Influence of Coagulation Bath Temperature on the Structure and Dielectric Properties of Porous Polyimide Films in Different Solvent Systems

Panpan Zhang,* Ke Zhang,* Xi Chen, Shuliang Dou, Jiupeng Zhao, and Yao Li*

**ABSTRACT:** In this work, the effect of coagulation bath temperature in different solvent systems [1,4-butyrolactone (GBL)/N,N-dimethylacetamide (DMAC)] on the structure and dielectric properties of polyimide (PI) films was investigated for the first time. The solubility parameter was introduced to explain the formation process of porous PI films. The results showed that the changed tendency of the dielectric constant versus temperature is opposite for the single-solvent system and cosolvent system. For a single DMAC and GBL solvent, the dielectric constants of the films decreased with increasing temperature. In contrast, the dielectric constants increased with the increase in temperature for the GBL/DMAC cosolvent system. Moreover, the measured porosities were applied to estimate the dielectric constants of the PI films. This showed that the porosity increased with increasing temperature for a single-solvent system, while it decreased for a cosolvent system. Scanning electron microscopy images suggested that the variation trends are derived from the different solvent systems. This study reveals the effect of coagulation bath temperature on the structure and dielectric properties of porous PI films and provides the guidance for the design and optimization of architectures for high-performance porous films.

1. INTRODUCTION

The phase-inversion process has been commonly applied to prepare a variety of asymmetric films since the development of asymmetric-type films by Loeb and Sourirajan.1−4 In the phase inversion process, an initially homogeneous polymer solution is cast onto a clean substrate, followed by soaking in a coagulation bath, leading to the formation of a thin film. With the diffusion exchange of the solvent and nonsolvent and the solidification of the phase-separation solution, the porous film is finally formed. Thus, the structures and performance of the asymmetric film are strongly controlled by kinetics and thermodynamics during the phase-separation process. The thermodynamics is associated with the phase equilibrium among components in the casting solution; this can be explained by Flory–Huggins theory,5,6 and the mutual transport and diffusion of components are responsible for kinetics.7−10

Polyimides (PIs) as a kind of film materials have attracted extensive attention because of their good gas selectivity, outstanding chemical resistance, and excellent thermal stability.11−20 Much research on the formation of porous asymmetric PI films has been published in the literature.21−32 Ren et al. studied the formation process, combined with the morphology of BTDA/TDI/MDI co-PI asymmetric films.24 Wang et al. investigated how the composition in a coagulation bath and concentration of polymer solution upon casting affected the morphology of porous PI films.20 A variety of factors have been studied, which can be used to control the morphology of porous films, such as the molecular weight for polymeric additives,25 the viscosity of casting solutions,26 and the kind of solvent or nonsolvent.19,25 However, so far, less attention has been focused on the influence of coagulation bath temperature on the morphology and performance of porous PI films.26,27 Therefore, this is the first time that the influence of coagulation bath temperature on the dielectric constant and morphology of PI films for a single-solvent and cosolvent system has been reported to further regulate the formation of porous PI films upon comprehensive understanding.

In this study, the effects of coagulation bath temperature on the dielectric constant and the morphology of PI films were...
studied. It is found that for a single and cosolvent system, the impact of coagulation temperature on the morphology and dielectric constant was different. Furthermore, the porosity was measured to estimate dielectric permittivity of the porous film. It suggests that porosity increased with increasing temperature for the single-solvent system, while it decreased with temperature for the cosolvent system. The variation trend is derived from the different influences of the temperature on the structure and morphology. Hence, we can accurately regulate the porosity and performance through controlling the coagulation temperature, which is practical and meaningful in the preparation and application of porous films.

2. EXPERIMENTAL SECTION

2.1. Raw Materials. 4,4’-diaminodiphenyl ether (ODA) and 3,3’,4,4’-benzophenone tetracarboxylic dihydride (BTDA) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. 1,4-butyrolactone (GBL, 99.0%) and N,N-dimethylacetamide (DMAC, 99.5%) were provided by Chemical Industry Development Co., Ltd and Tianjin Guangfu Fine Chemical Industry Research Institute, respectively. Deionized water was employed as a nonsolvent gelation medium (18.25 MΩ). All materials were of analytical reagent (AR) grade, which can be used without further purification.

2.2. Synthesis Process of Polyamic Acid. PI prepared from BTDA and ODA was obtained through the following procedure. First, 20 mmol ODA (4.00 g) in the DMAC/GBL solution (100/0, 75/25, 50/50, 25/75, and 0/100) was stirred for 30 min in a dry nitrogen atmosphere. Next, 20 mmol BTDA (6.44 g) was added six times, followed by vigorous stirring of the solution for 6 h. Finally, homogeneous polyamic acid (PAA) was synthesized in solution. The intrinsic viscosity of PAA is in the following order: 0/100 > 25/75 > 50/50 > 75/25 > 100/0. Here, 100/0, 75/25, 50/50, 25/75, and 0/100 are the volume ratios of the solvents (GBL/DMAC).

2.3. Preparation Routes of Porous PI Films. A wet phase-inversion process was employed to prepare PI films. The PAA solution was coated on a clean glass plate and then soaked in a coagulation bath (deionized water), which was maintained at different temperatures (0, 25, 45, and 60 °C) and kept for 3 h, forming the porous structure. Then, the opaque films were obtained by drying under vacuum conditions at 60 °C for 1.5 h. Afterward, thermal imidization was performed at 100, 200, and 300 °C for 1 h in a drying oven with circulating air. Finally, a variety of porous PI films were obtained through the experimental process described above. The thickness and density of the porous films are shown in Tables S1 and S2. Figure 1 shows the preparation routes of the porous PI films.

2.4. Examination and Characterization. The chemical structures of the films were characterized by Fourier transform infrared spectroscopy (FTIR) (Nicolet Avatar-360) and X-ray diffraction (XRD) spectroscopy (Rigaku Dmax-rB). The cross-sectional structures of the PI films were analyzed through scanning electron microscopy (SEM) equipped with FEI Quanta 200FEG. The dielectric results for the PI films were obtained using an impedance analyzer equipped with Agilent4294A. For each sample, the dielectric measurements were repeated three times. The corresponding samples were sputtered with gold electrodes at the two sides of the films. The pore structures of the PI films were studied using a high-performance automatic mercury intrusion instrument (Auto-Pore IV 9500). The test temperature was 25, and the pressure was from 1 to 30,000 pisa. The pore-size distribution parameters of the sample such as porosity and apparent density were calculated based on the volume of mercury injected into the actual sample.

3. RESULTS AND DISCUSSION

3.1. Structure of PI Films. Figure 2 displays the FTIR spectra of porous PI films obtained from different solvents. It is found that the characteristic absorption peaks of asymmetric and symmetric stretching of C=O, C–N stretching, and C=O bending appear at 719, 1372, 1716, and 1776 cm⁻¹, confirming the successful formation of all porous PI films from PAA films.

The structures of porous PI films were examined by XRD patterns, as given in Figure 3. The porous PI films exhibit a broad peak centered at about 2θ = 16.5°, which is associated
with the crystallization region in the amorphous porous PI. However, compared with the diffraction peaks of the nonporous PI film\textsuperscript{33} ($2\theta = 18.7^{\circ}$), the peaks of porous PI exhibited a slight shift, which may be attributed to the fact that the introduction of air enhances the distance between the PI molecules in porous films indirectly.

### 3.2. Morphology of Porous PI Films

SEM photographs of the films were obtained to study the influence of coagulation bath temperature on the structure and morphology of porous PI films, as displayed in Figures 4 and 5. Figure 4 displays the cross-section of the PI films with a porous structure through the single solvent (GBL or DMAC) at temperatures of 0, 25, 45, and 65 °C in a coagulation bath. As reported previously,\textsuperscript{19} a morphology with a sponge-like structure is formed in the GBL/PI/water system, whereas a large amount of macrovoids in a finger-like structure are observed in the PI/DMAC/water system. Previous studies have demonstrated that a finger-like structure was achieved typically in various systems under the strong interaction between the solvents and the nonsolvent.\textsuperscript{26,34} However, we speculated that this phenomenon is mainly originated from the diverse solubility of PAA in DMAC and GBL. The solubility parameter of DMAC (22.7 MPa$^{1/2}$) is more similar to that of PAA (20.8 MPa$^{1/2}$) compared with GBL (25.2 MPa$^{1/2}$), according to parameter data of Hildebrand solubility.\textsuperscript{19} Thus, PAA is preferred to be dissolved in DMAC than in GBL. As an excellent solvent, the molecular chains of PAA are stretched in DMAC. As a poor solvent, the molecular chains of PAA are shrunk in GBL. Therefore, the valid occupied volume of DMAC around PAA is extremely larger than that of GBL per mole of PAA molecule. As a result, a large void like a finger-like structure is formed in the PAA/DMAC film, while a small void-like sponge-like structure is obtained in PAA/GBL when DMAC/water and GBL/water phase separation happened. Moreover, the overall finger-like and sponge-like structure of films barely changed as the coagulation bath temperature increased. However, it can be noted that the inside microstructures of the films are different. As the coagulation bath temperature increases, more cracks and micropores were observed on the internal surface of sponge-like and finger-like holes for PI/GBL and PI/DMAC films, respectively. This phenomenon may be attributed to the remarkable increase in diffusion and interaction between the solvent and nonsolvent induced by the rise of coagulation bath temperature.

Figure 5 shows the cross-sectional images of the porous PI films prepared using the GBL/DMAC cosolvent with various ratios at different temperatures. Some micropores can be noticed on the surface of the holes. Moreover, the overall structures of the porous films are obviously changed with the temperature. As the coagulation temperature increases, the ratio of the finger-like structure decreased, leading to the increased amount of the sponge-like structure. In particular, only a small finger-like structure can be observed when the temperature reaches up to 60 °C, and the finger-like structure became small, as shown in Figure 5c. The remarkable change...
in the overall finger-like structures of the films originates from two main reasons. The first one is competitive diffusion in the GBL/DMAC cosolvent system. The diffusion of GBL-water can suppress the formation of a finger-like structure derived from the DMAC/water phase separation. Second, the PAA/GBL/DMAC/water phase may not have enough time to grow macrovoids such as a finger-like structure with an increase in temperature. Therefore, the macrovoid structure will not be preferred because of the insufficient liquid–liquid phase separation and the early solidification of the phase-separated solution.29

3.3. Analysis of the Dielectric Constant and Porosity. The dielectric constants of the various porous PI films were obtained in the frequency range of 50 Hz to 1 MHz at room temperature, which are displayed in Figure 6. In Figure 6a–e, the relative dielectric permittivity of the films reduced slowly with increasing frequency because of the decrease in effective dipoles. First, almost all dipoles could keep up with the varied frequency under the condition of lower frequencies. However, they began to lag behind the frequency of the electric field with increased frequency rotation, resulting in the reduction of effective dipoles.35

Figure 6f exhibits the dependence of the dielectric constants of porous PI films on coagulation bath temperature at room temperature and 10 kHz. It can be noted that the changed tendency of the dielectric constant versus temperature is opposite for the single-solvent system and cosolvent system. For the single DMAC and GBL solvent, the dielectric constants of the films decreased with increasing coagulation temperature. In contrast, the dielectric constants increased with the increase in coagulation temperature for the GBL/DMAC cosolvent system. In addition, it can be noticed that all porous PI films showed low dielectric constants, ranging from 1.6–2.8. In particular, the dielectric constant of PI porous PI films obtained from the pure DMAC solvent (65 °C) is only 1.60 at 100 Hz, which is far lower than that of pure PI films.

In order to further analyze the causes of the differences in the dielectric constants of different PI films, the pore-size distributions of several main porous films were characterized. Figure S1 shows the internal pore-size distribution of the porous films when the coagulation bath temperature is 0 and 65 °C. It can be observed that the internal pore-size distribution of several porous films is relatively wide and micropores and nanopores coexist. Moreover, for the films prepared at different coagulation bath temperatures, the internal pore-size distribution is also slightly different. Among them, when the solvent ratio (GBL/DMAC) is 75:25, the pore-size distribution changes obviously with

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Figure 6. Dielectric constant of porous PI films obtained from the GBL/DMAC cosolvent with various volume ratios: (a) 100:0, (b) 75:25, (c) 50:50, (d) 25:75, and (e) 0:100, and (f) dependence of the dielectric constants of films on coagulation bath temperature.
coagulation bath temperature. As shown in Figure S1(c1,c2), when the temperature of the coagulation bath is 0 °C, the grading phenomenon of pores in the film is not particularly obvious. However, as the temperature increases to 65 °C, the grading phenomenon of the holes becomes very obvious. This is mainly because the high temperature can inhibit the formation of the macropore structure inside the film, which is more consistent with the phenomenon observed in SEM photos in Figures 4 and 5. For a single-solvent system, the increase in porosity is probably due to the increase in the temperature on the structure and morphology, as discussed above in Figures 4 and 5. For a single-solvent system, the temperature for a single-solvent system, while it decreases with temperature for a cosolvent system. When the temperature changes from 0 to 65 °C, the porosity of the PI film obtained from a single GBL solvent increases from 31.9 to 46.0. Meanwhile, the porosity of the PI film from the GBL/DMAC cosolvent (75:25) decreases from 63.8 to 38.6. However, the porosity is the main factor that determines the dielectric constant of the porous film,\(^{36}\) and the results shown in Figure 6f can be observed, that is, for the film prepared from a single-solvent system and cosolvent system, changed tendency of the dielectric constant versus temperature is the opposite. The relationship between porosity and dielectric constant can be explained by formula 1,

\[
\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N}{3\varepsilon_0}(\alpha_e + \alpha_d)
\]

(1)

where \(\varepsilon_r\) is the relative dielectric constant, \(\varepsilon_0\) is the vacuum permittivity, \(N\) is the molecule number in unit volume, and \(\alpha_e\) and \(\alpha_d\) are the electronic and distortion polarization in the molecule, respectively. According to eq 1, porosity directly affects \(N\) and then changes the dielectric constant (\(\varepsilon_r\)) of the PI.

The opposite trend is derived from the different effects of the temperature on the structure and morphology, as discussed above in Figures 4 and 5. For a single-solvent system, the increase in porosity is probably due to the increase in the cracks and microvoids on the inside surface of the film as the temperature increases. For the cosolvent system, the decrease in porosity mainly originates from the reduction of the macropores and finger-like structure in the films with increasing temperature. Moreover, it can be observed from Table 1 that the maximum difference value of the porosity is as high as about 1–25% for the films prepared from the same solvent system at different coagulation temperatures. Hence, for the different solvent systems, we can adequately adjust the porosity through controlling the coagulation temperature, which is practical and meaningful in the preparation and application of porous films.

### 4. CONCLUSIONS

In conclusion, a series of porous PI films with various GBL/DMAC cosolvents were prepared at different coagulation bath temperatures. We speculated that the different structures of porous films mainly originated from the diverse solubility of PAA in DMAC and GBL solvents. It is found that the effects of coagulation temperature on the morphology and dielectric constant were different for the single- and component-solvent system. Moreover, it can be noted that the changed tendency of the dielectric constant versus temperature is opposite for the single-solvent system and cosolvent system. For a single DMAC and GBL solvent, the dielectric constants of the films decreased with increasing coagulation temperature. In contrast, the dielectric constants increased with increase in coagulation temperature for the GBL/DMAC cosolvent system. In addition, it suggested that porosity increased with increasing temperature for a single-solvent system, while it decreases with temperature for a component cosolvent system, which confirmed the dielectric test results indirectly. The variation trends are derived from the different influences of the temperature on the structure and morphology. Moreover, the maximum difference value of porosity is as high as about 1–25% for the same films at different coagulation temperatures. Hence, for the different systems, we can adequately adjust the porosity and dielectric performance through controlling the coagulation temperature, which is meaningful in the preparation and application of porous PI films.

### ASSOCIATED CONTENT

- Supporting Information
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04103.
  Thickness and density of the porous films, internal pore-size distribution of the porous films using an automatic mercury intrusion instrument, and pore-size distribution of the films based on the data from the statistical analysis SEM photographs using ImageJ software (PDF).

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Table 1. Porosity of Porous PI Films Obtained from Different Cosolvents and Temperatures

| PI films (GBL/DMAC) | porosity (%) |
|---------------------|--------------|
|                     | 0 °C | 25 °C | 65 °C |
| 0.100               | 67.3 | 67.8 | 68.7 |
| 75:25               | 63.8 | 61.0 | 38.6 |
| 25:75               | 66.3 | 65.5 | 62.0 |
| 100:0               | 31.9 | 35.8 | 46.0 |

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The porosities of PI films with a porous structure are given in Table 1. It suggested that porosity increased with increasing temperature for a single-solvent system, while it decreased with temperature for a cosolvent system. Change of temperature for a cosolvent system. When the temperature changes from 0 to 65 °C, the porosity of the PI film obtained from a single GBL solvent increases from 31.9 to 46.0. Meanwhile, the porosity of the PI film from the GBL/DMAC cosolvent (75:25) decreases from 63.8 to 38.6. However, the porosity is the main factor that determines the dielectric constant of the porous film, and the results shown in Figure 6f can be observed, that is, for the film prepared from a single-solvent system and cosolvent system, changed tendency of the dielectric constant versus temperature is the opposite. The relationship between porosity and dielectric constant can be explained by formula 1.

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Notes
The authors declare no competing financial interest.

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