

Fabrication of Refractive Index Profiles in Poly (Methyl Methacrylate) using Ultraviolet Rays Irradiation

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We demonstrated that the refractive index of poly(methyl methacrylate) (PMMA) increased by simple ultraviolet rays irradiation. The index change, +1.0% was due to the change of chemical structure including elimination of the carbonyl group, followed by olefin formation, which were determined by Fourier-transform infrared rays and UV absorption spectra. A refractive index profile for 15- μm -thick PMMA was realized by irradiation for 4 h. Therefore, it is considered that the graded index (GI) profile of PMMA can be applied to microdevices such as a microspherical lens, single-mode waveguide and so on. [DOI: 10.1143/JJAP.41.876]

KEYWORDS: refractive index change, PMMA, photochemical reaction, graded index, microlens, waveguide

1. Introduction

Recently, with the development of opt-telecommunications technology, numerous materials have been investigated from the viewpoint of their application. Important properties of materials to be used to fabricate devices for opt-telecommunication are refractive index, transparency, and resistance to the environmental factors, and control of the refractive index of materials is one of the most important factors of all.

Many researchers have used photochemical reactions to control refractive indices.¹⁻¹⁷⁾ Photochemical reactions have several merits; one can limit the reaction to that of the desired materials in the irradiated area, and the irradiated pattern has an error of less than 1 μm . These materials with photochemical reactivity are applied to holography,¹⁾ switching devices,^{8,9)} grating,¹⁰⁾ waveguides^{11,12)} and so on. Devices, which have a graded index (GI) profile in the medium, have also been intensively investigated, because those devices overcome the demerits of the conventional one; a transmitted pulse in a GI optical fiber can retain its shape during propagation, and a GI lens is able to erase aberrations and to have larger refraction with a curvature. Until now, the ion exchange method¹⁸⁻²⁰⁾ and facial gel polymerization method²¹⁻²³⁾ have been reported, where dopants are diffused in host materials in order to fabricate the profiles. However, we first reported that it was possible to achieve the desired refractive index profile in a polymer using a photochemical reaction.²⁴⁾ Polymer films demonstrated decreasing refractive index on approaching a light source. This method does not require non-uniform diffusion of dopants, and possesses the above-mentioned merits of photochemical reactions. But some devices such as lenses and waveguides require reactions to increase their refractive indices. In most materials, the refractive index decreases upon irradiation, except in the case of photopolymerization.¹²⁾ It is, however, difficult to maintain a stable GI profile in a device with a monomer, since monomers involved in photopolymerization are often volatile.

We observed the refractive index of poly(methyl methacrylate) (PMMA), which is well known as a typical polymer

applied to optical devices, increased under irradiation. In this paper, it is reported how a photochemical reaction of PMMA increased the refractive indices, and that GI structures were fabricated by the utilization of this reaction.

2. Experiments

PMMA ($M_w = 170,000$ Mitsubishi Rayon) was used without further purification. Two grams of the polymer was dissolved in 5 ml of *N,N*-dimethyl formamide (DMF) or dichloromethane (DCM).

Films for UV absorption spectra and refractive index measurements were prepared by spin coating of the solution on a fused silica plate ($n = 1.4570$ at 632.8 nm), and their vacuum dried in 80°C for 3 d in the dark. A 250 W super high-pressure mercury lamp (SPIII-250 Ushio) was used as the light source, which irradiated a polymer film on a substrate. The lamp was used with an interference filter (F10.254.0-4 CVI Laser Corp.) and a polytetrafluoroethylene (PTFE) mask as shown in Fig. 1. The bandwidth of the light transmitted through the filter was about 10 nm. The light

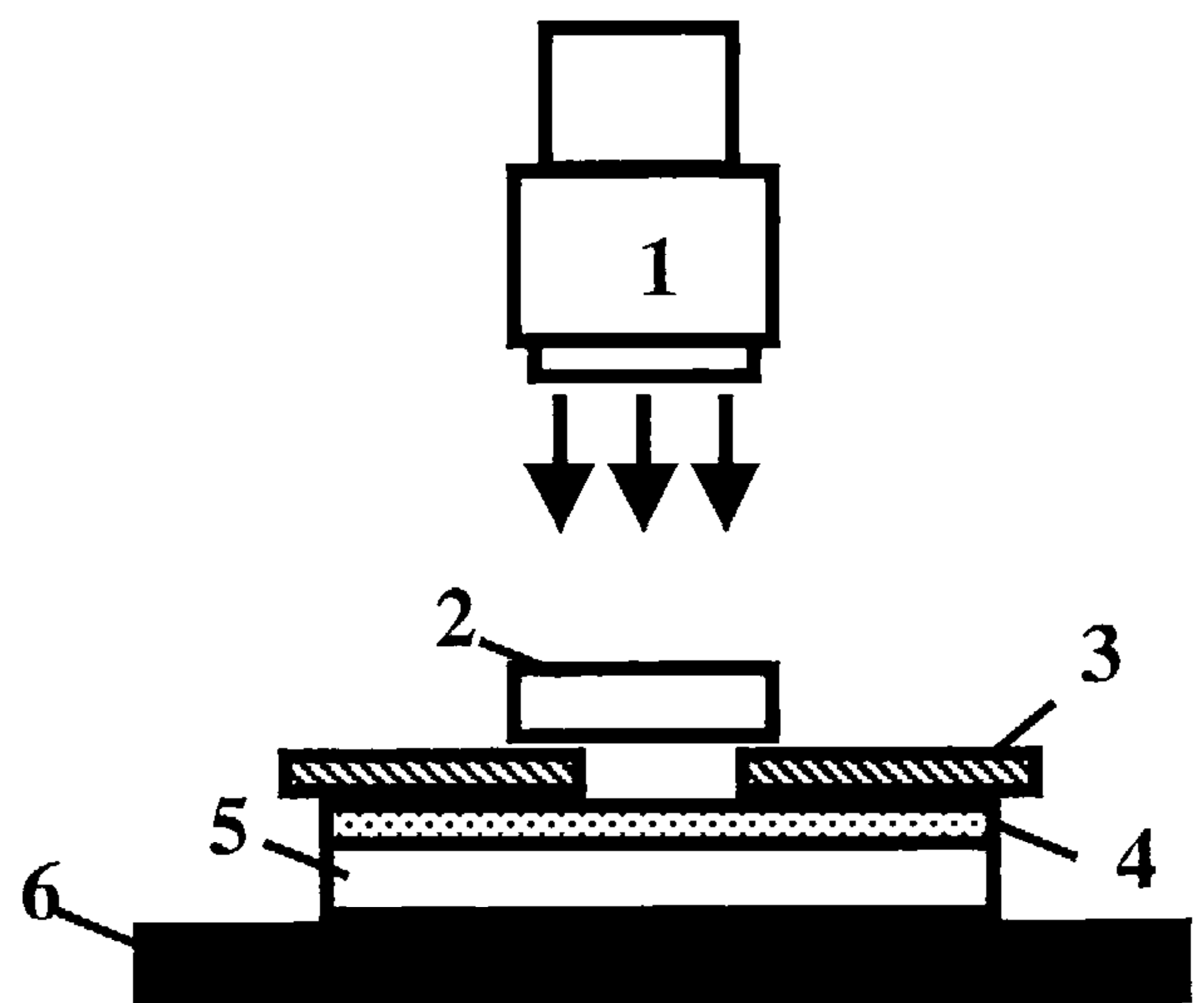


Fig. 1. UV irradiation setup: 1, UV light guide connected to super high-pressure mercury lamp; 2, interference filter at 365 nm; 3, PTFE mask; 4, spin-coated film on a substrate; 5, fused silica substrate; 6, iron plate.

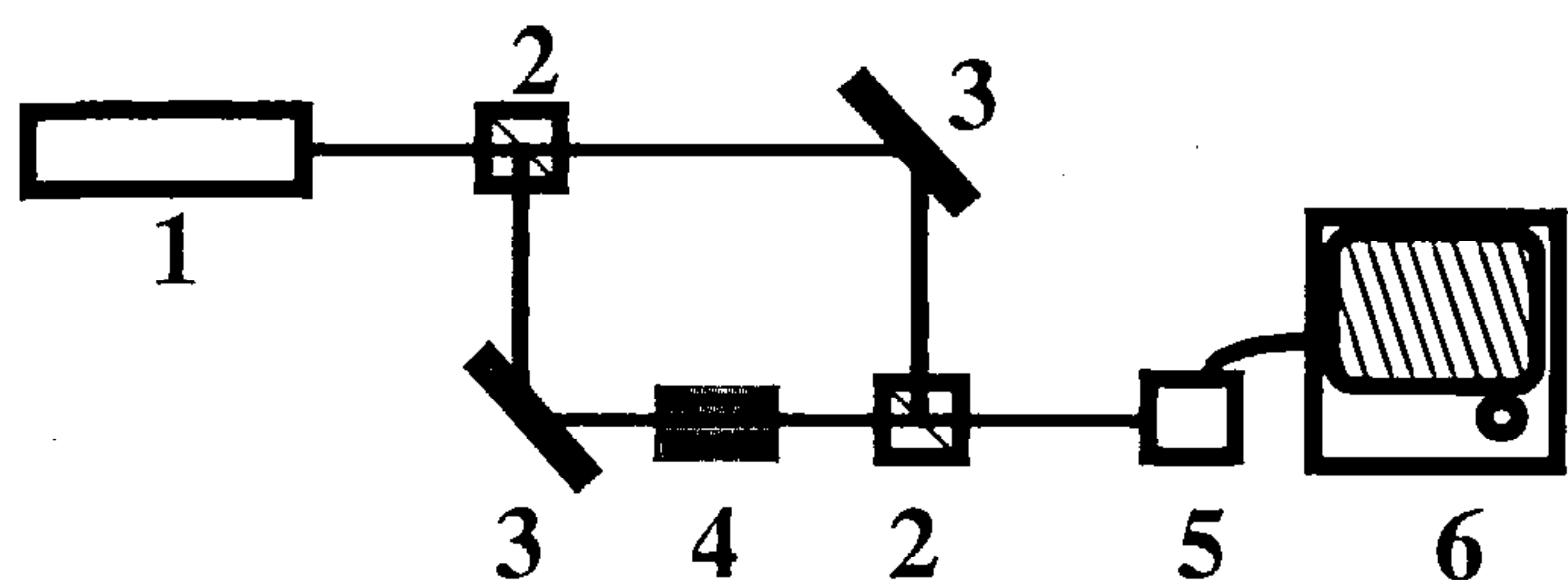


Fig. 2. Mach-Zehnder interferometer setup: 1, He-Ne laser source (632.8 nm); 2, beam splitter; 3, mirror; 4, sample holder; 5, CCD camera; 6, monitor.

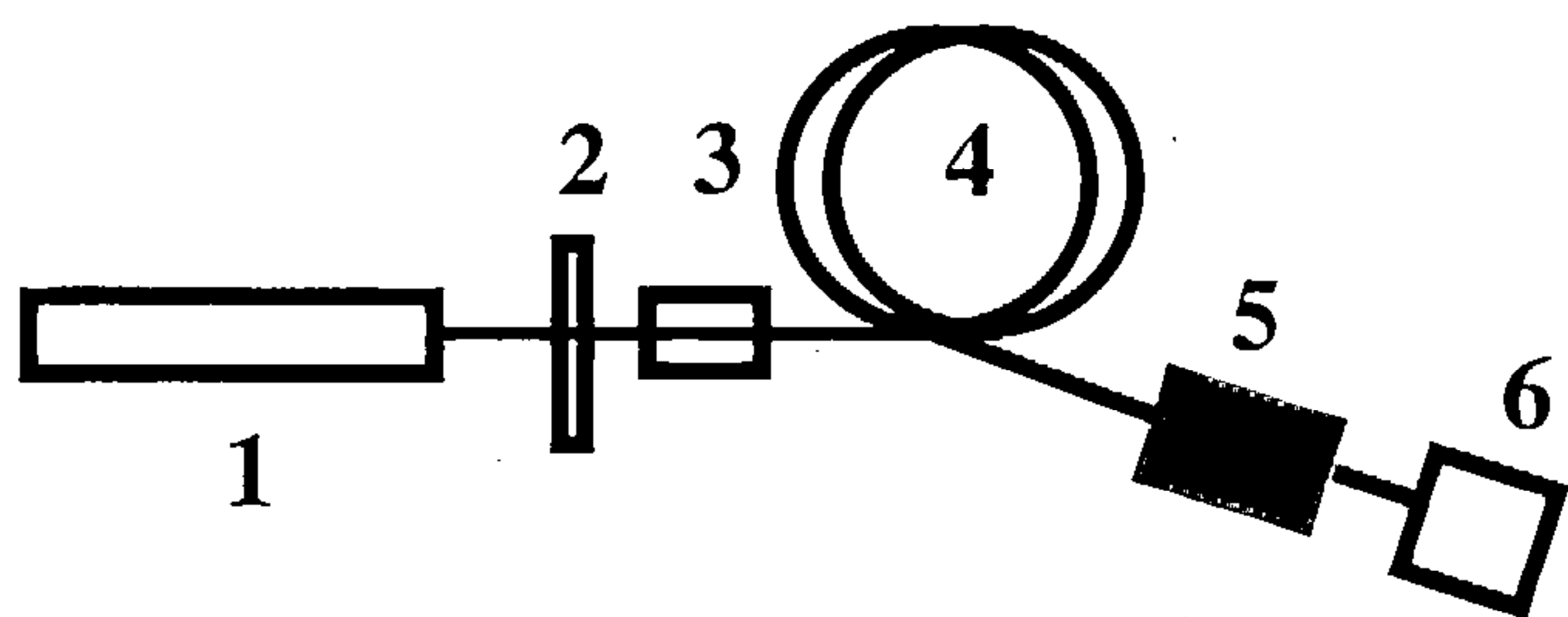


Fig. 3. Optical setup for transmission loss measurement: 1, He-Ne laser source (632.8 nm); 2, polarizer; 3, lens; 4, SM fiber; 5, sample holder; 6, power meter.

intensity was measured with a power meter (UIT-150 Ushio) and detectors (UVD-C254 Ushio). UV spectra were recorded with an UV/Vis/near infrared (NIR) spectrometer (V-570 Jasco). Fourier-transform infrared (FT-IR) spectra were recorded for spin-coated PMMA films on NaCl substrates by an FT-IR spectrometer (FT/IR-600 Jasco). Refractive index measurements were carried out by the m-line method.^{24,25)} A refractive index profile of depth less than 20 μm was measured using the Wentzel-Kramer-Brillouin (WKB) method.²⁶⁾ A refractive index profile of depth more than 0.1 mm was observed using a Mach-Zehnder interferometer (MZC-80 Mizojiri Optical) as shown in Fig. 2. Transmission loss was measured by the optical setup shown in Fig. 3. Molecular weight of PMMA was determined by gel permeation chromatography using tetrahydrofuran as an eluent, and polystyrene standards. The column effluent was monitored with an intelligent RI detector (830-RI Jasco).

3. Results and Discussion

3.1 Refractive index change of PMMA

Figure 4 shows the refractive index and film weight changes of PMMA film of 2 μm thickness at the irradiated area as a function of irradiation time. The refractive index was measured during 4 h UV irradiation of 30 mW/cm² at 254 nm. Concerning the variation of the refractive index, +1.0% is large enough for application to a waveguide. As shown in Fig. 4, a correlation was observed between the refractive index increase and the film weight decrease. PMMA has been utilized as a photo-resist material, based on the fact that UV light with shorter wavelength than 254 nm slowly decomposes the main chain. As shown in Fig. 5, it was reported that an ester group was first eliminated by UV irradiation at 254 nm (Norrish type I reaction), and that the other reactions also occur such as scission of the main chain,

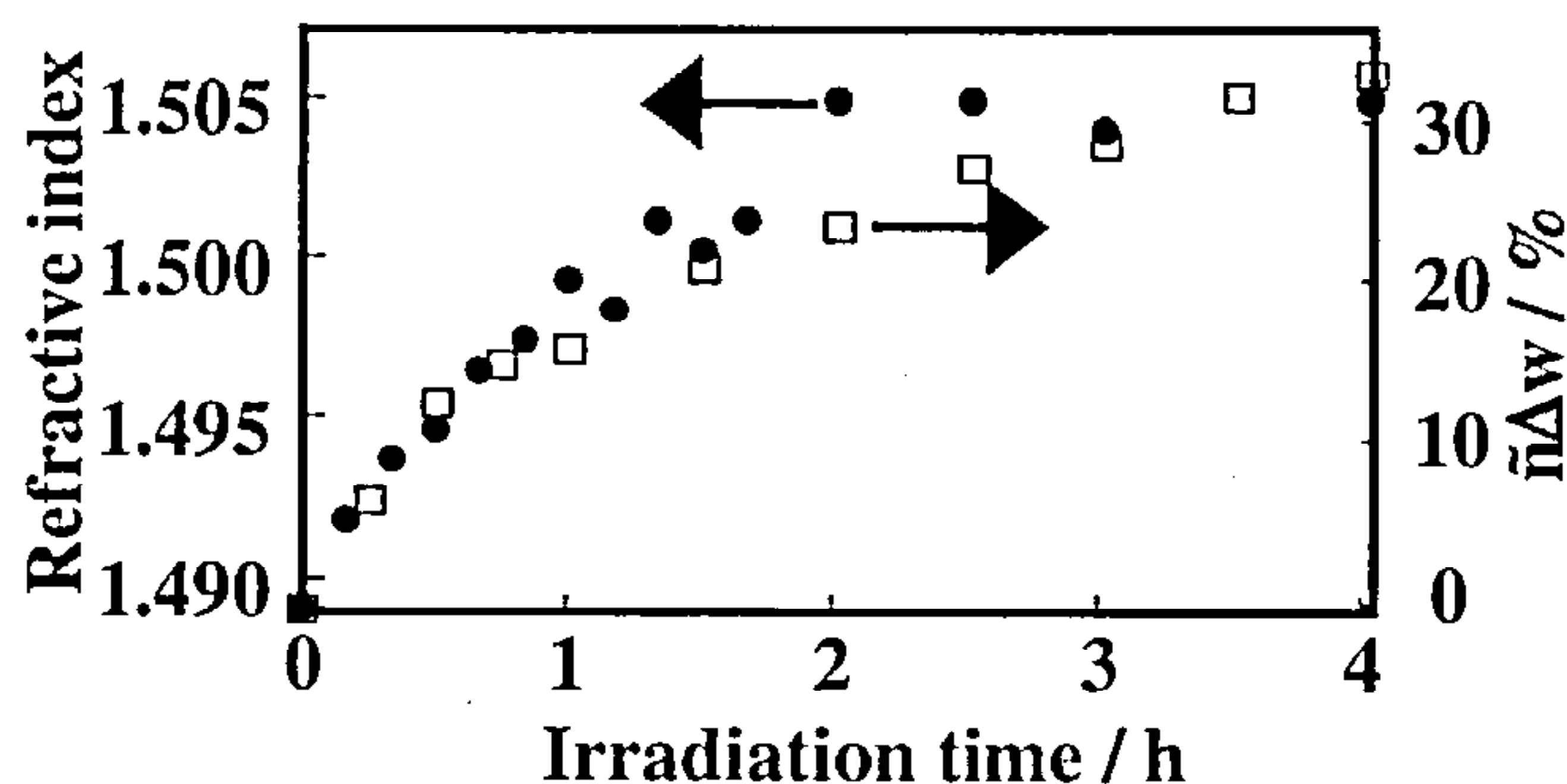


Fig. 4. Refractive indices and the change of weight of PMMA film with 2 μm thickness at irradiated area as a function of irradiation time. Irradiation wavelength is 254 nm. Irradiation intensity is 30 mW/cm² at 254 nm. Filled circles, ● denote refractive index at each irradiation time, and open squares, □ denote $-\Delta w$.

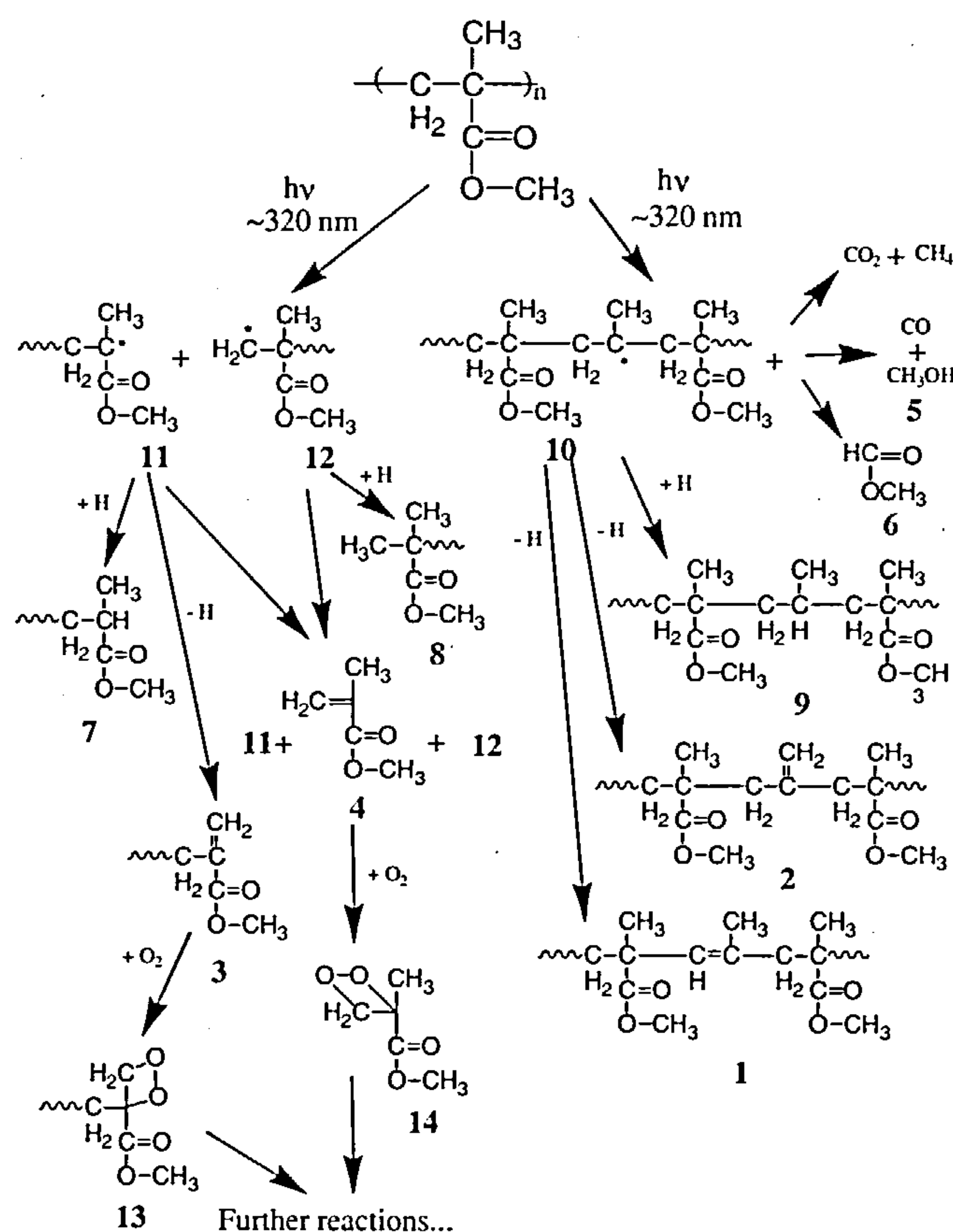


Fig. 5. Ester group first eliminated by UV irradiation at 254 nm.

production of a peroxidized group and so on.²⁷⁻³²⁾

Figure 6 shows the molecular weight of PMMA as a function of irradiation time. *M_n* of PMMA gradually decreased from 60,000 to 5,600 with increasing irradiation time. It was confirmed that the scission of the main chain occurred. Figure 7 shows FT-IR spectra of a PMMA film before and after irradiation. The intensity of the C=O stretching band observed in the original PMMA film at 1750 cm⁻¹ significantly decreased, and was accompanied by the peak broadening with increasing irradiation time. It is noteworthy that a weak absorption at 1660 cm⁻¹ of C=C stretching vibration appeared after UV irradiation. The result confirmed both the ester group elimination and the formation

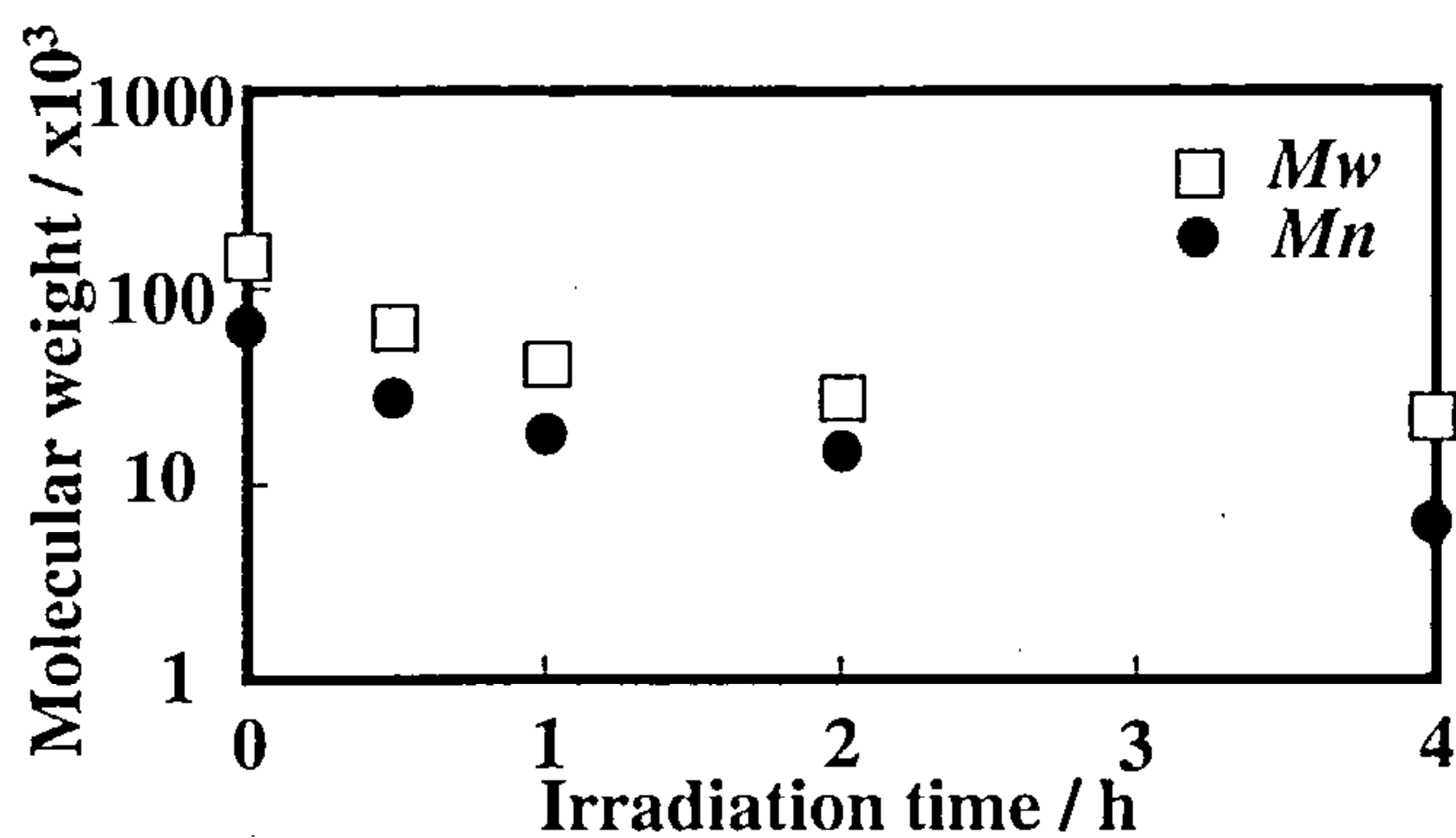


Fig. 6. Molecular weight of PMMA as a function of irradiation time. Filled squares, \blacksquare denote M_n , and open squares, \square denote M_w . Irradiation wavelength is 254 nm. Irradiation intensity is 30 mW/cm² at 254 nm.

of structures, 1–4. It is considered that volatile molecules formed in the decomposition process, for example CO, CO₂, HCOOCH₃ (b.p. 34°C), CH₃OH (b.p. 65°C) and MMA (b.p. 100°C), evaporated. As shown in Scheme I, monomeric

MMA is considered to be formed via the scission of a main chain, and the other volatile products resulted from the ester group elimination and subsequent reactions.

Figures 8(a) and 8(b) show UV absorption spectra of a film after irradiation (a; 0–2 h, b; 2–4 h). Absorption at 200 nm increased in the first 2 h, and peaked in the following 2 h. Absorption of about 200 nm is based on π – π^* transition of C = C bonds. In fact, according to the estimations of UV absorption for 1–14 determined by the Zerner intermediate neglect differential overlap (ZINDO) method of quantum chemical calculation, structures with absorption from 195–220 nm were only 1–4. Structures 1 and 2 have an absorption maximum at 195–205 nm and 3 and 4 have absorption at 205–215 nm. Predicted intensity of n – π^* transition based on carbonyl groups is far less than that of the above-mentioned π – π^* transitions.

Judging from the dependence of UV absorptions, the following photochemical process was considered. Weak absorptions of 254 nm and 308 nm due to ester group (n – π^*) or conjugated ester (π – π^*) such as structure 3, which originally exists as an end group resulting from disproportionation

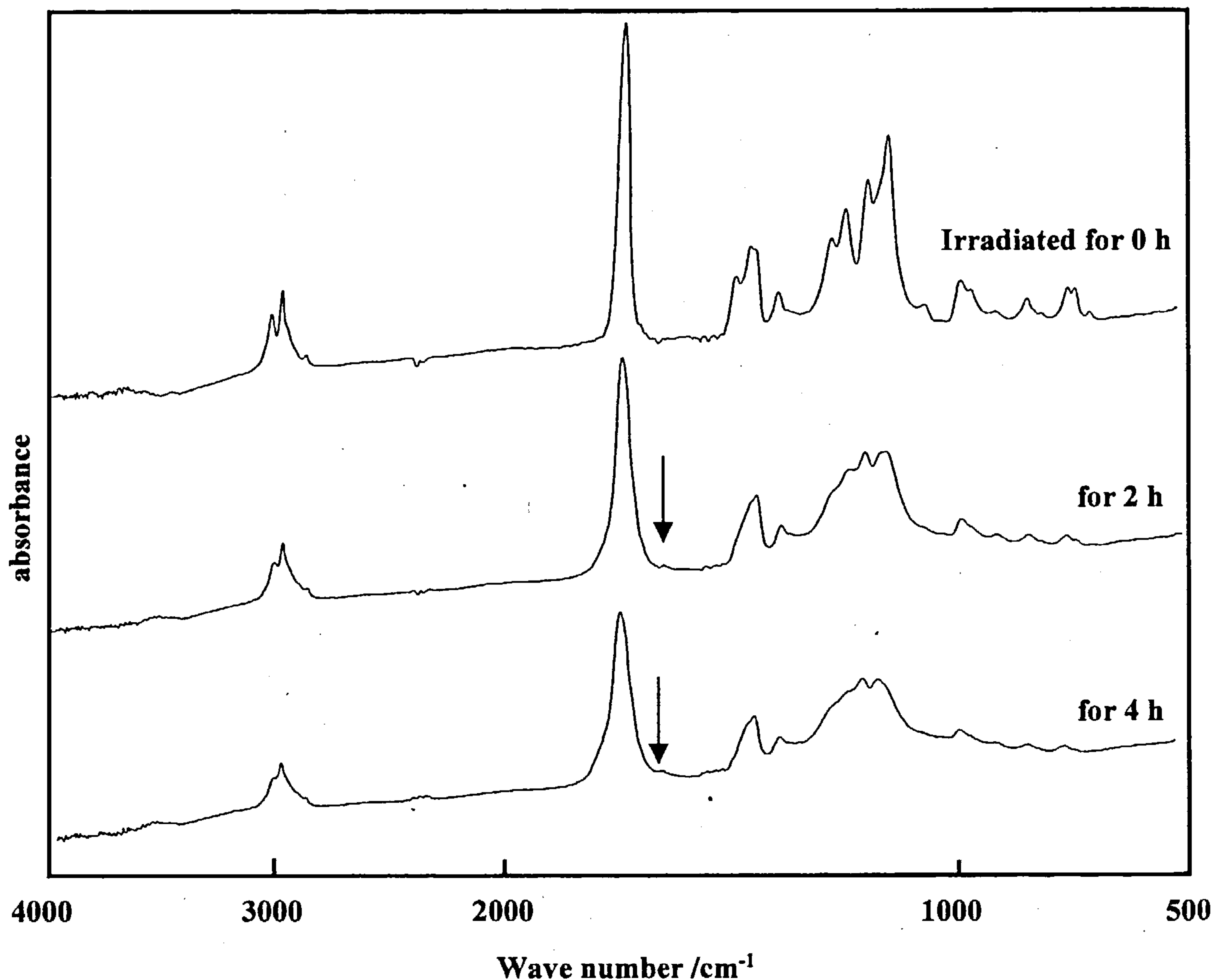


Fig. 7. FT-IR spectra of PMMA at each irradiation time. Irradiation wavelength is 254 nm. Irradiation intensity is 30 mW/cm² at 254 nm. Main absorption of PMMA is as follows; 1100–1300 cm⁻¹, and 1750 cm⁻¹ were caused by ester vibration. 2850–3000 cm⁻¹ were caused by C–H vibrations of –CH₂–, >C = CH₂, >C = CH–, >C–CH₃, and so on. 700–1000 cm⁻¹ were caused by C = C vibrations of >C = CH₂, >C = CH–, and so on.

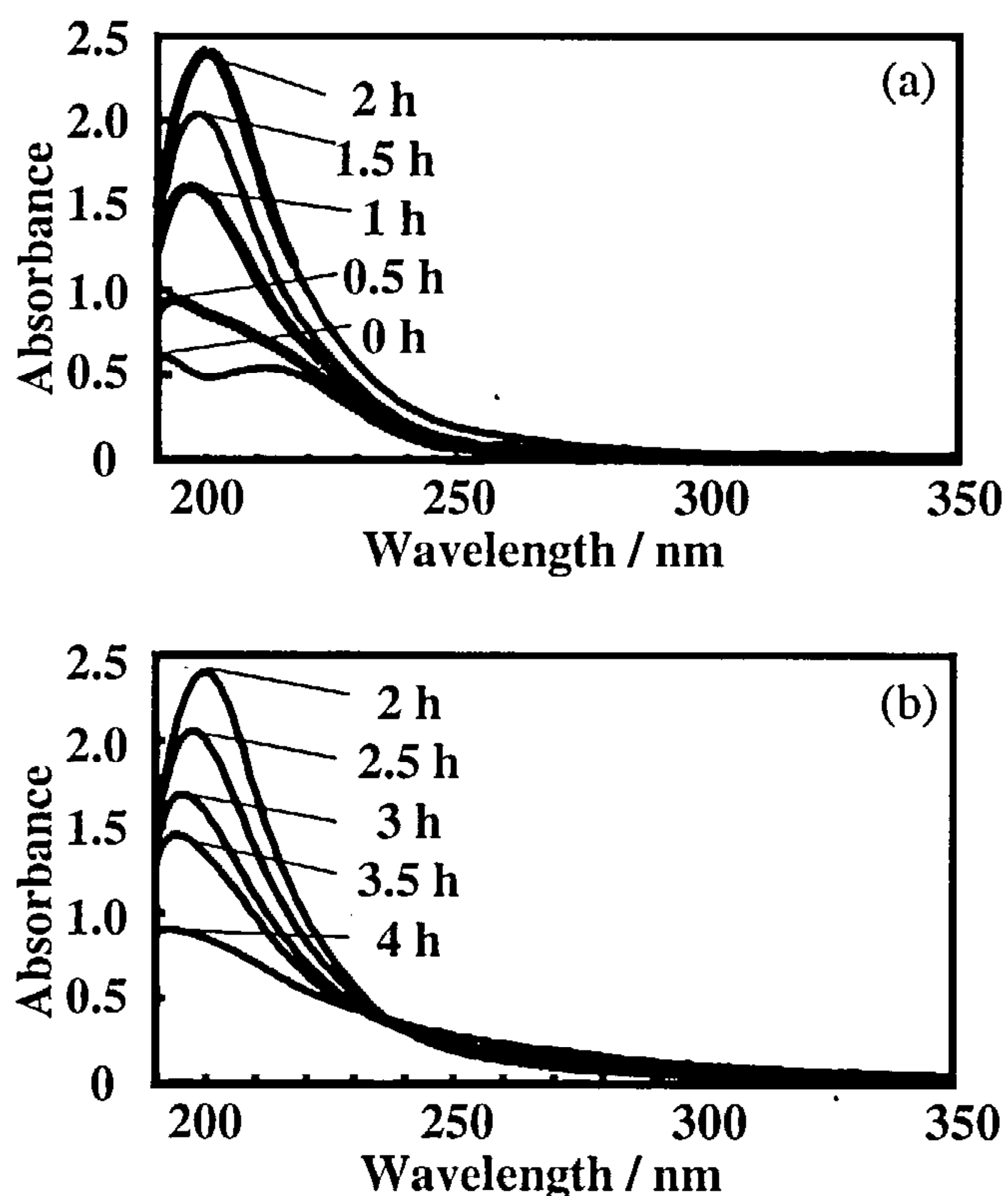


Fig. 8. (a) UV absorption spectra of PMMA at each irradiation time from 0 to 2 h, (b) UV absorption spectra of PMMA at each irradiation time from 2 to 4 h.

tiation in radical polymerization, triggered the reactions such as ester group elimination and main chain scission. These reactions increased the absorbance around 200 nm, as shown in Fig. 8(a). In the second stage (2–4 h), as the structures 1–3 sufficiently increased in number, an ester group elimination of repeating units adjoined to ones with C=C bonds increased gradually. The elimination of the next ester groups would produce a π -conjugated structure in the main chain, which has a strong absorption at a longer than 237 nm wavelength, according to the Woodward rule. Therefore, absorption at 237 nm or a longer wavelength also increased with the isosbestic point in Fig. 8(b).

The reason why PMMA changes the refractive index after irradiation is explained by the Lorenz–Lorentz equation as follows;

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi N \alpha, \quad (1)$$

where n , N , and α are the refractive index, number density of molecules and linear polarizability, respectively. Linear polarizability, α , depends on the state of the conjugated system. The number density of molecules, N , changed by decomposition, polymerization and so on. In the case of a polymer, a repeating unit (monomer) is considered as a molecule. For example, the number density increases in polymerization, because the distance between repeating units connected by covalent bonds become shorter resulting in the increase of the number density. The ester group elimination decreases the average volume of repeating units, which is one of the reasons why the refractive index increased. Resulting from Figs. 4 and 7(b), it was considered

that the change of N was dominant in the case of PMMA, because the refractive index variation correlated with the film weight, and there was no dependence between increasing π -conjugated structures and the refractive index.

3.2 Fabrication of Refractive Index Profile using PMMA

PMMA is well known as an organic optical material, because it has high transparency and easy processing. PMMA is applied to fabricate lenses and waveguides. If PMMA can be fabricated to obtain the desired refractive index profile, its application will further expand.

We tried to fabricate PMMA to obtain the refractive index profile using a photochemical reaction of PMMA. A PMMA sheet of 1 mm thickness is fabricated by hot pressing. Figure 9 shows the refractive index profile close to the irradiated PMMA surface. Under UV irradiation, the refractive index profile was obtained in the thickness direction. After irradiation for 4 h with a power of 30 mW/cm² at 254 nm, the maximum variation was 1%, and the thickness of the profile achieved was 15 μ m. This result indicates that this reaction can be applied to microoptical devices such as a microlens and waveguide for single-mode operation.

Next, PMMA bulk of size 15 \times 30 \times 3 mm³ was fabricated by a molding method. UV light of power 23 mW/cm² and 254 nm wavelength was irradiated onto the bulk for 24 h, through a photo-mask with 15 \times 1 mm² irradiation area. The irradiated bulk was set in a Mach–Zehnder interferometer as shown in Fig. 2, and an incident laser at 632.8 nm was irradiated from the side edge. Figure 10 shows the interference pattern in the cross section of the PMMA bulk. It is observed that the irradiated surface is concave due to degradation. Absorption increases gradually, because the reactions of PMMA produce π -conjugated structures with irradiation. Therefore, it was considered that the reactions causing a main chain scission were accelerated at the surface close to the light source. Though the refractive index profile was fabricated under a concave region, the maximum change of the index, 0.03% was very small. Transmission loss of

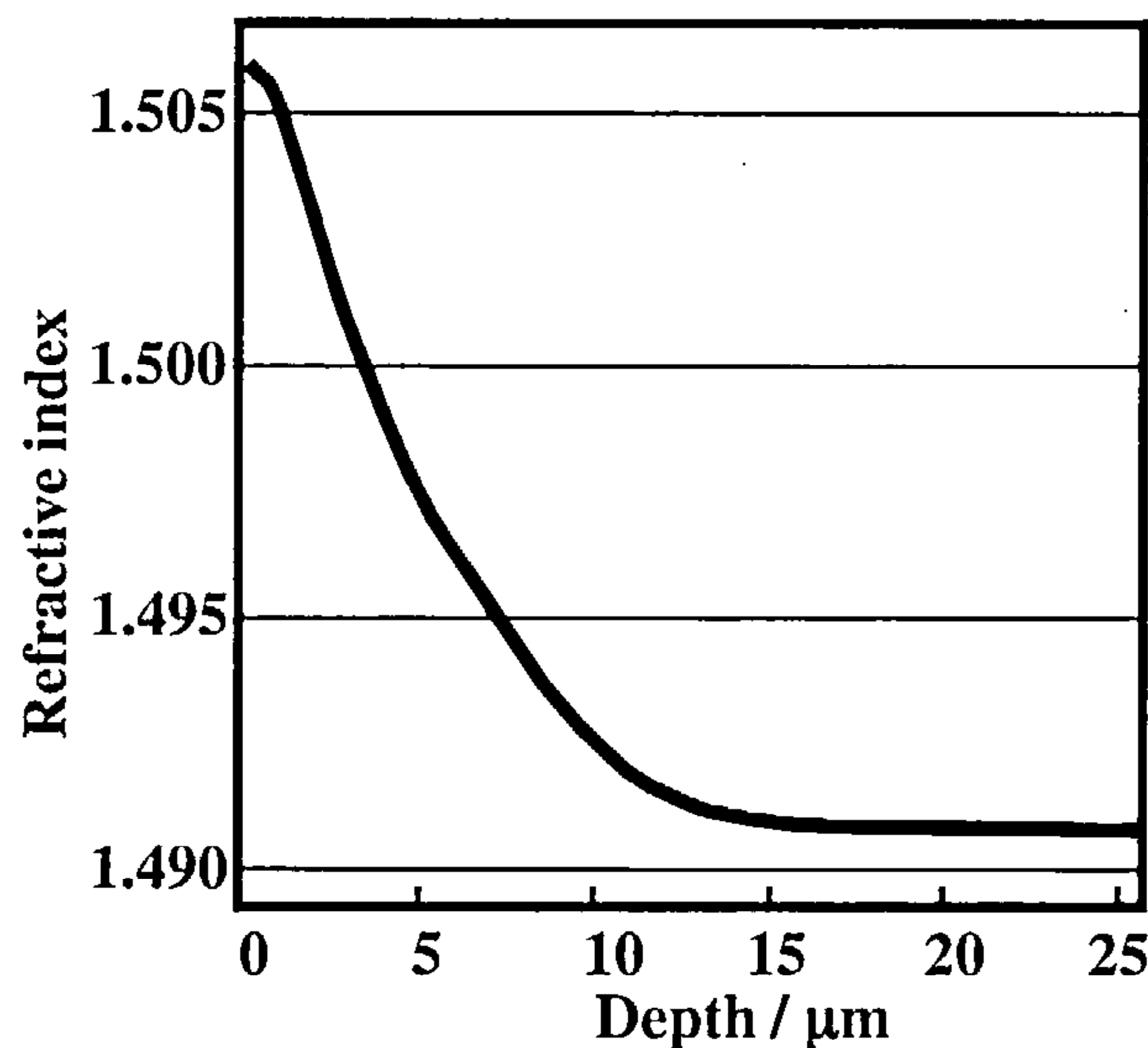


Fig. 9. The refractive index profile fabricated in the thickness direction of PMMA sheet by UV irradiation for 4 h. Irradiation wavelength is 254 nm. Irradiation intensity is 30 mW/cm² at 254 nm.

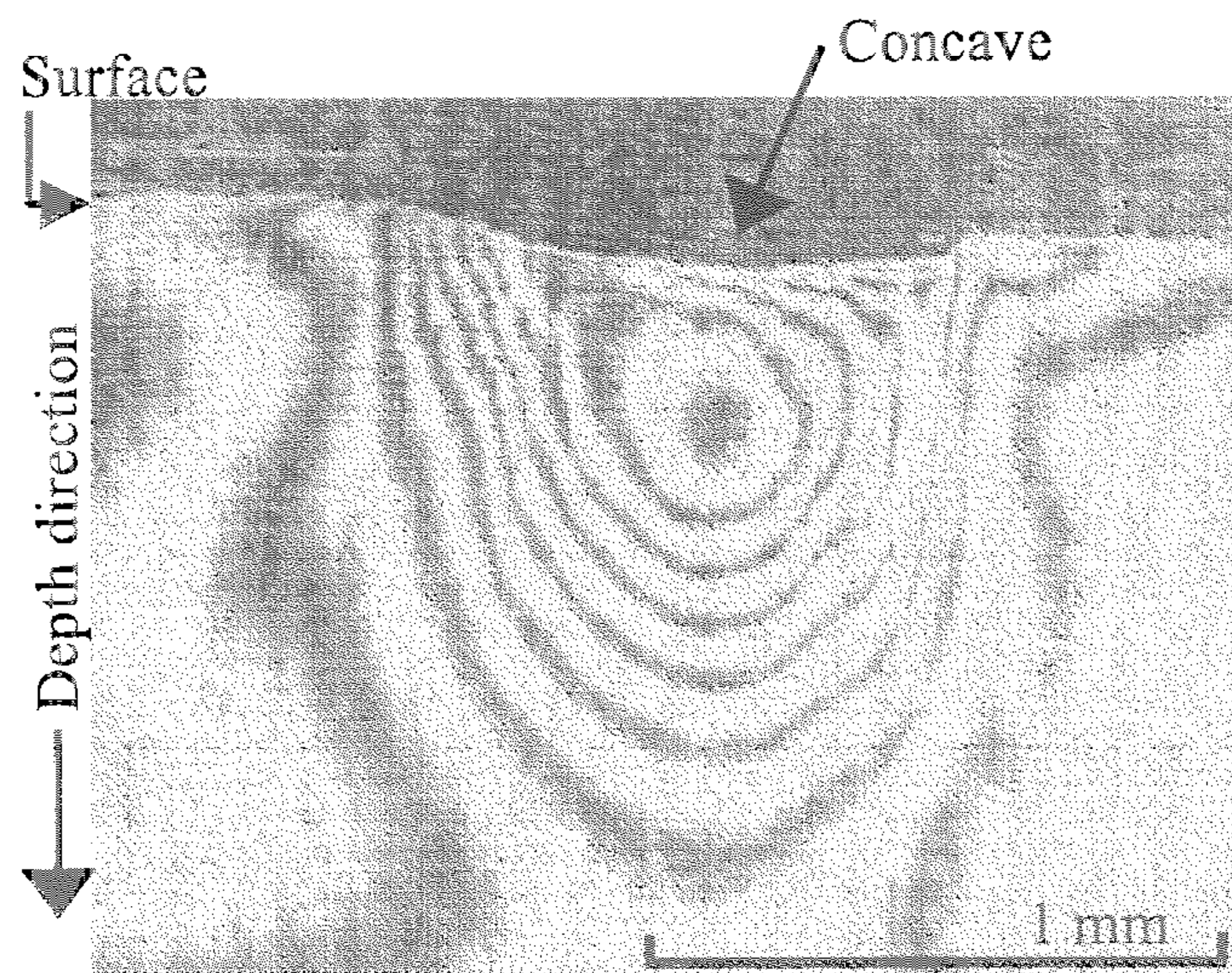


Fig. 10. Photograph of interference pattern through PMMA bulk in the cross section after irradiation with the power of 23 mW/cm^2 for 24 h. Irradiation wavelength is 254 nm.

this sample with an index profile was 0.32 dB/cm at 632.8 nm . Since the loss of a sample without the profile was 0.25 dB/cm , the loss slightly increased. However, 0.25 dB/cm is far larger than the natural loss of PMMA, about 100 dB/km . If samples with lower loss were to be fabricated, the loss of a sample with a profile would also decrease. Judging from these results, it is indicated that the refractive index increase would apply to optical devices of size over $100 \mu\text{m}$ rather than to microoptical devices.

4. Conclusions

UV light of 254 nm wavelength was irradiated onto PMMA for 120 min, and the refractive index increased by 1.0%. The variation was large enough to fabricate waveguides. It was indicated that the refractive index increase of PMMA was due to structural changes including the scission of the main chain, the elimination of the ester group, and subsequent formation of propylene and olefinic units, which was confirmed by FT-IR and UV absorption spectra. As reactions proceeded, absorption at wavelengths longer than 237 nm increased. It was considered that this phenomenon accelerated reactions near the film surface, which was rendered concave due to the decomposition of PMMA after irradiation for 24 h. On the other hand, a refractive index profile within a depth of $15 \mu\text{m}$ has been fabricated after irradiation for 4 h. Therefore, it is considered

that the GI profile of PMMA can be applied to microdevices such as a microspherical lens, waveguides for single-mode operation and so on.

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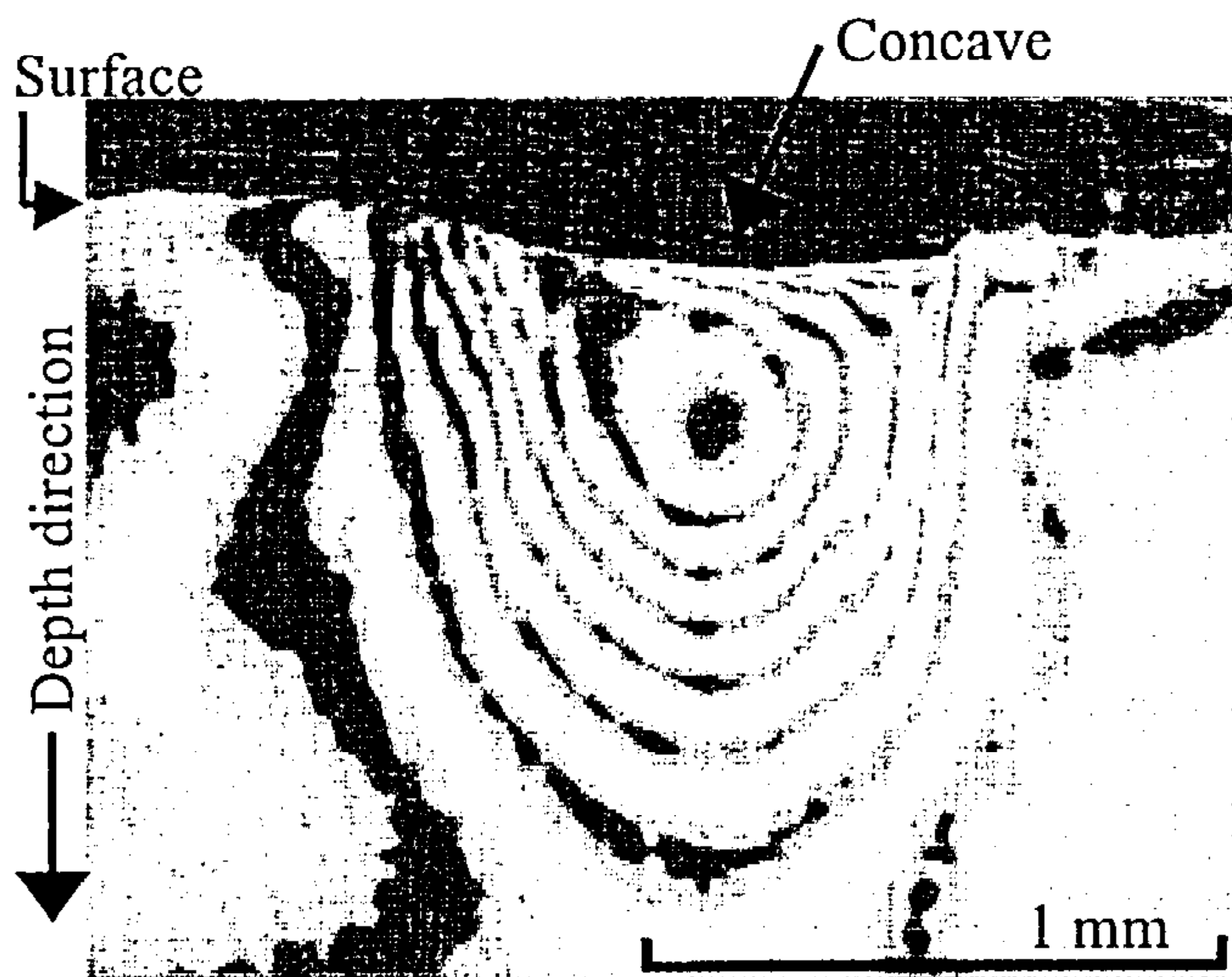


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