Wavelength Sensitivity of the Photodegradation of Poly(Methyl Methacrylate)

TAKUYA MITSUOKA, AYAKO TORIKAI,* and KENJI FUEKI

Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

SYNOPSIS

Poly(methyl methacrylate) (PMMA) was photolyzed with monochromatic light of wavelengths 260, 280, 300, 320, 400, and 500 nm in vacuo by the use of the Okazaki Large Spectrograph. UV spectral changes, the quantum yields of main-chain scission (ϕcs), and effects of wavelength were investigated. UV spectral changes around 280 nm were observed with irradiation at 260 nm. The ϕcs has a maximum value in case of irradiation with 300 nm light. It turned out that photodegradation of PMMA took place by irradiation of 260–320 nm light but did not by irradiation with the light longer wavelength than 340 nm. The average values of ϕcs obtained in this work were 0.84×10^{-4}, 1.06×10^{-4}, 4.21×10^{-4}, 1.23×10^{-4}, 0, and 0 for irradiations at 260, 280, 300, 320, 400, and 500 nm, respectively. It was found that the photo-induced side-chain scission initiates the main-chain scission of PMMA by irradiation of 260 and 280 nm light.

INTRODUCTION

Polymer materials are used extensively under terrestrial sunlight. Studies on photodegradation of polymer materials are important for basic research and industrial fields. Fundamental studies on photodegradation of polymers are required for various applications of polymer materials. These studies are valid for the development of photostable polymers, photoresistant, photodegradable polymers, estimation of the lifetime of polymers, and so on. Efficiency of light-induced degradation to a polymer material expressed as a function of the wavelength of the incident light gives crucial information on spectral sensitivity of the material. Such a study can be possible using monochromatic light with a high intensity. Recently, a large spectorograph was built at the National Institute for Basic Biology (NIBB) in Okazaki, Japan, and named the Okazaki Large Spectorograph (OLS).[1] Using the OLS, we can get monochromatic light at any desired wavelength between 250 and 1000 nm with high light intensities.

We have reported the effect of wavelength and light intensity on the photodegradation of poly(methyl methacrylate) (PMMA) in the presence of air.[2] Although the rate of photodegradation of polymers accelerates in the presence of air, the degree of degradation of photoirradiated PMMA, estimated by viscosity average molecular weight, is reported to be about the same when irradiation was carried out using a medium-pressure mercury lamp.[3] In this article, we attempt to clarify the effect of wavelength on photodegradation in the absence of oxygen and to propose a photodegradation mechanism of PMMA.

EXPERIMENTAL

Sample Preparation

PMMA powder ($\overline{M}_v$ = 637,000) supplied from Nakarai Chemicals Ltd. was dissolved in acetone and then purified by reprecipitation from methanol. Spectro-grade acetone and special-grade methanol were supplied from Nakarai 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} torr) for 24 h. The thickness of films was 0.10 mm for UV spec-

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 47, 1027–1032 (1993)
 CCC 0021-8995/93/061027-06

troscopic and viscosity measurements. Sample film was cut into strips of 4.0 × 0.8 cm and put into a flat quartz cell and degassed to 10^{-5} torr for 24 h. Samples had been stored in the dark until irradiation.

Irradiation

Monochromatic light irradiation to samples was carried out using the OLS at the NIBB. The spectrograph has two Xe short-arc lamps (30 and 6 kW) as its light sources. Radiation from these sources was dispersed into the spectrum by using double-blazed plane grating with 1200 lines/mm. A spectrum covering UV, visible, and near infrared regions (250–1000 nm) is projected onto a 10-m focal curve. The detailed description of the spectrograph was reported by Watanabe et al.[1] and is shown in Figure 1. Irradiation of monochromatic light with any desired wavelength was made by placing the samples

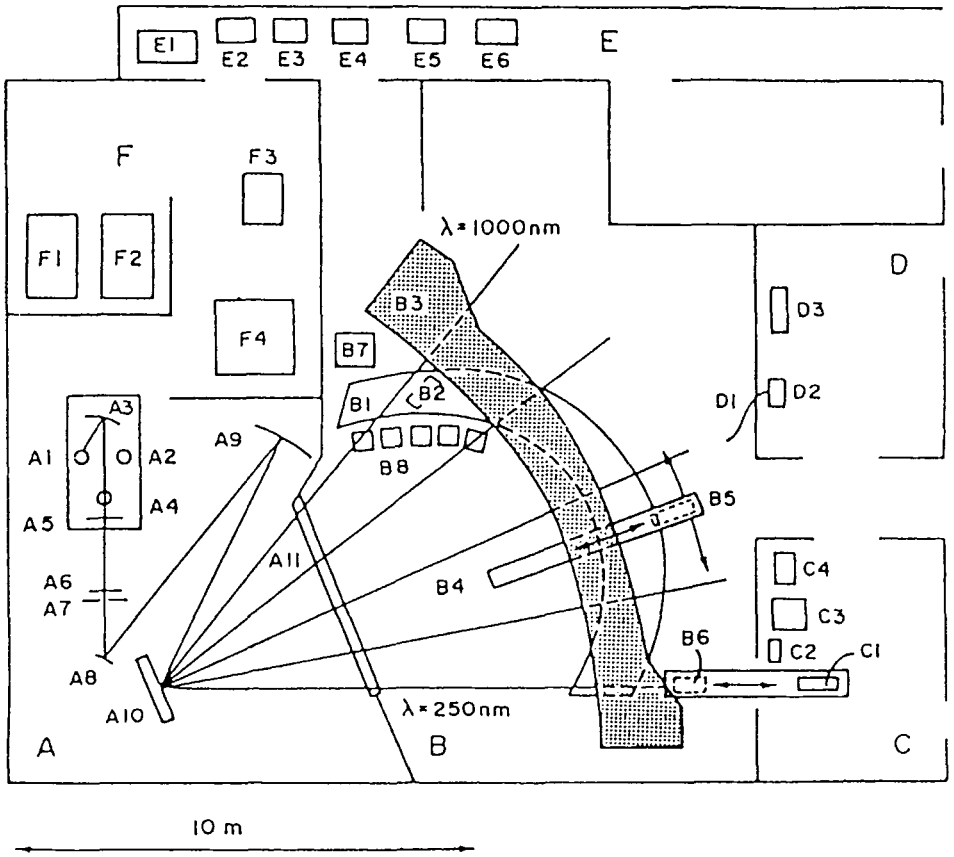


Figure 1 Spectral arrangement of the Okazaki Large Spectrograph. A, monochromator room; B, irradiation room; C, sample box preparation room; D, optical fiber room; E, microcomputer room; F, power supply room. A1, 30 kW xenon short-arc lamp; A2, 6 kW xenon short arc-lamp for low-energy irradiations; A3, rotatable condensing mirror; A4, medium-pressure mercury lamp for wavelength calibration; A5, shutter; A6, heat-absorbing filter; A7, entrance slit; A8, plane mirror; A9, condensing mirror; A10, double-blazed plane grating; A11, window; B1, focal curve stage; B2, sample box; B3, x-axis frame; B4, y-axis frame; B5, arm; B6, origin; B7, interface for entrance slit control; B8, interface for connector drive; C1, trolly; C2, control panel; C3, cathode ray tube (CRT) terminal; C4, printer; D1, optical fiber bundle (11 m long); D2, optical fiber outlet unit; D3, panel for monitoring; E1, 16-bit host microcomputer; E2, dater typewriter; E3, CRT terminal; E4, printer; E5, numerical control device (NC) for automatic carrier system; E6, NC interface; F1, air cooling system; F2, power supply for lamps; F3, control panel for lamps; F4, water cooling unit for lamps.

at appropriate positions on the 10-m focal curve. The wavelength dispersion is about 0.8 nm/cm. The beam was focused onto the sample at each wavelength by using a surface mirror.

A schematic illustration of sample irradiation is shown in Figure 2.

The stability of the source was continuously monitored during irradiation at preselected wavelengths. Constant intensity was obtained in this experiment. Irradiations of samples were carried out at wavelengths of 260, 280, 300, 320, 400, and 500 nm in vacuo. Four samples were irradiated at the same time, varying with light intensities at each wavelength. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. The temperature of the samples was kept at 23°C at each wavelength. Immediately after irradiation, the samples were put into black paper envelopes and stored in a desiccator at ambient temperature.

Measurements

UV spectra of photo-irradiated samples were taken on a Hitachi model 323 spectorophotometer. Viscosities of the samples were measured with a Ubbelohde's viscometer at 25 ± 0.01°C using acetone as a solvent. The viscosity average molecular weight, M_v, was calculated from the intrinsic viscosity ($[\eta]$) using eq. (1).[4]

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

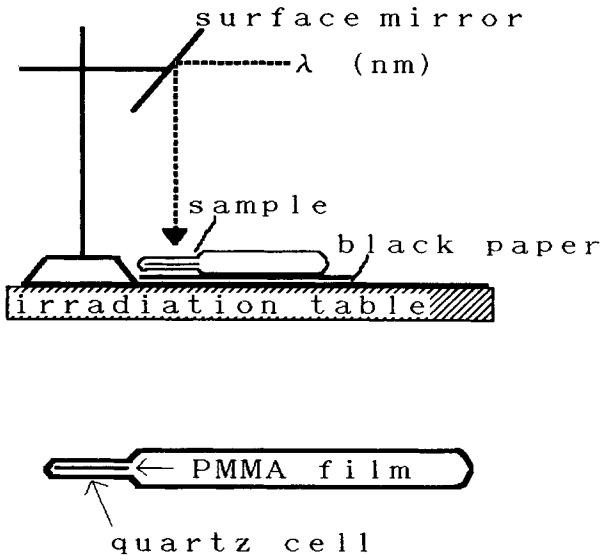


Figure 2 Schematic illustration of sample irradiation.

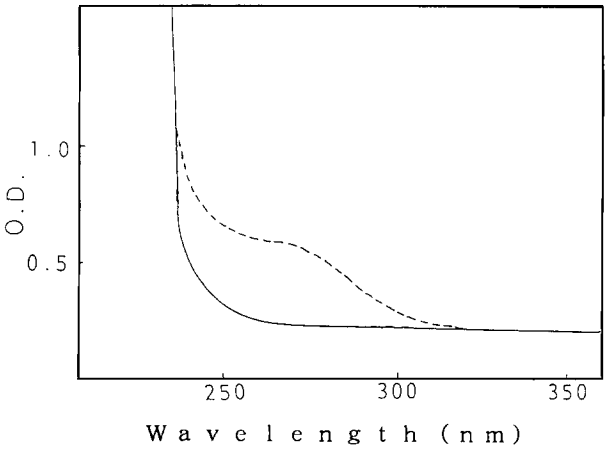


Figure 3 Ultraviolet spectra of photoirradiated PMMA at 260 nm at 23°C in vacuo. (——), unirradiated; (- - - - -), irradiated, total photon number, 6.32×10^{19} photons/cm^2.

RESULTS AND DISCUSSION

A UV spectrum of PMMA film irradiated with 260 nm light is shown in Figure 3. A typical spectrum of PMMA film photoirradiated with other wavelength light is shown in Figure 4.

The increase in optical density around 280 nm was found by irradiation of 260 nm monochromatic light. Such a large change was not caused by irradiation of wavelength light other than 260 nm. This fact suggests the side-chain scission of PMMA and the production of new chemical species having λ_{max} at 280 nm. Photodegradation processes of PMMA are summarized as follows.[2,5-7]

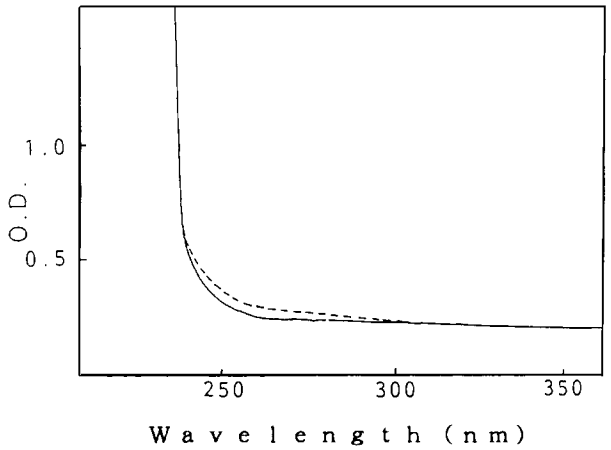
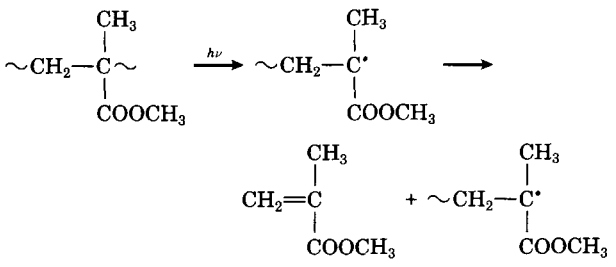
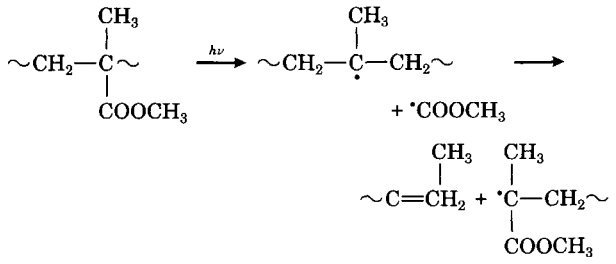


Figure 4 Ultraviolet spectra of photoirradiated PMMA at 300 nm at 23°C in vacuo. (——), unirradiated; (- - - - - -), irradiated, total photon number, 4.21×10^{19} photons/cm^2.

I Homolitic main-chain scission.

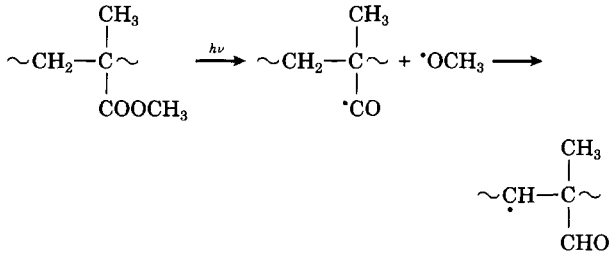


II Ester side-chain scission.

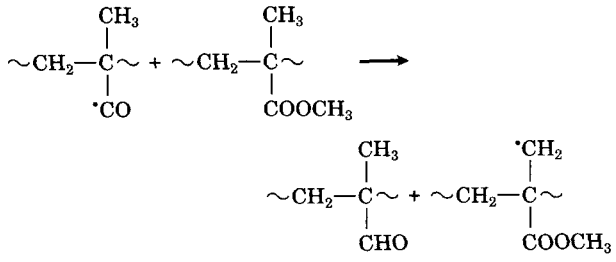


Reaction II has side reaction possibility as follows.[7,8]

II Side reaction (a).



II Side reaction (b).



These side reactions generate CHO group in products that might cause change of the UV spectrum at 280 nm.

Quantum Yield of Main-Chain Scission

PMMA films were irradiated with monochromatic light to a total photon number of 4.21×10^{-4} photons/cm^2 at each wavelength (260, 280, 300, 320, 400, and 500 nm). The effect of wavelength on the degradation of PMMA was estimated based upon the number of main-chain scissions, calculated using eq. (2).

$$N_{cs} = \frac{\overline{M}_{v_0}}{\overline{M}_v} - 1 \tag{2}$$

where N_{cs} and $\overline{M}_{v_0}$ are the number of main-chain scissions and initial molecular weight, respectively. The quantum yield of main-chain scission (ϕcs) was calculated using the following equation:

$$\phi cs = N \frac{W}{w_0} \frac{\overline{M}_{v_0}/\overline{M}_v - 1}{I_{\text{obs}} \cdot t} \tag{3}$$

where N and W are Avogadro's number and polymer weight, respectively, and w_0 is the weight of one polymer molecule unirradiated, t is irradiation time. The observed photon intensity (I_{obs}) is calculated from the incident photon intensity (I_0) and the optical density (OD) at each wavelength and given by eq. (4).

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

The average values of ϕcs at each irradiation wavelength are plotted against irradiation wavelength in Figure 5, which shows that the maximum ϕcs value

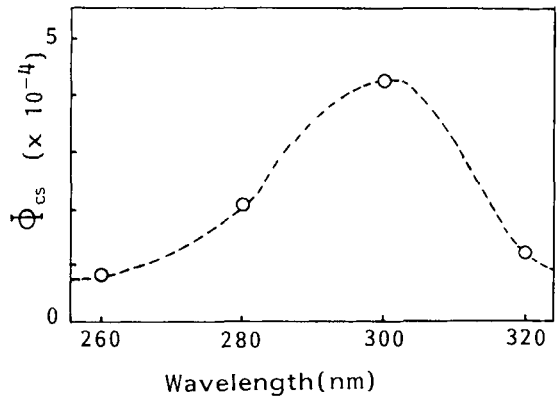


Figure 5 Effect of wavelength on the quantum yield of main-chain scission (ϕcs) of photoirradiated PMMA in vacuo, 4.21×10^{19} photons/cm^2.

was obtained after irradiating at 300 nm light and that main-chain scission did not take place by irradiation of the light of wavelengths at 400 and 500 nm. The result is that main-chain scission of PMMA takes place by irradiation with the light of wavelength below 320 nm. The wavelength effect on photodegradation behavior of PMMA in vacuo has been demonstrated in the present experiment. Figure 5 shows that the ϕcs value is the greatest in the case of irradiation with 300 nm light. This fact implies that the most efficient main-chain scission of PMMA can be attained by irradiation of 300 nm light. When irradiations are carried out at 400 and 500 nm light, ϕcs values are found to be zero. Judging from these results, reaction (I), direct main-chain scission takes place mainly with irradiation of the light of 300 nm while main-chain scission following side-chain scission takes place with irradiation of the light of wavelength shorter than 280 nm. Because side reactions (a) and (b) have been found to take place with irradiation of the light of wavelength shorter than 280 nm. Photodegradation of PMMA can take place with irradiating the light of wavelength shorter than 320 nm.

Comparison of ϕcs In Vacuo with Those in Air

Quantum yields of main-chain scission (ϕcs) at specified irradiation wavelengths in air and in vacuo are shown in Table I. Comparing this table, ϕcs values at 260 nm and 280 nm in air are almost twice as large as those in vacuo, while ϕcs values at 300 nm in air is about the same as those in vacuo. We attempt to explain the difference between the ϕcs (in air) and ϕcs (in vacuo) obtained with irradiation of 260 nm and 280 nm light. Recently, we investigated the wavelength effect on the electron spin resonance spectra of photoirradiated PMMA at 77 K in vacuo. When irradiating at 260 nm light, the radicals produced from the side-chain and 280 nm scission, i.e., $\cdot CH_3$ and $\cdot COOCH_3$, were detected adding to the radical due to homolytic main-chain scission. Only the radical due to homolytic main-chain scission was produced with irradiation of 300 nm light.

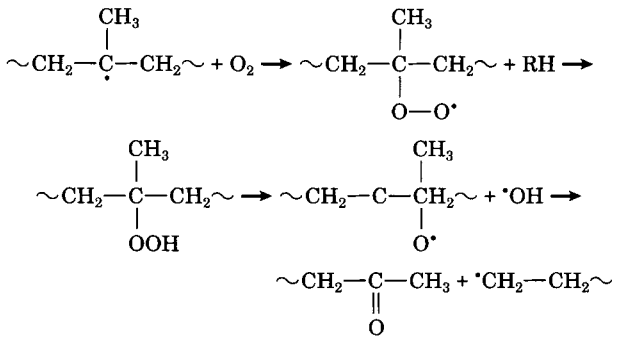
Table I Quantum Yields of Main-Chain Scission (Φcs) at Specified Irradiation Wavelengths in Air and In Vacuo

	Wavelength (nm)		
$\Phi cs \times 10^4$	260	280	300
In air*	2.07	2.34	4.31
In vacuo	0.84	1.06	4.21

* Ref. 2.

When irradiating in air, the oxygen addition reaction to an on-chain radical may occur according to the following scheme.[10]

II Side reaction (c).



After irradiating at 260 nm and light 280 nm in the presence of O_2, ester side-chain scission takes place according to side reaction (c); therefore, ϕcs values are increasing compared with those in vacuo. Homolytic main-chain scission which takes place with irradiation of 300 nm light, induces first direct main-chain scission (I) following peroxide formation. ϕcs values obtained with irradiation at 300 nm in air are not so large compared with those in vacuo.

SUMMARY

The quantum yields of main-chain scission (ϕcs) photoirradiated in vacuo were determined, respectively, at irradiation wavelengths of 260, 280, 300, 320, 400, and 500 nm. UV spectral change was found by irradiation of 260 nm monochromatic light. Such a large change was not caused by irradiation of wavelength lights other than 260 nm. The threshold wavelength of photodegradation of PMMA in the absence of oxygen was determined to be around 320 nm.

The authors thank Dr. Masakatu Watanabe and Mamoru Kubota of the National Institute for Basic Biology for their advice and help in carrying out irradiations. This study was carried out under the NIBB Cooperative Research Program for the Okazaki Large Spectrograph (89-50390-508). The present work was partially supported by a Grant-in-Aid for Scientific Research No. 03650720 from the Ministry of Education, Science and Culture.

REFERENCES

1. M. Watanabe, M. Furuya, Y. Miyoshi, Y. Inoue, I. Iwahashi, and K. Matsumoto, *Photochem. Photobiol.*, **36,** 491 (1982).
2. A. Torikai, M. Ohono, and K. Fueki, *J. Appl. Polym. Sci.*, **41,** 1023 (1990).
3. A. Torikai, A. Hozumi, and K. Fueki, *Polym. Degrad. Stab.*, **16,** 13 (1986).
4. Chem. Soc. Jpn., *Kagaku Binran,* Maruzen, Tokyo, 1980, p. 763.
5. A. Gupta, R. Lian, F. D. Tsay, and J. Moacanin, *Macromolecules,* **13,** 1696 (1980).
6. A. Torikai and K. Fueki, *Polym. Photochem.*, **2,** 297 (1982).
7. J. F. McKellar and N. S. Allen, *Photochemistry of Man-Made Polymer,* Applied Science, London, 1979, p. 89.
8. R. B. Fox, L. G. Isaocs, and S. Stones, *J. Polym. Sci., Polym. Chem. Educ.*, **1,** 1079 (1963).
9. T. Mitsuoka, A. Torikai, and K. Fueki, *Polym. Preprints Jpn.*, **39,** 1846 (1990).
10. W. Schnabel, *Polymer Degradation,* Macmillian, New York, 1981, p. 114.

Received December 11, 1991
Accepted April 28, 1992