

Solid state coagulation of rigid-rod polymer thin films

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A novel coagulation processing scheme has been developed to fabricate optical quality polymer thin films for non-linear optical applications. In this process, termed solid state coagulation, an optically isotropic polymer solution is rapidly frozen into a solid mixture to preserve the molecular dispersion of the polymer in the solvent. It is then coagulated at a cryogenic temperature in a proper coagulant to extract the frozen solvent without disrupting the molecular distribution of the polymer. Thin films of rigid-rod poly(*p*-phenylene benzobisthiazole) (PBZT) prepared by this technique showed an optical attenuation coefficient of about 300 cm^{-1} (or 1300 db cm^{-1}), significantly lower than the 990 cm^{-1} (or 4300 db cm^{-1}) obtained from the thin films prepared by the conventional solution-state coagulation process. Wide angle X-ray scattering confirmed that the domain structures in the solid-state coagulated PBZT thin films are smaller and less ordered than those in the solution-state coagulated thin films. This solid state coagulation processing scheme is particularly valuable for polymer systems, such as rigid-rod polymers, ladder polymers, crystalline polymers and polymer blends of incompatible systems, which cannot be processed with significant optical clarity by melt processing or solution casting. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Organic polymers are considered to be the most promising candidates for non-linear optical (NLO) applications because they afford a large non-linear susceptibility, a fast femtosecond response time and a high laser threshold¹. A second-order NLO material requires a non-centrosymmetrical dipole orientation of its chromophores². The dipole orientation is normally introduced by a poling process to align the dipole moments of the chromophores using a powerful electric field at or above the glass transition temperature of the host polymer. However, the oriented dipole moments tend to relax over time under processing or use conditions to a more random state, resulting in the reduction of the second-order NLO effects. Hence, the second-order NLO materials have been strategically prepared by using high glass transition temperature polymers as *host matrices* or by incorporating NLO chromophores into rigid-chain polymers as main chain or side-chain copolymers to enhance their temporal stability³. Current technical emphasis in the development of third-order NLO materials is to enhance their NLO susceptibility, which generally leads to polymers of rigid molecular structures and extended π -electron conjugation^{4,5}.

In addition to NLO activity, optical clarity at the wavelength of interest is a primary concern for practical application of an NLO material. Organic polymers for NLO applications are normally fabricated into thin films by one of three methods: melt processing, solution casting and coagulation. Processing of conjugated rigid-chain polymers, such as poly(*p*-phenylene benzobisthiazole) (PBZT), into a useful form for a specific application could be a challenge because they degrade upon heating before they melt and they undergo a phase separation transition upon increasing solution concentration^{6,7}. Optical quality thin films of conjugated rigid-chain polymers have been prepared by a coagulation process instead of melt processing or solution casting. In principle, solution-coagulated polymer thin films suffer the same phase separation problem as that encountered by solution-cast thin films, but the degree of phase separation and the domain structure in the coagulated thin films may be controlled to some extent by selecting a specific film-forming mechanism during coagulation^{8–11}.

In this paper, we present a new coagulation scheme called solid state coagulation for processing optical quality thin films of conjugated rigid-chain polymers. The film-forming mechanism consists of a rapid freezing of an optically transparent polymer solution to preserve the molecular dispersion of the polymer in the solvent and a solid state coagulation to extract the frozen solvent

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without disrupting the molecular distribution of the polymer. The optical quality and the supramolecular structure of the rigid-rod PBZT thin films prepared by this solid state coagulation process were compared with those prepared by conventional solution state coagulation.

EXPERIMENTAL

Materials

The feasibility of the solid state coagulation technique for fabricating optical quality polymer thin films was demonstrated on conjugated rigid-rod polymer PBZT. The PBZT was obtained from Stanford Research Institute, which had an intrinsic viscosity of 16 dl g^{-1} corresponding to a weight-average molecular weight of about $27\,000 \text{ g mol}^{-1}$ ¹². The solvent was methanesulfonic acid (MSA) obtained from Aldrich Chemical Corporation. It had been distilled at 120°C under reduced pressure prior to use. Solutions of PBZT were prepared at concentrations of 1, 2 and 3 wt%, respectively, by mixing a predetermined amount of PBZT with MSA at 40°C . They were stirred under dry nitrogen purge for at least 5 days, examined for optical isotropy with a polarized optical microscope and then stored in a dry nitrogen environment until being used.

Coagulation

Thin films of PBZT were prepared by both solid state and solution state coagulations. Initially, a spacer of known thickness was used to doctor blade a thin layer of PBZT solution on a silicon wafer. In the process of solution state coagulation, the doctor-bladed solution was immediately immersed in a water bath to coagulate the polymer from the liquid solution. In the process of solid state coagulation, the doctor-bladed solution was plunged into a cryogenic acetone bath to quench the solution into a frozen mixture. The temperature of the cryogenic bath was controlled with dry ice at about -80°C . The frozen MSA was then extracted from the solid mixture by the acetone at a subambient temperature. Such a process was designated solid state coagulation because the PBZT solution was in a frozen state during the film-forming process of coagulation. The coagulated polymer thin films were then washed in a large volume of distilled water for at least 2 days to remove residual MSA. After washing, the wet PBZT thin films were mounted on 1 in (2.5 cm) diameter glass rings and dried under ambient conditions for optical and morphological characterizations. PBZT thin films of various thicknesses were fabricated to determine their optical loss due to surface reflection and that due to internal absorption and scattering.

Characterization

A u.v./vis./near i.r. spectrophotometer (Perkin Elmer Lambda 9) was used to determine the percentage transmission ($T\%$) of the coagulated PBZT thin films over a wavelength range from 250 to 2500 nm. The interference fringes observed in the transmission spectrum were used to determine the film thickness by using the equation $2n_2d = m\lambda$, where n_2 is the refractive index of the film, d is the thickness of the film, m is the interference order and λ is the wavelength at which the transmission extreme is observed^{9,13}. In this study, the film thickness was determined based on an n_2 value of

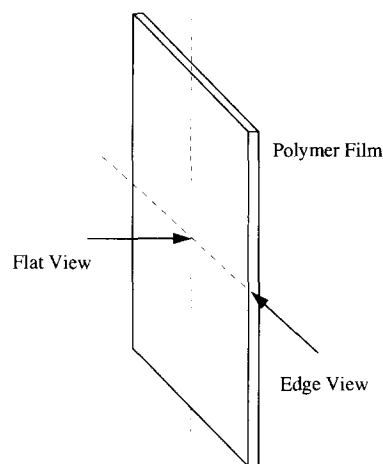


Figure 1 Position of the X-ray beam with respect to PBZT film

1.85 at wavelengths above 1000 nm ^{9,14}. The $T\%$ is related to the relative optical transmission (I_t/I_0) by $T\% = 100I_t/I_0$, where I_t and I_0 are the intensities of the transmitted and the incident wave, respectively. For an electromagnetic wave travelling normal to a free standing film in air, the relative optical transmission may be expressed as⁹

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

where n_1 is the refractive index of air and α is the optical attenuation coefficient of the film. The optical loss of the coagulated PBZT thin films due to surface reflection, $2(n_2 - n_1)^2/(n_2 + n_1)^2$, and that due to internal absorption and scattering, $e^{-\alpha d}$, were estimated, respectively, from the intercept and the slope of the $\ln(I_t/I_0)$ versus d plot.

Wide-angle X-ray scattering (WAXS) technique was used to investigate the effect of different coagulation schemes on the supramolecular structure of coagulated PBZT thin films. A $\text{CuK}\alpha$ radiation was generated from a Rigaku rotation anode unit (RU-200BVH X-ray generator) at 40 kV and 200 mA and monochromatized with graphite crystals. As shown in Figure 1, WAXS patterns of the various PBZT thin films were taken with the X-ray beam respectively in plane (edge view) and normal to the plane (flat view) of the film. The scattering patterns were recorded on photographic films using a Statton camera. The camera was evacuated to eliminate possible blackening of the films due to air scattering. The distance from the PBZT sample to the photographic film was 5.33 cm.

RESULTS AND DISCUSSION

In a coagulation process, a non-solvent diffuses into a polymer solution and mixes with the solvent. The mixing reduces the thermodynamic power of the solvent causing the polymer to precipitate. When a rigid-rod polymer precipitates, it forms a domain structure of polymer aggregates. The size of the aggregates is determined by the mobility of the rigid-rod molecules in the solution during coagulation. Intuitively, the polymer aggregation can be inhibited by a high solution viscosity or equivalently, a high polymer concentration. This concept has been applied to fabricate rigid-rod molecular

composites, i.e. composite materials of flexible-chain polymers molecularly reinforced with rigid-rod polymers, by using the most concentrated and yet optically isotropic solutions¹⁵.

It is understood that thick polymer components cannot be coagulated with significant optical clarity because the slow diffusion of nonsolvent into a thick polymer solution will drive the polymer to phase-separate into large aggregates. The polymer aggregates will scatter the light of a wavelength comparable with the size of the aggregates. Therefore, rigid-rod molecular composites are normally fabricated into fibres or thin films via a rapid coagulation process to minimize the degree of phase separation^{15,16}. In this study, PBZT thin films with a thickness from 0.7 to 8.2 μm were prepared. Since the thin films were dried on glass rings, they underwent an enormous reduction in film thickness but not in surface area.

The relative optical transmission (I_t/I_0) of the various PBZT thin films measured at 600 nm is shown in Figure 2 in logarithmic scale as a function of film thickness (d). The data for the films prepared by solution state coagulation are indicated by open symbols. Judged from the intercept at zero film thickness, the PBZT thin films are estimated to have an optical loss due to surface reflection of about 19–23%. This value agrees with those previously reported for coagulated PBZT thin films, 18% at a wavelength of 1000 nm and 20–25% at a wavelength of 600 nm⁹. The refractive index of the various PBZT thin films in the out-of-plane direction therefore may be estimated to be 1.99. This value is slightly lower than that (2.1) reported for extruded PBZT thin films at the same wavelength^{9,14}.

The optical attenuation coefficients (α) estimated from the slopes in Figure 2 for the thin films coagulated from the 1, 2 and 3 wt% solutions are 2000, 890 and 990 cm^{-1} (or 8700, 3870 and 4300 dB cm^{-1}), respectively. The difference in the α values is likely due to a different scattering loss rather than a different absorption loss in the various PBZT thin films. It implies that the domain

structures in the coagulated PBZT thin films are not identical. The better optical quality obtained from the PBZT thin films coagulated from more concentrated (i.e. the 2 and the 3 wt%) solutions may be attributed to their higher solution viscosity, which to some extent restricted the mobility, and thus the degree of phase separation, of the PBZT molecules during coagulation. However, it should be noted that PBZT molecules of high molecular weights do not require long-range mobility to become phase separated in solutions of significantly high concentrations. For example, the PBZT used in this study undergoes a phase transformation with increasing solution concentration from an optically isotropic state to a biphasic state at about 5 wt%¹⁷. This effect may counterbalance that of high solution viscosity, giving rise to the comparable optical properties of the PBZT thin films coagulated from the 2 and the 3 wt% solutions.

The concept of solid state coagulation originated from previous work on processing of rigid-rod molecular composites. It was found that when a composite solution of PBZT and nylon 6/6 in MSA was poured into liquid nitrogen, the solution immediately froze into a transparent solid mixture. The transparency suggested that the three constituents of the solution were molecularly dispersed such that there were no large domains that would scatter visible light. Therefore, a rigid-rod molecular composite may be obtained if the frozen solvent can be removed without disrupting the molecular distribution of the polymers. A two-step film-forming mechanism was established to coagulate rigid-rod molecular composites: (1) an optically isotropic composite solution is rapidly frozen into a solid mixture to preserve the molecular dispersion of the polymers in the solvent and (2) the solid mixture is coagulated in a proper non-solvent at a cryogenic temperature to extract the frozen solvent without disrupting the molecular dispersion of the polymers. This process was not pursued further for coagulating monolithic structural components because a very long time was required to coagulate a thick piece of

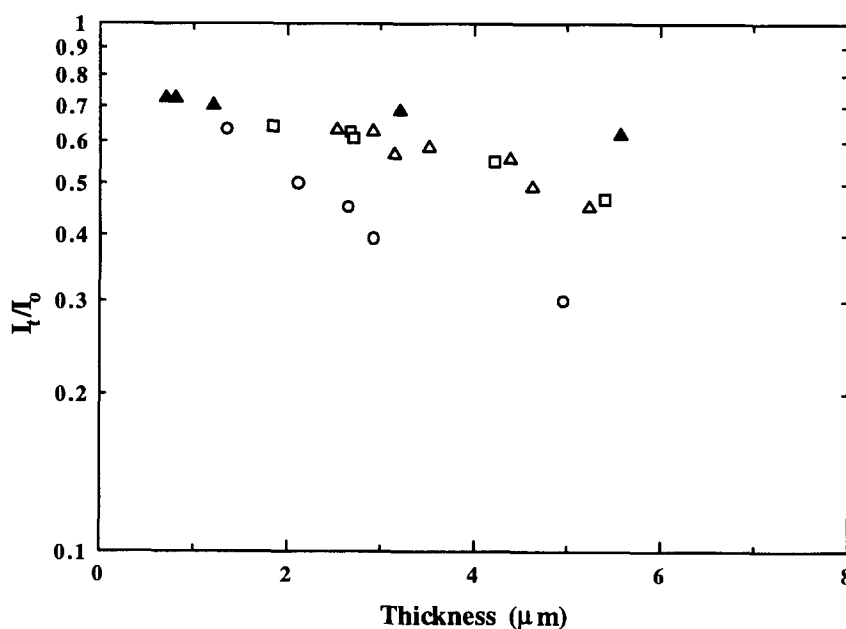


Figure 2 Relative optical transmission of PBZT thin films prepared by solution state coagulation (open symbols) and that by solid state coagulation (solid symbols) as a function of film thickness and solution concentration: (O) 1 wt%; (\square) 2 wt%; and (Δ) 3 wt%

rigid-rod molecular composite. Nonetheless, the process is feasible for fabricating polymer thin films with controlled supramolecular structures. In the current study, the two-step film-forming process was effected simultaneously by subjecting the polymer solution directly to the coagulant at a subambient temperature. In this process, the heat transfer occurs much faster than the diffusion-based mass transfer of the coagulant and the dissolved solvent.

The relative optical transmission of the PBZT thin films prepared by solid state coagulation from the 3 wt% solution is also included in *Figure 2* (solid symbols). The reflection optical loss of these thin films, estimated by extrapolating the optical loss of zero film thickness, is about 26%. The reflective index of these films is estimated to be 2.13, comparable to that of extruded PBZT thin films. The optical attenuation coefficient of the solid state coagulated PBZT thin films is estimated (from the slope of $\ln I_t/I_0$ versus d) to be 300 cm^{-1} (or 1300 dB cm^{-1}), significantly lower than that obtained from the solution state coagulated PBZT thin films (990 cm^{-1} or 4300 dB cm^{-1}). It indicates that the phase aggregation of PBZT in solid state coagulated thin films is less significant than that in solution state coagulated thin films.

WAXS revealed ordered structures in coagulated PBZT fibres and thin films¹⁸. The structural order in highly oriented PBZT fibres was reported to fit in a non-primitive, monoclinic unit cell whose lattice dimension is $a = 11.79\text{ \AA}$, $b = 3.539\text{ \AA}$, $c = 12.514\text{ \AA}$ and $\gamma = 94.0^\circ$. Based on this unit cell, the two strong equatorial reflections in the fibre diffraction pattern are from (010) and (200) planes, corresponding respectively to the face-to-face and side-by-side packing of the benzobisthiazoles of PBZT molecules. *Figure 3* shows the flat-view WAXS patterns obtained from the solution state coagulated (*Figure 3a*) and the solid state coagulated (*Figure 3b*) PBZT thin films. Both films exhibited a scattering pattern of concentric rings, indicating that their PBZT molecules formed ordered domains which were randomly oriented throughout the film with respect to the direction of the X-ray beam. *Figure 3a* appears to show a strong (010) reflection and a relatively weak (200) reflection. This is due to the molecular orientation of

PBZT in the ordered domains. It will be further discussed in the following section that most PBZT molecules are oriented with their chain axis parallel to the film surface and their molecular basal plane (i.e. benzobisthiazole plane) perpendicular to the film surface. With such an arrangement, the (200) planes that satisfy the Bragg condition to scatter the flat-view X ray are limited. The three weak reflections in *Figure 3a*, based on their d spacings, may be assigned to the first, the third, and the fifth layer line reflections of PBZT repeat units. A similar but more diffuse scattering pattern, especially the (010) reflection, was observed for the solid state coagulated thin film. It suggests that the structural order in the solid state coagulated thin films is less significant than that in the solution state coagulated thin films.

Figure 4 shows the edge-view WAXS patterns obtained from the solution state coagulated (*Figure 4a*) and the solid state coagulated (*Figure 4b*) PBZT thin films. The two scattering patterns are very similar only the one from the solid state coagulated thin films is more diffuse. Both films showed weak layer line reflections in the meridional direction, indicating their PBZT molecules in ordered domains were to some degree oriented with their chain axis parallel to the film surface. The weak reflection intensity is due to a global randomness of the PBZT chain orientation in the plane of the film. The strong and broad (200) reflection in the equatorial direction suggests that a majority of the PBZT molecules in the ordered domains is oriented with their molecular basal plane normal to the film surface. Under this condition, the (010) planes of the PBZT molecules would also be oriented normal to the film surface. However, the planes are randomly oriented with respect to the edge-view X ray giving rise to the weak (010) reflection in the meridional direction. The broad (010) reflection in the equator suggests that significant (010) planes are oriented parallel to the film surface. The stronger (010) reflections in the meridian and the equator than in the off-axis directions imply a discrete orientation of the ordered PBZT domains. This discrete orientation may be related to the process by which the ring-mounted PBZT films were fabricated. These PBZT films may be considered biaxially stretched films since they have undergone an enormous thickness reduction during drying on

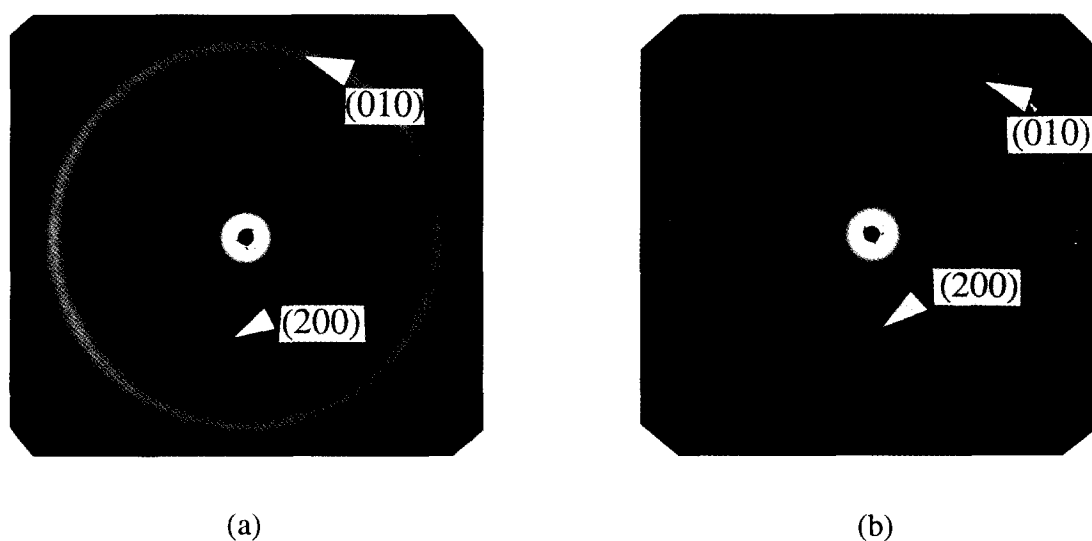


Figure 3 Flat-view WAXS patterns of (a) solution state coagulated and (b) solid state coagulated PBZT thin films

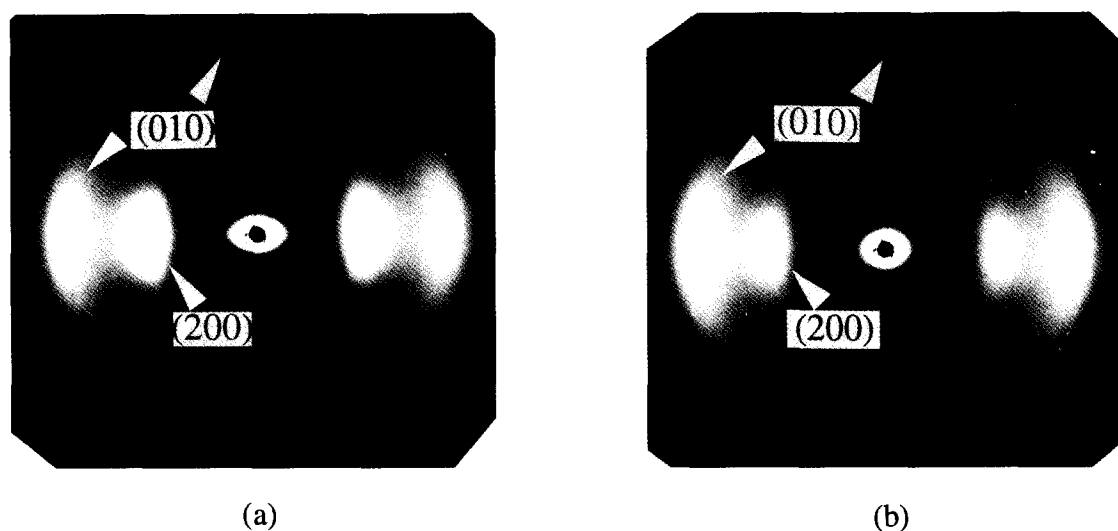


Figure 4 Edge-view WAXS patterns of (a) solution state coagulated and (b) solid state coagulated PBZT thin films

the glass rings. It might be due to this drying process that most ordered PBZT domains were stretched with their (010) planes lying either parallel or perpendicularly to the film surface. The more diffuse scattering pattern of Figure 4b compared to Figure 4a indicates that the PBZT aggregates in the solid state coagulated thin films are smaller and less ordered than those in the solution state coagulated thin films. This result supports the hypothesis that the mobility and thereby the degree of phase separation of PBZT molecules may be controlled by solid state coagulation to fabricate optical quality thin films.

Over the last few years, the optical quality of coagulated PBZT thin films has been significantly improved (from an α value of above 8600 dB cm^{-1} to the current 1300 dB cm^{-1}) and so has the third order NLO susceptibility (from 10^{-12} to 5×10^{-10} esu). However, the ultimate optical quality achievable for the rigid-rod PBZT polymer is not yet known. It is speculated that the major contribution to the optical loss α in the solid state coagulated PBZT thin films at 600 nm is from intrinsic absorption of the polymer rather than scattering loss due to the domain structure of PBZT aggregates. In order to separate the absorption loss from the scattering loss in the conjugated PBZT, its attenuation coefficient will be compared with that of nonconjugated rigid-rod polymers, such as polybenzobisthiazoles with bicyclooctane (BCO) or diadamantane (DA) bridges^{19,20}. Both BCO-PBZT and DA-PBZT have molecular structures similar to the conjugated PBZT but they do not absorb visible light because their aliphatic BCO and diadamantane moieties break the π -electron delocalization along the otherwise conjugated polymer backbone. Results of this study will be reported elsewhere.

CONCLUSIONS

Thin films of rigid-rod PBZT were prepared from MSA solutions by using both solution state and solid state coagulation processes. At the wavelength of 600 nm, the thin films prepared by solution state coagulation from 1, 2 and 3 wt% solutions showed an optical attenuation coefficient of 8700, 3870 and 4300 dB cm^{-1} , respectively. The increase of optical clarity with increasing solution

concentration to about 2 wt% is probably due to the high solution viscosity of the more concentrated solution, inhibiting the polymer mobility during coagulation to form large aggregates. The PBZT molecules in a solution whose concentration is close to the critical phase separation concentration conceivably do not require a long-range mobility to become phase-separated. This factor may counterbalance the effect of high solution viscosity and give rise to the comparable optical quality of the PBZT thin films coagulated from the 2 and the 3 wt% solutions. The PBZT thin films prepared from the 3 wt% solution by solid state coagulation showed an optical attenuation coefficient of 1300 dB cm^{-1} . This is the best optical quality ever measured for PBZT thin films in the out-of-plane direction. The WAXS pattern of the solid state coagulated thin films is similar to that of the solution state coagulated thin films but more diffuse. It suggests that the domain structure of PBZT aggregates in the solid state coagulated thin films is smaller and less ordered than that in the solution-state coagulated thin films. The flat-view WAXS patterns indicated that the coagulated PBZT films were composed of locally ordered domains which are randomly oriented in the plane of the films. The edge-view WAXS patterns showed that most PBZT molecules in the ordered domains are oriented with their chain axis parallel to the film surface and their molecular basal plane perpendicular to the film surface.

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