in the absence of oxygen, being bleached by oxygen, since, in at least one case,<sup>3</sup> the decay in color is accompanied by a corresponding decay in magnetic susceptibility, and since, in at least one case, ultraviolet irradiation produces the same transient species; (2) that in addition to the transient species a molecular (i.e., nonradical) product is produced in the irradiation of secondary amides which has an absorption maximum at ca. 240 m $\mu$  and which appears to be in the amine portion of the molecule; (3) that the transient species responsible for the colors are, for the most part, in the amine portion of the molecule and, on the basis of spectral shifts and chemical considerations, probably in the carbon atom  $\alpha$  to the amide nitrogen.

Let us finally consider the possibility that free radicals are produced in many other locations, but that the most stable position is on the carbon  $\alpha$  to the nitrogen. In the absence of significant back reaction or termination, the rate of disappearance by chain transfer of non- $\alpha$ -radicals R<sub>n</sub> is given by:

$$-(d[R_n]/dt) = k_{tr}[A][R_n] \quad (1)$$

where [A] is the concentration of  $\alpha$ -methylene groups and  $k_{tr}$  is the abstraction rate constant. For a value of [A] of  $10^{-2}$  moles/cm.<sup>3</sup> (for example), 95% of the non- $\alpha$ -radicals will have disappeared in  $3 \times 10^2/k_{tr}$  seconds. If  $k_{tr}$  at 25°C. were 10 cm.<sup>3</sup>/mole-sec. (for example), the time required would be 30 sec. Thus, it is possible that several

types of free radicals are produced, but only one detected if the radical production and detection are not carried out at very low temperatures.

## References

1. J. F. Fowler and M. J. Day, *Nucleonics*, **13**, No. 12, 52 (1955).
2. A. Chapiro, *J. chim. phys.*, **53**, 895 (1956).
3. R. G. Bennett, R. L. McCarthy, B. J. Nolin, J. Zimmerman, *J. Chem. Phys.*, **29**, 249 (1958).
4. M. E. Jayco and W. M. Garrison, *J. Chem. Phys.*, **25**, 1084 (1956).
5. H. W. Starkweather, Jr., and R. E. Moynihan, *J. Polymer Sci.*, **22**, 363 (1956).

## Synopsis

Differential spectra have been obtained of a number of irradiated polyamides and monomeric amides. These spectra indicate that both free radical and molecular products are produced as primary products. The transient colored products (which are believed to be free radicals) and molecular products appear to be in the amine portion of the molecule for the most part. The approximate  $G$  yield for radical production in nylon 66 is 5.8, and the approximate molar extinction coefficient of the free radical at 355 m $\mu$  is 690.

## Résumé

Des spectres différentiels ont été obtenus pour un certain nombre de polyamides irradiés et d'amides monomériques. Ces spectres indiquent que des radicaux libres et des espèces moléculaires sont produits en premier lieu. Des produits intermédiaires colorés (qui sont supposé être des radicaux libres) et des espèces moléculaires semblent être pour la plus grande partie dans la portion amine de la molécule. La valeur approximative de  $G$  pour la production de radicaux dans le nylon 66 est 5,8 et le coefficient d'extinction molaire du radical libre à 355 m $\mu$  est égal à 690.

## Zusammenfassung

Eine Vergleich der Spektren einer Anzahl bestrahlter Polyamide und monomere Amide wurde durchgeführt. Diese Spektren sprechen sowohl für die Bildung freier Radikale als auch von Molekeln als Primärprodukte. Die unbeständigen gefärbten Produkte (die als freie Radikale betrachtet werden) und die molekularen Produkte scheinen sich zum grösseren Teil im Aminteil der Molekel zu befinden. Der ungefähre  $G$ -Wert für die Radikalerzeugung in Nylon 66 beträgt 5,8 und der ungefähre molare Extinktionskoeffizient des freien Radikals bei 355 m $\mu$  ist 690.

Received April 3, 1959