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Study on the thermo-optic properties of DR1/PMMA composite*

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This paper reports that the thermo-optic coefficient (dn/dT) as well as thermal expansion coefficients (β) of DR1/PMMA polymer film are measured for both TE (transversal electric) and TM (transversal magnetic) polarizations by using an attenuated total reflection configuration at the wavelengths of 832nm. The thermo-optic coefficients of DR1/PMMA are negative and as high as the order of $10^{-4}/^{\circ}$C. The influences of dopant concentration, poling process and photobleaching process on the thermo-optic properties of DR1/PMMA are also investigated.

Keywords: thermo-optic effect, polymer thin film
PACC: 7820N, 7865T

1. Introduction

Along with the successful invention of lasers, rapid development in optic communication causes the larger requirement for optic control and optic transfer devices. More and more optic–electronic devices based on different fabrication techniques have been invented.[1,2] Recently polymer-based optical waveguides for fabrication of thermo-optic devices have attracted great interest in the telecommunication application areas, such as digital optical switch, Mach-Zehnder interferometer type optical switch and optical cross-connects[3−5] due to the high thermo-optic coefficient (TOC) of the polymer, which is one order of magnitude larger than those for silica material. As DR1 (disperse red 1)/PMMA, which is azo dye dopant PMMA composite, is widely used, it is important to study the thermo-optic properties of this kind of polymer film. In this paper, measurements of dn/dT as well as β of DR1/PMMA film have been performed for both transversal electric (TE) and transversal magnetic (TM) polarizations in metal cladding optical waveguide by using an attenuated total reflection (ATR) configuration at the wavelengths of 832nm. Comparing with other technique such as the Abbe refractometer method,[6] we find that this method can study the thermo-optic properties and its anisotropy in waveguide configuration which is very close to a real environment for practical application. The TOC of pristine PMMA film measured by this method are $dn_{\rm TM}/dT = -1.27\times10^{-4}/^{\circ}$C and $dn_{\rm TE}/dT = -1.21\times10^{-4}/^{\circ}$C which are very close to the value reported in the literature ($-1.20\times10^{-4}/^{\circ}$C).[7] So that using the ATR method to measure TOC of polymer film is reliable. In addition, the influences of dopant concentration, poling process and photobleaching process on the thermo-optic properties of DR1/PMMA are also investigated. Chemical structure of the DR1 ($C_{16}H_{18}N_4O_3$, N - Ethyl-N- (2-hydroxyethyl) - 4- (-4-nitrophenylazo) aniline) is shown in Fig.1, which exhibits an absorbance at 502 nm. The most widely quoted theory of thermo-optic effect in polymer materials[6,8,9] is that of Prod'homme.[10] According to his theory, the TOC dn/dT of a polymeric material can be expressed as

$$\frac{dn}{dT} = -\eta\beta, \tag{1}$$

with

$$\eta = \frac{(n^2-1)(n^2+2)}{6n}, \tag{2}$$

where T is the temperature, n is the refractive index, β is the thermal expansion coefficient. In polymeric

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film, and according to the Lorentz–Lorenz[11] relation in optical polymer, the function $(n^2+2)/(n^2-1)$, which is proportional to the specific volume, is linear in the various temperature ranges where there is no phase transition.[12] Therefore the thermal expansion coefficient can be directly obtained as $\beta = a/b$[12] from the phenomenological expression

$$f_{\mathrm{LL}} = \frac{n^2+2}{n^2-1} = aT + b. \tag{3}$$

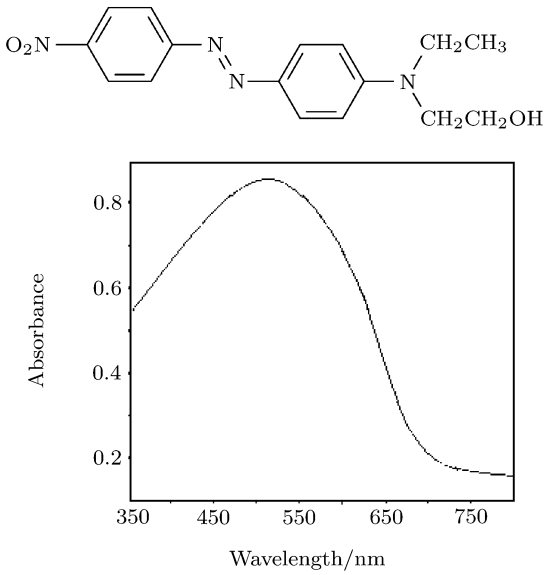


Fig.1. Molecular structure of disperse red 1 (DR1) and its absorbance at visible and UV light range.

2. Experiment setup

As shown in Fig.2, experimental sample consists of a glass prism (ZF7) on its base precoated a thin silver film of about 50nm by a sputtering machine. The polymer film is spin coated onto the silver film. The refractive index of the glass prism is calculated from a dispersion formula offered by supplier (ZF7, $n = 1.7892 \pm 0.0002$ at λ=832nm). The dielectric permittivities of the gold film (ε=–29+1.5i at λ=832nm) are related with the experimental condition and usually measured by Chen's technique.[13] In this configuration, the silver film serves as a coupling layer and a cladding of the polymer waveguide as well. The prism–waveguide coupling system is mounted on a brass plate heated by an auto-controlled ceramic heater. Temperature is measured by a thermocouple directly attached to the polymer film. In the experiment, a collimated light beam from a diode laser passes through a polarizer and is then incident upon the interface between the prism and the silver film with an appropriate angle. Reflected light is detected with a photodiode and averaged to reduce the noise. Angular scan is carried out by a $\theta/2\theta$ computer-controlled goniometer, a series of dips in reflectivity due to resonant transfer of energy into guide modes are generated on a computer screen and saved in a data file. Variation of refractive index of the polymer film with temperature can be determined through monitoring the angular shift of the resonant dips (as shown in Fig.3).

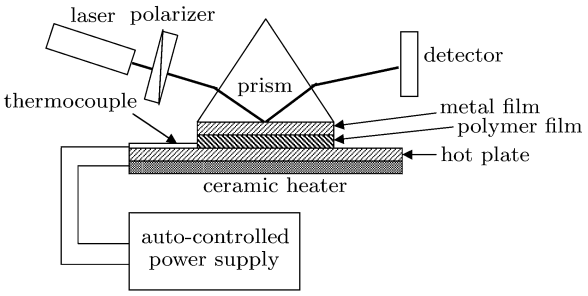


Fig.2. Attenuated total reflection (ATR) setup with temperature control.

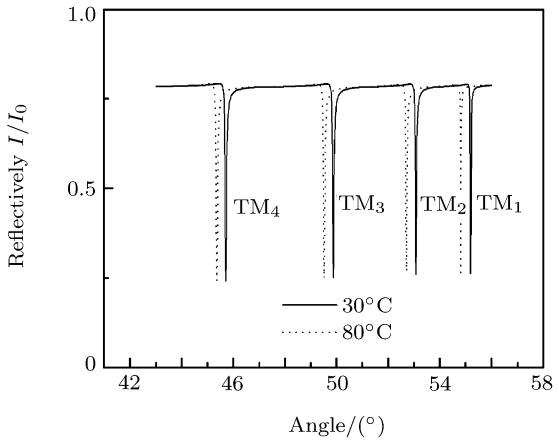


Fig.3. Reflectivity vs angle of incidence at T=30°C and at T=80°C of a sample of PMMA with TM polarization. Refractive index changes from n=1.48996 at 30°C to n=1.48362 at 80°C.

3. Results and discussions

3.1. The influence of dopant concentration on the TOC of DR1/PMMA film

Before the measurement, DR1/PMMA solution is prepared by dissolving the pristine PMMA powder in monochlor-benzene, mixing with different amounts of DR1 powder for different dopant concentrations.

These solutions are stirred by magnetic stirrer for 12h to make the PMMA and DR1 dissolving completely, and stewing for 72h, and then filtered by 0.45μm pore size syringe filters. These prepared polymer solutions are then spin coated onto the silver film with the spin speed of 1200rad/m, the samples are then baked in a vacuum oven at 50°C for 12h. The film thickness is measured by the M-line technique.[14] Due to the same spin speed, thicknesses of the DR1/PMMA films for different dopant concentrations are controlled in a narrow range of 4.6–4.8μm. In the measurements, in order to eliminate the effect of absorbed moisture,[15] data are taken in the cooling cycle with the temperature ranging from 70°C to 30°C at 5°C intervals. Variations of refractive index n and $f_{\rm LL}$ with temperature of DR1/PMMA film with 10% dopant concentration are shown in Fig.4 and Fig.5. Same process is performed for the measurement of TOC and thermal expansions of DR1/PMMA films with different dopant concentrations. The results are shown in Fig.6 and Table 1.

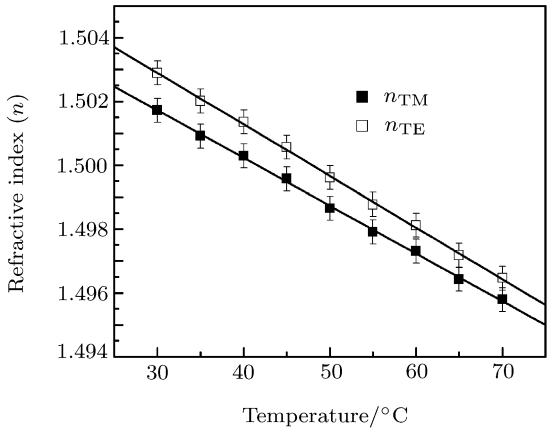


Fig.4. The variation of refractive index n of DR1/PMMA (with 10% dopant concentration) film with temperature at the wavelength of 832nm.

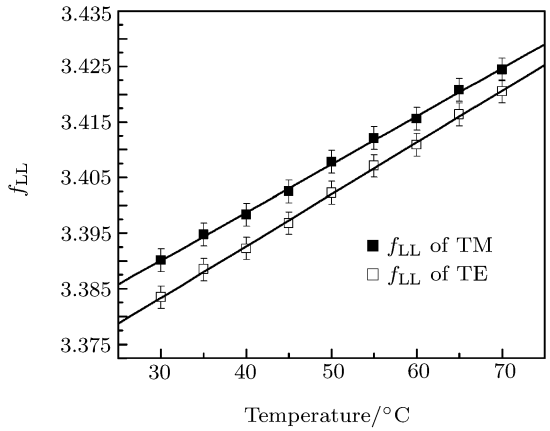


Fig.5. The variation of $f_{\rm LL}$ of DR1/PMMA (with 10% dopant concentration)film with temperature at the wavelength of 832nm.

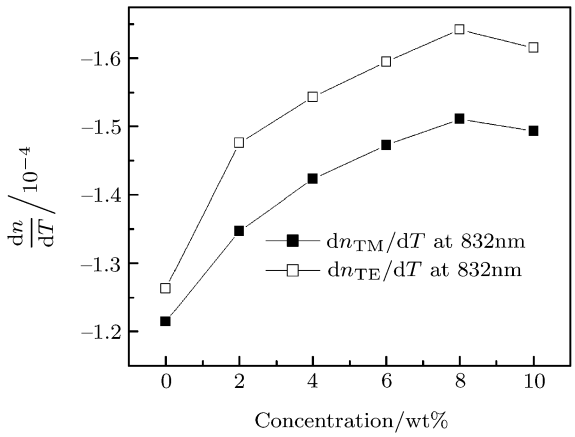


Fig.6. The variation of TOC of DR1/PMMA film with dopant concentration for both TE and TM polarization at the wavelength of 832nm.

Table 1. The refractive indices and thermal expansion coefficients of DR1/PMMA film with different dopant concentrations for both TE and TM polarization at the wavelength of 832nm.

oncentration/wt%	0	2	4	6	8	10
$n_{\rm TM}$	1.49462	1.49788	1.49884	1.49968	1.50065	1.50172
$n_{\rm TE}$	1.49543	1.49889	1.49981	1.50078	1.50188	1.50289
$\beta_{\rm TM}/(10^{-4}/°{\rm C})$	2.135	2.352	2.453	2.535	2.590	2.561
$\beta_{\rm TE}/(10^{-4}/°{\rm C})$	2.210	2.545	2.652	2.745	2.811	2.755

The results show that the absolute value of TOC of DR1/PMMA film does not always increase with the increasing wt% of the dopant. We believe that there are two main effects which exert the combined influences on the TOC of the DR1/PMMA system, one is the plasticization effect of the polymer which increases the thermal expansion; another is the thermal isomerization effect of the chromophore DR1 which restrains the thermal expansion. At the beginning of increasing the dopant concentration, the plasticization effect is dominant and β increases. When the dopant concentration increases further, the thermal isomerization effect is enhanced and becomes dominant at last, thus β decreases. We find that the maximum ab-

solute value of the TOC of the DR1/PMMA is at the concentration of 8wt% of the DR1.

The absolute value of TOC of TE polarization is always larger than that of TM polarization. According to Eq.(3), anisotropy in TOC can be expressed as follows:

$$\Delta \mathrm{d}n/\mathrm{d}T = -\eta\Delta\beta - \beta\Delta\eta, \tag{4}$$

where

$$\Delta \mathrm{d}n/\mathrm{d}T = (\mathrm{d}n/\mathrm{d}T)_{\mathrm{TE}} - (\mathrm{d}n/\mathrm{d}T)_{\mathrm{TM}},$$

$$\Delta\beta = \beta_{\mathrm{TE}} - \beta_{\mathrm{TM}}, \quad \Delta\eta = \eta_{\mathrm{TE}} - \eta_{\mathrm{TM}}.$$

From Table.1, we find that $\eta\Delta\beta$ is two orders of magnitude larger than $\beta\Delta\eta$. Therefore it is apparent that the anisotropy in TOC of DR1/PMMA films is mainly caused by the anisotropy in thermal expansion.

3.2. The influence of poling on the TOC of DR1/PMMA film

In order to investigate how poling will affect the thermo-optic properties of the DR1/PMMA film, a corona poling is carried out in an oven by applying a voltage of 2.5kV to a discharge needle at the temperature 105°C (glass transition temperature T_{g} of DR1/PMMA) for 30min. While the electric field is maintained, cooling down to room temperature allows to freeze-in the polar orient. In order to validate the effectivity of the poling procedure, the electric-optic coefficient is measured to be γ_{33} = 3.1pm/v and γ_{31}=1.1pm/v by the improved ART technique.[16] The TOC and its anisotropy of poled films are measured by the same method as that used for the unpoled DR1/PMMA film. The experimental results are shown in Table 2.

Table 2. Film thickness d, refractive indices n and TOC $\mathrm{d}n/\mathrm{d}T$ of DR1/PMMA (with 10% dopant concentration) film for TE and TM polarization at the wavelength of 832nm, $\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$, $\Delta(\mathrm{d}n/\mathrm{d}T) = \mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T - \mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$.

	d/μm	n_{TM}	n_{TE}	Δn	TOC/(10^{-4}/°C)		
					$\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$	$\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T$	$\Delta\mathrm{d}n/\mathrm{d}T$
Unpoled DR1/PMMA film	4.7	1.50172	1.50289	0.00117	–1.493	–1.605	–0.112
Poled DR1/PMMA film	4.5	1.50955	1.50712	–0.00243	–1.394	–1.444	–0.050

After poling the DR1/PMMA film with 10% dopant concentration, it is found that with the decreasing of the film thickness, refractive indices n_{TM} and n_{TE} are reasonably increased, but the absolute value of both $\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$ and $\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T$are decreased due to the decreasing of thermal expansion β. Since DR1/PMMA is a thermoplastic polymer, which has flexible structure, and can be treated by heat-poling without changes in polymer characteristics or properties of the original polymer.[17] During the poling, the chromophores are effectively orientated (the poling orientation is perpendicular to the film plane). This procedure increases the polarizability of the TM polarization, synchronously, the refractive index of the polymer for the TM polarization increases significantly. The orientation of chromophores causes the molecular arrangement regular and compact which contribute the film thickness decreasing and the density increasing. This procedure makes both n_{TE} and n_{TM} increasing, the increasing speed of n_{TM} is greater than that of n_{TE}, as a result, the sign of the birefringence ($\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$) is reversed. The regular and compact molecular arrangement also causes the decreasing of the thermal expansion β, and therefore the absolute value of both $\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$ and $\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T$ is decreased.

The unexpected result is that the absolute value of anisotropy of TOC ($\Delta\mathrm{d}n/\mathrm{d}T$) of polymer films decreases after poling while the absolutely value of birefringence increases. It can be explained that although the absolute value of both $\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T$ and $\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$ decreases due to the decreasing of thermal expansion after poling, the decreasing value of $|\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T|$ is smaller than that of $|\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T|$ because of the significant increasing of n_{TM}.

3.3. The influence of photobleaching process on the TOC of DR1/PMMA film

The DR1/PMMA film with 10% dopant concentration is irradiated by the Hg lamp (P_{bleach}=

80mW/cm^2), which radiates the light with the wavelength region from 295nm to 450nm. In order to well understand the influence of photobleaching process on the TOC, it is necessary to measure the refractive index profile formed by photobleaching in DR1/PMMA film. The refractive index profile of DR1/PMMA film is determined by measuring the effective refractive indices of the waveguide modes with ATR configuration by using M-line method at the wavelength of 832nm. The spatial variation of refractive index inside the film is determined by using the inverse ATM method.[18] Figure 7 shows the refractive index profiles of DR1/PMMA film exposed by UV light for different times. From Fig.7, we find that the spatial variation of the refractive index of DR1/PMMA film shows a graded refractive index distribution as a function of bleaching time. This conclusion is consistent with the previously reported results for other polymer films[19] and can be well explained. It is considered that in the absorbing material film, the photons responsible for the bleaching reaction penetrate into the film gradually, the penetration depth increases with the increasing of the bleaching time until the film is full bleached and has a uniform refractive index distribution. The TOC of the full bleached film is then measured by the same method as that used in the original DR1/PMMA film. Moreover, for comparison, the TOC of pristine PMMA film is also measured. The experimental results are shown in Table 1.

The refractive index of the full bleached DR1 / PMMA for TM polarization is reduced from n=1.50172 to n=1.49201 (for TE polarization from n=1.50289 to n=1.49274), this may result from an irreversible decomposition of the chromophore accompanied by a broadening of the polymer molecular weight distribution.[19]

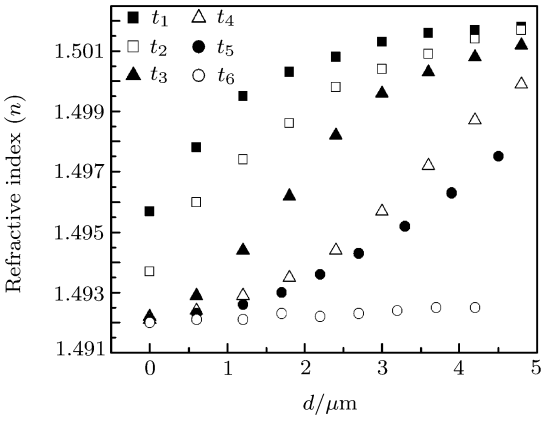


Fig.7. The spatial variation of the refractive index n inside DR1/PMMA film at the wavelength of 832nm for TM polarization photobleached by UV light for different times: t_1=5h, t_2=12h, t_3=24h, t_4=40h, t_5=60h, t_6=96h.

The absolute value of TOC (both for TE and TM polarization) of the full bleached DR1/PMMA film decreases. According to Eq.(1), this is caused by the decreasing of both refractive index and the thermal expansion coefficient. This can be explained that the dopant DR1 increases the plasticization effect of the PMMA composite and the plasticization effect increases the thermal expansion coefficient. Thus, the bleaching process makes the DR1 molecular decomposition and reduces the thermal expansion coefficient.

Decrease of the absolute value of anisotropy in TOC of the full bleached DR1/PMMA film is also observed. Table 3 shows that the anisotropy of both refractive index and thermal expansion coefficient slightly decreases when the DR1/PMMA film is full bleached. Therefore, according to the Eq.(4), reduction of the absolute value of anisotropy of the TOC is expected.

Table 3. The TOC ($\mathrm{d}n/\mathrm{d}T$), thermal expansion (β), refractive index of DR1/PMMA (with 10% dopant concentration) film and the full bleached DR1/PMMA film for both TM and TE polarizations at the wavelength of 832nm, $\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$, $\Delta\beta = \beta_{\mathrm{TE}} - \beta_{\mathrm{TM}}$.

	n_{TM}	n_{TE}	Δn	$\mathrm{d}n_{\mathrm{TM}}/\mathrm{d}T$ /(10^{-4}/°C)	$\mathrm{d}n_{\mathrm{TE}}/\mathrm{d}T$ /(10^{-4}/°C)	β_{TM} /(10^{-4}/°C)	β_{TE} /(10^{-4}/°C)	$\Delta\beta$ /(10^{-4}/°C)
DR1/PMMA (10%wt)	1.50172	1.50289	0.00117	–1.493	–1.605	2.561	2.755	0.194
Full bleached DR1/PMMA	1.49201	1.49274	0.00073	–1.312	–1.374	2.287	2.382	0.095

4. Conclusion

In general, we investigated the influence of dopant concentration, poling process and photobleaching process on the thermo-optic properties of DR1/PMMA film by using ATR configuration at the wavelengths of 832nm. To our knowledge, it is reported for the first time. The TOC of DR1/PMMA is negative and as high as the order of $10^{-4}/^{\circ}$C. The experimental results will be useful for the design of high-performance thermo-optic polymer devices.

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