Effect of Photodegradation on Dynamic Mechanical Properties of Nylon 6

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Synopsis

Changes in the dynamic mechanical properties of nylon 6 (α-form) under ultraviolet light irradiation were investigated. On irradiation with spectrally dispersed ultraviolet light in the wavelength range of 219–415 nm, the dynamic modulus E' and the density of nylon 6 were increased below about 300 nm. It was found that the increment in E' and the density were the result of crosslinking. When E' was measured with time elapsed during irradiation by light of 253.7 nm, E' initially decreased with time, increased at a longer time, and then reached a limiting value asymptotically. From the result of the change in E' with time, it was assumed that the scission and crosslinking reactions occur simultaneously during ultraviolet light irradiation. Thus, the change in E' with elapsed time was expressed by the equation $E'_t = E'_0 \exp(-k_1 t) + E'_\infty [1 - \exp(-k_2 t)]$, where E'_t is the dynamic modulus at time t, E'_0 is the E' at $t = 0$, E'_∞ is the limiting value of E', and k_1 and k_2 are the rate constants. The apparent activation energies for k_1 and k_2 were 3.23 and 2.50 kcal/mole, respectively, and the former value agreed with the activation energy for the scission of the amide groups. The effects of the photodegradation on the temperature dispersion of nylon 6 were also investigated. On irradiation with light at 253.7 nm, the α-relaxation which appeared at about 90°C was broadened and the intensity of the γ-relaxation at −95°C in the tan δ-versus-temperature curve was lowered. The β-relaxation which appeared at −45°C for the wet nylon 6 decreased its intensity.

INTRODUCTION

It is well known that the properties of polymer materials are changed under ultraviolet light irradiation. The photodegradation of polyamide has been widely investigated by many workers using various methods, for example, ultraviolet spectrometry,[1,2] phosphorescence emission study,[3] ESR,[4–7] electron microscopy,[8,9] viscosity,[10–12] and analysis of evolved gases.[13,14] However, there are very few reports related to the change in the mechanical property during the photodegradation. Stephenson, Moses, and Wilcox[15] examined the effects of ultraviolet light irradiation in nitrogen and *in vacuo* on change in tensile strength and elongation. In general, when the crosslinking reaction occurs, tensile strength should increase and elongation should tend to decrease, since the molecular chain stiffened. However, it is difficult to evaluate exactly a slight change in strength, elongation, and modulus during the photodegradation under the mechanical measurement of large deformation owing to the formation of cracks. On the other hand, the dynamic mechanical measurement under small deformation may be available to evaluate the scission or the crosslinking reaction during the degradation.

In this report, changes in the dynamic mechanical properties of nylon 6 under ultraviolet light irradiation were investigated. It is uncertain whether crosslinking or scission occurs on ultraviolet light irradiation. For example, several

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authors proposed scission at the amide groups.[6,13,14] However, crosslinking mechanisms were also proposed.[13,16,17] These differences seem to arise from the irradiated wavelength. It was reported that crosslinking occurs below about 300 nm.[18] Thus, in order to study the wavelength dependence of the photo-degradation, the change in the dynamic modulus E' was measured at each wavelength using spectrally dispersed ultraviolet light. E' was also measured isothermally during the photodegradation with elapsed time, and a kinetic study was carried out. Also, the effect of the photodegradation on the temperature dependence of the dynamic viscoelastic properties for dry and wet nylon 6 was studied.

EXPERIMENTAL

Material

The nylon 6 film used in this work was Toray nylon CM 1021 without additives and was supplied by Toray Ind. Inc. The thickness of the sample was 30 μm. A weight-average molecular weight Mw which calculated from eq. (1)[19] was 35,880 as a criterion.

$$M_w = 22.3 \times 10^3 [\eta]^{1.33} \tag{1}$$

The intrinsic viscosity $[\eta]$ was measured at 25°C in m-cresol.

The original sample has a single equatorial reflection at $2\theta = 21.3°$ in the x-ray diffraction pattern as shown in Figure 1. From the fact that the meridional reflection of the 0,14,0 planes occurred at $2\theta = 77.6°$, the fiber repeat distance (b axis) which had hydrogen bonds between antiparallel chains was 17.2 Å. Therefore, the original sample was not the γ-form but had a pseudohexagonal structure.[20] Since the original sample was unstable for heat or moisture, it was converted to the stable α-form by refluxing in ethyl alcohol for 72 hr (Fig. 1).
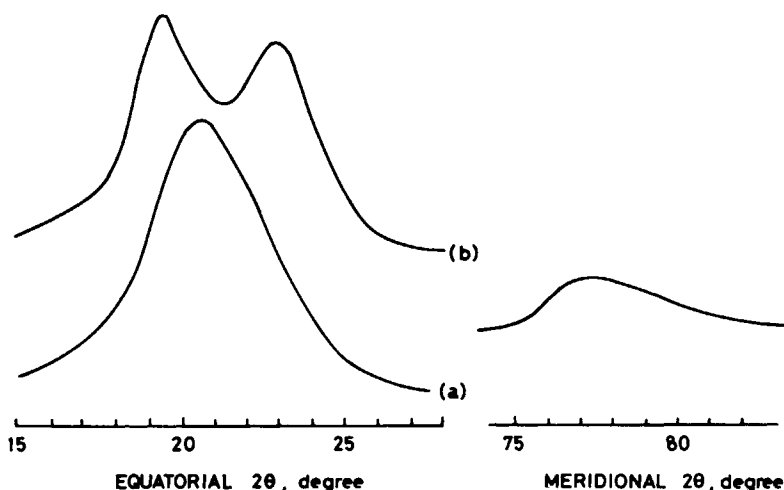

Fig. 1. X-ray diffraction pattern of (a) original nylon 6 and (b) α-form nylon 6 converted by ethyl alcohol treatment.
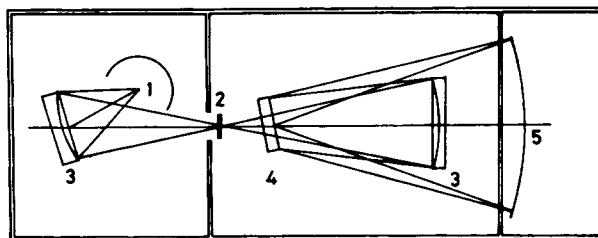
Fig. 2. Apparatus for irridation with spectrally dispersed ultraviolet rays: 1, xenon lamp (2 kW); 2, slit; 3, concave mirror; 4, grating; 5, sample.

Measurements

For irradiation with spectrally dispersed ultraviolet light, an apparatus as shown in Figure 2 was used (Nihonbunko Co., model CRM-FA). . This apparatus is composed of a 2-kW xenon lamp, a slit, concave mirrors, and a grating.   Ultraviolet light from the xenon lamp was dispersed into spectra by the grating. The sample was set vertically where the ultraviolet light dispersed into the spectra was focused.   The wavelengths used in this work were from 219 to 415 nm.   The sample for the measurements of the ultraviolet spectrum, the x-ray diffraction, the intrinsic viscosity, and the temperature dispersion were prepared by irradiating them in air with light at 253.7 nm, using a low-pressure mercury lamp.

The dynamic viscoelastic properties were measured by Rheovibron DDV-IIC (Toyo Baldwin Co., Ltd.).   Figure 3 shows the apparatus which measured the dynamic modulus during irradiation with light at 253.7 nm.   The furnace was modified for irradiation.   It was equipped with a low-pressure mercury lamp and a filter to cut the heat ray from the lamp.   The temperature dispersion was also measured by this apparatus at 110 Hz and at a heating rate of 2°C/min.

The x-ray diffraction patterns were measured by 30 kV, 25 mA, using a Ni-filtered CuK_α beam.   The x-ray instrument used was a Rigakudenki model 3D-F equipped with a Geiger–Müller counter.

The ultraviolet spectrum was measured by using a Hitachi double-beam spectrometer model 356.

The density of nylon 6 was measured at 25°C by the flotation method in benzene and nitrobenzene mixtures.
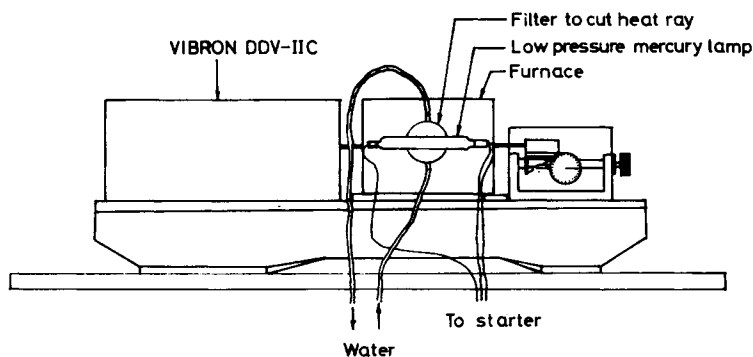

Fig. 3. Dynamic viscoelastic apparatus equipped with irradiation apparatus.

RESULTS AND DISCUSSION

Figure 4 shows the ultraviolet spectra of unirradiated and irradiated nylon 6 films 30 μm thick. Irradiation was made at 45°C for 10, 20, and 40 hr using the low-pressure mercury lamp with 253.7 nm wavelength. The progress of the photodegradation is accompanied by a maximum in absorption at about 295 nm in the spectrum. Moore[13] mentioned that this maximum is due to uncharacterized complex groupings introduced during manufacture by the thermal process of polymerization and that they act as photosensitizers. According to Margolin et al.,[21] it originates in an unknown substance formed during thermo-oxidation or photo-oxidation. It is also reported that a peak at 295 nm is due to pyrrole rings or peroxy radicals formed during oxidation reaction.[22]

Figure 5 shows the changes in E' as a function of the wavelength of irradiation. The irradiation of nylon 6 film was made by spectrally dispersed ultraviolet rays, and changes in E' were measured at each irradiating wavelength. The vertical axis in Figure 5 is denoted as the ratio of the dynamic modulus of the irradiated sample, E'_{irr}, to that of the unirradiated one, E'_{unirr}. As the irradiation proceeds, the modulus increases below about 300 nm, and two peaks are observed at 250 and 290 nm. The appearance of the photodegradation curve as a function of the irradiating wavelength such as Figure 5 (Mullen and Searle[23] called it the ultraviolet activation spectrum) corresponds to the ultraviolet spectrum expressed by the absorbance.[24,25] The peak at about 290 nm in Figure 5 then agrees with the maximum in absorption at 295 nm in the ultraviolet spectrum (Fig. 4), which appeared to be due to the formation of substances acting as photosensi-
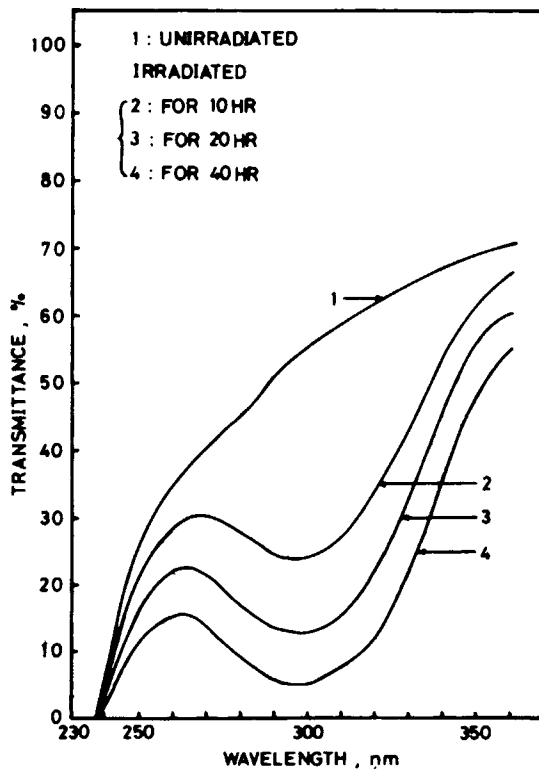

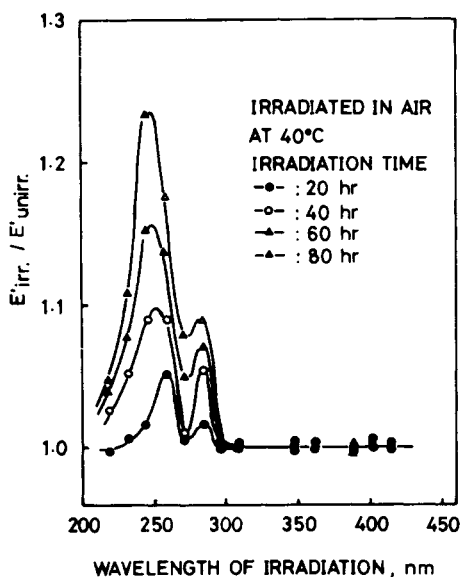Fig. 4. Ultraviolet spectra of irradiated and unirradiated nylon 6.

Fig. 5. Wavelength dependence of photodegradation on change in dynamic modulus.

tizers.   Below about 240 nm, the photodegradation is limited to near the surface layer of the film and proceeds generally to a small extent, since ultraviolet rays do not pass through the 30-μm film, as shown in Figure 4.   Therefore, the maximum appears at about 250 nm.

The change in density plotted against the wavelength of irradiation agrees well with the change in the modulus (Fig. 5) as shown in Figure 6.   The change in the density is also observed below 300 nm, and two peaks appear at 250 and 290 nm. For the increment in modulus or density under photodegradation, there are two
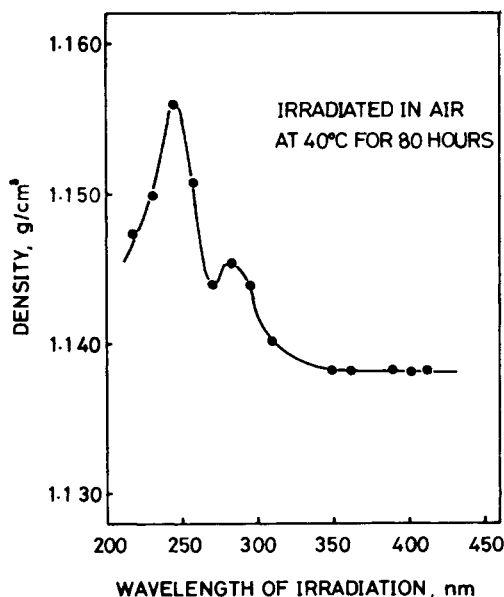

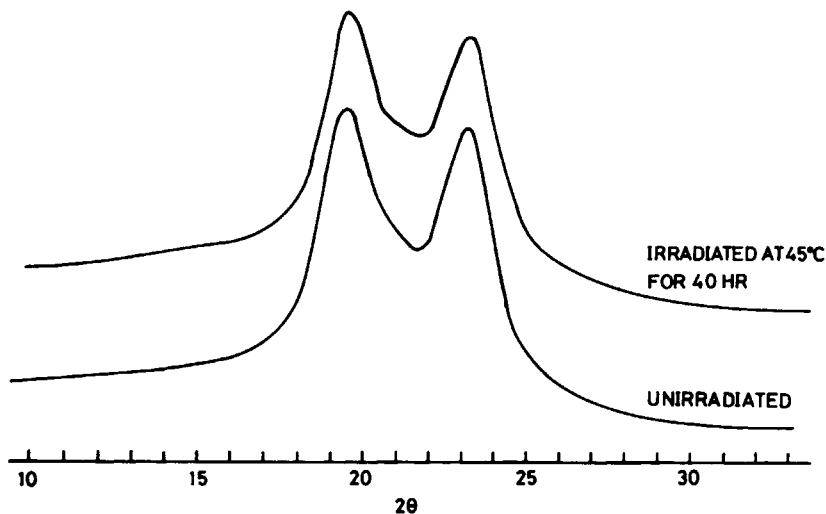Fig. 6. Change in density as function of irradiating wavelength.

Fig. 7. X-ray diffraction pattern for irradiated and unirradiated nylon 6.

possible explanations; one is crosslinking and the other is crystallization. If changes in crystal occur during the photodegradation, the x-ray diffraction pattern must be changed. However, as shown in Figure 7, the x-ray diffraction pattern is unchanged by irradiation.

The change in intrinsic viscosity $[\eta]$ of nylon 6 during the photodegradation with light at 253.7 nm is shown in Figure 8. The irradiation was made at 45°C in air by using the low-pressure mercury lamp. The viscosity increased with irradiation time. The $[\eta]$ of the sample irradiated for 10 hr was measured on a soluble part. The film irradiated above 20 hr could not be dissolved in m-cresol. Thus, it is clear that on irradiation with light below 300 nm, crosslinking occurs causing the increase in modulus and density.

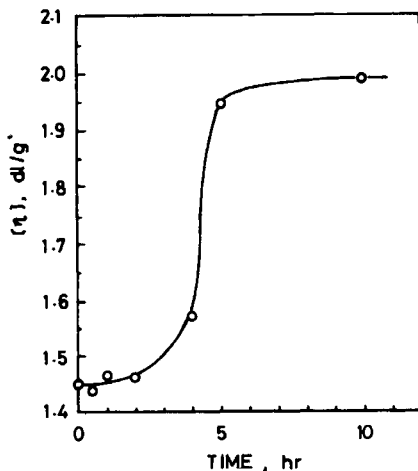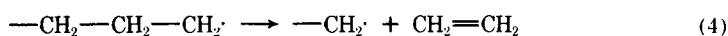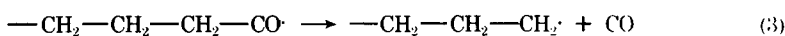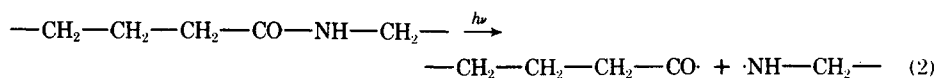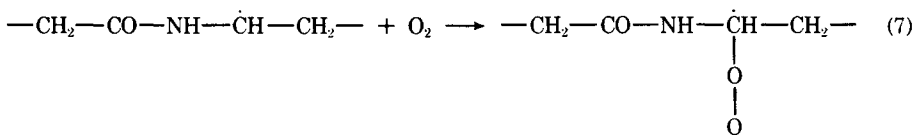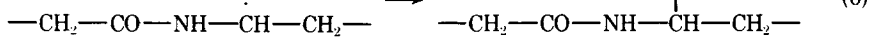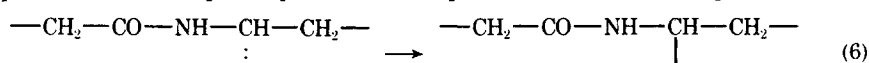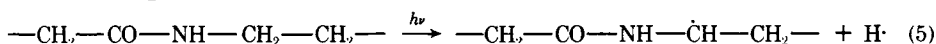According to the mechanism,[16,18,26] besides crosslinking, scission occurs si-

Fig. 8. Change in intrinsic viscosity $[\eta]$ during photodegradation.
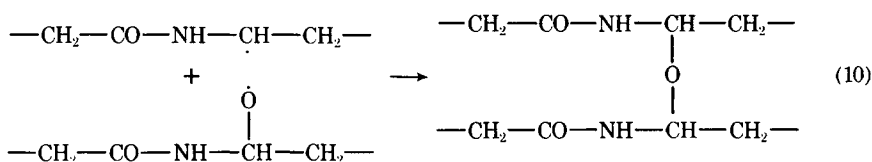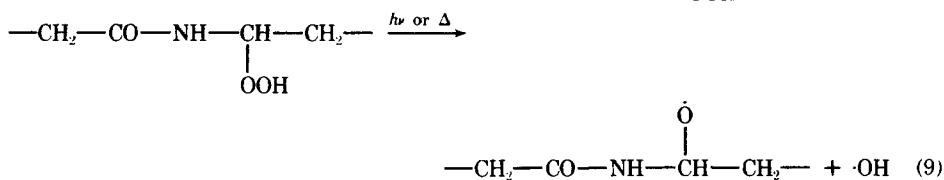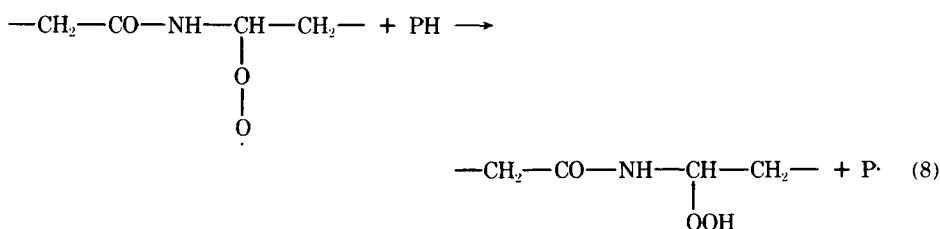
multaneously due to photo-oxidation as follows:

Scission Reaction:

$$—CH_2—CH_2—CH_2—CO—NH—CH_2— \xrightarrow{h\nu}$$

$$—CH_2—CH_2—CH_2—CO\cdot + \cdot NH—CH_2— \quad (2)$$

$$—CH_2—CH_2—CH_2—CO\cdot \longrightarrow —CH_2—CH_2—CH_2\cdot + CO \quad (3)$$

$$—CH_2—CH_2—CH_2\cdot \longrightarrow —CH_2\cdot + CH_2{=}CH_2 \quad (4)$$

Crosslinking Reaction:

$$—CH_2—CO—NH—CH_2—CH_2— \xrightarrow{h\nu} —CH_2—CO—NH—\overset{\cdot}{C}H—CH_2— + H\cdot \quad (5)$$

$$\begin{array}{c} —CH_2—CO—NH—\overset{\cdot}{C}H—CH_2— \\ \vdots \\ —CH_2—CO—NH—\overset{\cdot}{C}H—CH_2— \end{array} \longrightarrow \begin{array}{c} —CH_2—CO—NH—CH—CH_2— \\ | \\ —CH_2—CO—NH—CH—CH_2— \end{array} \quad (6)$$

$$—CH_2—CO—NH—\overset{\cdot}{C}H—CH_2— + O_2 \longrightarrow \begin{array}{c} —CH_2—CO—NH—\overset{}{C}H—CH_2— \\ | \\ O \\ | \\ \overset{\cdot}{O} \end{array} \quad (7)$$

If PH is the polymer molecule,

$$\begin{array}{c} —CH_2—CO—NH—CH—CH_2— \\ | \\ O \\ | \\ \overset{\cdot}{O} \end{array} + PH \longrightarrow \begin{array}{c} —CH_2—CO—NH—CH—CH_2— + P\cdot \\ | \\ OOH \end{array} \quad (8)$$

$$\begin{array}{c} —CH_2—CO—NH—CH—CH_2— \\ | \\ OOH \end{array} \xrightarrow{h\nu \text{ or } \Delta} \begin{array}{c} \overset{\cdot}{O} \\ | \\ —CH_2—CO—NH—CH—CH_2— + \cdot OH \end{array} \quad (9)$$

$$\begin{array}{c} —CH_2—CO—NH—CH—CH_2— \\ + \\ \overset{\cdot}{O} \\ | \\ —CH_2—CO—NH—CH—CH_2— \end{array} \longrightarrow \begin{array}{c} —CH_2—CO—NH—CH—CH_2— \\ | \\ O \\ | \\ —CH_2—CO—NH—CH—CH_2— \end{array} \quad (10)$$

In order to investigate how crosslinking and scission occur during the photo-degradation, the change in E' is measured isothermally with irradiation time. Figure 9 shows the change in E' with elapsed time during the course of irradiation with 253.7 nm light at 120°C in air. E' decreases initially with time, increases at a longer time region, and then reaches a limiting value. However, when the lamp is turned off at 300 min, E' increases considerably. The initial decrease in E' reflects the scission reaction of the main chain. The increase in E' from about 60 min is due to the crosslinking reaction. For explanation of the final increase in E' from 300 min in darkness, it may be considered that when the irradiation is stopped, the free radicals formed and trapped in the immovable
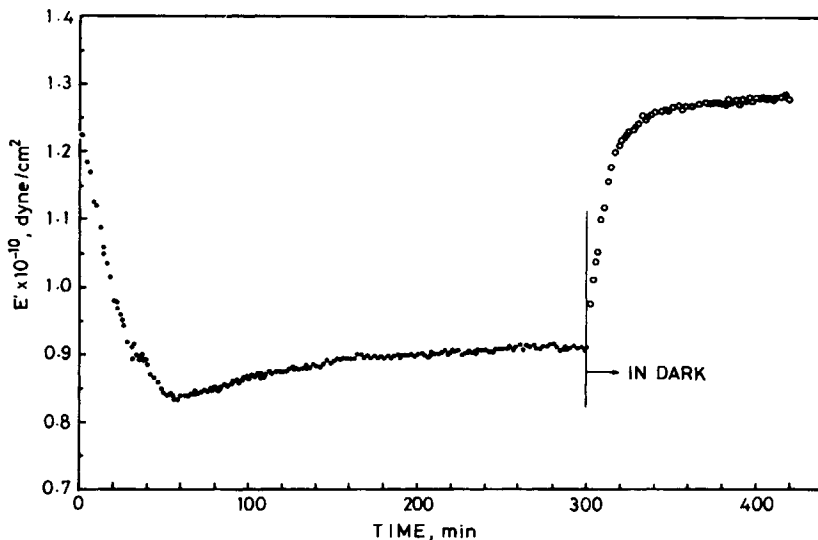
Fig. 9. Change of E' with elapsed time during irradiation with light at 253.7 nm and 120°C in air.

network chains during irradiation are recombined gradually to lead to the increase in E'. Shinohara and Dallantine[27] reported that free radicals, —CH$_2$—CO—N=CH—ĊH—CH$_2$—, formed by high-energy radiation such as γ-ray, were stable even above room temperatures due to the restriction of the motion of the polymer chain, except near or above the melting point (215°C).

From the isothermal change in E' during the photodegradation, the rate constants are calculated. As shown in Figure 10, it is supposed that scission and crosslinking occur simultaneously and the decrease and the increase in E' can be written by an equation of first-order reaction.[28] The decrease in E' by the scission reaction can be expressed as follows:

$$-dE_1'/dt = k_1 E_1' \tag{11}$$

where E_1' is the dynamic modulus at time t when only scission occurs and k_1 is the rate constant. If $E_1' = E_0'$ at $t = 0$, then eq. (11) can be solved as eq. (12):

$$E_1' = E_0' \exp(-k_1 t) \tag{12}$$

The increase in E' caused by the crosslinking reaction is written by eq. (13) in the same manner as in the case of the thermal degradation of poly(vinyl chloride)[29]:

$$d(E_\infty' - E_2')/dt = k_2 (E_\infty' - E_2') \tag{13}$$

where E_2' is the dynamic modulus at time t when only the crosslinking reaction occurs, E_∞' is the limiting value of E_2', and k_2 is the rate constant. From eq. (13) we can obtain eq. (14) since $E_2' = 0$ at $t = 0$:

$$E_2' = E_\infty' [1 - \exp(-k_2 t)] \tag{14}$$

If the increase and the decrease in E' occur simultaneously, the change in E' as a whole can be expressed as eq. (15) by adding eqs. (12) and (14):

$$\begin{aligned} E_t' &= E_1' + E_2' \\ &= E_0' \exp(-k_1 t) + E_\infty' [1 - \exp(-k_2 t)] \end{aligned} \tag{15}$$
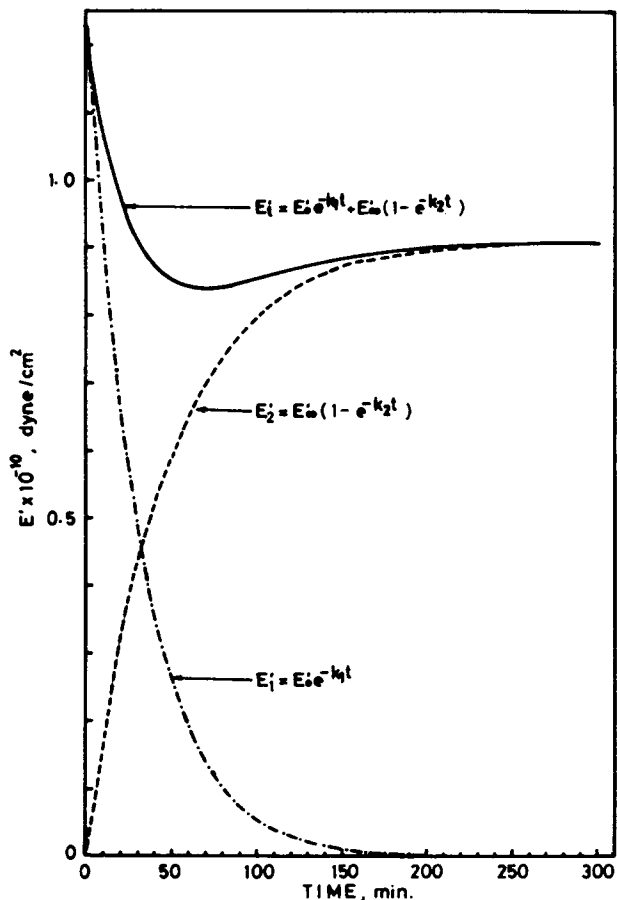
Fig. 10. Kinetic analysis of photodegradation of nylon 6.

The rate constants k_1 and k_2 can be determined by a trial-and-error method using the experimental values of E'_0 and E'_∞. At first some values are choosen for k_1 and k_2, and then the values of E'_t are calculated at each time by eq. (15). The calculations are continued until the calculated values of E'_t fit well with the experimental values changing k_1 and k_2.

Figure 11 shows the changes in E' during photodegradation at various temperatures from 100 to 130°C. At each temperature, it is suggested that scission and crosslinking occur simultaneously. The plots are the experimental values, and the solid lines are calculated from eq. (15). It is found that eq. (15) fits the experimental values well.

The rate constants k_1 and k_2 at various temperatures were obtained and are collected in Table I. The temperature dependence of the rate constants is shown in Figure 12. The apparent activation energies for k_1 and k_2 are 3.23 and 2.50 kcal/mole, respectively, from the slope of the straight lines. It is known that the activation energy of the scission reaction by the photodegradation is estimated to be 5.5% of the bond energy of the dissociating linkage.[30] If the scission reaction occurs mainly at the amide groups, the activation energy is calculated as 2.92 kcal/mole since the bond energy of the amide group is 53 kcal/mole.[22] Hence,
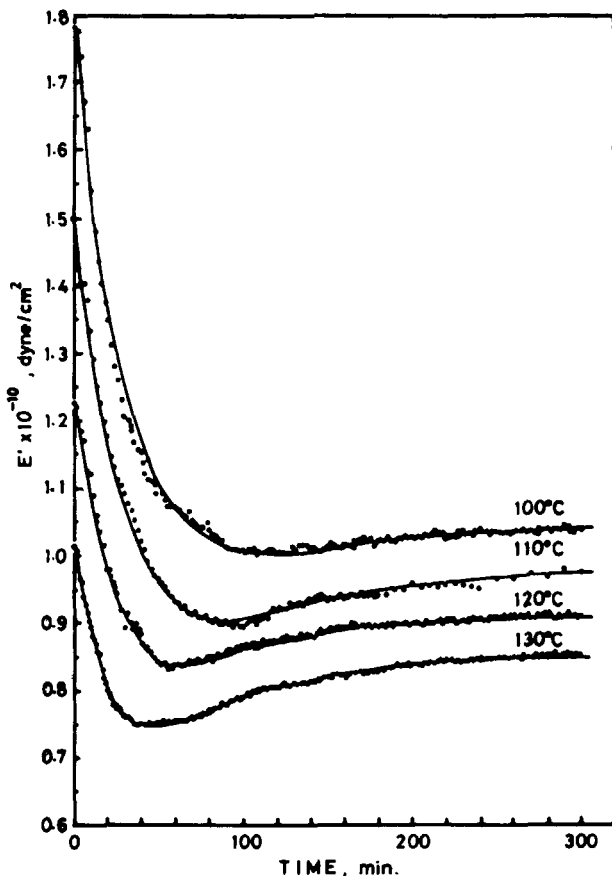
Fig. 11. Change in E' during photodegradation at various temperatures. Plots are experimental values and solid lines are calculated from eq. (15).

the value of 3.23 kcal/mole agrees with the activation energy for the scission of the amide groups.

We found that on irradiation of nylon 6 with light below 300 nm, crosslinking and scission occurred simultaneously and consequently led to recombination reaction. It is interesting to know the effect of the photodegradation on the temperature dispersions of nylon 6. Figure 13 shows the temperature dependence of the dynamic viscoelastic properties of the unirradiated and the photo-
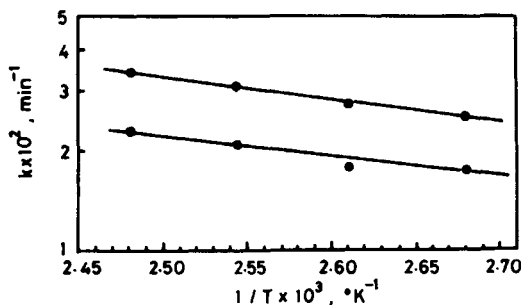

Fig. 12. Temperature dependence of k_1 and k_2.

TABLE I
Rate Constants at Various Temperatures

Temperature, °C	Rate constant, min^{-1}	
	k_1	k_2
100	2.50×10^{-2}	1.75×10^{-2}
110	2.75×10^{-2}	1.80×10^{-2}
120	3.10×10^{-2}	2.10×10^{-2}
130	3.45×10^{-2}	2.20×10^{-2}

degraded nylon 6 in the dry state. Ultraviolet light irradiation was made at 45°C for 5, 10, and 15 hr using the low-pressure mercury lamp. The sample irradiated above 20 hr became so brittle in the dry state that it was impossible to measure the temperature dispersion. In the dry state, two peaks are observed at 90°C (α-relaxation) and -95°C (γ-relaxation) in the tan δ-versus-temperature curve accompanying the decrement in E'.

About the rise of the α-relaxation there are many opinions, for example, segmental motions in the amorphous regions as a consequence of the breaking of hydrogen bonds between chains,[31-37] movement of the strained amorphous segments,[38] or glass transition of the polymer.[39-41] We consider that the α-relaxation is due to large-scale segmental motions in the amorphous regions in the vicinity of the glass transition temperature. Hydrogen bonds are broken as a consequence of segmental motion as reported by Williams and Delatycki[42] relating to epoxy–diamine networks. However, according to the thermal analysis of polyamides, an endothermic peak due to the glass transition appeared at about 40–50°C[43-46] and it increased to about 90°C by heat treatment.[45] This increment is considered to be a drying process rather than the formation of hydrogen bonds, being consistent with the result of the viscoelastic measurement.[47] In the temperature dispersion of the wet nylon 6, two peaks appeared above room temperature at about 30 and 90°C,[39,47] but the former one, which was caused by plasticization, disappeared upon heat treatment.[39,48] The γ-relaxation at -95°C involves the motion of methylene groups between the amide groups in the amorphous regions.[31-42]
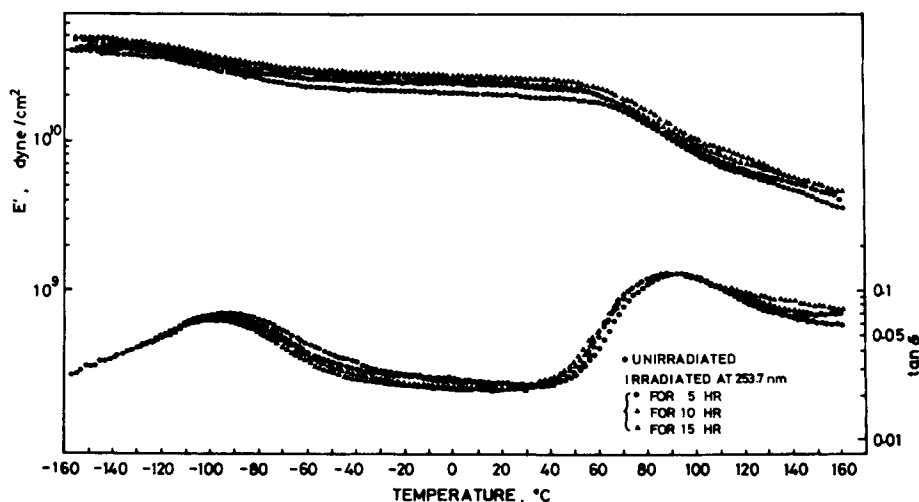

Fig. 13. Temperature dispersions of irradiated and unirradiated nylon 6 in dry state.

As the photodegradation proceeds, the α-peak in the tan δ curve is broadened, but the peak temperature and the intensity do not change.   Deeley, Woodward, and Sauer[34] reported that the α-peak was broadened by the high-energy radiation.   Prevorsk, Butler, and Reimschuessel[39] also reported that crosslinking with toluene diisocyanate led to a broadening of the α-peak.   The cause of broadening of the α-peak by the photodegradation is considered as follows.   During the progress of the photodegradation, various radicals are formed by many kinds of the scission reaction as shown in eqs. (2) to (4), and these lead to the formation of structures with various chain lengths which have various glass transition temperatures.

The γ-peak decreases in intensity and becomes sharper on irradiation with ultraviolet light.   According to the mechanism of the photodegradation of polyamide, the crosslinking reaction occurs at the methylene groups as shown in eqs. (6) and (10).   As the number of the movable methylene groups decreases, the intensity of the γ-relaxation is lowered.   The dynamic modulus increases upon photodegradation in the observed temperature range, reflecting the stiffening process by the crosslinking.

It is well known that the β-relaxation of nylon 6 appears only in the wet state. Figure 14 shows the γ-relaxation at $-100°C$ and the β-relaxation at $-45°C$ for the irradiated and the unirradiated wet nylon 6.   These samples were placed in a vessel containing a saturated aqueous solution of sodium chloride and conditioned at $30°C$ for a week.   The relative humidity was 76%, and the moisture content of the sample was about 3% by weight.
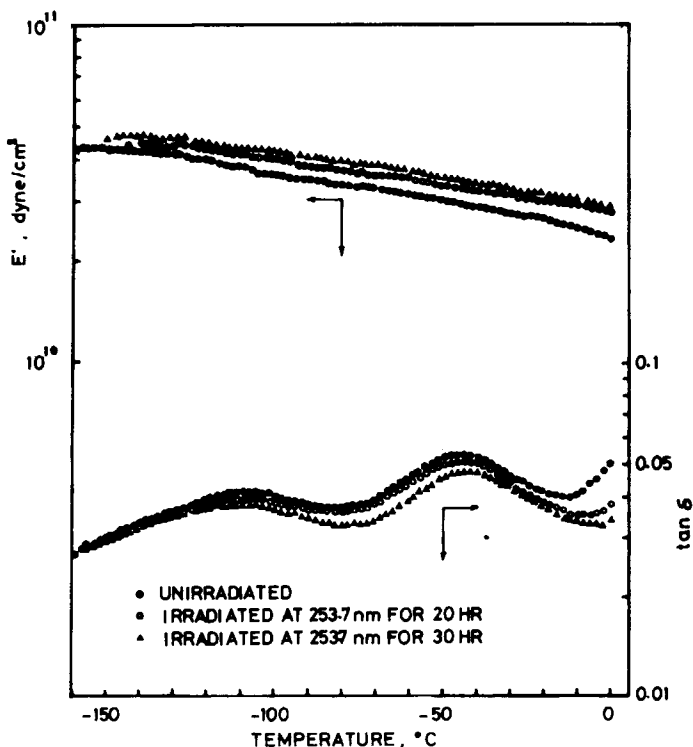

Fig. 14. Temperature dispersions of irradiated and unirradiated nylon 6 in wet state.

In the wet state the γ-relaxation shifts to a lower temperature and its intensity decreases. According to Woodward, Crissman, and Sauer,[33] the addition of water breaks hydrogen bonds in the amorphous region; this tends to keep the hydrocarbon portion of adjacent chains separated and therefore leads to a better packing of these portions in the water-containing nylon. Also, addition of water to nylon acts to decrease the methylene groups motion. However, the effect of the photodegradation on the γ-relaxation is the same as that of the dry nylon 6.

The rise of the β-relaxation has not yet been satisfactorily explained, and there is controversy as to whether the β-relaxation is caused by the presence of low molecular weight substances in the polyamide or is the result of conformational changes in chain segments. There are many opinions about the assignment of the β-relaxation, for example, the rotational motion of water molecules which are bound to amide groups by hydrogen bonds,[31,40] the segmental motion involving the cooperation of methylene groups and adjacent amide groups not bonded with amide groups on nearby chains,[32–36,41] the motion of the water/polymer complex,[49] and kinetic units containing amide groups which are firmly bonded to neighboring molecules.[50] Recently, Kapur, Rogers, and Baer[37] reported that the composite mechanism, which involves the forming and breaking of hydrogen bonds between carbonyl groups and the water molecules which bridge them and the major contribution of absorbed water to the composite mechanism, arises from the icelike defects which tightly bound water forms with nylon.

Under ultraviolet light irradiation, the β-relaxation in the tan δ-versus-temperature curve decreases in intensity as shown in Figure 14. This change may be attributed to the decrease in the number of the amide groups by the scission reaction as in eq. (2) and to the decrease in the number of the methylene groups which move cooperatively with the amide groups by the crosslinking reaction. The change in the dynamic modulus by the photodegradation is the same as that in the dry state.

CONCLUSIONS

The relationship between the dynamic mechanical properties and the photodegradation of nylon 6 was investigated and the following conclusions were obtained:

(1) The modulus of the elasticity and the density of nylon 6 are increased by the photodegradation with light below 300 nm according to the crosslinking reaction.

(2) The change in E' during irradiation with light at 253.7 nm is expressed by the equation $E'_t = E'_0 \exp(-k_1 t) + E'_\infty [1 - \exp(-k_2 t)]$, reflecting scission and crosslinking.

(3) The activation energies for k_1 and k_2 are 3.23 and 2.50 kcal/mole, respectively.

(4) The activation energy of 3.23 kcal/mole agrees with that for scission of the amide groups.

(5) Under photodegradation, the α-relaxation is broadened, the β-relaxation decreases in height, and the γ-relaxation decreases in intensity and becomes sharper.

This study was part of an investigation on "Durability of Polymer Materials," which was carried out as cooperative work among the institutes in the Agency of Industrial Science and Technology, Ministry of International Trade and Industry, Japan.

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