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Void formation in coagulated rigid-rod polymer thin films

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Large voids of about 100 μm are often found in rigid-rod polymer thin films coagulated from isotropic solutions. To understand the mechanism of this void formation so as to improve the optical quality of coagulated rigid-rod polymer thin films, surface and internal structures of various coagulated poly(*p*-phenylene benzobisthiazole) solutions were investigated on freeze-dried films by high resolution scanning electron microscopy. The films coagulated immediately from doctor-bladed solutions exhibited surface crinkles and large internal voids, while the films coagulated from the doctor-bladed solutions that had undergone a surface treatment in an atmosphere containing the vapour of a non-solvent showed a surface network structure but no large internal voids. Results support that the large voids were formed due to a large-scale coagulant incursion during coagulation. The absence of the large voids in the films coagulated from the surface-treated solutions is attributed to the surface network structure being strong enough to regulate the incursion of coagulant during the film forming process at coagulation.

(Keywords: rigid polymer; coagulation; optical quality)

INTRODUCTION

Organic polymers have been recognized as the most promising class of non-linear optical materials[1,2]. Their high laser threshold and femtosecond response time give them apparent advantages over conventional inorganic materials and multiple quantum wells. Although the molecular or the electronic structure required for producing large third-order non-linearities in organic polymers is not yet clear, it is generally believed that conjugated polymers with extended π-electron delocalization will exhibit large third-order non-linearities. However, a high degree of p orbital alignment in these polymers will also increase polymer chain rigidity and, thus, difficulties in polymer processing.

Rigid-rod polymers, such as poly(*p*-phenylene benzobisthiazole) (PBZT) and poly(*p*-phenylene benzobisoxazole) (PBO), are heterocyclic aromatic polymers with extended π-conjugation. These polymers are high in mechanical strength, thermal stability and chemical resistance, but low in solubility and processability. They usually do not show a glass transition or melting temperature below their thermal degradation temperature and can only be solution processed[3,4]. Recently, a very large third-order non-linearity, $\chi^{(3)} \sim 4.5 \times 10^{-10}$ esu, was measured for the extruded and then coagulated PBZT thin films[5]. This value is about two orders of magnitude higher than that previously reported[6]. The enhancement in $\chi^{(3)}$ was attributed to the improvement in optical quality of the PBZT films. The extruded and then coagulated PBZT thin films were not flawless; they typically showed defects characterized as large voids, small particles, lines parallel to and lines transverse to the extrusion direction[7].

Very recently, a processing scheme that is capable of coagulating void-free rigid-rod polymer thin films was developed[8]. This processing scheme involves a relaxation treatment of rigid-rod polymer solutions in an environment containing the vapour of a non-solvent prior to coagulation. In this study, we investigated the surface and the internal structures of various coagulated PBZT solutions on freeze-dried films by high resolution scanning electron microscopy to understand the mechanism of void formation. The objective was to optimize the optical quality of coagulated rigid-rod polymer thin films through elimination of the large voids.

EXPERIMENTAL

Materials and processing

Rigid-rod polymer PBZT was selected for morphological studies after coagulation from an isotropic methanesulfonic acid (MSA) solution. This PBZT, obtained from Stanford Research Institute, had an intrinsic viscosity of 16 dl g^{-1} in MSA at 30°C, corresponding to a weight average molecular weight of 27 000 g mol^{-1} (ref. 9). A 1 wt% solution was prepared by mixing a predetermined weight of PBZT in distilled MSA at room temperature under dry nitrogen atmosphere. After the

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solution was determined to be homogeneous with a polarized optical microscope, it was deaerated and filtered through a glass frit of 20–50 μm pore size using vacuum. This solution could be readily doctor-bladed into a thin layer on a glass microscope slide. To gauge the solution thickness, layers of Scotch® tape were pasted along the edges of the glass slide and used as a spacer. The doctor-bladed solution was coagulated via one of three routes: (1) immediately coagulated in distilled water; (2) coagulated in distilled water after undergoing a 5 min relaxation over a large beaker of water (a moist environment); (3) slowly coagulated in air by absorption of moisture and then washed in water.

Freeze-drying of coagulated PBZT films

Freeze-drying has been successful in removing fluids from biomaterials without apparent damage to the original structure. This process was also used in the present study to dry the coagulated PBZT films for morphological determination of the void formation mechanism in the coagulated rigid-rod polymer thin films. The coagulated wet films were first immersed in acetone for 2 h to change from a water medium to an acetone medium. The films were then soaked in benzene for 2 days to change the medium again from acetone to benzene. Eventually, the benzene-containing PBZT films were frozen in liquid nitrogen and then dried by sublimation of the benzene at −80°C under vacuum. After the films were dried for approximately 5 days, the temperature was slowly brought up to room temperature. These films were kept under vacuum until they were ready for morphological studies.

High resolution scanning electron microscopy and optical microscopy

A high resolution scanning electron microscope (SEM, Hitachi model S900) was used to examine the surface and the internal structures of the freeze-dried PBZT films. A layer of tungsten 30 Å thick was sputtered on the SEM specimens. Micrographs were taken at 2 kV from two different areas of the films, i.e. the doctor-bladed surface and the cross-sectional area of the films. These two areas were expected to have different morphologies because they were coagulated at different stages of the coagulation process. The coagulation of the PBZT solution in water was investigated *in situ* with an optical microscope (Nikon, Metaphot). A drop of the 1 wt% PBZT solution was sandwiched between a glass slide and a cover glass. The glass slide was then placed in a Petri dish of distilled water. The diffusion of water into the solution, as shown by the propagation of the coagulation front, was observed with the microscope and recorded photographically on Polaroid films.

RESULTS AND DISCUSSION

The PBZT thin films prepared by immediate coagulation of the doctor-bladed solution showed large voids. The SEM micrograph of such a void, taken from the cross-section of a freeze-fractured PBZT film, is shown in *Figure 1*. The thickness of this film is approximately 60 μm, indicating that the freeze-drying process preserved the wet film structure of PBZT. The void is cone-shaped, from a side view, with a base of about 70 μm in diameter. The tip of the cone was located near the doctor-bladed surface while the base was located near the surface that had been in contact with the glass slide. The void, from the tip to the base, extended across almost the entire film thickness. In fact, the size of the voids was found to be dependent on the thickness of the film: the thicker the film, the larger the voids. The PBZT films that were coagulated from the moisture-treated solutions and that were slowly coagulated in air did not show large voids. However, these films had the poorest optical transparency among the various films.

Figure 1 Large voids observed in the immediately coagulated PBZT films

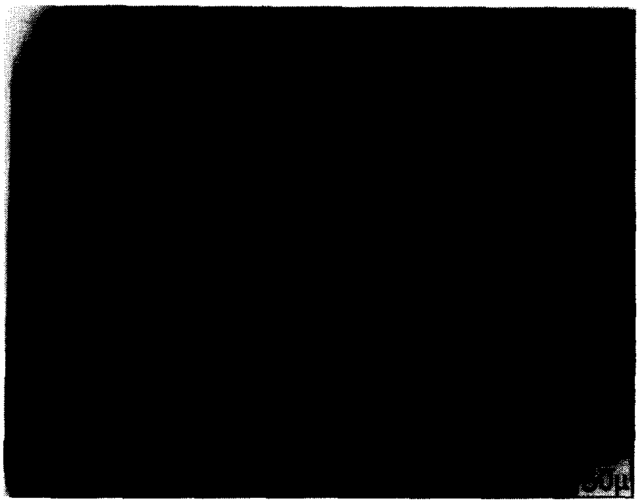

Figure 2 Coagulation progression of thick PBZT solution

The coagulation process of the PBZT solution in water was investigated *in situ* with an optical microscope. The PBZT solution was sandwiched between a glass slide and a cover glass. Once the PBZT solution was immersed in water, a coagulation front developed and began to propagate into the solution. The coagulated portion could be readily identified as a band of orange-red colour in contrast to the greenish yellow colour of the solution. The colour change was due to the deprotonation of PBZT from MSA by the infiltrated water. The progression of the coagulation was recorded on Polaroid films and is shown in *Figure 2*. It serves as an example for coagulation of very thick films. The coagulation developed a path of

Figure 3 Surface structures of various coagulated PBZT films: (a) immediately coagulated after doctor-blading; (b) moisture-treated and then coagulated in water; (c) coagulated in air and then washed in water

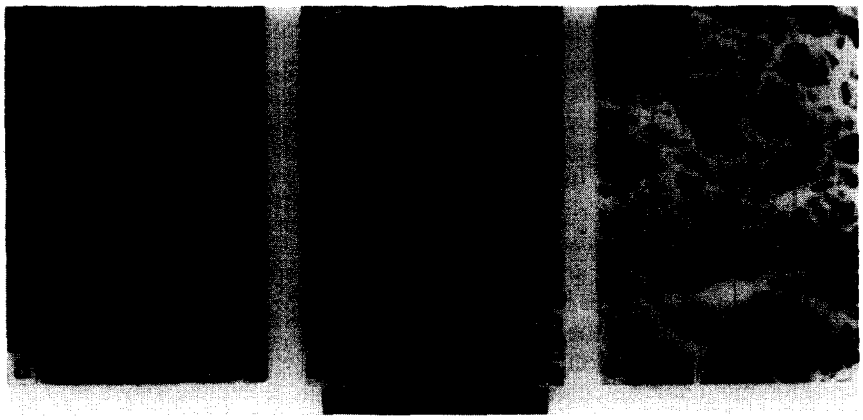

Figure 4 Internal structures of various coagulated PBZT films: (a) immediately coagulated in water; (b) moisture-treated and then coagulated in water; (c) coagulated in air and then washed in water

tear-drop pattern over a distance of about 200 μm beginning at the boundary between the solution and water. However, the first 50–100 μm of the tear-drop pattern bears a close resemblance to the cone-shaped voids found in the immediately coagulated films. The shape and the size of the tear-drop pattern suggest that the size of the large voids may increase with the thickness of the PBZT films but it reaches a limit in very thick films.

The surface structures of the three different types of coagulated PBZT films are shown in *Figure 3*. The immediately coagulated films showed crinkles on an otherwise smooth surface (*Figure 3a*). The smooth surface probably resulted from rapid coagulation of the PBZT solution in water causing the molecular dispersion of PBZT to be frozen in the films. Judging from *Figures 1* and *3a*, the tip of the cone-shaped voids must be located beneath the crinkles. The films coagulated from the moisture-treated solutions showed a fibrous network structure (*Figure 3b*). The network structure was likely caused by a low degree of phase separation of PBZT due to the moisture absorbed in the solution during the moisture treatment. The pore size of the network was approximately 200–300 nm, smaller than the wavelength of visible light, rendering a low optical loss of the film. The PBZT films coagulated in air showed a structure of large interconnected domains (*Figure 3c*). The domain structure is composed of fibrous networks, indicating that the domains resulted from further phase separation of the network structure during the prolonged, slow coagulation of PBZT in the moist environment.

The internal structures of the various coagulated PBZT films are shown in *Figure 4*. The immediately coagulated films (*Figure 4a*) and the films coagulated from moisture-treated solutions (*Figure 4b*) showed a similar internal structure of a fine network. This indicates that the internal solution morphology and the rate of coagulation were similar for the two solutions. Therefore, it may be concluded that the moisture absorbed in the moisture-treated solutions was mainly on the surface. This statement agrees with the surface network structure observed for the PBZT films coagulated from the moisture-treated solutions. The films slowly coagulated in air showed a much coarser network and their fibrils were significantly larger than those in the immediately coagulated films and the films coagulated from moisture-treated solutions. Again, the large fibrils suggest a greater degree of phase separation of PBZT in the slowly coagulated films. The low optical transparency of this type of film is probably due to the large domains and the spaces that strongly scatter light.

It is a common occurrence for large voids to form in coagulated rigid-rod polymer thin films. Two mechanisms have been proposed to explain the void formation in these films. One attributes void formation to expansion of entrapped air or moisture during the exothermic process of coagulation[10]. In the other, voids result from large-scale coagulant incursion due to the instability of the coagulation process[11]. Based on the first argument, large voids formed due to entrapped air or moisture might be eliminated once the entrapped air or moisture was removed. It was found that the PBZT films coagulated from doctor-bladed solutions that had been deaerated with high vacuum exhibited about the same amount of large voids, while the PBZT films coagulated from the doctor-bladed solutions that had been allowed to relax in a moist environment did not show large voids. These two observations suggest that a reduction in the air content in the PBZT solution will not reduce the amount of large voids and that an increase in the moisture content could actually result in the elimination of the large voids. Therefore, the void formation in the coagulated PBZT films is unlikely to be due to the entrapped air or moisture in the solution.

Previous coagulation studies on PBZT solutions indicated that a very thin layer of PBZT coagulated immediately at the boundary between the solution and coagulant when they were first in contact[11]. The coagulation process continued with coagulant diffusing through that coagulated PBZT layer. However, the instability of this coagulation process could result in the breakage of the coagulated PBZT layer and, thus, allow a large-scale incursion of coagulant at the early stage of coagulation. It is possible that the polymer solution might yield to the coagulant incursion and migrate around the coagulant towards the opposite direction of the incursion. This movement could make a crinkle on the solution surface and leave a large void in the solution. For the thin layer of PBZT solution, the coagulant penetrated through most of the solution, except for that adhering to the glass slide. The large cone-shaped voids probably resulted from a sudden stop of the coagulant as it neared the glass slide.

By comparing the surface and the internal structures of the immediately coagulated PBZT films with those of the films coagulated from the moisture-treated solutions, it was concluded that an absence of the large voids in the latter films was due to a strengthened surface structure of the moisture-treated solutions. As indicated in *Figure 2b*, this surface structure is a network of aggregated PBZT molecules resulting from a low degree of phase separation of the solution caused by absorbed moisture, which reduced the thermodynamic quality of MSA as a solvent for PBZT. The surface network structure was strong enough to maintain its integrity and regulate water incursion during the film-forming process at coagulation. Because of the low degree of phase separation, the PBZT aggregates were so small compared to the wavelength of visible light that they could not be detected by normal optical means.

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