Photodegradation of Poly(methyl Methacrylate) by Monochromatic Light: Quantum Yield, Effect of Wavelengths, and Light Intensity

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Synopsis

Poly(methyl methacrylate) (PMMA) was photolyzed with monochromatic light of wavelengths 260, 280, and 300 nm by the use of the Okazaki large spectrograph. The quantum yield of main-chain scission (Φ_{cs}), effects of wavelength, and incident photon intensity on the photodegradation were investigated. It turned out that photodegradation of PMMA took place by the irradiation of 260–300 nm light, but did not by the irradiation at $\lambda \geq 320$ nm. The number of main-chain scission (N_{cs}) has a maximum value in the case of the irradiation with 280 nm light. Under the same conditions of wavelength and total photon intensity, a longer-term irradiation with a weaker incident photon intensity tends to yield a greater amount of main-chain scission. A linear relationship was found between the number of main-chain scission and the incident photon intensity. The average values of Φ_{cs} obtained in this work were 2.1×10^{-4}, 2.4×10^{-4}, and 4.1×10^{-4}, respectively, for the irradiations at 260, 280, and 300 nm. It was found that the photoinduced side-chain scission initiates the main-chain scission of PMMA.

INTRODUCTION

Studies on photodegradation of polymers are important not only academically but also industrially. Many kinds of useful polymers for industrial purposes have been developed recently. Fundamental studies on photodegradation are required to obtain photostable polymers and to estimate the lifetime of polymer materials. Until now, photodegradation of polymers has been mainly investigated by using a light source[1-5] such as 254 nm light from a low-pressure mercury lamp, polychromatic light from a high- or medium-pressure mercury lamp, and banded light through cutoff filters. Monochromatic light with a high intensity can not be obtained by conventional irradiation techniques.

Recently a large spectrograph was built at the National Institute for Basic Biology (NIBB) in Okazaki, Japan and named as the Okazaki large spectrograph (OLS). Using the OLS, we can get monochromatic light at any desired wavelength between 250 and 1000 nm with high light intensities.

Effects of wavelength and light intensity on photodegradation of polymers can be studied with such high intensity monochromatic light. In particular, the quantum yield of photodegradation can be determined reliably.

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In this work we have studied specifically the photodegradation of PMMA, which is a plastic widely used for its stiffness and clarity in various industrial fields. This work is the first application of OLS to basic research on polymer degradation.

EXPERIMENTAL

Sample Preparation

Poly(methyl methacrylate) powder (M_v = 838,000) supplied from Nakarai Chemicals Ltd. was dissolved in acetone and then purified by reprecipitation from methanol. Spectrograde acetone and methanol were supplied from Kishida Chemicals Ltd. and used as received. PMMA films were cast from an acetone solution of purified PMMA powder on a flat glass dish and dried under vacuum (10^{-4} mm Hg) for 24 h. Absorption spectrum of unirradiated PMMA coincided with that of the purified PMMA.[6] The thickness of films used was 0.01 mm for Fourier transform infrared (FTIR) spectroscopic measurements and 0.09 mm for ultraviolet (UV) spectroscopic and viscosity measurements. Samples have been stored in the dark till irradiations were made.

Irradiation

Monochromatic light irradiation to samples were carried out using the OLS at NIBB. The spectrograph has two Xe short arc lamps (30 and 6 kW) as its light sources. Radiation from these sources was dispersed into a spectrum by using a double-blazed plane grating with 1200 lines/mm. A spectrum covering UV, visible, and near infrared region (250–1000 nm) is projected onto a 10-m-long focal curve. The detailed description of the spectrograph was reported by Watanabe et al.[7] Irradiation of monochromatic light with any desired wavelength was made by placing the samples at appropriate positions on a 10-m-long focal curve. The wavelength dispersion is about 0.8 nm/cm. The beam was focused at each wavelength by using a surface mirror (20 × 10 cm). The stability of the source was continuously monitored during the irradiation at preselected wavelengths. A long-term variation of ca. 2% in the light intensity over a 10 h period was observed in this system.

Irradiations to the samples were carried out at wavelengths of 260, 280, 300, 320, 340, 400, and 500 nm in air. Four samples were irradiated at the same time and with varying light intensities at each wavelength. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. A neutral density filter was placed at appropriate position to obtain any desired photon intensity. The temperature of the samples was kept at 23°C at each wavelength during irradiation. Immediately after irradiations, the samples were put in black paper envelopes and stored in a desiccator at an ambient temperature.

Measurements

FTIR spectra of photoirradiated samples were taken on a Nicolet MX-1 FTIR spectrophotometer. A Hitachi model 323 spectrophotometer was used to take UV spectra of the samples.

The degree of main-chain scission was followed by viscosity measurements with an Ubbelohde's viscometer at 25 ± 0.01°C using acetone as a solvent. The viscosity-average molecular weight, $\overline{M_v}$, was calculated from the intrinsic viscosity ($[\eta]$) using[8]

$$[\eta] = 7.5 \times 10^{-5}(\overline{M_v})^{0.70} \tag{1}$$

RESULTS AND DISCUSSION

UV and FTIR Spectra

A UV spectrum of PMMA film irradiated with 260 nm light is shown in Figure 1. Unirradiated PMMA has an absorption maximum at $\lambda = 277$ nm which is attributed to carbonyl group in ester side chain. This spectrum coincides with that obtained by Gupta et al.[6] On photoirradiation, this band shifts to a shorter wavelength ($\lambda_{max} = 267$ nm). The same shift of the band was found in the case of the photoirradiation with 280 and 300 nm. No shift was observed when photoirradiation was carried out with the light of wavelengths longer than 320 nm. The decrease of absorbance at 277 nm (ΔOD_{277}) and the increase of that at 267 nm (ΔOD_{267}) are plotted at each irradiation wavelength in Figure 2. The results show that the decrease of OD_{277} and the increase of OD_{267} are almost complementary except for 300 nm light irradiation. This fact suggests the side-chain scission of PMMA and the production of new chemical species having λ_{max} at 267 nm.

Side-chain scission of ester groups is observed in a FTIR spectrum of photoirradiated PMMA (Fig. 3). In this spectrum, a band around 1190 cm^{-1} attributed to ν_{C-O-C} decreases in its intensity with the irradiation of 260 nm

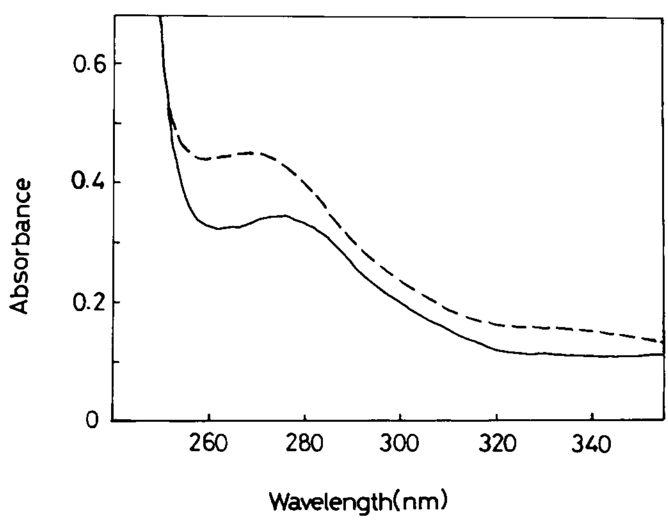


Fig. 1. Optical absorption spectra of unirradiated (—) and photoirradiated (---) PMMA with the light of wavelength 260 nm at 23°C in air. Total photon intensity, 3.83×10^{19} photons/cm^2.

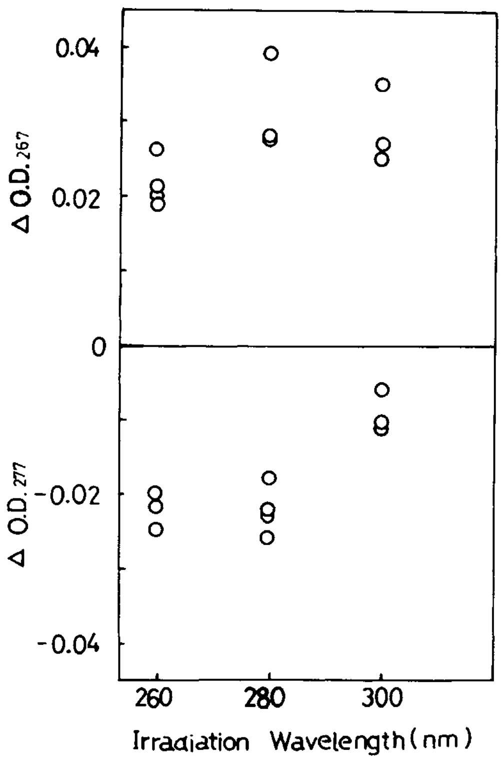


Fig. 2. Changes in optical densities at 284 and 267 nm by photoirradiation with the light of wavelengths 260, 280, and 300 nm at 23°C in air.

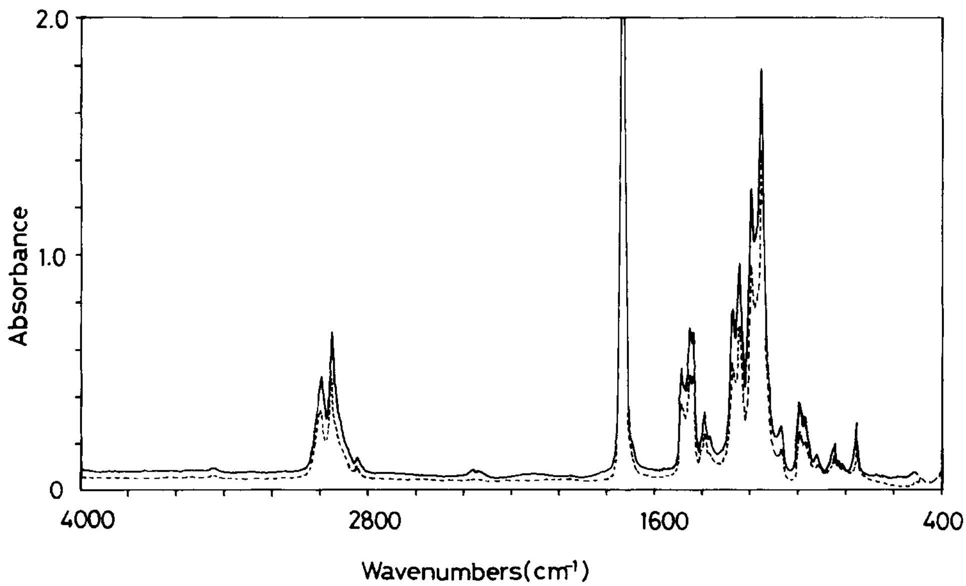
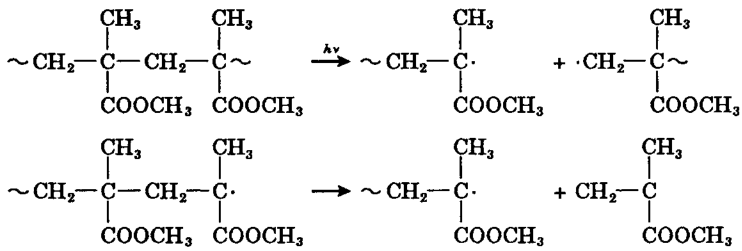


Fig. 3. FTIR spectra of unirradiated (—) and photoirradiated (---) PMMA with the light of wavelength 260 nm at 23°C in air. Total photon intensity, 3.83×10^{19} photons/cm^2.

light. A similar decrease was found when the irradiation was carried out with 280 or 300 nm light.

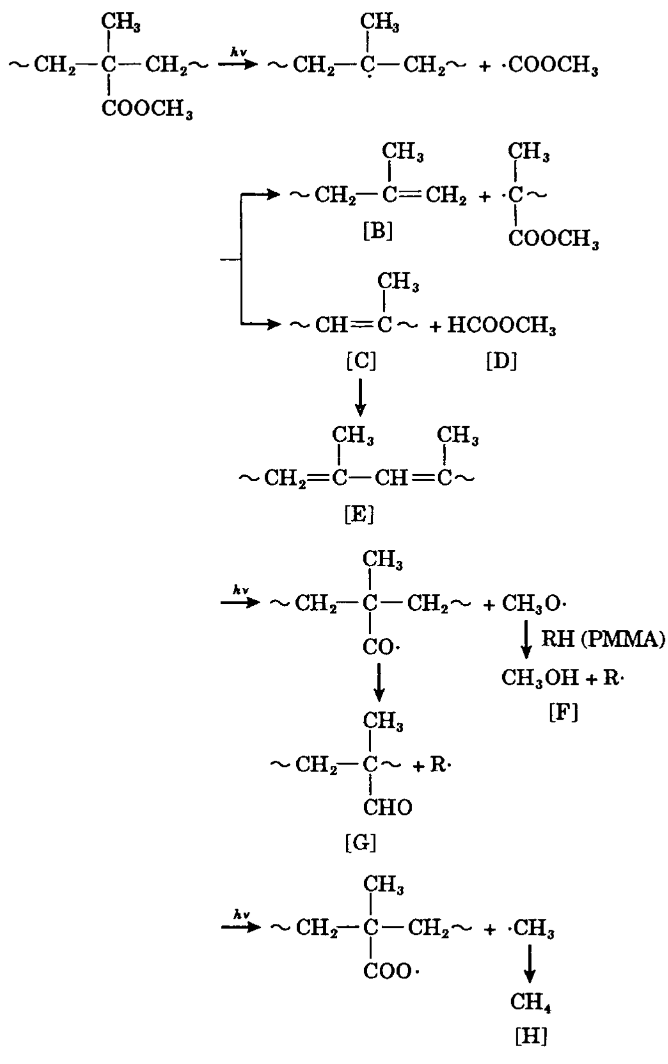
Photodegradation processes of PMMA is summarized as follows[6,9,10]:

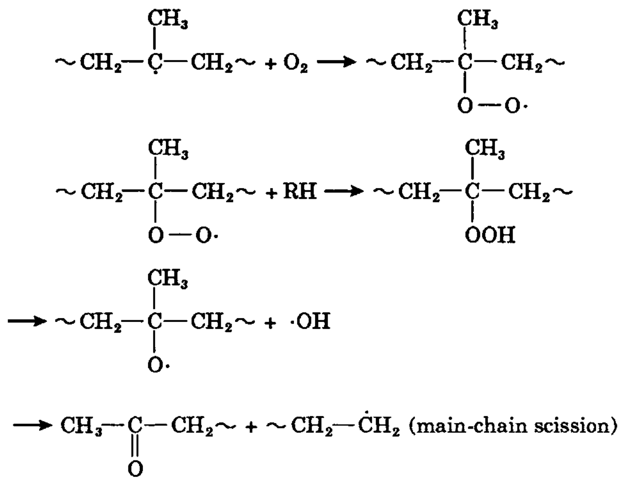
I. Direct main-chain scission:



[A]

II. Main-chain scission following side-chain scission:





[I]

Stable products [A]-[I] are expected to be produced as a result of photodegradation of PMMA.

Considering the position of λ_{max} in the UV spectrum obtained in the present study, product [G] or [I] seems to be the chemical species observed. It has been reported[11] that formaldehyde (HCHO) has its λ_{max} at 295 nm and λ_{max} shifts to shorter wavelengths by introducing alkyl groups in the hydrogen position, and that acetone (CH_3COCH_3) has its λ_{max} at 278.9 nm. Substituting CH_3 groups of acetone by alkyl groups, the band may shift to shorter wavelengths. Since the band of newly produced species extends over 260–280 nm, ketone-type [I] and aldehyde-type [G] compounds may be attributable to this band.

Effect of Irradiation Wavelength

PMMA films were irradiated with the monochromatic light to the total photon intensity of 3.83×10^{19} photons/cm^2 at each wavelength (260, 280, 300, 320, 340, 400, and 500 nm). The effect of wavelength on the degradation of PMMA was estimated based on the number of main-chain scission, which is calculated using

$$N_{cs} = \frac{\overline{M_{v0}}}{\overline{M_v}} - 1 \qquad (2)$$

where N_{cs} and $\overline{M_{v0}}$ are the number of main-chain scission and initial molecular weight, respectively. The average values of N_{cs} at each irradiation wavelength are plotted against irradiation wavelength in Figure 4 along with the absorption spectrum of an unirradiated PMMA film. Figure 4 shows that the main-chain scission of PMMA takes place by the irradiation of light with wavelengths below 320 nm. It can be seen from Figure 4 that the efficiency of main-chain scission represented by N_{cs} parallels the absorbance at each wavelength in the UV-absorption spectrum. The results indicate that the main-chain scission of PMMA takes place as a result of direct photon absorption by carbonyl chromophores in PMMA.

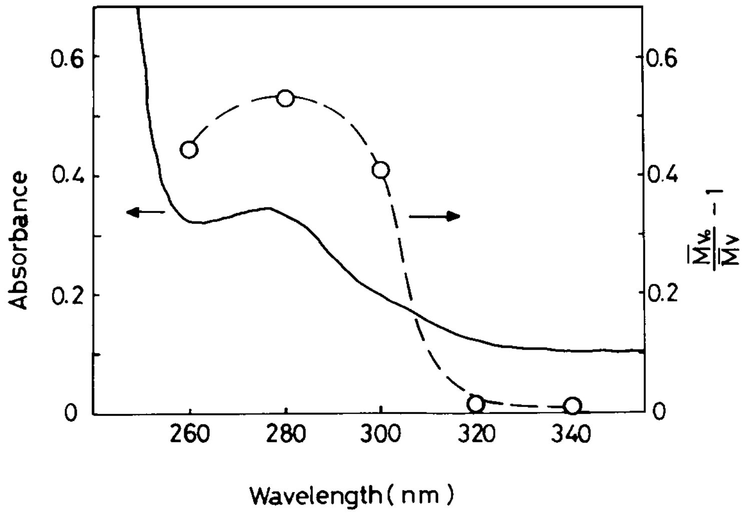


Fig. 4. Optical absorption spectrum of unirradiated PMMA (—) and changes in number of main-chain scission (-O-) with irradiation wavelength.

The wavelength effect on photodegradation of PMMA has been clearly demonstrated in the present experiment. This is the first study that has unambiguously shown the dependence of photodegradation of PMMA on wavelength.

Effect of Light Intensity

The effect of light intensity on photodegradation of PMMA is a factor to be explored for further developing the practical use of PMMA. To fix the total photon intensity, there are two procedures: One is a long-term irradiation with a low photon intensity and the other is a short-term irradiation with a high photon intensity. Here the "photon intensity" is defined by the number of incident photon per unit time and unit area of the sample. Such an effect was estimated by molecular weight change of PMMA.

The results are shown in Figures 5 and 6, respectively, for the irradiation wavelengths of 260 and 300 nm. A linear relationship between $\overline{M_v}$ and photon intensity was observed. When compared at the same wavelength and total photon intensity, the decrease of molecular weight tends to be greater for lower photon intensities. A similar trend was also found in the case of the irradiation with 280 nm light. This trend may be explicable, if some product formed by slow processes further absorbs photons and contributes to degradation of the polymer since longer time is required in the case of the irradiations with lower photon intensities.

The implications of these results are significant for an understanding of photodegradation of PMMA under sunlight, where the incident photon intensity is very low compared with the present experiment, and for an estimate of the lifetime of this polymer material under terrestrial sunlight.

Quantum Yield of Main-Chain Scission

The quantum yield of main-chain scission (Φ_{cs}) was calculated using the following equation:

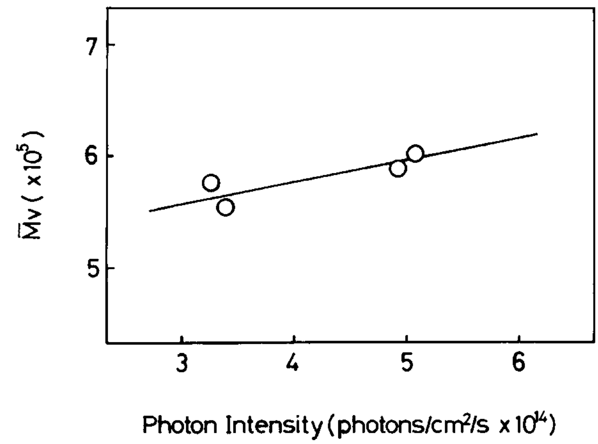


Fig. 5. Effect of incident photon intensity on changes in viscosity-average molecular weight ($\overline{M_v}$). Irradiation wavelength, 260 nm; total photon intensity, 3.83×10^{19} photon/cm^2.

$$\Phi_{cs} = N \frac{w}{w_0} \frac{\overline{M_{v0}}/\overline{M_v} - 1}{I_{abs} \cdot t} \tag{3}$$

where N and w are Avogadro's number and polymer weight, respectively, and t is the irradiation time. The absorbed photon intensity (I_{abs}) is calculated from the incident photon intensity (I_0) and the optical density (OD) at each wavelength and given by

$$I_{abs} = I_0(1 - 10^{-OD}) \tag{4}$$

The results are summarized in Table I. Although the number of main-chain scission (N_{cs}) has the largest for the irradiation with 280 nm light, Φ_{cs} is the

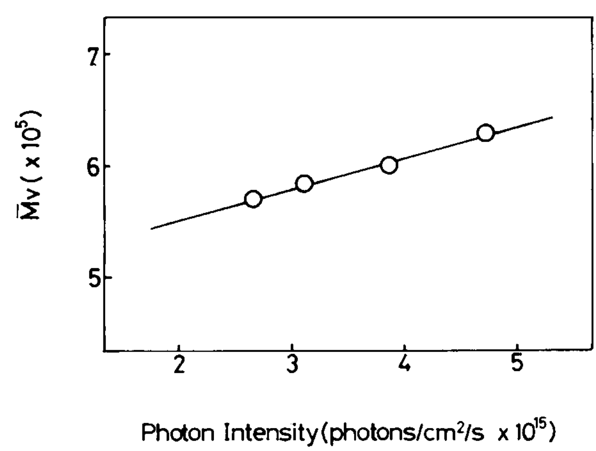


Fig. 6. Effect of incident photon intensity on changes in viscosity-average molecular weight ($\overline{M_v}$). Irradiation wavelength, 300 nm; total photon intensity 3.83×10^{19} photons/cm^2.

TABLE I
Quantum Yields of Main-Chain Scission (Φ_{cs}) at Specified Irradiation Wavelengths

Wavelength (nm)	Incident photon intensity (photons/cm^2 s)	Quantum yield Φ_{cs}
260	3.27×10^{14}	2.27×10^{-4}
	3.38×10^{14}	2.22×10^{-4}
	4.93×10^{14}	1.94×10^{-4}
	5.07×10^{14}	1.84×10^{-4}
280	1.33×10^{15}	2.63×10^{-4}
	1.66×10^{15}	3.05×10^{-4}
	1.85×10^{15}	1.54×10^{-4}
	2.26×10^{15}	2.12×10^{-4}
300	2.68×10^{15}	4.66×10^{-4}
	3.12×10^{15}	4.23×10^{-4}
	3.87×10^{15}	4.05×10^{-4}
	4.74×10^{15}	3.47×10^{-4}

greatest in the case of the irradiation with 300 nm light. This fact implies that the most efficient main-chain scission of PMMA can be attained by the irradiation of 300 nm light. The Φ_{cs} values obtained by the irradiation of 260 nm light or 280 nm light are similar to each other as shown in Table I.

Quantum yield of main-chain scission of PMMA has been reported by Schultz et al.[12] by the irradiation of 214–229 nm wavelength light, and they obtained somewhat larger value (0.03) than those in this work.

The absorption spectrum of unirradiated PMMA was already shown in Figure 1. Judging from this spectrum, the absorbed total photon number may be greater at 260 or 280 nm than at 300 nm. Processes other than main-chain scission seem to participate more in the case of photodegradation at 260 or 280 nm, leading to lower values of Φ_{cs} at these wavelengths.

SUMMARY

It was found that main-chain scission of PMMA took place by the irradiation of light with wavelengths shorter than 320 nm. Ketone-type and aldehyde-type compounds seem to be produced by photodegradation of PMMA. When compared at the same wavelength and same total photon intensity, a longer-term irradiation with a weaker photon intensity tends to yield a greater amount of main-chain scission. The quantum yields of main-chain scission were determined to be 2.1×10^{-4}, 2.4×10^{-4}, and 4.1×10^{-4}, respectively, at irradiation wavelengths 260, 280, and 300 nm.

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