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Refractive index changes in photochromic diarylethene derivatives in polymethylmethacrylate films

Takashi Yoshida [a], Koichi Arishima [a], Fumihiro Ebisawa [a], Mitsutoshi Hoshino [a], Ken Sukegawa [a], Atsushi Ishikawa [b], Tatsuya Kobayashi [b], Makoto Hanazawa [b], Yukio Horikawa [b]

[a] *NTT Opto-Electronics Laboratories, Nippon Telegraph and Telephone Corporation, Tokai, Naka-gun, Ibaraki 319-11, Japan*

[b] *Development Laboratory, Kanebo Ltd., 1-5-90 Tomobuchi-cho, Miyakojima-ku, Osaka 534, Japan*

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Abstract

We investigated photochromism and the refractive index change Δn in polymethylmethacrylate (PMMA) films made using 16 compounds of 1,2-diarylethene derivatives. The derivatives were classified as maleic anhydride or hexafluorocyclopentene diarylethene in type according to their structure.

In PMMA films, the photochromic reactivity of maleic anhydride diarylethene derivatives strongly depends on their substituent structure. On the contrary, the photochromism of hexafluorocyclopentene diarylethene derivatives is observed in PMMA films regardless of their substituent.

We found that Δn increased in proportion to the absorbance charge increase. Moreover, both Δn and ΔA were also proportional to the concentrations of the photochromic compounds. We believe that both Δn and ΔA are related to changes in the molecular structure of 1,2-diarylethene derivatives.

We fabricated one transparent PMMA film of each type. Each film contained a high concentration of dispersed diarylethene derivatives. The changes in refractive index and absorbance of the maleic anhydride diarylethene type saturated at more than 15 wt.%. However, the changes in the hexafluorocyclopentene diarylethene type with a long alkyl chain were in proportion to the concentrations of the compound, and we obtained the largest refractive index change (0.0018) yet reported for 1,2-diarylethene derivatives in transparent PMMA films.

Keywords: 1,2-diarylethene derivatives; Optical switch; Photochromism; Optical waveguide; Reversible refractive index charge

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1. Introduction

Materials whose refractive index can be changed have been studied for optical applications. The refractive index change Δn in organic photochromic (PC) compounds have led to proposals for their use in a number of optical waveguide components, because a refractive index change in an optical waveguide shifts the phase of the signal light. In addition, the reversible refractive index change of PC compounds allows the light phase shift to be controlled. However, almost all conventional organic PC compounds have poor thermal stability, and the refractive index change caused by light irradiation is unstable at room temperature. Recently, thermally irreversible PC compounds, 1,2-diarylethene derivatives, have been developed and good durability has been reported in PC reaction cycles [1–6]. Once closed these 1,2-diarylethene derivatives are thermally stable but exhibit reversible photochromism with high conversion efficiency. We have reported that a self-holding PC optical switch (Mach–Zehnder type) can be obtained by using the diarylethene compound as the optical waveguide material [7].

PC compounds for use in optical devices must be self-holding, be capable of a large number of PC cycles and exhibit a large refractive index change. In order to miniaturize optical waveguide devices, the large Δn caused by a PC reaction is very important because it means that sufficient light phase shift can be obtained in a short-length waveguide. Another important requirement for optical devices is that the PC compounds can function in a solid, such as a polymer.

The 1,2-diarylethene derivatives satisfy the requirements of self-holding and a high number of PC cycles [8]. However, the large Δn (e.g. about 10^{-3}) is not provided by these PC compounds owing to the low PC reaction efficiency in the polymer film. The PC reaction characteristics of 1,2-diarylethene derivatives have been studied in hexane, benzene and acetonitrile solutions [9]. Moreover, the refractive

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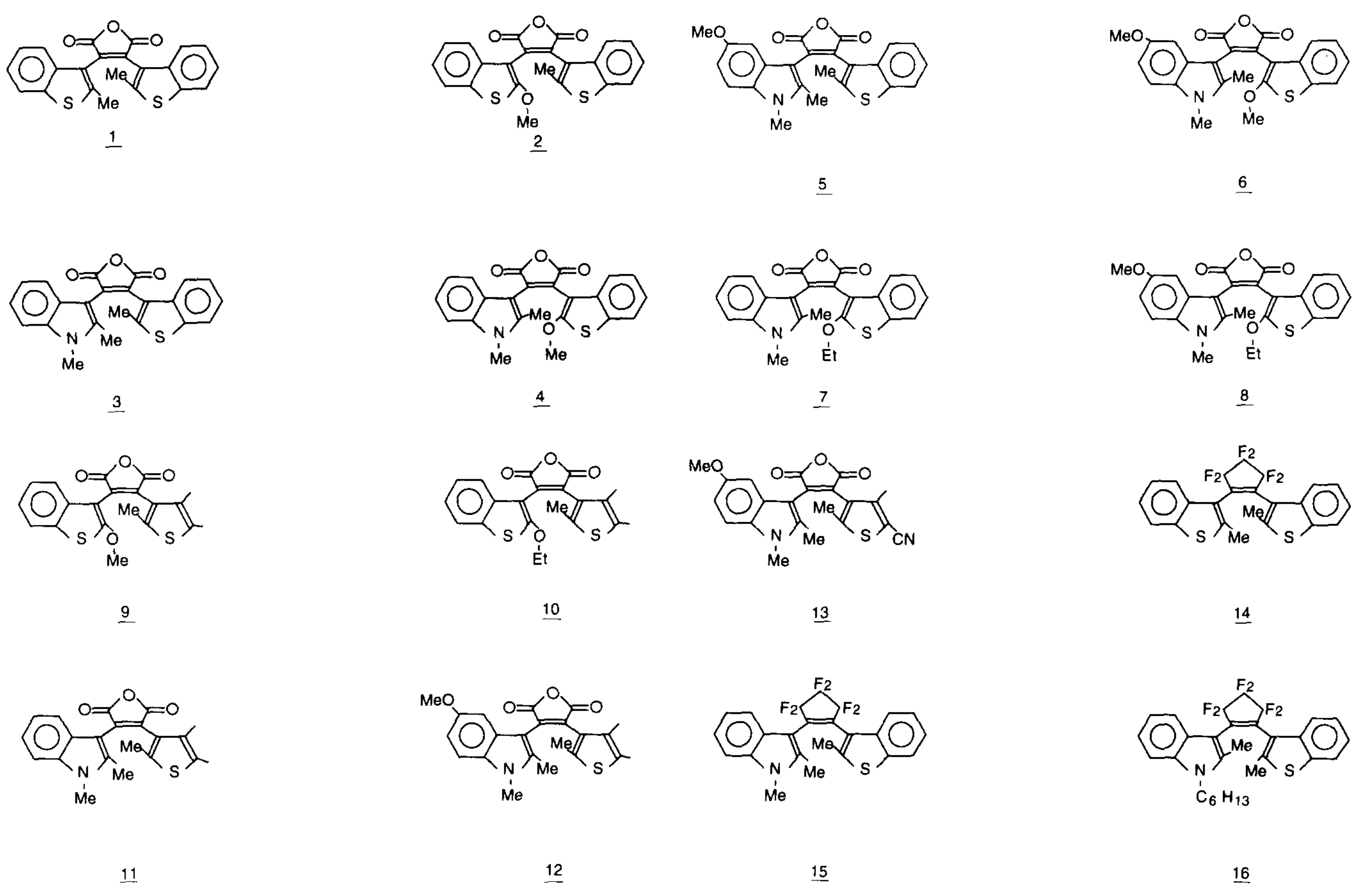

Fig. 1. The structure of 1,2-diarylethene derivatives. There are two groups which consist of the maleic anhydride diarylethene (**1–13**) and the hexafluorocyclopentene diarylethene (**14–16**) derivatives. In the maleic anhydride diarylethene derivatives group, there are four subgroups; they have two benzo[*b*]thiophene rings (**1** and **2**), an *N*-methyl indoline and a benzo[*b*]thiophene ring (**3**, **4**, **5**, **6**, **7** and **8**), a benzo[*b*]thiophene and trimethyl thiophene ring (**9** and **10**) and an *N*-methyl indoline and a trimethyl thiophene ring (**11**, **12** and **13**).

index change in polymer has been examined for a few compounds [2,3].

In this paper, we report on the photochromism and Δn of 1,2-diarylethene derivatives. We obtain a high Δn of 1,2-diarylethene derivatives contained in polymethylmethacrylate (PMMA) causing sufficient phase shift in the signal light in a waveguide. A large Δn of more than 10^{-3} was realized with a large PC compound concentration in PMMA.

2. Experimental details

2.1. Materials

We studied 16 compounds of 1,2-diarylethene derivatives, whose structures are shown in Fig. 1. The 16 compounds were the maleic anhydride diarylethene derivatives (**1–13**) and the hexafluorocyclopentene diarylethene derivatives (**14–16**). The maleic anhydride diarylethene derivatives were purchased from Kobe Tennenbutsu Kagaku Ltd. (Kobe, Japan). The hexafluorocyclopentene diarylethene derivatives were synthesized with a conventional method [10].

These PC compounds were dispersed in PMMA solutions. The total weight ratio of these PC compounds and PMMA was 20 wt.% in PMMA solutions containing 40 wt.% chlorobenzene and 40 wt.% 4-methyl-2-pentanone. The concentrations of the PC compounds varied from 5 to 50 wt.% against PMMA. Sample films on fused quartz plates or on silicon wafers were made with the spin coating method. The film thickness was 4 μm. PMMA ($M_w = 101\,000$, $M_n = 48\,300$) was the secondary standard grade of Aldrich Ltd.

2.2. Photochromism measurement

We investigated the photochromism of 1,2-diarylethene derivatives using the apparatus shown in Fig. 2 equipped with a light irradiation and absorption spectra observation system. The change ΔA in absorbance was observed simultaneously with light irradiation in this system. There was no stray light, because the sample film was irradiated obliquely and there was a light trap at the opposite side of the light source.

We arranged two light sources, a 500 W Xe lamp and a 350 W superhigh pressure Hg lamp. The use of optical fibre bundles made it easy to change between the two light sources. This provided a UV to visible light irradiation wavelength range.

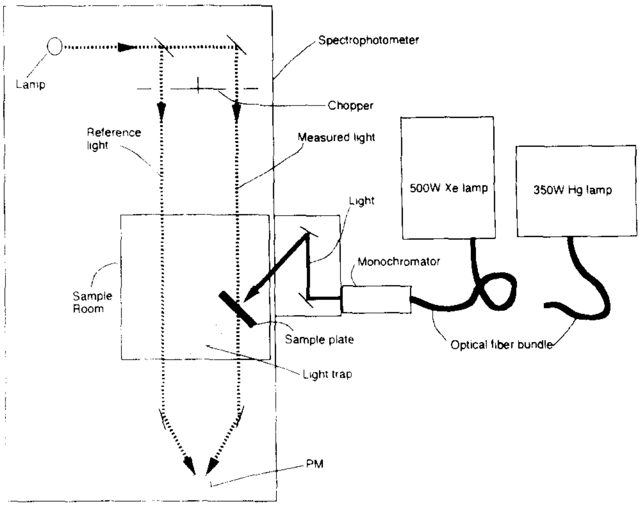

Fig. 2. Irradiation and observation apparatus.

The irradiated area of the sample films was 2.0 cm × 1.8 cm, and the light power was almost uniform throughout this area. The bandwidth of the irradiating light was about 20 nm. The absorption spectra of the films on the fused quartz plates were obtained using a Shimadzu UV-3100 spectrophotometer.

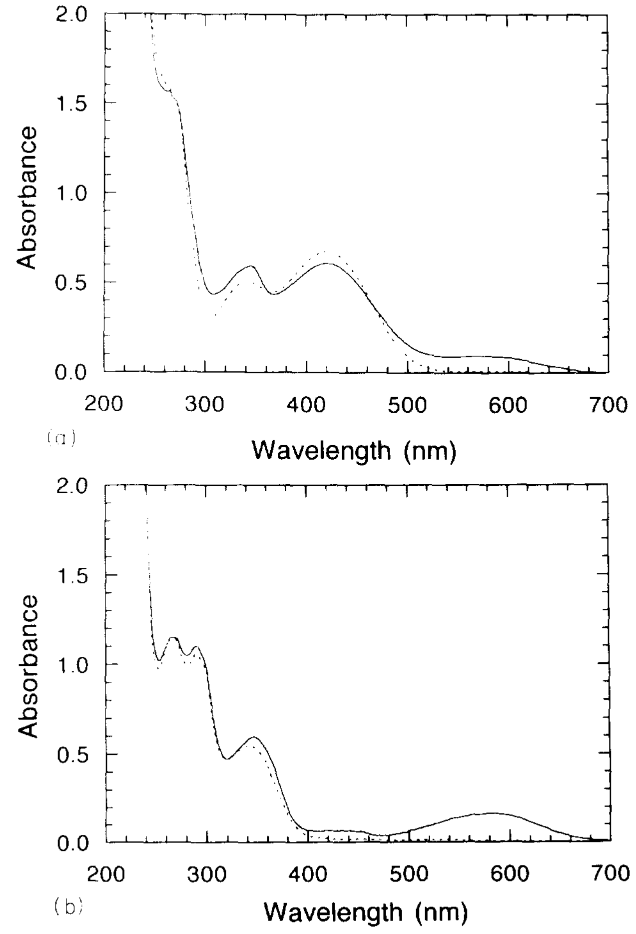

Fig. 3. UV–visible spectra of typical 1,2-diarylethene derivatives: (a) **9**; (b) **15**; -----, open form; ——, closed form.

Table 1
Light irradiation and photochromic observation wavelengths

Derivative	Light irradiation wavelength (nm)	Observation wavelength (nm)
1 and **2**	420	540
3–8	460	540
9	420	580
10	420	570
11–13	460	540
14	365	530
15 and **16**	365	580

The UV–visible spectra of typical 1,2-diarylethene derivatives are shown in Fig. 3. The maleic anhydride diarylethene films were irradiated at their peak wavelength between 420 nm and 460 nm. The hexafluorocyclopentene diarylethene films were irradiated with UV light, because the hexafluorocyclopentene diarylethenes did not exhibit photochromism with visible light, only with UV irradiation.

Table 1 shows the light irradiation wavelengths for the 1,2-diarylethene derivatives and the wavelengths at which photochromism was observed.

2.3. Refractive index changes with photochromic reaction in polymethylmethacrylate films

The refractive indices of these 1,2-diarylethene derivative films on silicon wafers were measured with the prism coupling method (Metricon model 2010 prism coupler) at 1300 nm. The light was produced by the apparatus shown in Fig. 2 and the light wavelengths for the irradiation were the same as those shown in Table 1.

3. Results and discussion

3.1. Photochromism in polymethylmethacrylate films

For optical devices, it is important that PC materials are capable of functioning in a polymer film, such as the PMMA film. The PC characteristics of 1,2-diarylethene derivatives are usually studied in solution and the reaction properties such as conversion efficiency have not been studied in polymer films. It is believed to be impossible to estimate the PC reaction in a polymer from results obtained in solution. This is because the reaction occurs in a free volume of polymer and so the conversion efficiency will be reduced. Therefore, we studied the PC compounds (maleic anhydride diarylethene (**1–13**) and the hexafluorocyclopentene diarylethene derivatives (**14–16**)) in PMMA films.

Figs. 4 and 5 show the absorption change in maleic anhydride diarylethene derivatives in relation to exposure time at the wavelengths shown in Table 1. In hexane solution, all the maleic anhydride derivatives exhibited photochromism. As shown in Fig. 5, some compounds which have an *N*-methyl

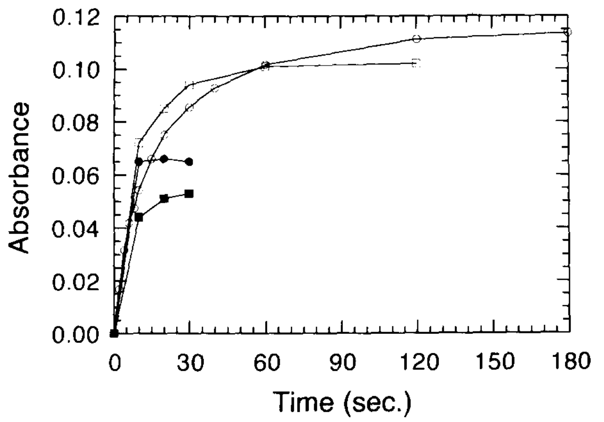

Fig. 4. Photochromism of the maleic anhydride diarylethenes in PMMA films: ●, **1**; ■, **2**; ○, **9**; □, **10**.

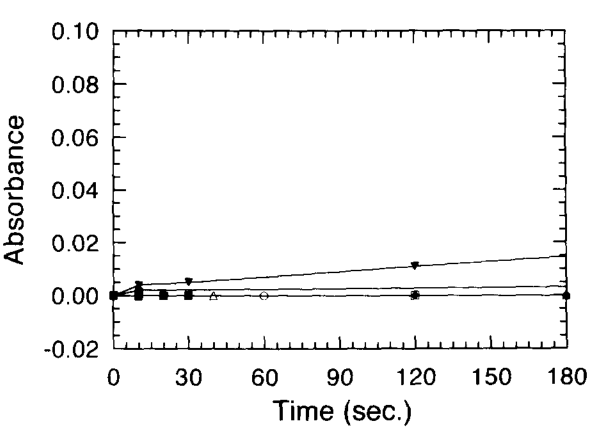

Fig. 5. Photochromism of the maleic anhydride diarylethenes in PMMA films: ●, **3**; ■, **4**; ○, **5**; □, **6**; ◇, **7**; △, **8**; ▲, **11**; ▼, **12**; ◆, **13**.

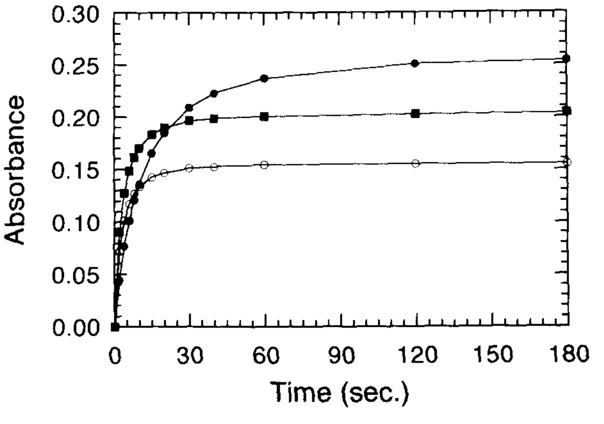

Fig. 6. Photochromism of the hexafluorocyclopentene diarylethenes in PMMA films: ●, **14**; ■, **15**; ○, **16**.

indoline substituent were not PC. However, the other compounds (**1**, **2**, **9** and **10**), which do not have an *N*-methyl indoline substituent, were PC (Fig. 4). This result suggests that maleic anhydride 1,2-diarylethene derivatives with *N*-methyl indoline substituent cause hardly any PC reaction in polymer films.

On the contrary, all the hexafluorocyclopentene diarylethene derivatives exhibited photochromism (Fig. 6), despite the fact that **15** and **16** both have an *N*-methyl indoline substituent.

The PC reaction of 1,2-diarylethene derivatives is known to be affected by the polarity of the solvent and the PC reaction efficiency is reduced in a polar solvent [9]. We compared the photochromism of diarylethene derivatives in PMMA films with that in solutions in order to evaluate the polarity of PMMA with a PC reaction. In the non-polar solvent hexane, they were all (**1–16**) PC. By contrast, in the polar solvent acetone **1**, **2**, **9**, **10** and **14–16** exhibited photochromism and **3–8** and **11–13**, with an *N*-methyl indoline substituent, did not. This result in the polar solvent was the same as that for PMMA film. This identical behaviour in polar solvent and PMMA film suggests that the PC reaction of 1,2-diarylethene derivatives in PMMA is influenced by the polarity of PMMA owing to the carbonyl group which PMMA contains. As a result, maleic anhydride 1,2-diarylethene derivatives with thiophene groups and hexafluorocyclopentene diarylethene derivatives are suitable as the refractive index control material for optical waveguide devices because of their highly PC reactivity in films made of a polar polymer such as PMMA.

The PC reaction response is also an advantageous characteristic in relation to optical devices. The thermal irreversibility of diarylethene derivatives has led to the development of polymer materials whose refractive indices can be controlled by light irradiation. The adjusted refractive index is suitable and self-holding without providing any power supplement. In terms of applications to such self-holding optical waveguide devices as optical switches, the switching speed must be less than several tens of seconds because the switching time is negligible compared with the holding time.

In Figs. 4 and 6, the saturation times of PC reactions were several tens of seconds. This value is sufficient for optical devices containing self-holding light phase shift material. These saturation phenomena are believed to be caused by the PC equilibrium which results from a balance between the irradiating light wavelength and the polarity of the polymer.

3.2. Refractive index change in polymethylmethacrylate films

The refractive index of 1,2-diarylethene derivatives becomes high when they are in closed form. We investigated the refractive index changes (Δn at 1300 nm) by using the PC reactions of diarylethene derivatives in PMMA films. A large refractive index change is expected in a material which is soluble in PMMA polymer at a high concentration and with high conversion efficiency. The molecular refractive index change in the reaction is also considered to affect the total Δn in the polymer but, in this study, the molecular refractive index change cannot be evaluated clearly from conversion efficiency owing to the difficulty in determining the extinction coefficient of 1,2-diarylethene derivatives in PMMA film.

Table 2
Refractive index change of 10 wt.% derivatives in polymethylmethacrylate films at 1300 nm

Derivative	Refractive index change $\Delta n \times 10^4$
1	1.0
2	2.0
9	5.0
10	1.0
14	3.0
15	8.0
16	6.0

Δn values of the maleic anhydride and hexafluorocyclopentene diarylethene derivatives (**1**, **2**, **9**, **10** and **14–16** at 10 wt.%) are shown in Table 2.

The Δn values in Table 2 are measured with the same concentration of 1,2-diarylethene derivatives and considered to indicate the differences in conversion efficiency. Maleic anhydride diarylethene derivatives with a methoxy group in a thiophene ring (**2** and **9**) exhibit a relatively high Δn. Hexafluorocyclopentene diarylethene derivatives with *N*-alkyl indoline exhibit a higher Δn than maleic anhydride diarylethene derivatives and the highest Δn value is obtained with **15**.

In PMMA films, the Δn value of **14–16**, with a hexafluorocyclopentene structure, was larger than that of **1**, **2**, **9** and **10**, with a maleic anhydride structure.

Fig. 7 shows the relation between ΔA and Δn of **2**, **9** and **16** together with their PC reactions. It is interesting that the $\Delta n/\Delta A$ plots for three compounds are on the same line. This fact indicates that both Δn and ΔA are closely related to the change in molecular structure, which is proportional to the dipole moment of compounds caused by the PC reaction.

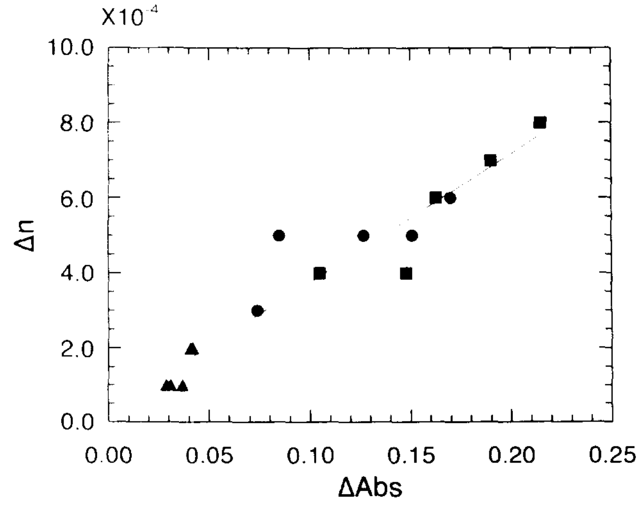

Fig. 7. The relation between refractive index change Δn and the absorbance change ΔA in PMMA films: ▲, **2**; ●, **9**; ■, **16**.

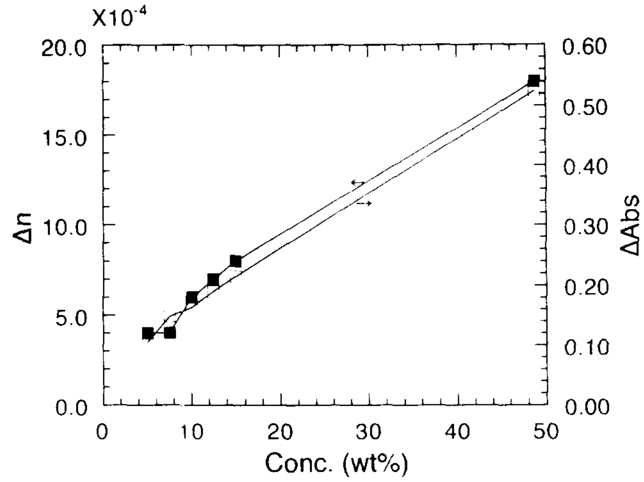

Fig. 8. The refractive index change Δn and absorbance change ΔA in PMMA films: □, ■, **16**.

3.3. High concentration effect in polymethylmethacrylate films

Δn values of these derivatives at 10 wt.% did not satisfy optical device requirements. The proportional relation between Δn and ΔA in Fig. 7 suggests that the refractive index change of diarylethene-derivative-containing PMMA film is easily estimated by ΔA measurement. A refractive index change of more than 10^{-3} is required for a material for optical waveguide devices [7]. Therefore, it is estimated that a ΔA value of more than 0.3 is required for device application. The Δn value was proportional to the concentration of PC compound in PMMA film, supporting the contentions that there is no molecular aggregation of diarylethene derivatives and that all molecules are dispersed uniformly in PMMA film. We therefore investigated a way of increasing Δn to, for example, 50 wt.%, by means of the high concentration effect in PMMA film.

We tried to disperse 50 wt.% of the diarylethene derivatives (**1**, **2**, **9**, **10** and **14–16**) in PMMA. There were many crystalline islands in all the PMMA films, except for **9** and **16**, suggesting that they had good solubility in PMMA. The Δn and ΔA values of **9** increase in proportion to concentration less than 15 wt.% and were saturated at 15 wt.%, suggesting that the molecules of diarylethene derivative **9** in PMMA film did not cause a sufficient PC reaction in high concentration film. The largest Δn was obtained with **16** at 50 wt.%.

Fig. 8 shows the Δn and ΔA values of **16**–PMMA film. They were proportional to the concentration of **16**, and we obtained the polymer film with the largest refractive index change (0.0018) at a concentration of 50 wt.%.

The structure of **16** is like that of **15** with an additional long alkyl chain. The additional long alkyl chain is considered to improve the solubility of **15** and to prevent the aggregation of diarylethene molecules in PMMA. Therefore, adding a long alkyl chain to a PC compound and dispersing this PC compound in polymer film at a high concentration is a good method for achieving a large refractive index change.

4. Conclusions

We investigated the PC characteristics of 16 1,2-diarylethene derivatives, maleic anhydride and hexafluorocyclopentene diarylethene derivatives, in PMMA and evaluated their potential for application as optical waveguide device materials.

The photochromism of the hexafluorocyclopentene diarylethene derivatives was hardly affected by the polarity of the PMMA environment as compared with the maleic anhydride derivatives.

The plots of $\Delta n/\Delta A$ for the three PC compounds were on the same line. The fact indicates that both Δn and ΔA are closely related to the change in molecular structure, which is proportional to the dipole moment of the compounds. The Δn value of a film containing 1,2-diarylethene derivative is easily evaluated from ΔA.

We were able to obtain a transparent PMMA film of highly concentrated **16** with a long alkyl chain. Adding a long alkyl chain to a PC compound and dispersing this compound in polymer at a high concentration is a good way to achieve a large refractive index change. We measured the largest refractive index change (0.0018) for **16** in PMMA films.

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