

## Material Investigation of Alicyclic Methacrylate Copolymer for Polymer Waveguide Fabrication

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We investigated the physical and chemical properties of alicyclic methacrylate copolymers and their changes under deep-UV exposure. It was shown that alicyclic methacrylate copolymers have a better thermal stability and a higher refractive index than conventional poly(methyl methacrylate) (PMMA). Fourier transform IR (FTIR) spectra show the scission of the carbonyl group of the alicyclic methacrylate copolymers by deep-UV exposure similar to that of PMMA. This structural modification results in a local and controllable increase in refractive index in the exposed areas of the polymer surface. We fabricated polymer waveguides from alicyclic methacrylate copolymers by conventional photolithography using quartz/chromium mask. The minimum propagation loss of the straight waveguide with a 7.5  $\mu\text{m}$  width was 2 dB/cm at 1550 nm. [DOI: 10.1143/JJAP.45.2572]

**KEYWORDS:** polymer waveguide, alicyclic methacrylate copolymer, PMMA, deep-UV exposure, refractive index, glass transition temperature

### 1. Introduction

Fiber to the home (FTTH) is becoming more and more popular. The demand for high-speed communication networks has increased not only in offices but also in homes. For the backbone of such networks, glass optical fibers are used, because of their low propagation loss. However, polymer waveguides are not suitable for long-range communication, because of their large propagation loss, but they have other merits such as a low fabrication cost and a high flexibility and are suitable for local area networks.<sup>1)</sup>

Polymers can easily be combined with other materials. It is also possible to introduce special functions into polymers such as biocompatibility. The combination of polymers with fluidics and biological substances offers the possibility to build a biosensor with various optical components.

Poly(methyl methacrylate) (PMMA) has been investigated for the fabrication of polymer waveguides. PMMA is a very common polymer and exhibits a significant increase in refractive index with deep-UV exposure.<sup>2)</sup> Compared with other optical polymers, such as polycarbonate, PMMA has a lower refractive index (1.49) and an insufficient thermal stability [glass transition temperature ( $T_g$ ), 105 °C]. Polymers that possess higher refractive indexes and  $T_g$ s are required for practical applications.<sup>3)</sup>

Polymer waveguides have been fabricated by various techniques including reactive ion etching or photobleaching, laser direct writing, electron-beam direct writing and replication techniques such as casting, injection molding and hot embossing.<sup>4)</sup> Owing to the simplicity of the method, we have chosen conventional deep-UV exposure in fabricating the waveguides. This technique has several advantages over common methods because only a single polymer layer is used, which serves as the substrate and waveguide as well, and no further etching or development steps are required.

In this paper, we report on the chemical and physical properties of alicyclic methacrylate copolymers and the fabrication of polymer waveguides.

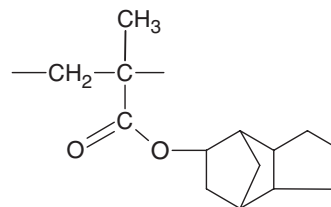


Fig. 1. Main structure of alicyclic methacrylate.

### 2. Experimental

#### 2.1 Materials and analysis

Alicyclic methacrylate copolymers were obtained from Hitachi Chemical as the OPTOREZ-Series (OZ-1000, OZ-1100, OZ-1310, and OZ-1330).<sup>5–7)</sup> The main structure of the alicyclic methacrylate part is shown in Fig. 1.

For refractive index measurement and waveguide fabrication, 500- $\mu\text{m}$ -thick polymer plates were fabricated by hot embossing (HEX03, Jenoptik). Spin coating was used to fabricate thin films, for UV spectral measurement and differential scanning calorimetry (DSC) measurement. Therefore, the OPTOREZ-Series copolymers were dissolved in anisole.

For deep-UV modification, commercial UV-exposure equipment (UVAPRINT CM, Dr. Hönle) was used. A 100 W/cm mercury xenon arc lamp (F-Lamp, Dr. Hönle) combined with a cold mirror with reflectance in the range of 220–420 nm was used in the exposure system. The resulting output was 0.6 mW/cm<sup>2</sup> at 240 nm. The exposure was performed under vacuum condition. The UV spectra of polymer films spin-coated on quartz glass were measured with a Perkin-Elmer Lambda 2 UV/vis spectrometer. Refractive index measurement was carried out by m-line spectroscopy using a self-made prism coupler arrangement. Fourier transform IR (FTIR) spectra were recorded with a Bruker IFS 66. The samples for FTIR were prepared on a gold-sputtered Si wafer by spin coating.  $T_g$  was determined by differential scanning calorimetry (DSC-204 Phoenix, Netzsch Gerätebau).

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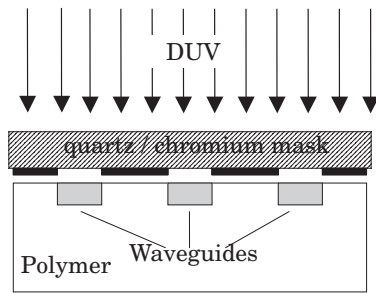
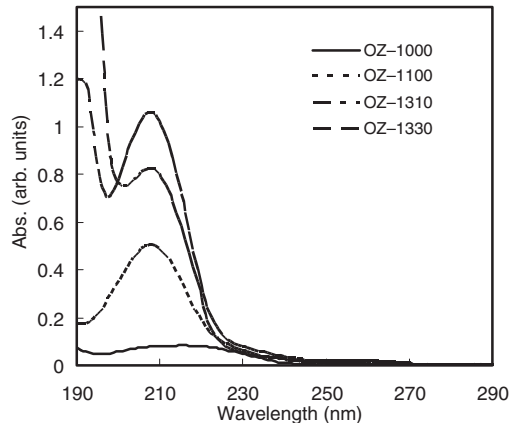


Fig. 2. Scheme of waveguide fabrication by quartz/chromium mask.

Fig. 3. UV absorption spectra of approx. 0.5- $\mu\text{m}$ -thick alicyclic methacrylate copolymers films (OPTOREZ-Series OZ-1000, OZ-1100, OZ-1310, and OZ-1330).

## 2.2 Waveguide fabrication

The structuring of the waveguides was carried out by conventional photolithography using a quartz/chromium mask, as shown in Fig. 2. The UV irradiation results in a local and controllable increase in refractive index in the exposed areas of the polymer surface, which generates integrated optical waveguide structures in a planar polymer plate. The width of the waveguides was 7.5  $\mu\text{m}$ . The exposure dose was 8.64 J/cm<sup>2</sup>. All transmission experiments were carried out using randomly polarized light.

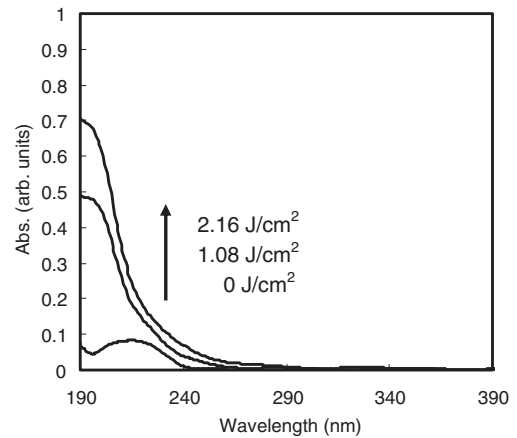
## 3. Results and Discussion

### 3.1 UV spectroscopy

Figure 3 shows the UV spectra of alicyclic methacrylate copolymers with thicknesses of approximately 0.5–0.6  $\mu\text{m}$ . All polymers absorb UV light below 240 nm with a shoulder peak at around 210 nm. That means these polymers absorb short-wavelength deep-UV light and a photochemical reaction is initiated.

Figure 4 shows the absorption spectra of OZ-1000 for different exposure doses. Henzi *et al.* have reported that the absorption peak of PMMA at 190–290 nm increases with increasing exposure dose under vacuum condition.<sup>8,9)</sup> Similar to that of PMMA, the intensity of absorption of the shoulder peak of OZ-1000 increases with increasing exposure dose. The increasing absorption peak below 200 nm represents the generation and reaction of unsaturated bonds. This peak is due to the  $\pi$ - $\pi^*$  transition of C=C bonds.

To achieve a single-mode waveguide using a given refractive index profile, the geometry of the waveguide

Fig. 4. UV absorption spectra of approx. 0.5- $\mu\text{m}$ -thick OZ-1000 after different exposure doses.

structure must be adjusted. The width of the waveguide is determined by the structural design of the photomask used in standard UV lithography. If the process tolerances are known, then the structural dimensions of the photomask can be adjusted to produce the exact width required for single-mode waveguide propagation. However, the depth of the waveguide is determined by the penetration depth of deep-UV light into the polymer. To achieve single-mode waveguide propagation behavior in this direction, penetration depth should be accurately adjusted. As shown in Fig. 4, the absorption peak becomes larger with increasing UV exposure dose. This means that it is possible to control penetration depth by adjusting exposure dose. Thus, after being exposed to a certain UV exposure dose, UV light is absorbed in a very thin layer at the polymer surface but it cannot reach the deeper areas of the polymer. The depth of the waveguide can therefore be controlled by adjusting exposure dose.

### 3.2 FTIR spectroscopy

To investigate the photochemical reaction of alicyclic methacrylate copolymers in detail, we measured their FTIR spectra. Figure 5 shows the FTIR spectra of OZ-1000 films at different exposure doses. With increasing exposure dose, the intensity of the carbonyl band in the pendant group at 1750–1735 cm<sup>-1</sup> decreases, indicating a change of the chemical environment. Furthermore, the intensity of the

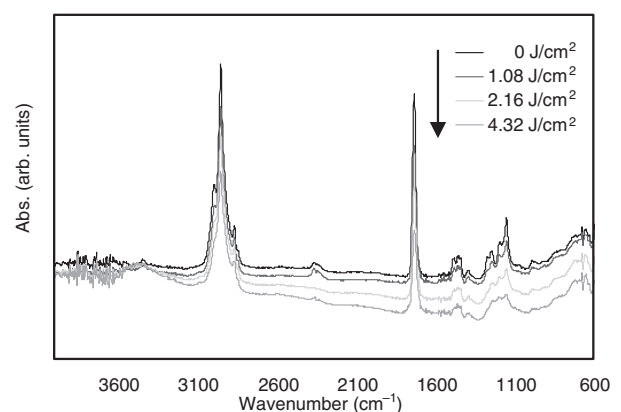


Fig. 5. FTIR spectra of OZ-1000 after different exposure doses.

Table I. Glass transition temperatures of OZ-Series before and after exposure.

Sample name	$T_g$ before exposure (°C)	$T_g$ after exposure (°C)
OZ-1000	125.3	110.2
OZ-1100	130.5	123.7
OZ-1310	129.9	130.8
OZ-1330	120.1	107.0

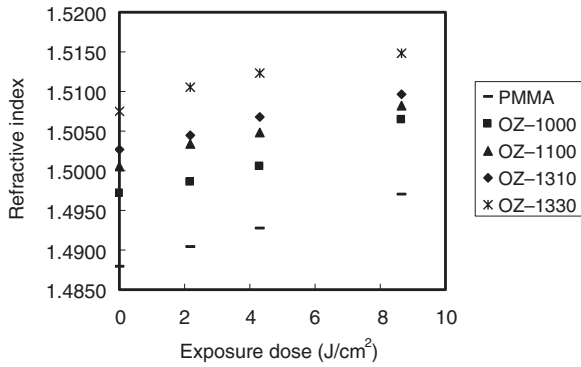


Fig. 6. Effective refractive index of OZ-Series as function of exposure dose.

C–H stretching and bending absorption bands at  $2960\text{--}2850\text{ cm}^{-1}$  and  $1500\text{--}1350\text{ cm}^{-1}$ , respectively and that of the C–O stretching bands at  $1270\text{--}1150\text{ cm}^{-1}$  decrease substantially. The intensity of the O–H stretching band at  $3500\text{ cm}^{-1}$  increases with increasing exposure dose. This suggests the formation of alcohol derived from the scission of the carbonyl group.<sup>10)</sup>

### 3.3 DSC

Table I shows the changes of  $T_g$  of the OZ-Series copolymers before and after exposure. The exposure dose was  $4.32\text{ J/cm}^2$  and the sample thickness was  $20\text{ }\mu\text{m}$ . Except for OZ-1310,  $T_g$  decreased after exposure, but the decrease in  $T_g$  is relatively small compared with that for PMMA. The  $T_g$  of PMMA was  $105\text{ }^\circ\text{C}$ , after exposure at  $4\text{ J/cm}^2$ , it was approximately  $80\text{ }^\circ\text{C}$ . In the case of PMMA, the cleavage of pendant methylester groups and a decrease in molecular weight caused a reduction in  $T_g$ .<sup>8)</sup>

### 3.4 Refractive index

Figure 6 shows effective refractive index of the lowest-order mode at  $633\text{ nm}$  as function of exposure dose for the OZ-Series copolymers. By increasing exposure dose, effective refractive index becomes larger in all samples. No birefringence can be found in the range of the measurement resolution  $\pm 10^{-4}$ . Independent of OZ grade, the investigated materials show comparable behaviors, but slightly different dose dependences.

### 3.5 Waveguide performance

A waveguide has a graded index profile with an exponential decay.<sup>11)</sup> We have measured the performance of a straight waveguide consisting of OZ-1100. Figure 7 shows the near-field pattern of the straight waveguide at  $1550\text{ nm}$ . Figure 8 shows the intensity profile of the straight

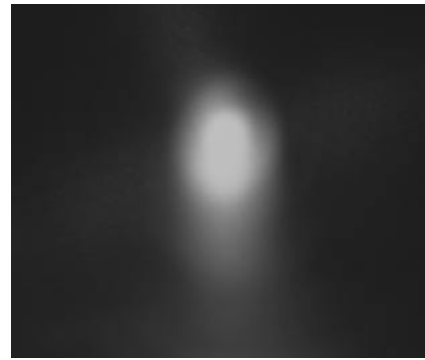
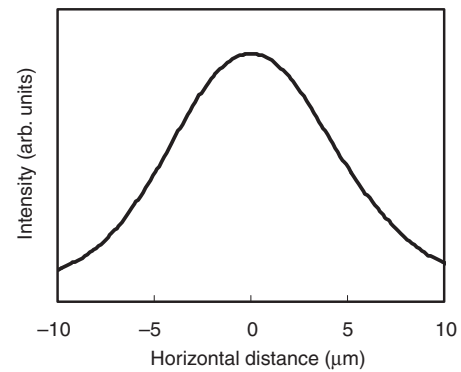
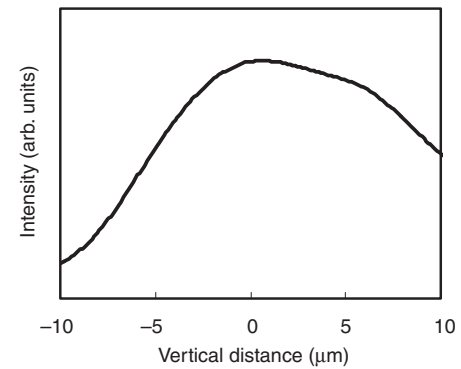


Fig. 7. Near-field photograph of straight waveguide.



(a)



(b)

Fig. 8. Intensity profiles of straight waveguide in both (a) horizontal and (b) vertical directions.

waveguide in both vertical and horizontal directions. From the intensity profile of the vertical direction, this waveguide does not seem to be single-mode. The optimizations of waveguide structure design and the UV exposure conditions are needed for further evaluation of the waveguide.

The minimum waveguide loss that we have obtained so far was  $2\text{ dB/cm}$  at  $1550\text{ nm}$ . The exposure dose for this sample was  $8.64\text{ J/cm}^2$ . The polarization dependent loss was less than  $0.15\text{ dB}$ . In the case of a PMMA waveguide, the waveguide loss was  $1\text{ dB/cm}$  at  $1550\text{ nm}$ . This difference may be due to the chemical structure of the OPTOREZ-Series copolymers. OPTOREZ-Series copolymers contain alicyclic groups and have more C–H bonds than PMMA, which cause higher intrinsic material losses owing to vibrational overtones. In addition, the conditions of waveguide fabrication from OPTOREZ-Series copolymers have not been optimized

yet. Polymer films from the OPTOREZ-Series copolymers were prepared by hot embossing. These films have a higher roughness than commercially available PMMA sheets. We believe that waveguide loss can be reduced by decreasing the roughness of the polymer substrate.

#### 4. Conclusions

We investigated the physical and chemical properties of alicyclic methacrylate copolymers and their changes under deep-UV exposure. It was shown that alicyclic methacrylate copolymers have a better thermal stability and a higher refractive index than PMMA. FTIR spectra show the scission of carbonyl group of the alicyclic methacrylate copolymers by deep-UV exposure. The refractive index of the alicyclic methacrylate copolymers increased with exposure dose. These show that alicyclic methacrylate copolymers can be applied as polymer waveguides with deep-UV exposure similar to PMMA.

Thus far, the minimum waveguide loss of OZ-1100 was 2 dB/cm at 1550 nm. This shows that alicyclic methacrylate copolymers are promising materials for polymer waveguides.

Future work will focus on improving hot embossing in order to reduce the surface roughness of the polymer films. The optimizations of the waveguide structure and UV

exposure conditions are also needed in order to obtain a better waveguide performance.

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- 1) L. Eldada, R. Blomquist, L. W. Shacklette and M. J. McFarland: *Opt. Eng.* **39** (2000) 596.
- 2) W. J. Tomlinson, I. P. Kaminow, E. A. Chandross, R. L. Fork and W. T. Silfvast: *Appl. Phys. Lett.* **16** (1970) 486.
- 3) M. Zhou: *Opt. Eng.* **41** (2002) 1631.
- 4) H. Ma, A. K.-Y. Jen and L. R. Dalton: *Adv. Mater.* **14** (2002) 1339.
- 5) F. Kanega, H. Kawai and H. Kokame: *Hitachi Chemical Tech. Rep.* **11** (1988) 35 [in Japanese].
- 6) H. Kawai, M. Suzuki and A. Yoshida: *Hitachi Chemical Tech. Rep.* **28** (1997) 21 [in Japanese].
- 7) Y. Yamashita, M. Suzuki, A. Yoshida and S. Iwata: *Hitachi Chemical Tech. Rep.* **37** (2001) 17 [in Japanese].
- 8) P. Henzi, D. G. Rabus, K. Bade, U. Wallrabe and J. Mohr: *Proc. SPIE* **5454** (2004) 64.
- 9) P. Henzi, D. G. Rabus, U. Wallrabe and J. Mohr: *Proc. SPIE* **5451** (2004) 24.
- 10) C. Wochnowski, S. Metev and G. Sepold: *Appl. Surf. Sci.* **154–155** (2000) 706.
- 11) D. G. Rabus, P. Henzi and J. Mohr: *IEEE Photonics Technol. Lett.* **17** (2005) 591.