

Optical loss in rod-like polymer thin films

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Optical thin films of three rod-like polymers, a rigid-rod polymer poly(p-phenylene benzobisthiazole) (PBZT), a diadamantane-substituted PBZT (DMT-PBZT) and a bicyclo[2.2.2]octane-substituted PBZT (BCO-PBZT), at different thicknesses were prepared with the solid-state coagulation process. In contrast to PBZT, DMT-PBZT and BCO-PBZT do not have a π -conjugated backbone because of their aliphatic DMT and BCO moieties. The PBZT thin films showed an out-of-plane optical attenuation coefficient (α_o) of 1300 dB cm⁻¹ at 600 nm wavelength while the α_o value of the DMT-PBZT and the BCO-PBZT thin films at 600 nm wavelength could not be determined due to their weak absorption in the visible light region. However, the in-plane optical attenuation coefficient (α_i) of the BCO-PBZT thin films was determined to be about 11.4 dB cm⁻¹ by waveguide measurement at 632 nm. By comparing the optical transmission of the PBZT thin films to that of the DMT-PBZT and the BCO-PBZT thin films, it is concluded that the optical loss in the PBZT thin films is mainly due to intrinsic absorption of the polymer. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

For the past decade, conjugated polymers have been extensively studied for their unique combination of electronic, electrical, and optical properties^{1,2}. Poly(p-phenylene benzobisthiazole)(PBZT) is a hetero-aromatic rigid-rod polymer with extended π -conjugation along the polymer backbone. Besides excellent thermal and mechanical properties³, PBZT was recently found to have interesting nonlinear optical activity^{4,5} and electrical conductivity with electrochemical doping^{6,7}. Optical thin films of PBZT were normally prepared by coagulation from its isotropic methanesulfonic acid solutions. Initial studies showed that these thin films had a third-order nonlinear optical (NLO) susceptibility ($\chi^{(3)}$) of 6×10^{-12} esu^{4,5}. Since then, the $\chi^{(3)}$ value of PBZT thin films has been increased to 4.5×10^{-10} esu along with the improvement in optical quality of these thin films^{8–11}. The state-of-the-art α_o value of the PBZT thin films is 1300 dB cm⁻¹ at 600 nm wavelength achieved by the thin films prepared using the solid-state coagulation process¹². In this process, a thin layer of an optically isotropic PBZT solution is first frozen into a transparent solid mixture to preserve the molecular dispersion of the polymer in the solvent. The solvent is then extracted from the frozen mixture without disrupting the molecular distribution of the polymer.

Despite the high $\chi^{(3)}$ value of the PBZT thin films, their state-of-the-art α_o value is still far from the 1 dB cm⁻¹ desired for practical applications. Therefore, it is in our interest to understand if and how the optical quality of the PBZT thin films can be further improved. In this study, thin films of PBZT, DMT-PBZT¹⁴ and BCO-PBZT¹⁵ were prepared at various thicknesses by the solid-state coagulation process for optical characterization. Neither the DMT-substituted nor the BCO-substituted polymers absorb visible light because of the aliphatic nature of the DMT and the

BCO moieties which break the otherwise p-conjugated PBZT backbone. Although the substituted PBZT polymers showed different optical absorption to that of the rigid-rod PBZT, they maintained the same chain rigidity and liquid crystalline characteristic of PBZT. Therefore, it is reasonable to assume that the DMT-PBZT and the BCO-PBZT have a supramolecular structure resembling that of PBZT in solid state. Comparing the optical transmission of the PBZT thin films with that of the DMT-PBZT and the BCO-PBZT thin films allows us to differentiate the optical loss in the PBZT thin films due to the intrinsic absorption of the material and that due to the scattering from the aggregated domains of rigid-rod molecules.

EXPERIMENTAL METHOD

Materials

The three rod-like polymers, PBZT, DMT-PBZT and BCO-PBZT, were obtained from the Polymer Branch, Air Force Materials Directorate. Their chemical structures are shown in *Figure 1*. The PBZT has a π -conjugated backbone and therefore its thin films show a yellowish colour. On the contrary, the films of the rigid-rod polymers substituted with the aliphatic DMT and BCO moieties appear to be colourless. All the three polymers are soluble in methanesulfonic acid (MSA). The MSA, obtained from the Aldrich Chemical Corporation, had been distilled before it was used to prepare the polymer solutions for thin film fabrication.

Thin film fabrication

In this study, thin films of the rod-like polymers were prepared from a 3 wt% MSA solution by using the solid-state coagulation process. The solution was prepared by mixing a predetermined weight of the polymer in the distilled MSA at 40°C under a dry nitrogen blanket for at least five days. The solution had been examined with a polarized optical microscope to ensure its optical isotropy

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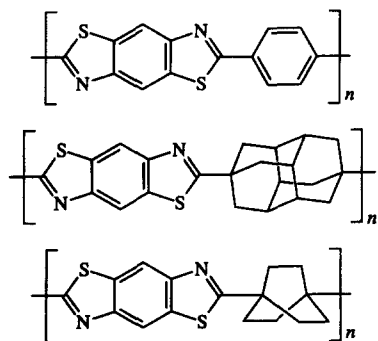


Figure 1 Chemical structures of PBZT, DMT-PBZT, and BCO-PBZT polymers

and homogeneity. In the process of thin film preparation, a thin layer of the polymer solution was first spin-coated on a silicon wafer and then plunged into a coagulation bath of acetone and dry ice at approximately -80°C . The MSA in the frozen polymer solution was subsequently extracted by the acetone at a subambient temperature. The coagulated polymer thin film was then washed in a large volume of distilled water for at least two days to remove residual MSA. The wet film was eventually mounted on a one-inch diameter glass ring and air-dried for optical evaluation. The detailed procedures for thin films fabrication by solid-state coagulation process have been reported elsewhere¹².

UV-visible spectroscopy

The thickness of the various rod-like polymer thin films was determined with a Sloan Dektak II profilometer. A Perkin Elmer UV/Vis/NIR spectrophotometer (Lambda 9) was used to measure the percent optical transmission ($T\%$) of these thin films over a wavelength ranging from 250 to 2500 nm. The $T\%$ is related to the relative optical transmission (I_t/I_o) by the equation $T\% = 100 I_t/I_o$, where I_t and I_o are the intensities of the transmitted and the incident light, respectively. For an electromagnetic wave travelling normal to a flat film in air, the relative optical transmission may be expressed as¹³

$$\frac{I_t}{I_o} = \left[1 - \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \right]^2 e^{-\alpha d} \quad (1)$$

where n_1 and n_2 are the refractive indices of air and the film, respectively, and α is the optical attenuation coefficient of the film. By using this relationship, the optical loss of the rod-like polymer thin films due to surface reflection, $(n_2 - n_1)^2/(n_2 + n_1)^2$, and that due to internal absorption and scattering, $e^{-\alpha d}$, were estimated from the intercept and the slope of the $\ln(I_t/I_o)$ versus d plot, respectively.

Waveguide

The polymer thin films prepared in this study had a thickness ranging from a few tenths of a micron to about seven microns. For the highly transparent polymer thin films, such as those of DMT-PBZT and BCO-PBZT, the α value was not readily estimated from the slope of their $\ln(I_t/I_o)$ versus d plot over the narrow thickness range. Therefore, waveguide measurements were used to determine the optical attenuation coefficient of the BCO-PBZT thin films. A coagulated BCO-PBZT thin film, after being thoroughly washed with distilled water, was laid on a silicon wafer that had a silica (SiO_2) surface layer of two microns.

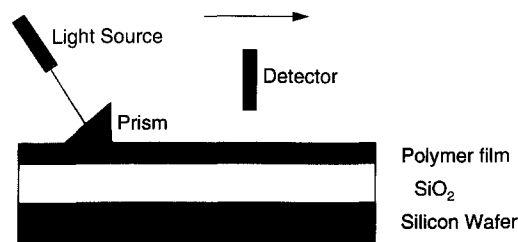


Figure 2 The schematic diagram of a polymer film optical waveguiding set-up

After the film was dried at ambient conditions, it adhered to the silicon wafer. The optical attenuation coefficient of the film was measured using out-of-plane scattering technique with the optical set-up illustrated in *Figure 2*. A laser beam ($\lambda = 632 \text{ nm}$) was coupled into the BCO-PBZT thin film with a rutile prism coupler. The optical intensity scattered from the laser beam that travelled in the BCO-PBZT thin film was monitored with a Silicon Photodetector. This optical intensity was fitted according to the Beer's law, equation (1), as a function of propagation distance of the laser beam to estimate the in-plane optical attenuation coefficient of the BCO-PBZT thin film.

RESULTS AND DISCUSSION

PBZT belongs to a class of heterocyclic-aromatic rigid-rod polymers. It is thermally intractable, because it does not melt upon heating to its thermal degradation temperature³. PBZT is soluble in strong protic acids, such as MSA, polyphosphoric acid and sulfuric acid, and concentrated PBZT solutions are nematic liquid crystalline. High-strength, high-modulus fibers and thin films have been processed from these highly anisotropic liquid crystalline solutions. However, these fibers and thin films do not have the desired optical clarity for specific applications. Therefore, optical quality PBZT thin films are normally prepared by coagulation from isotropic solutions. Many coagulation schemes were used to produce optical quality PBZT thin films. The primary approaches have been by controlling the mobility of the polymer molecules to prevent them from forming aggregates and domains that are large enough to scatter the light of interest. Our recent investigation showed that the PBZT thin films produced by the solid-state coagulation process exhibited the smallest optical attenuation coefficient.

The relative optical transmission of the PBZT, DMT-PBZT and BCO-PBZT thin films at 600 nm wavelength is shown in *Figure 3* as a function of the film thickness. Based on the slope of the $\ln(I_t/I_o)$ versus d plot, the out-of-plane optical attenuation coefficient estimated for the PBZT thin films is 1300 dB cm^{-1} . This out-of-plane optical attenuation coefficient is the smallest ever obtained for coagulated PBZT thin films, but it is still much too large compared to the desired 1 dB cm^{-1} for practical applications. The optical attenuation coefficient of the DMT-PBZT and BCO-PBZT thin films could not be determined based on the slope of the $\ln(I_t/I_o)$ versus d plot over the film thickness range. It indicates that the optical loss due to absorption and scattering in the two polymer thin films was very small.

Figure 4 shows the absorption spectra of the PBZT, DMT-PBZT and BCO-PBZT thin films prepared by the solid-state coagulation process. The PBZT absorption spectrum shows a λ_{max} around 430 nm and an absorption

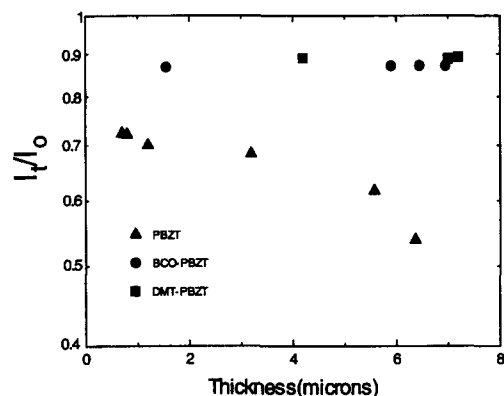


Figure 3 Relative optical transmission of PBZT, DMT-PBZT, and BCO-PBZT thin films prepared by solid-state coagulation as a function of film thickness

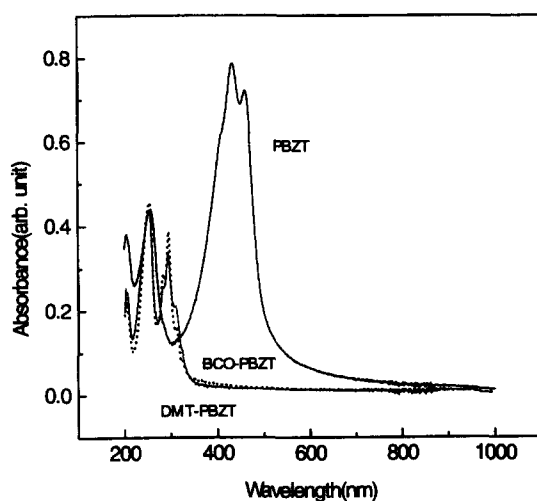


Figure 4 Absorption spectra of PBZT, DMT-PBZT, and BCO-PBZT polymers

tail that extends through the visible into the near infrared region. Therefore, there is definite absorption of PBZT at a wavelength of 600 nm. The DMT-PBZT and BCO-PBZT thin films show a λ_{\max} around 300 nm and did not show any significant absorption at a wavelength above 400 nm. The fact that the DMT-PBZT and BCO-PBZT thin films lack an absorption at wavelengths above 400 nm supports the observation in *Figure 3* that the two polymer thin films have a very low optical loss due to absorption at 600 nm wavelength. However, in order for the BCO-PBZT and DMT-PBZT thin films to have the low optical attenuation coefficient, the polymer thin films must also have a low scattering loss from the large polymer aggregates or domains.

A planar waveguide experiment was used to determine the optical attenuation coefficient of the DMT-PBZT and BCO-PBZT thin films. *Figure 5* shows the propagation of a laser beam ($\lambda = 632$ nm) in a BCO-PBZT thin film. The red propagation streak revealed in *Figure 5* indicates that the laser beam travelled about 7 mm in the BCO-PBZT thin film. It also indicates that there must be laser light scattered from the BCO-PBZT thin film in order for us to see it. The optical intensity that scattered from the travelling laser beam in the BCO-PBZT thin film is shown in *Figure 6*. The scattering intensity shows a slight oscillation that is believed to be caused by waveguide thickness variations. The optical

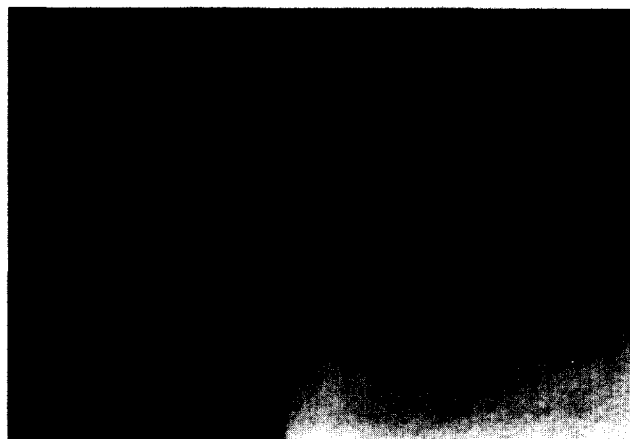


Figure 5 The streak observed on the BCO-PBZT thin film at 632 nm

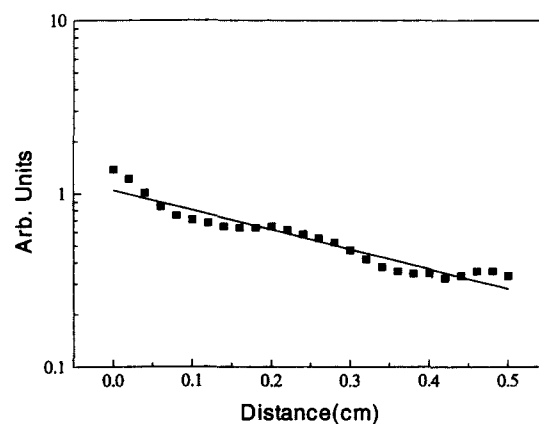


Figure 6 The detected streak intensity of BCO-PBZT polymer at the wavelength of 632 nm as a function of propagated distance

loss of the polymer thin film was estimated to be about 11.4 dB cm^{-1} from the curve of the scattering intensity *versus* propagation distance (actually ranging from 9 to 13 dB cm^{-1} along the propagation streak).

Judged from the molecular structures and liquid crystalline solution behavior of PBZT, DMT-PBZT and BCO-PBZT, the three polymers are expected to have a similar morphological arrangement in their thin films. However, the optical attenuation coefficient of the BCO-PBZT thin films (11.4 dB cm^{-1}) obtained from the waveguide experiment was found to be significantly smaller than that of the PBZT thin films (1300 dB cm^{-1}) obtained from UV/Vis/NIR absorption spectrum. Furthermore, the PBZT thin films did not show the propagation streak of the laser beam in the waveguide experiment. Two explanations may be possible. One is that the PBZT thin film had very low scattering loss and therefore the light propagation in the film could not be seen. The other is that the PBZT thin film had very high absorption loss and therefore the laser light intensity diminished rapidly in the film. Based on the experience of the waveguide measurement on the BCO-PBZT thin films, we know the first explanation is not possible for the PBZT thin films. Therefore, it is concluded that the optical loss in the PBZT thin films at 600 nm wavelength was mainly due to intrinsic absorption of the polymer. As a result, the optical clarity of PBZT thin films at 600 nm is not expected to be further improved solely by refining the processing techniques.

CONCLUSIONS

Thin films of rod-like polymers PBZT, BCO-PBZT and DMT-PBZT have been prepared by a unique solid-state coagulation process. In this process, a thin layer of an isotropic polymer solution is first frozen into a transparent solid mixture to preserve the molecular dispersion of the polymer in the solvent. The solvent is then extracted from the frozen mixture without disrupting the molecular distribution of the polymer. DMT-PBZT and BCO-PBZT have a molecular structure similar to that of PBZT, but they do not absorb visible light because their aliphatic DMT and BCO moieties break the otherwise π -conjugated polymer backbone. The solid-state-coagulated PBZT thin films showed an optical attenuation coefficient of 1300 dB cm^{-1} at 600 nm wavelength from their UV/Vis/NIR absorption spectra and the BCO-PBZT thin films showed an optical attenuation coefficient of 11.4 dB cm^{-1} at 632 nm wavelength from waveguide experiment. The results suggest that the solid-state coagulation process was capable of producing polymer thin films with minimal phase aggregation and the primary optical loss in the PBZT thin films was due to intrinsic optical absorption of the polymer.

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