Processing of optical quality rigid-rod polymer thin films

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A novel process for the fabrication of optical quality thin films of rigid-rod polymers by coagulation from an isotropic solution is reported. This process consists of the following steps: (1) extrusion or doctor-blading of an isotropic rigid-rod polymer solution into a uniform thin solution layer; (2) relaxation of the solution in an atmosphere containing the vapour of a non-solvent for an appropriate length of time; and (3) coagulation of the solution in a non-solvent bath. Thin films of rigid-rod poly(*p*-phenylene benzobisthiazole) (PBZT) thus prepared do not show the large voids or line defects commonly observed in the extruded and subsequently coagulated PBZT thin films. A processing window based on the solution thickness and relaxation duration is outlined for a 1 wt% PBZT solution in methanesulfonic acid to fabricate void-free PBZT thin films up to 6 μm in thickness at room temperature. Optical spectra and micrographs show that the PBZT thin films prepared by the current process compare favourably with those extruded and then coagulated in terms of low optical loss and fewer defects.

(Keywords: rigid-rod polymer; PBZT; optical quality)

INTRODUCTION

In recent years non-linear optics has emerged as a new frontier of scientific research for technological development of photonics by which information may be acquired, stored, processed and transmitted through photons[1,2]. Organic polymers typically have the desirable mechanical integrity, flexibility, light weight, low linear optical loss, and low temperature solution or melt processibility. Interest in highly conjugated polymers for non-linear optical applications stems from the potential combination of the typical polymer properties with the unique electronic and optical characteristics of conjugated polymers. Their π-electron delocalization can lead to large optical non-linearities and their femtosecond response time is by far the fastest compared to inorganic materials and multiple quantum wells.

Poly(*p*-phenylene benzobisthiazole) (PBZT) belongs to a class of heteroaromatic rigid-rod polymers with extended π-conjugation along the polymer backbone. It has excellent mechanical strength and thermal stability[3]. Because PBZT does not have a glass transition or melting temperature below its thermal degradation temperature, optical quality thin films of PBZT have been fabricated by coagulation from methanesulfonic acid (MSA) or polyphosphoric acid (PPA) solutions or, recently, by spin-casting from organic solvents with Lewis acids[4,5]. Over the last few years, third-order non-linear optical susceptibility, $\chi^{(3)}$, measured for PBZT thin films by degenerate four-wave mixing[6,7] or third-harmony generation techniques[8,9] showed significant increase from 6×10^{-12} to 4.5×10^{-10} esu. This increase of $\chi^{(3)}$ values is attributed to the improvement in optical quality of the PBZT thin films. Therefore, the question whether the optical quality of PBZT thin films can be further improved to show intrinsic $\chi^{(3)}$ of PBZT arises naturally.

Judging from the large $\chi^{(3)}$ value and the relatively small optical loss in waveguiding, the PBZT thin films extruded and coagulated from isotropic MSA solutions seem to have the best optical quality to date among the various PBZT thin films, although they were selected from a large number of films based on their superior optical quality[10]. Normally, the extruded and coagulated PBZT thin films show four defects characterized as large voids of $\sim20\,\mu$m, small particles of $\sim1\,\mu$m, and lines parallel to and lines transverse to the extrusion direction[11]. Those defects might significantly contribute to the optical loss (α) of the PBZT thin films resulting in a decreased figure of merit $\chi^{(3)}/\alpha$ and possibly a reduced $\chi^{(3)}$.

In the present paper, we report a novel process to fabricate optical quality rigid-rod polymer thin films. This process is derived from the extrusion and coagulation process by introducing an intermediate step of solution relaxation in an environment containing a non-solvent vapour to modify the solution morphology after extrusion so the film forming process during coagulation can be controlled. The objective is to improve the optical quality of PBZT thin films by eliminating the

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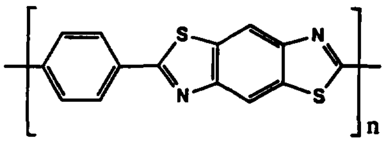

Figure 1 Molecular structure of rigid-rod polymer PBZT

above-mentioned defects in the extruded and coagulated PBZT thin films, leading to measurement of the intrinsic $\chi^{(3)}$ of PBZT.

EXPERIMENTAL

Materials and processing

Rigid-rod polymer PBZT (*Figure 1*) obtained from SRI International and MSA obtained from Aldrich Chemical Company were used in the current study. The PBZT had an intrinsic viscosity of $16\,\mathrm{dl\,g^{-1}}$ in MSA at 30°C, corresponding to a weight average molecular weight of $\sim 27\,000\,\mathrm{g\,mol^{-1}}$ (ref. 12). A solution of 1 wt% PBZT was prepared in distilled MSA by stirring at room temperature under a dry nitrogen atmosphere. The solution became homogeneous in a few days and was optically isotropic. The solution was then filtered through a sintered glass filter (25–50 μm pore size) and reserved as the stock solution for PBZT thin film fabrication.

Thin films of PBZT were prepared by the following procedure: (1) doctor-blading the PBZT solution into a thin layer on a glass microscope slide; (2) relaxing the doctor-bladed solution in a humid environment over a large beaker of water for a selected length of time; and (3) coagulating the PBZT thin film in a distilled water bath to remove MSA. The doctor-blading method was used to simulate the solution extrusion process for the sake of conserving time and material. The thickness of the films was controlled by a spacer made up of one to eight layers of Scotch® tape (*Figure 2*). Each layer of the Scotch® tape amounts to $\sim 60\,\mu$m in thickness. The relaxation in the humid environment is in accord with the film extrusion process, in which the solution was extruded on a rotating drum half immersed in a coagulation bath. The coagulated polymer thin film was mounted on a glass ring cut from a 2.54 cm diameter glass tube and allowed to air-dry. It should be noted that the PBZT thin films thus prepared result in a large reduction in film thickness but not in surface area.

Optical characterizations

An optical microscope (Nikon Metaphot) was used to examine the surface and internal defects of the PBZT thin films using both transmitted and reflected light. A u.v./vis./n.i.r. spectrophotometer (Perkin Elmer Lambda 9) was used to characterize transmission (T%) of the PBZT thin films over a wavelength range from 200 to 2500 nm. The total optical loss of the PBZT thin films, including surface reflection and internal scattering and absorption, was determined from the T% in the optical spectra as a function of wavelength and film thickness. The optical loss due to surface reflection was determined by extrapolating the total optical loss to zero film thickness. The film thickness was estimated from the interference fringes observed in the transmission optical spectrum using the equation:

$$2nd = m\lambda_m \qquad (1)$$

where n is the index of refraction, d is the film thickness, m is the interference order, and λ_m is the wavelength at which the transmission extreme is observed.

RESULTS AND DISCUSSION

Optical micrographs of ring-mounted PBZT thin films

The line defects of the extruded and then coagulated PBZT thin films, especially the die marks along the extrusion direction, clearly indicated that the viscosity of the PBZT solution was too high for the solution to relax into a smooth surface prior to coagulation. Previous coagulation studies[13] on PBZT solutions showed that a very thin surface layer of PBZT formed immediately upon coagulation on the polymer solutions. The instability of the continuing coagulation process resulted in a large scale incursion of coagulant by breaking through that thin surface layer. These observations provided reasons for us to speculate that the void formation in the extruded and coagulated PBZT thin films might be due to the severe water incursion because of surface imperfection. While reducing solution concentration was not desirable for a number of reasons, e.g. it generates too much waste solvent and the dilute solution may not have enough integrity to form a thin film during coagulation, we chose to relax the extruded PBZT solution to improve its surface structure. To be in accord with the film extrusion conditions, a doctor-bladed PBZT solution was kept over a large beaker of water until it started to show precipitation of PBZT due to absorption of moisture. The thin film coagulated from this moisture-treated solution showed opaqueness in PBZT-precipitated areas but exceptionally high transparency in some other areas. This suggested that an appropriate relaxation in a humid environment has significant effect on the optical quality of coagulated PBZT thin films.

As a base line characterization, *Figure 3* shows the optical micrograph of a ring-mounted PBZT thin film prepared by immediate coagulation of the 1 wt% PBZT solution after doctor-blading with a 240 μm spacer. The micrograph exhibits large voids ($\sim 100\,\mu$m) and small

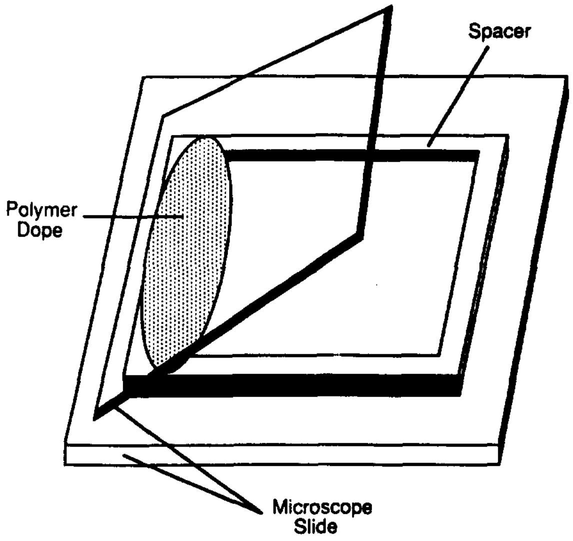

Figure 2 Thin film fabrication of PBZT by doctor-blading

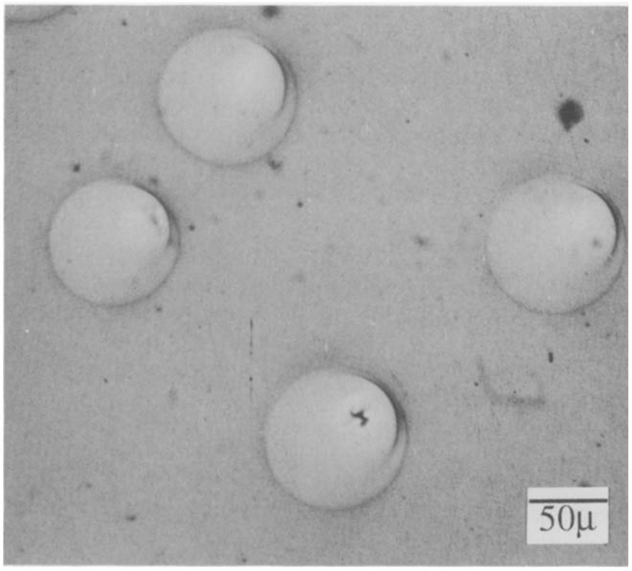

Figure 3 Structure of ring-mounted PBZT film coagulated immediately after doctor-blading

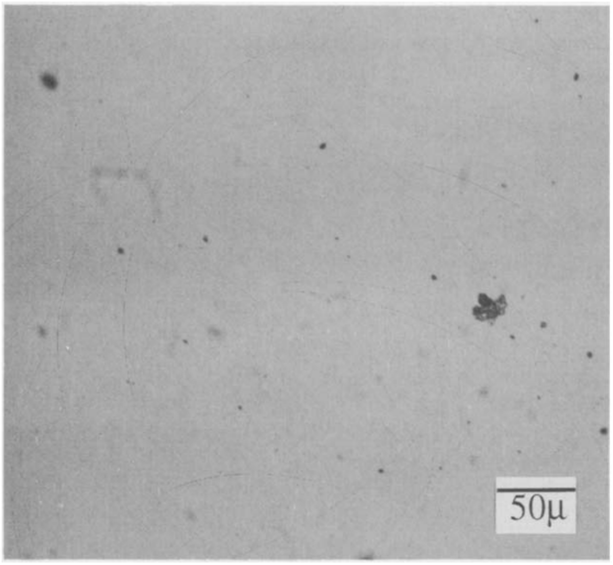

Figure 4 Structure of ring-mounted PBZT film coagulated after being relaxed in a humid environment for 5 min

particles (a few μm) but no apparent line defects. This morphology is typical for the ring-mounted PBZT thin films that were coagulated immediately after doctor-blading. The PBZT solution did show surface line marks after doctor-blading, they were probably stretched out during drying on the glass ring. The size of the voids is found to be dependent on the thickness of the doctor-bladed solution, the thicker the solution the larger the voids. Since the thickness of the ring-mounted films ($\sim$1–6 μm) is much less than the size of the voids, the voids must assume the shape of a disc. The disc-shaped voids are likely to result from the large thickness reduction during drying. The various defects found in the doctor-bladed and coagulated thin films are common to the extruded and coagulated PBZT thin films.

An optical micrograph of a ring-mounted PBZT thin film prepared from the solution which has been doctor-bladed with a spacer of 240 μm and then relaxed in the humid environment for 5 min prior to coagulation is shown in *Figure 4*. This micrograph exhibits only small particles. These particles could be impurities or gel in the PBZT polymer or dust from the air or water and may be removed through purification of the PBZT polymer or processing in a clean room. The small particles are not considered as significant as the large voids in affecting the optical quality of the PBZT thin films. An optical micrograph of the ring-mounted PBZT thin film coagulated from the solution which had been allowed to relax under a dry nitrogen atmosphere, a dry environment, for 5 min after doctor-blading is shown in *Figure 5*. This micrograph exhibits both the large voids and the small particles. It was noticed that the surface marks on the doctor-bladed solutions disappeared after relaxation in either the dry or the humid environment, suggesting that the formation of large voids in *Figure 5* was not due to surface defects. Therefore, the elimination of the large voids from the PBZT thin film shown in *Figure 4* has to do with the water absorbed in the solution.

It was initially speculated that the water absorbed in the thin PBZT solution layer might have caused PBZT molecules to aggregate into a network structure throughout the solution which provided the mechanical integrity of the solution to inhibit the formation of large voids. To verify this hypothesis, water was added to and mixed with the 1 wt% PBZT solution by a small amount (0.05 wt%) at a time to fabricate PBZT thin films. The water-mixed solutions were optically transparent indicating that if there were PBZT aggregates, they were probably too small to be detected by optical means. All the thin films coagulated immediately after doctor-blading from the water-mixed solutions exhibited large voids. Some of the films prepared from the PBZT solutions that were mixed with an excessive amount of water showed cloudiness due to the phase separation of PBZT molecules into large aggregates or domains. These results seem to suggest that the water mixed in the PBZT solutions does not promote a network structure of PBZT with enough mechanical strength to prevent the void formation. Instead, the morphology of the water-mixed

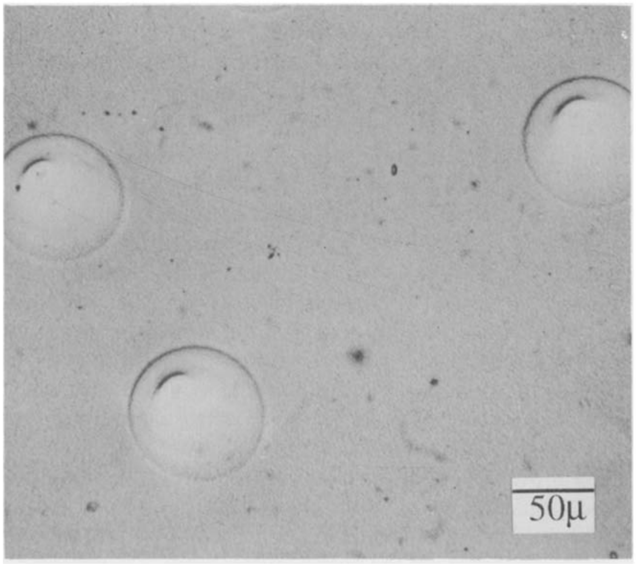

Figure 5 Structure of ring-mounted PBZT film coagulated after being relaxed in a dry environment for 5 min

Table 1 Processing window for 1 wt% PBZT solution

Film thickness (μm)	Time (min) 0	1	3	5	7
0.62	V	G	G	PS	PS
1.06	V	V	G	PPS	PS
2.12	V	V	G	G	G
2.75	V	V	V	G	G
4.66	V	V	V	G	G
5.86	V	V	V	G	G

G, good optical quality; V, voids; PS, phase-separated; PPS, partially phase-separated

PBZT solutions is more likely to consist of localized PBZT aggregates or domains and coagulant can penetrate through the boundary between these aggregates or domains.

It may be argued that the large voids in the coagulated PBZT thin films are due to evaporation of entrapped air or water molecules during the exothermic coagulation process. This argument does not seem to be valid because if the voids are originated from the evaporation of entrapped air then all the PBZT thin films, no matter if they were coagulated immediately after doctor-blading or coagulated after relaxation in the dry or the humid environment for any length of time, should exhibit the large voids. If the large voids are originated from the evaporation of water in the solution then the moisture-treated solution should have more large voids than the solution relaxed in dry nitrogen atmosphere after coagulation. It is considered now that the water absorbed by the PBZT solution during relaxation is mainly on the surface. It allows PBZT molecules to form a strong surface network which regulates the incursion of water and, thus, prevents a large scale migration of PBZT molecules during coagulation. The surface and the internal structures of the various coagulated PBZT solutions are being investigated on freeze-dried samples using a high resolution scanning electron microscope to elucidate the mechanism of void formation. The results will be reported separately.

The processing window for 1 wt% PBZT/MSA solution

The optical quality of the PBZT thin films fabricated from the 1 wt% solution by utilizing the current doctor-blading, relaxation and coagulation process is listed in *Table 1*. It covers the films prepared from solution thickness of 60–480 μm (controlled by one to eight layers of Scotch® tape) with a relaxation in the humid environment for 0–7 min. Conceptually, a rapid coagulation is preferred to fabricate optical quality PBZT thin films from isotropic solutions so the isotropic dispersion of PBZT molecules in the solutions can be preserved while a slow coagulation allows PBZT molecules to phase-separate leading to non-transparent thin films. This may well explain the reason why the PBZT thin films coagulated in the mixtures of water and MSA show phase-separated network structure and poor optical quality[14].

The relaxation duration in the humid environment and its relationship with the solution thickness are critical to the coagulation of void-free PBZT thin films. If the duration is not sufficiently long, the PBZT solution cannot escape the void formation during coagulation and if the duration is overly long, the slow coagulation due to the absorption of moisture results in phase-separated PBZT thin films with poor optical quality. In general, a thinner film requires a shorter relaxation duration and a thicker film requires a longer relaxation duration. The optical quality of the PBZT thin films shown in *Table 1* reveals the processing window for the 1 wt% PBZT solution to fabricate void-free PBZT thin films up to 6 μm at room temperature. The relaxation duration ranges from 1 to 7 min depending on the solution thickness. However, it must be emphasized that very thick PBZT films of good optical quality cannot be prepared by a coagulation process because of the inevitable slow diffusion of water into the solution at the late stage of coagulation.

Transmission u.v./vis./n.i.r. spectra of PBZT films coagulated from moisture-treated solutions

The transmission u.v./vis./n.i.r. spectrum of a ring-mounted PBZT thin film is shown in *Figure 6*. This film was coagulated from a doctor-bladed solution of ~180 μm after a moisture treatment for 5 min. The optical spectrum shows the constructive and destructive interference fringes. Based on equation (1), the film thickness can be readily calculated from the wavelengths of two consecutive transmission extremes, λ_m and λ_{m+1}, by using the equation:

$$d=\frac{\lambda_m\lambda_{m+1}}{2n(\lambda_m-\lambda_{m+1})} \tag{2}$$

if the refractive indices at the two wavelengths are equal. The extruded and then coagulated PBZT thin films showed a decrease of refractive index with increasing wavelength to an asymptotic value at ~1000 nm[7]. This value is 1.96 and 1.80, respectively, at the two principal directions with respect to the extrusion direction. For an isotropic PBZT film, a refractive index of 1.88 seems to be a reasonable estimation. It is essentially identical to the arithmetic and the geometric average of 1.96 and 1.80 and it is very close to the average (1.87) calculated from the index of ellipsoid with refractive indices of 1.96 and 1.80. Therefore, the thickness of the ring-mounted PBZT

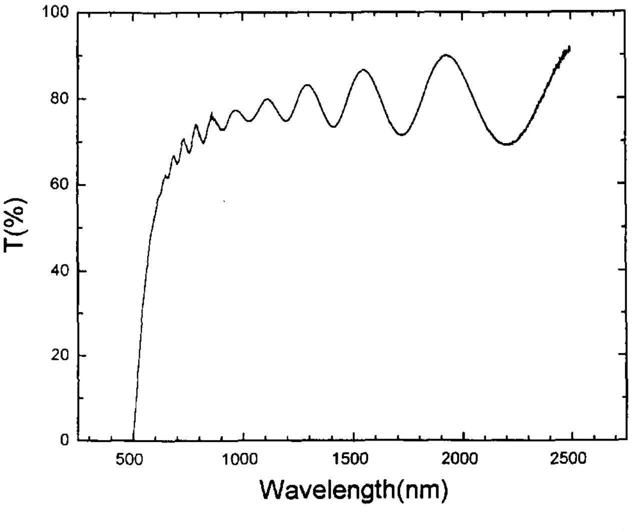

Figure 6 Optical transmission spectrum of ring-mounted PBZT film coagulated from 180 μm moisture-treated polymer solution

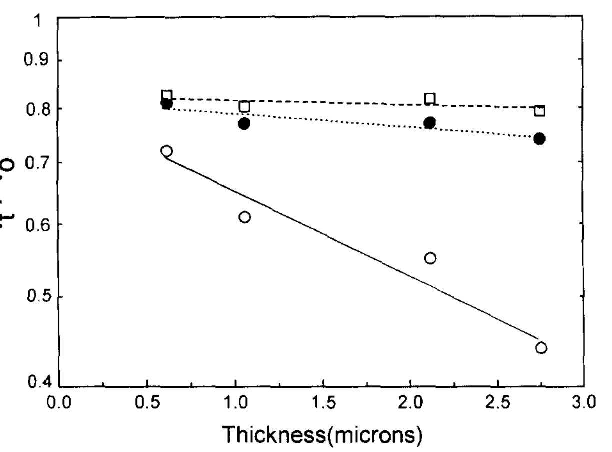

Figure 7 Plot of I_t/I_0 in logarithmic scale of the ring-mounted PBZT films in relation to film thickness and wavelength: (○) 600 nm; (●) 1000 nm; (□) 2000 nm

film shown in *Figure 6* is estimated to be 2.1 μm from equation (2). The thickness calculated for the various ring-mounted PBZT films is summarized in *Table 1*.

As a first approximation, the T% of the ring-mounted PBZT thin films in relation to the wavelength is assumed to be the medium between the two curves constructed, respectively, from the constructive and the destructive extremes of the interference fringes in the optical spectrum. The T% is related to the relative intensity I_t/I_0 of the transmitted light to the incident beam by T% = 100 I_t/I_0. The I_t/I_0 thus obtained for the PBZT thin films is shown in logarithmic scale in *Figure 7* as a function of wavelength of the light and the film thickness. It reveals that the I_t/I_0 is sensitive to film thickness only at wavelengths of <1000 nm. At longer wavelengths, the insensitivity of I_t/I_0 to film thickness indicates that the optical loss at these wavelengths is mainly due to surface reflection rather than internal absorption and scattering.

Surface reflection occurs when an electromagnetic wave crosses an interface between two media of different refractive indices. For a beam travelling normally to the interface of a free standing film in air, the fraction reflected is governed by the equation:

$$\frac{I_r}{I_0}=\frac{(n_2-n_1)^2}{(n_2+n_1)^2} \tag{3}$$

where I_r is the intensity of reflected light, and n_1 and n_2 are the refractive indices of air and the film, respectively. The optical attenuation due to the absorption of a material is described by Beer's law:

$$\frac{I_t}{I_0}=e^{-\alpha d} \tag{4}$$

where I_t is the intensity of transmitted beam, α is the optical attenuation coefficient, and d is the thickness of that material. By assuming that the doctor-bladed and then coagulated PBZT films are structurally uniform, then the intensity attenuation of a beam propagating normally through such a film can be analysed as illustrated in *Figure 8* based on equations (3) and (4). The intensity of the transmitted beam is, therefore, related to the intensity of the incident beam by the equation:

$$\frac{I_t}{I_0}=\left[1-\frac{(n_2-n_1)^2}{(n_2+n_1)^2}\right]^2 e^{-\alpha d} \tag{5}$$

It is clear from equation (5) that there exists a linear relationship between ln (I_t/I_0) and d, so the optical attenuation coefficient α can be determined from the slope of the semilogarithmic plot of ln (I_t/I_0) *versus* d. When the d in equation (5) is substituted with 0, the equation reduces to the description of the relative intensity of the transmitted beam which has the intensity of incident beam less than the optical loss due to the surface reflection at the two interfaces of the free standing film. Therefore, the optical loss due to the surface reflection of the PBZT films can be determined from the intercept of the semilogarithmic plot at zero film thickness.

By extrapolating the I/I_0 in *Figure 7* to zero film thickness, the optical loss of the PBZT films due to surface reflection is found to be 20% at 600 nm wavelength and 18% at longer wavelengths. This optical loss calculated from equation (5) is 25% at 600 nm ($n_2=2.1$) and 18% at longer wavelengths ($n_2=1.88$), in good agreement with that extrapolated from the I/I_0 in *Figure 7*. The optical attenuation coefficient of the PBZT thin films estimated from the slope of $\ln(I_t/I_0)$ *versus* d is $\sim 2000\ \mathrm{cm}^{-1}$ at 600 nm and $350\ \mathrm{cm}^{-1}$ at 1000 nm. The $350\ \mathrm{cm}^{-1}$ optical attenuation corresponds to a $1500\ \mathrm{dB\ cm}^{-1}$ optical loss. This out-of-plane optical loss is 25 to 75 times greater than the in-plane optical loss (20–$60\ \mathrm{dB\ cm}^{-1}$) measured by waveguide experiment of extruded and coagulated PBZT films[10]. The in-plane and out-of-plane structural order of the coagulated PBZT thin films is being investigated to understand the origin of the anisotropy in the optical loss.

Although the present film fabrication process is very effective in eliminating the large voids in the coagulated rigid-rod polymer thin films, the optical quality of these films is by no means ultimate because many important factors, including the types of solvent and coagulant, solution concentration, relaxation temperature and non-solvent vapour pressure, have not been optimized. It is understood that aggregates and small voids are inevitable in the coagulated rigid-rod polymers because of their rigid molecular structure. But for optical applications, their size has to be small compared to the wavelength of interest. Intuitively, the size of the small voids and even the size of the aggregates in the rigid-rod polymer thin films may be reduced by coagulating the solution at a higher concentration, because a higher solution viscosity may slow down the rate of phase separation. The relaxation conditions may be optimized

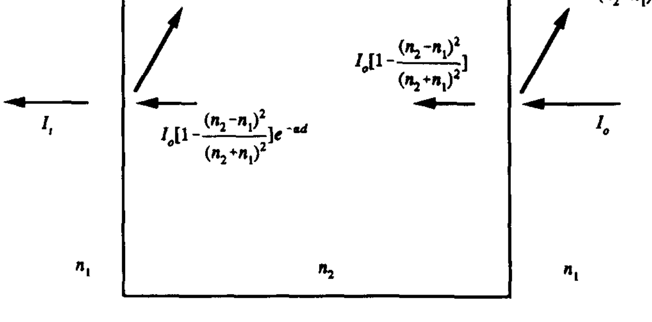

Figure 8 Intensity attenuation of a beam propagating normally through a free standing film due to surface reflection and internal absorption

by varying and controlling the type of non-solvent, temperature, non-solvent vapour pressure and relaxation duration. In fact, all these parameters may be integrated into the film extrusion process to fabricate the ultimate optical quality rigid-rod polymer thin films.

CONCLUSIONS

The optical quality of the rigid-rod PBZT thin films coagulated from an isotropic MSA solution after doctor-blading was examined. The thin films that were coagulated immediately after doctor-blading and that were coagulated after relaxing in a dry environment showed large voids and small particles while the thin films that were coagulated after relaxing in a humid environment for an appropriate duration showed only small particles. It is believed that the moisture-treated PBZT solutions form a surface network structure due to absorption of water in the humid environment. This network structure is strong enough to regulate the water incursion during coagulation and thus prevents the formation of large voids due to a large scale migration of PBZT molecules.

A processing window is outlined for a 1 wt% PBZT solution at room temperature based on solution thickness and relaxation duration in the humid environment. The best optical quality films are those prepared from a solution thickness of 60–240 μm with a relaxation time of 1–5 min. The optical loss of the PBZT thin films due to surface reflection is ~20% at 600 nm wavelength and 18% at longer wavelengths and the optical attenuation coefficient is ~2000 cm^{-1} at 600 nm wavelength and 350 cm^{-1} at 1000 nm wavelength. Rigid-rod polymer thin films with ultimate optical quality may be obtained through the optimization of the current thin film fabrication process.

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