NOTE

Electron Spin Resonance Studies of Poly(methyl methacrylate) Irradiated with Monochromatic Light

INTRODUCTION

Recently, we studied the wavelength sensitivity of photodegradation of poly(methyl methacrylate) (PMMA)[1,2] in the presence and absence of oxygen. By comparing the quantum yield of main-chain scission (ϕcs) in vacuum and that in air irradiated at the same wavelength, the following conclusions were obtained:

1. Main-chain scission of PMMA takes place by the irradiation of light of a wavelength shorter than 320 nm.
2. There are two processes which cause main-chain scission of PMMA.

The main processes of photodegradation of PMMA are reported to be as follows[1-5]:

1. Ester side-chain scission followed by main-chain scission which forms small radicals such as $\cdot COOCH_3$, $\cdot CHO$, and $\cdot CH_3$.
2. Direct main-chain scission producing the scission-type radical of PMMA which gives a well-known nine-line ESR spectrum.

Judging from the ϕcs values obtained in the previous experiments,[2] direct main-chain scission takes place mainly on irradiation of 300 nm light, while main-chain scission following side-chain scission takes place with the light of a wavelength shorter than 280 nm.

In this study, we attempted to clarify the precursors of the photodegradation and to confirm the previous results. Monochromatic light irradiations to PMMA at 77 and 296 K in vacuum were carried out for this purpose.

EXPERIMENTAL

PMMA was prepared by the radiation-induced polymerization of the methyl methacrylate (MMA) monomer. MMA supplied by Tokyo Kasei Co. Ltd. was purified by vacuum-distillation after removing inhibitors by a conventional method. Fleshly distilled monomer was deaerated by repeated freeze–thaw cycles and sealed off under vacuum (10^{-5} Torr). MMA was irradiated with γ-rays from a Co-60 source in vacuum at room temperature with a dose rate of 3.7×10^2 Gy/h and total dose to 5.4×10^3 Gy. PMMA prepared in this way was dissolved in acetone and then purified by reprecipitation from methanol. After washing the precipitate with methanol, it was dried under vacuum (10^{-4} Torr) for 24 h.

PMMA films were cast from an acetone solution of purified PMMA powder on a flat glass dish. After evaporating the solvent, they were dried under vacuum (10^{-4} Torr) for 24 h. The thickness of films was ca. 0.1 mm. A strip of 3×60 mm film was used for the ESR measurement.

Samples were irradiated with monochromatic light using an Okazaki Large Spectrograph (OLS). A detailed explanation of the OLS has already been given.[2] Irradiations of monochromatic light with any desired wavelengths between 250 and 1000 nm can be made by placing the samples at appropriate positions on the 10 m focal curve. The stability of the source was continuously monitored during irradiations at preselected wavelengths. Irradiations to samples were carried out at wavelengths of 260, 280, 300, 320, 400, and 500 nm in vacuum at 77 and 296 K. A quartz lens was used to obtain higher photon intensity for the irradiations at 77 K. The light intensity at each sample position was measured by a Riken HK-1 photon density meter. The ESR spectra of photoirradiated samples were taken on a Brucker ER 200D ESR spectrometer at 77 and 296 K in vacuum.

RESULTS AND DISCUSSION

On photoirradiation of PMMA film at 77 K in vacuum, the ESR spectra shown in Figure 1 were obtained. The spectra obtained by the irradiation of 260 nm light [Fig. 1(1)] consists of a singlet and a quartet superimposed on the nine-line (scission-type) spectrum. Furthermore, we could also find a doublet arising from $\cdot CHO$ (coupling constant = 126 + 2.0 G) in the spectrum (Fig. 2).[3]

The four-line spectrum indicated as M in Figure 1 can be assigned to $\cdot CH_3$. The origin of the unresolved singlet spectrum indicated by the arrow in Figure 1 is not clear; it might be attributed to $\cdot COOCH_3$.[6]

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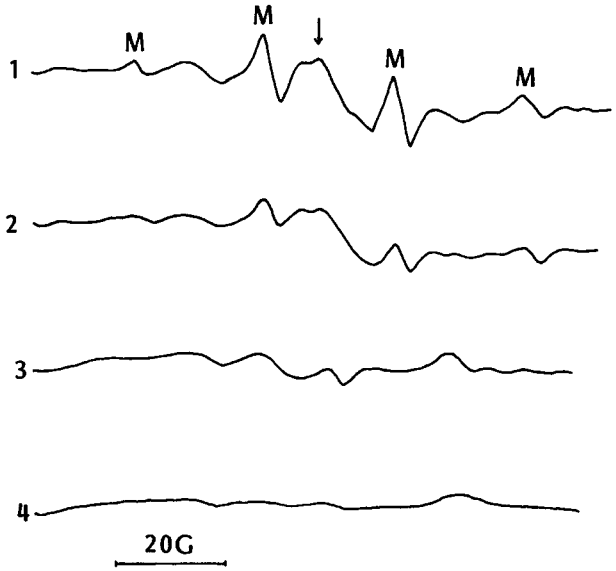
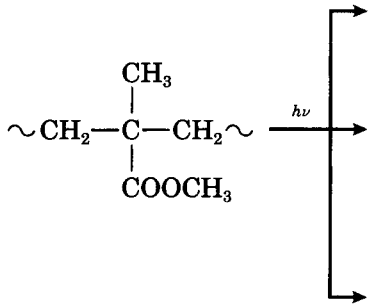
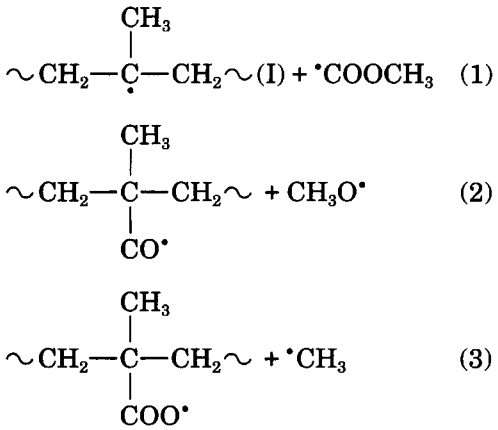


Figure 1 ESR spectra of photoirradiated PMMA at 77 K in vacuum. Irradiation wavelength: (1) 260 nm; (2) 280 nm; (3) 300 nm; (4) 320 nm. Total photon fluence: (1) 9.8×10^{19} photons/cm^2; (2) 2.6×10^{20} photons/cm^2; (3) 2.8×10^{20} photons/cm^2; (4) 3.4×10^{20} photons/cm^2.

These radicals are considered to be produced by ester side-chain cleavage of PMMA,[5] i.e.,

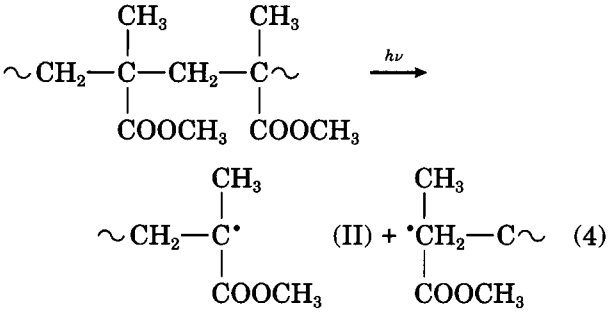




On warming the sample to room temperature, these radicals disappear, leaving the weak nine-line spectrum.

Figure 2 ESR spectrum of photoirradiated PMMA at 77 K in vacuum. Irradiation wavelength, 260 nm. Total photon fluence, 9.8×10^{19} photons/cm^2. Arrows indicate the doublet (•CHO).

The small radicals such as •CH$_3$ and •CHO were also found by irradiating the PMMA with 280 nm light. When the irradiations were carried out with the 300 nm light, such small radicals could not be detected. Only a weak nine-line spectrum (II) produced by reaction (4) was observed:



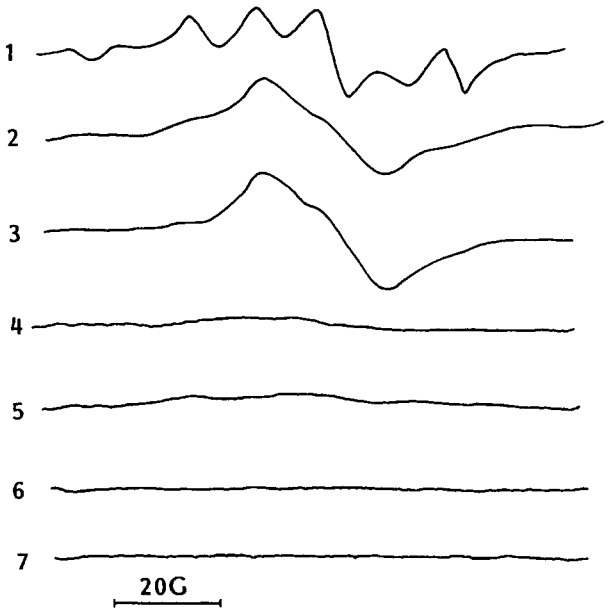


Figure 3 ESR spectra of photoirradiated PMMA at 296 K in vacuum. Irradiation wavelength: (1) 260 nm; (2) 280 nm; (3) 300 nm; (4) 320 nm; (5) 340 nm; (6) 400 nm; (7) 500 nm. Total photon fluence: (1) 4.9×10^{18} photons/cm^2; (2–7) 2.3×10^{19} photons/cm^2.

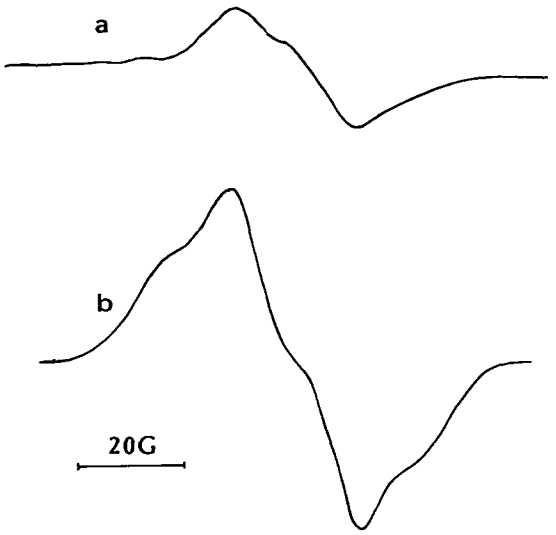
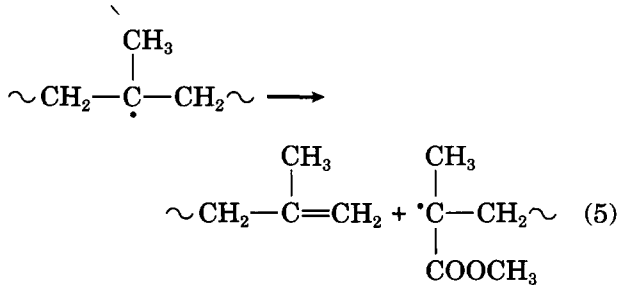


Figure 4 (a) ESR spectrum of PMMA photoirradiated at 300 nm in vacuum. (b) Simulated spectrum of the allyl radical.

Furthermore, no radical species was found by irradiating PMMA samples with the light of wavelength longer than 320 nm.

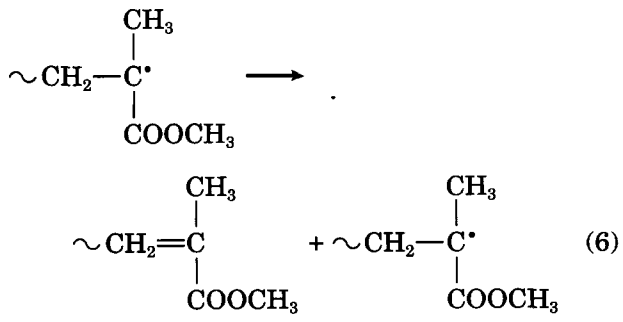
The main-chain scission of PMMA is considered to begin from radicals (I) and (II) according to the following scheme[3]:

1. Ester side-chain scission:



(5)

2. Homolytic main-chain scission:



(6)

Process 1 takes place on irradiation of PMMA with the light of wavelengths of 260 and 280 nm, while process 2 is responsible for the main-chain scission on irradiation of 300 nm light.

These observation support our previous results, which are given below:

1. Ester-side chain scission followed by main-chain scission is the main process for the photodegradation of PMMA, when the irradiations were carried out with 260 and 280 nm light.
2. The threshold wavelength of photodegradation of PMMA in the absence of oxygen was determined to be around 320 nm.[2]

On photoirradiation of PMMA film in vacuum at 296 K with monochromatic light, the ESR spectra were obtained as shown in Figure 3. The spectrum obtained with the irradiation of 260 nm light can be attributed to the scission-type radical of PMMA produced by reaction (4).

On photoirradiation of PMMA film with the light of 280 and 300 nm, a type of spectrum other than that of the scission-type radical was detected. This spectrum may be attributed to an allyl-type radical produced by long-term exposure to the light. Total fluence of photon numbers are about five times larger in the case of irradiations at 280 and 300 nm than that of 260 nm.

The spectrum obtained on irradiation of 300 nm light is compared with the simulated spectrum of the allyl radical[7] in Figure 4. An allyl-type radical formation with long-term exposure to light is confirmed from spectra (a) and (b) in this figure.

Although the mechanism of allyl-type radical formation was not fully elucidated, the wavelength sensitivity of radical formation is confirmed by ESR spectra irradiated and measured at 296 K. The experimental results obtained from ESR spectra at 296 K also support our previous conclusion that the threshold wavelength of photodegradation of PMMA in the absence of oxygen was determined to be around 320 nm.

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