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## Refractive index decrease during photocrosslinking in photopolymers suitable for holographic recording

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### SUMMARY:

Photosensitive polymers of cyclobutane formation type have been found to show a decrease in their refractive indices with progress of photocrosslinking, when studied by the waveguide method. The decrease in refractive index is considered to be due to a decrease of exaltation in molar refraction. This phenomenon is of potential importance in holographic recording.

### Introduction

In holographic recording, optical information is stored as interference fringes in the holographic media. It is known that the diffraction efficiency of the phase hologram is in principle higher than that of the amplitude hologram<sup>1)</sup>. Phase holograms can be classified into two groups; one is the refractive index modulation in which the interference fringe due to differences in light intensity is recorded as spatial distributions of the refractive index of the medium to be recorded; the other is relief type hologram in which the interference fringe is recorded as spatial distributions of thickness of the medium. Dichromated gelatin is used for the refractive index modulation type holograms, in which a photocrosslinking reaction is utilized for producing the index modulation, and has been known to be superior in terms of diffraction efficiency. However, this material has deficiencies such that complicated procedures are required for preparation of the recording film and fixation of the optical image or information. Much effort has therefore been devoted to developing alternative organic materials utilizing photochemical reactions<sup>2)</sup>. So far, the authors have developed recording materials which consist of two monomers with large differences in photosensitivities and refractive indices, in an effort to produce high refractive index modulation<sup>3)</sup>. In the course of searching such materials for refractive index modulation, we have become interested in the variation of the refractive indices accompanied by the photocrosslinking of the photosensitive polymers.

Generally, the relationship connecting the refractive indices  $n$  of materials, the molar volume  $V$ , and the molar refraction  $[R]$  can be expressed by the Lorentz-Lorenz equation as follows:

$$[R] = [(n^2 - 1)/(n^2 + 2)] \cdot V = [(n^2 - 1)/(n^2 + 2)] \cdot M/d = 4\pi N_A a/3 \quad (1)$$

where  $M$  is the molecular weight,  $d$  is the density,  $N_A$  is the Avogadro number, and  $a$  is the molecular polarizability. Assuming that the molar refraction can be repro-

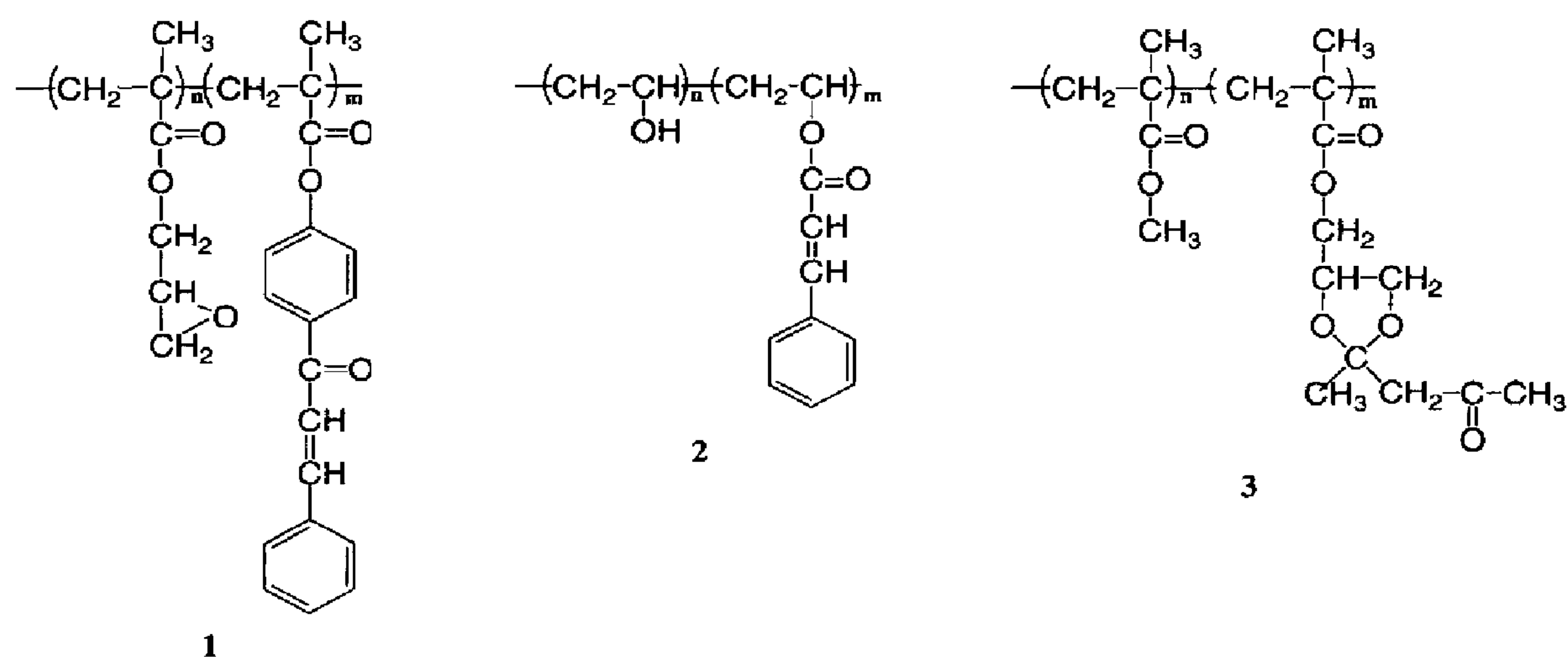


duced by simple addition of the constituent atomic refraction and bond refraction and the constituent atoms do not change during the reaction, the difference in the refractive index of the polymer, before and after the photocrosslinking, originates only from the difference in the density of the polymer. However, photocrosslinking usually causes an increase in the density of the materials and hence a decrease in film thickness. Therefore, the change in thickness cancels the change in the refractive index, and the optical path length shows little change since the efficiency of the holographic phase recording is directly related to the optical path difference obtained from the simple product of the film thickness and refractive index of the materials.

For efficient phase recording, it is desired to vary either the thickness or refractive index. For producing large refractive index changes during the photocrosslinking reaction, systems with large variation in contribution from the bond refraction to the total molar refraction are considered to be most effective. For this purpose, we need a system where large changes in the molecular polarizability occur during the photo-reaction. We therefore selected a cyclobutane ring formation reaction between polymer chains, and examined the variation of thickness and refractive index with photocrosslinking of polymer thin films having photosensitive side chains.

### Experimental part

Three kinds of polymer were used for the present study; poly[4'-methacryloyloxychalcone-*co*-(glycidyl methacrylate)] (ARG; chalcone component: about 30 mol-%) (**1**) obtained from Sampo Chemical Co., Ltd., poly[(vinyl cinnamate)-*co*-(vinyl alcohol)] (SPR; cinnamoyl component: about 77 mol-%) (**2**) obtained from Sampo Chemical Co., Ltd., and poly([2-methyl-2-(2-oxopropyl)-1,3-dioxolan-4-yl]methyl methacrylate)-*co*-(methyl methacrylate)) (OPM-MMA; 1,3-dioxolanyl component: about 10 mol-%) (**3**) synthesized in our laboratory<sup>4)</sup>, which is a photocleavage-type polymer used as a reference material.



The polymers having structures **1**, **2**, and **3** have broad absorption bands around 310 nm<sup>5)</sup>, 320 nm<sup>6)</sup>, and 285 nm<sup>4)</sup>, respectively, in the ultraviolet region. These polymers are known to be crosslinked under irradiation of the light in the wavelength corresponding to the absorption bands.



Thin films of the polymer used were prepared by casting a solution of the polymers on quartz plates, and drying them under reduced pressure. The thicknesses of the molded films used were in the range of two to six micrometers.

The thicknesses and refractive indices of the polymer thin films were measured using the prism coupling waveguide method<sup>7)</sup> at a wavelength of 514,5 nm generated from an Ar<sup>+</sup> ion laser source. The crosslinking reactions in the thin films progressed with irradiation by an ultrahigh pressure 250 W mercury lamp provided by a UIS-251H illumination apparatus obtained from Ushio electric Co., Ltd. The variation of the film thickness and refractive index was measured intermittently after specific time intervals for the same sample. For polymers 1 and 2, the infrared spectra were simultaneously measured to monitor the progress of the crosslinking. A Nicolet 60 SX FT-IR spectrometer was used for the infrared spectral measurements.



## Results and discussion

The photosensitive polymers 1 and 2 having cinnamoyl structures are known to crosslink to form cyclobutane ring structures by the photodimerization reaction of the C=C double bonds in solid state<sup>5,6,8)</sup>. Therefore, the progress of the photodimerization reaction can be monitored by the disappearance of the C=C double bonds. Infrared absorption bands characteristic of the C=C bonds can be found at 1335 and 1329 cm<sup>-1</sup> in the spectra for polymers 1 and 2, respectively. Figs. 1a and 1b show the variations of absorbances of the characteristic bands in the infrared spectra of ARG and SPR thin films, respectively, with irradiation time, indicating a monotonic decrease in concentration of C=C double bonds with irradiation time.

Figs. 2a and 2b show the variation of film thickness and refractive index of ARG and SPR thin films, respectively, with irradiation time. Both films exhibit a decrease in thickness, which correlates well with the decrease in concentration of C=C double bonds as shown in Fig. 1. It is obvious that the decrease in thickness is ascribed to an increase of the density accompanied by photocrosslinking in these polymers. A decrease in the refractive index is also observed concurrently with the progress of the photocrosslinking for the two polymers. On the other hand, for the OPM-MMA thin film, which is a photocleavage-type polymer with 1,3-dioxolanyl structure, the thickness is found to decrease and the refractive index is increased as shown in Fig. 3.

Here we discuss the changes in the refractive index accompanied by crosslinking between photosensitive functional groups for the polymers with cinnamoyl structures, ARG and SPR. Molar refraction can be approximately calculated by summing the atomic refractions of the constituent atoms and additional contributions from bonding regions. However, in case of the conjugated organic compounds with C=C and/or C=O double bonds, the measured molar refraction often gives a larger value than the calculated values. In order to elucidate this phenomenon, we have introduced a rather classical but useful concept named "exaltation"<sup>9)</sup>. In this case, exaltation is defined as the differences between the calculated molar refractions and those actually found. Generally, this exaltation strongly occurs for systems with long conjugated structure. In other words, conjugated materials usually have larger refractive indices than the non-conjugated ones.

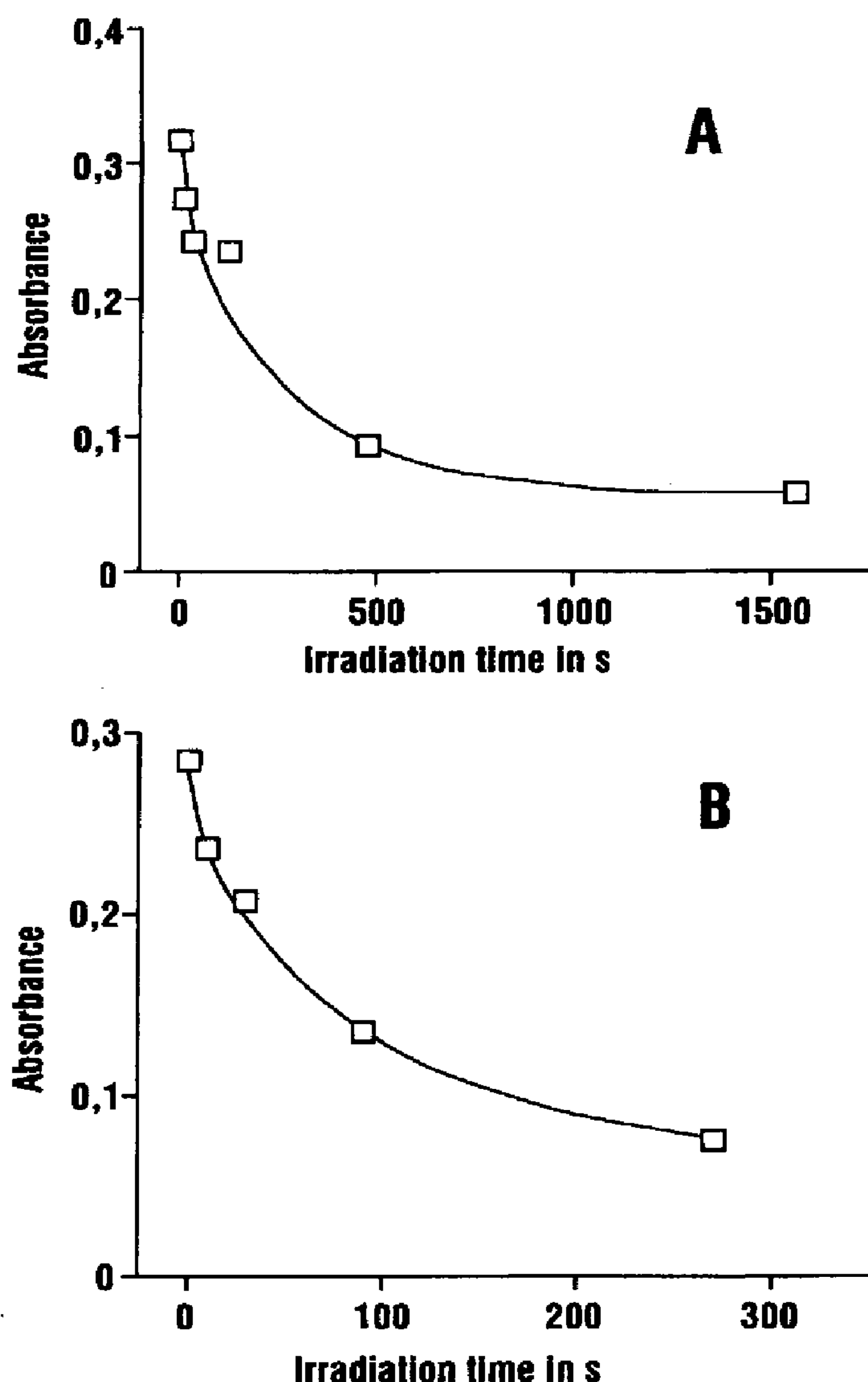


Fig. 1. Variations of absorbances of the 1335 and 1329  $\text{cm}^{-1}$  bands in the infrared spectra with irradiation time of UV light for (A) poly[4'-methacryloyloxychalcone-*co*-(glycidyl methacrylate)] (ARG) and (B) poly[(vinyl cinnamate)-*co*-(vinyl alcohol)] (SPR), resp.

Tab. 1 shows the densities, refractive indices, and molar refractions of two representative compounds with cinnamoyl structures and the corresponding saturated compounds with hydrocinnamoyl structures in liquid state. The cinnamoyl compounds have higher refractive indices and their exaltations show higher values around  $4.0 \text{ cm}^3$ , while the saturated hydrocinnamoyl compounds have lower refractive indices and their corresponding exaltations are nearly  $0 \text{ cm}^3$ . From these observations, we consider that for polymers with cinnamoyl structures the exaltation value decreases due to the destruction of the structures conjugated with phenyl and carbonyl groups and the formation of cyclobutane rings through dimerization of the  $\text{C}=\text{C}$  double bonds of cinnamoyl structures. The decrease in the refractive index due to ring formation is thus sufficient to offset the contribution from the increase in density due to crosslinking.

In contrast, for polymers with photosensitive 1,3-dioxolanyl rings, the ring is photocleaved to generate radicals. These radicals react as a hydrogen abstraction reagent to give rise to crosslinking<sup>10)</sup>. For the OPM-MMA polymer, photocrosslink-

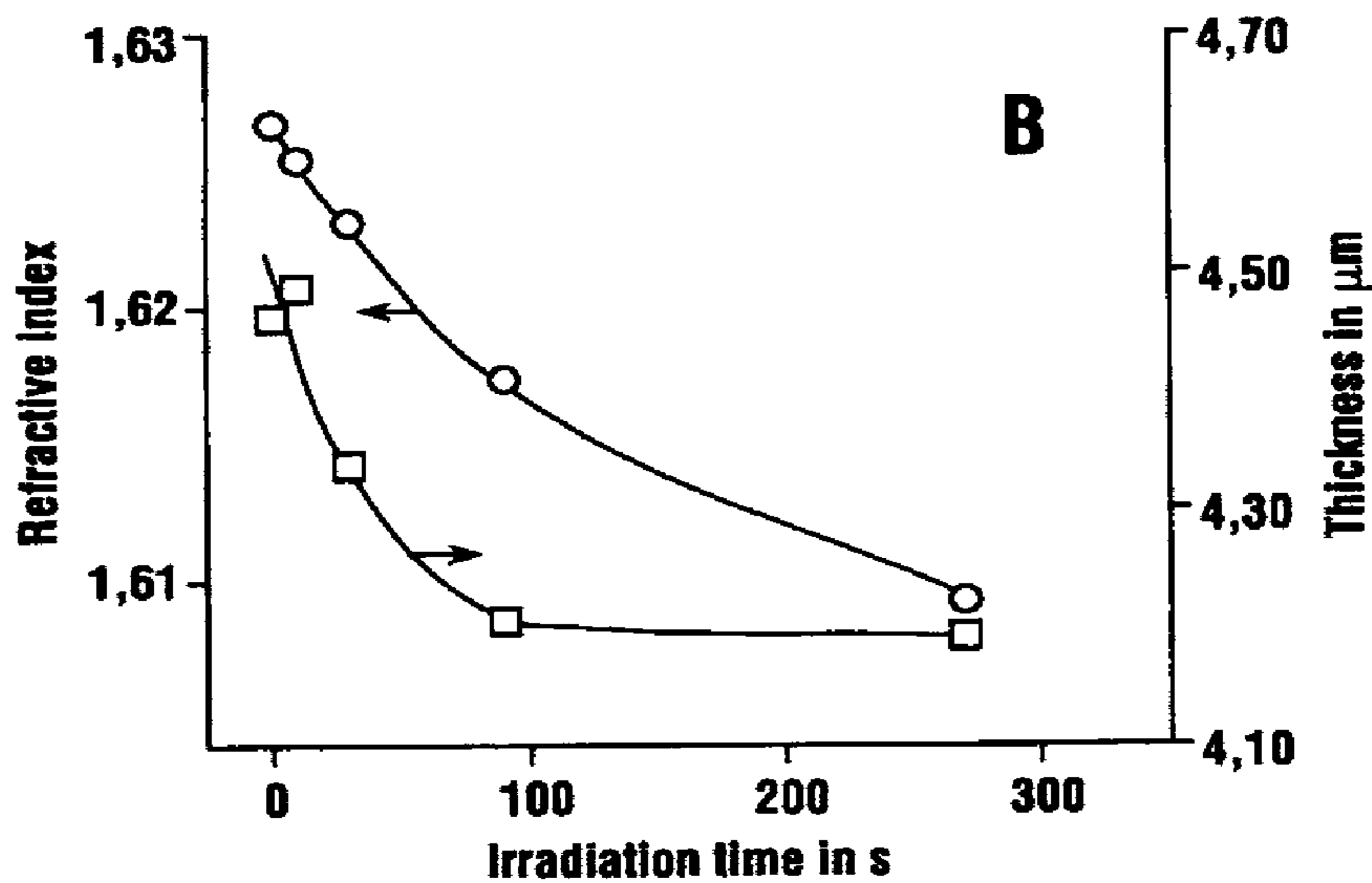
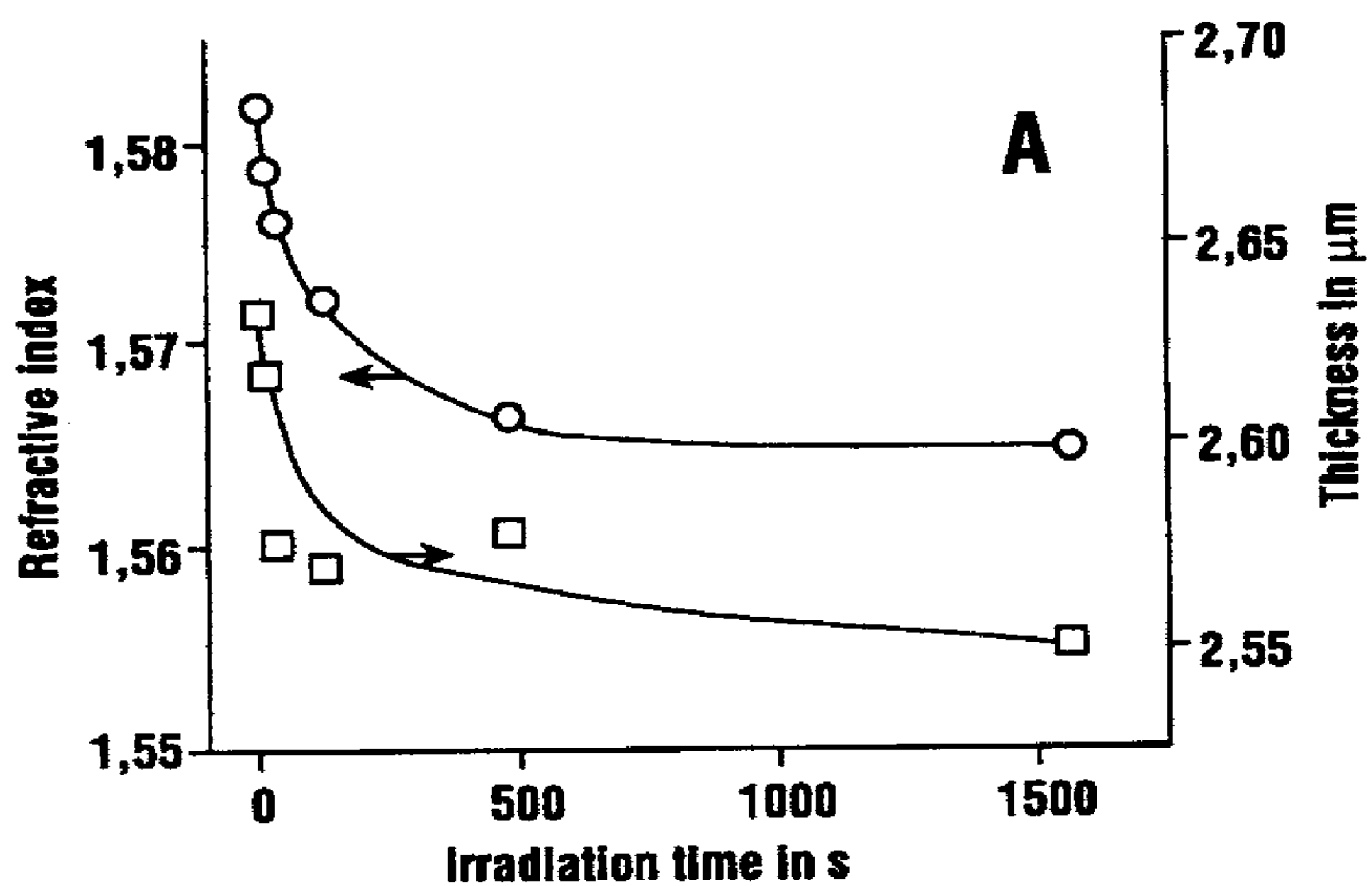


Fig. 2. Variations of film thickness and refractive index with irradiation time of UV light for (A) ARG and (B) SPR

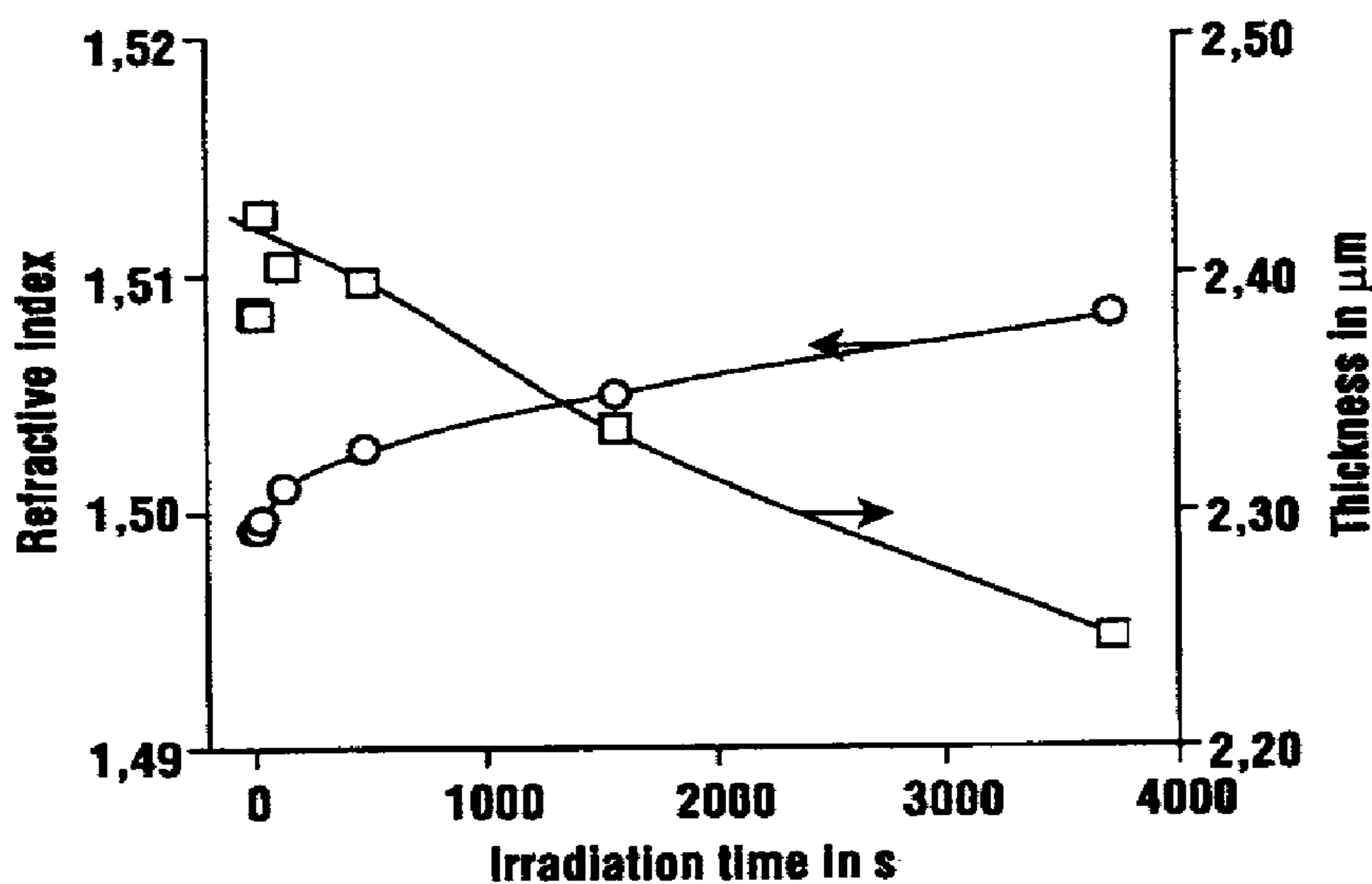


Fig. 3. Variations of film thickness and refractive index with irradiation time of UV light for OPM-MMA, which has 1,3-dioxolanyl group in the side chain



Tab. 1. Densities, refractive indices, molecular weights and molar refractions of compounds with cinnamoyl structure and corresponding saturated hydrocinnamoyl compounds

Compounds	$\frac{d_4^{20}}{\text{g/cm}^3}$	$n_D^{20}$	Molecular weight	Molar refraction [R] in cm <sup>3</sup>		Exaltation in cm <sup>3</sup>
				obs.	calc. <sup>a)</sup>	
ethyl <i>trans</i> -cinnamate	1,0490 <sup>b)</sup>	1,55982 <sup>b)</sup>	176,22	54,30	50,69	+3,61
ethyl 3-phenylpropionate	1,0147 <sup>c)</sup>	1,49542 <sup>c)</sup>	178,23	51,26	51,18	+0,08
<i>trans</i> -cinnamaldehyde	1,0497 <sup>d)</sup>	1,61949 <sup>d)</sup>	132,16	44,20	39,80	+4,40
3-phenylpropionaldehyde	1,019 <sup>e)</sup>	1,5230 <sup>c)</sup>	134,18	40,23	40,28	-0,05

a) Calculated for the atomic refractions of A. I. Vogel, *J. Chem. Soc.* 1833 (1948).

b) *Beilsteins Handbuch der Organischen Chemie* 9, 581 (1926).

c) *Beilsteins Handbuch der Organischen Chemie* 9, 511 (1926).

d) *Beilsteins Handbuch der Organischen Chemie* 7, 348 (1925).

e) Aldrich Catalog Handbook of Fine Chemicals 780 (1994–1995).

ing should contribute only to increase in the density and a rise in the refractive indices, as shown in Fig. 3.

As mentioned before, the optical path difference, which is the difference in the product of the refractive index and film thickness, is the essential figure of merit for the diffraction efficiency for the phase-type holographic recording. In these polymers with cinnamoyl structures, both decreases in the refractive index and film thickness contribute simultaneously to decreases in the optical path length. This behavior is attractive for phase-type holographic recording that utilizes optical path difference. Since the optical path difference between the irradiated and unirradiated parts is several percent of the original optical path length, application of this mechanism is expected to contribute to the improvement of the efficiency of holographic recording. Both ARG and SPR examined here have been developed as photoresist materials sensitive to ultraviolet light. It is believed that photopolymers sensitive to visible light, where photoreaction mechanisms are similar to those polymers with suitable deactivating or fixing methods for such photosensitive groups, constitutes promising holographic recording materials of the future.

- 1) H. M. Smith, "Holographic Recording Materials" chap. 1, H. M. Smith, Ed., Springer-Verlag, Berlin 1977
- 2) For example, "Holographic Materials", T. J. Trout, Ed., Proc. SPIE, vol. 2405, SPIE, Bellingham 1995
- 3) H. Tanigawa, T. Ichihashi, A. Nagata, *Kogaku (Jap. J. Opt.)* 20, 227 (1991)
- 4) A. Nagata, K. Uchida, J. Iyoda, *Kobunshi Ronbunshu* 42, 101 (1985)
- 5) T. Ichihashi, W. Kawai, *Kobunshi Kagaku* 27, 833 (1970)
- 6) E. M. Robertson, W. P. Van Deusen, L. M. Minsk, *J. Appl. Polym. Sci.* 2, 308 (1959)
- 7) R. Ulrich, R. Torge, *Appl. Opt.* 12, 2901 (1973)
- 8) P. L. Egerton, E. Pitts, A. Reiser, *Macromolecules* 14, 95 (1981)
- 9) W. Hüchel, "Theoretical Principles of Organic Chemistry", Elsevier, Amsterdam 1958, pp. 222–228
- 10) G. F. D'Alelio, R. J. Caiola, *J. Polym. Sci., Part A-1* 5, 287 (1967)