

## Special Issue: Polymers for Microelectronics

**Guest Editors:** Dr Brian Knapp (Promerus LLC) and  
Prof. Paul A. Kohl (Georgia Institute of Technology)

### EDITORIAL

#### Polymers for Microelectronics

B. Knapp and P. A. Kohl, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41233](https://doi.org/10.1002/app.41233)

### REVIEW

#### Negative differential conductance materials for flexible electronics

A. Nogaret, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40169](https://doi.org/10.1002/app.40169)

### RESEARCH ARTICLES

#### Generic roll-to-roll compatible method for insolubilizing and stabilizing conjugated active layers based on low energy electron irradiation

M. Helgesen, J. E. Carlé, J. Helt-Hansen, A. Miller, and F. C. Krebs, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40795](https://doi.org/10.1002/app.40795)

#### Selective etching of polylactic acid in poly(styrene)-block-poly(D,L)lactide diblock copolymer for nanoscale patterning

C. Cummins, P. Mokarian-Tabari, J. D. Holmes, and M. A. Morris, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40798](https://doi.org/10.1002/app.40798)

#### Preparation and dielectric behavior of polyvinylidene fluoride composite filled with modified graphite nanoplatelet

P. Xie, Y. Li, and J. Qiu, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40229](https://doi.org/10.1002/app.40229)

#### Design of a nanostructured electromagnetic polyaniline–Keggin iron–clay composite modified electrochemical sensor for the nanomolar detection of ascorbic acid

R. V. Lilly, S. J. Devaki, R. K. Narayanan, and N. K. Sadanandhan, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40936](https://doi.org/10.1002/app.40936)

#### Synthesis and characterization of novel phosphorous-silicone-nitrogen flame retardant and evaluation of its flame retardancy for epoxy thermosets

Z.-S. Li, J.-G. Liu, T. Song, D.-X. Shen, and S.-Y. Yang, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40412](https://doi.org/10.1002/app.40412)

#### Electrical percolation behavior and electromagnetic shielding effectiveness of polyimide nanocomposites filled with carbon nanofibers

L. Nayak, T. K. Chaki, and D. Khastgir, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40914](https://doi.org/10.1002/app.40914)

#### Morphological influence of carbon modifiers on the electromagnetic shielding of their linear low density polyethylene composites

B. S. Villacorta and A. A. Ogale, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41055](https://doi.org/10.1002/app.41055)

#### Electrical and EMI shielding characterization of multiwalled carbon nanotube/polystyrene composites

V. K. Sachdev, S. Bhattacharya, K. Patel, S. K. Sharma, N. C. Mehra, and R. P. Tandon, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40201](https://doi.org/10.1002/app.40201)

#### Anomalous water absorption by microelectronic encapsulants due to hygrothermal-induced degradation

M. van Soestbergen and A. Mavinkurve, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41192](https://doi.org/10.1002/app.41192)

#### Design of cyanate ester/azomethine/ZrO<sub>2</sub> nanocomposites high-k dielectric materials by single step sol-gel approach

M. Ariraman, R. Sasi Kumar and M. Alagar, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41097](https://doi.org/10.1002/app.41097)

#### Furan/imide Diels–Alder polymers as dielectric materials

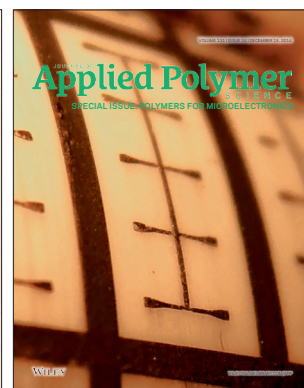
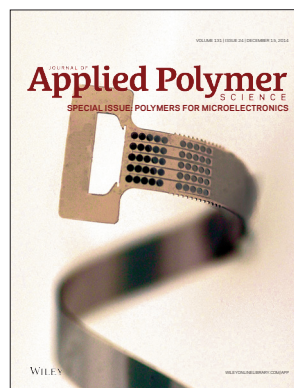
R. G. Lorenzini and G. A. Sotzing, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40179](https://doi.org/10.1002/app.40179)

#### High dielectric constant polyimide derived from 5,5'-bis[(4-amino) phenoxy]-2,2'-bipyrimidine

X. Peng, Q. Wu, S. Jiang, M. Hanif, S. Chen, and H. Hou, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40828](https://doi.org/10.1002/app.40828)

#### The influence of rigid and flexible monomers on the physical-chemical properties of polyimides

T. F. da Conceição and M. I. Felisberti, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40351](https://doi.org/10.1002/app.40351)



## Special Issue: Polymers for Microelectronics

**Guest Editors:** Dr Brian Knapp (Promerus LLC) and  
Prof. Paul A. Kohl (Georgia Institute of Technology)

### Development of polynorbornene as a structural material for microfluidics and flexible BioMEMS

A. E. Hess-Dunning, R. L. Smith, and C. A. Zorman, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40969](https://doi.org/10.1002/app.40969)

### A thin film encapsulation layer fabricated via initiated chemical vapor deposition and atomic layer deposition

B. J. Kim, D. H. Kim, S. Y. Kang, S. D. Ahn, and S. G. Im, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40974](https://doi.org/10.1002/app.40974)

### Surface relief gratings induced by pulsed laser irradiation in low glass-transition temperature azopolysiloxanes

V. Damian, E. Resmerita, I. Stoica, C. Ibanescu, L. Sacarescu, L. Rocha, and N. Hurduc, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41015](https://doi.org/10.1002/app.41015)

### Polymer-based route to ferroelectric lead strontium titanate thin films

M. Benkler, J. Hobmaier, U. Gleißner, A. Medesi, D. Hertkorn, and T. Hanemann, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40901](https://doi.org/10.1002/app.40901)

### The influence of dispersants that contain polyethylene oxide groups on the electrical resistivity of silver paste

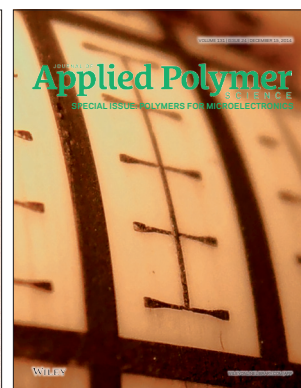
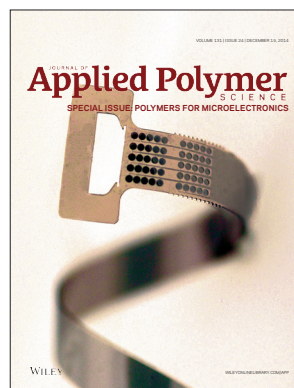
T. H. Chiang, Y.-F. Chen, Y. C. Lin, and E. Y. Chen, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41183](https://doi.org/10.1002/app.41183)

### Quantitative investigation of the adhesion strength between an SU-8 photoresist and a metal substrate by scratch tests

X. Zhang, L. Du, and M. Zhao, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.41108](https://doi.org/10.1002/app.41108)

### Thermodynamic and kinetic aspects of defectivity in directed self-assembly of cylinder-forming diblock copolymers in laterally confining thin channels

B. Kim, N. Laachi, K. T. Delaney, M. Carilli, E. J. Kramer, and G. H. Fredrickson, *J. Appl. Polym. Sci.* 2014, DOI: [10.1002/app.40790](https://doi.org/10.1002/app.40790)



## High Dielectric Constant Polyimide Derived from 5,5'-Bis[(4-amino) phenoxy]-2,2'-Bipyrimidine

Xinwen Peng, Qiong Wu, Shaohua Jiang, Muddasir Hanif, Shuiliang Chen, Haoqing Hou

Chemistry and Chemical Engineering College, Jiangxi Normal University, Nanchang Jiangxi 330022, People's Republic of China

Correspondence to: S. Jiang (E-mail: s.jiang19830913@gmail.com or shaohua.jiang@uni-bayreuth.de)

and H. Hou (E-mail: haoqing@jxnu.edu.cn)

**ABSTRACT:** Polyimides (PIs) are highly desirable materials due to their excellent physical, chemical properties, and widespread applications. In this article, a new PI containing bipyrimidine units was prepared from a newly synthesized 5,5'-bis[(4-amino) phenoxy]-2,2'-bipyrimidine and 3,3',4,4'-biphenyltetracarboxylic dianhydride via a two-step method. The as-synthesized PI not only showed high thermal stability and excellent mechanical properties, but also possessed high dielectric constant (7.1, 100 Hz) and low dielectric loss (below 0.04) in a wide frequency range from 100 Hz to  $10^5$  Hz. The obtained PI promises potential applications in electronic products. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40828.

**KEYWORDS:** dielectric properties; mechanical properties; polyimides; thermal properties

Received 16 February 2014; accepted 6 April 2014

DOI: 10.1002/app.40828

### INTRODUCTION

The mostly used high dielectric constant materials for high energy density capacitors are ceramics.<sup>1–4</sup> However, the disadvantages of percolative, fragile, and heavy nature of the ceramic materials limited their applications to some extent. To overcome such limitations, particular polymers, such as biaxially oriented polypropylene (BOPP), polyester (PET), polycarbonate (PC), polyphenylenesulfide (PPS), aromatic polyurea, polyaniline, and polyvinylidene fluoride (PVDF), have been explored as candidates for high dielectric constant materials due to their advantages of easy processing, mechanical flexibility, and low cost.<sup>5–13</sup> Among these polymers, polyaniline has dielectric constant of 1.18 at 1 MHz while BOPP, PET, PC, PPS, and aromatic polyurea possess the dielectric constant ranging from 2.2 to 4.2 at 1000 Hz.<sup>5–13</sup> Especially, PVDF and its copolymer (P(VDF-TrFE) and P(VDF-TrFE-CFE) (TrFE: trifluoroethylene; CFE: chlorofluoroethylene)) have super high dielectric constant in the range of 12–52 due to their high dipole density.<sup>5</sup> Owing to the high dielectric permittivity, PVDF has been widely used to make flexible composites by addition of fillers, such as metals, ceramics, carbon-based materials, and organic fillers<sup>13–16</sup> for applications as high dielectric constant materials.

Because of the good thermal stabilities, good mechanical properties, excellent chemical resistance, and electrical properties, aromatic polyimides (PIs) have been extensively applied in the

fields of aviation, automotive, and electronic industries.<sup>17–20</sup> However, the aromatic PIs generally show low dielectric constant in the level of 2.5–3.5,<sup>21–23</sup> and thus do not meet the requirement for use in electromechanical devices for energy conversion. For the use in such application, the dielectric permittivity of PIs should be substantially increased, and the excellent thermal, mechanical, and chemical resistance properties should be retained as well.

In this article, we describe the synthesis and characterization of a novel PI with excellent dielectric permittivity (7.1, 100 Hz) and low dielectric loss ( $<0.04$ ) in a wide frequency range from 100 Hz to  $10^5$  Hz, as well as excellent thermal and mechanical properties. The PI is synthesized from a newly synthesized 5,5'-bis[(4-amino) phenoxy]-2,2'-bipyrimidine (BAPBP) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) via a two-step method.

### EXPERIMENTAL

#### Materials

2-Chloropyrimidine and BPDA were obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Triphenylphosphine,  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ , zinc powder, liquid bromine were purchased from J&K Chemical Ltd. *N,N*-Dimethylformamide (DMF) and *N,N*-diethylacetamide (DMAc) were purified using  $\text{CaH}_2$  and then distilled under reduced pressure and then stored in the presence

Additional Supporting Information may be found in the online version of this article.

© 2014 Wiley Periodicals, Inc.

of 4 Å molecular sieves. All other reagents and solvents were obtained from China National Pharmaceutical Group Corporation.

### Synthesis of 2,2'-Bipyrimidine (2)<sup>24–28</sup>

Under N<sub>2</sub> atmosphere, the purified DMF (850 mL) was added to a round bottom flask. After dried under vacuum for 20 min, NiCl<sub>2</sub>·H<sub>2</sub>O (10.40 g, 0.044 mol), triphenylphosphine (45.90 g, 0.180 mol), and zinc powder (5.70 g, 0.088 mol) were added. With vigorous stirring for 30 min at room temperature, 2-chloropyrimidine (1, 20.00 g, 0.180 mol) was added and continuously stirred for 1 h. The mixture was reacted at 50°C for 50 h and then filtrated through Celite. The filter cake was washed by chloroform for three times and then the filtrate solution was extracted by chloroform for three times. The dark green crude solid was obtained after the chloroform evaporated under reduced pressure. The above crude product was suspended in ethylene diamine tetra acetic acid (EDTA) solution (75.00 g; NH<sub>3</sub>/water, 200 mL, 7 wt %). After stirring for 4 h and standing for 1 h, the aqueous layer was taken out and extracted with 200 mL of diethyl ether for three times. Subsequently, the diethyl ether solution was rotary evaporated and the residue was chromatographed through a silica gel column using dichloromethane as eluent. After that, the white product (2,2'-bipyrimidine) was obtained by rotary evaporation under reduced pressure. 2,2'-Bipyrimidine 11.3 g (88%), m.p. 111.7–112.3°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.47 (t, 4H, H<sub>4</sub>, H<sub>6</sub>), 9.04 (d, 2H, H<sub>5</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 121.54 (C<sub>2</sub>), 158.06 (C<sub>4</sub>, C<sub>6</sub>), 162.32 (C<sub>5</sub>). IR (KBr): 2997 (C–H, stretching), 1631, 1540, 1410, 1373 (Ar, stretching). Anal. calcd for C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>: C 60.75, H 3.82, N 35.43; found: C 60.64, H 3.88, N 35.48.

### Synthesis of 5,5'-Dibromo-2,2'-Bipyrimidine (3)<sup>24–28</sup>

2,2'-Bipyrimidine (2, 5.00 g, 0.032 mol) and bromine (5.05 g, 0.063 mol) were heated to 150°C in a hydrothermal reaction container and annealed for 15 h. The mixture was cooled and the hard solid was powdered and treated with Na<sub>2</sub>SO<sub>3</sub> solution to remove the unreacted bromine, finally basified with sodium hydroxide and filtered. The white solid product 5,5'-dibromo-2,2'-bipyrimidine was obtained by the chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>). 5,5'-Dibromo-2,2'-bipyrimidine 2.2 g (86%), m.p. 324.8–325.3°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 9.06 (s, 4 H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ): 121.55 (C<sub>5</sub>), 158.85 (C<sub>4</sub>), 159.70 (C<sub>2</sub>); IR (KBr): 3018 (C–H, stretching), 1542, 1526, 1412, 1382 (Ar, stretching), 642 (C–Br, stretch). Anal. calcd for C<sub>8</sub>H<sub>4</sub>N<sub>4</sub>Br<sub>2</sub>: C 30.42, H 1.28, N 17.73, Br 50.57; found: C 30.38, H 1.27, N 17.75, Br 50.60.

### Synthesis of 5,5'-Bis[(4-acetylamino) phenoxy]-2,2'-Bipyrimidine (5)

4-Acetaminophenol (4, 7.25 g, 0.048 mol) and 5,5'-dibromo-2,2'-bipyrimidine (3, 6.32 g, 0.02 mol) were dissolved in 150 mL of DMF. Anhydrous K<sub>2</sub>CO<sub>3</sub> (2.73 g, 0.02 mol) was added to the solution, and the mixture was refluxed at 140°C for 10 h. After cooling to room temperature, the mixture was poured into 5 wt % sodium hydroxide solution, and stirred for 2 h. The solid was filtered, washed repeatedly with distilled water. The white crystals of 5,5'-bis[(4-acetamin)phenoxy]-2,2'-bipyrimidine was recrystallized from DMF/ethanol. 5,5'-Bis[(4-acetamin)phenoxy]-2,2'-bipyrimidine 8.12 g (89%), m.p. 209.5–

210.3°C. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ): 2.06 (s, 6H), 7.22 (d, 4H), 7.69 (d, 4H), 8.69 (s, 4H), 10.52 (s, 2H). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ): 24.20 (CH<sub>3</sub>–C), 111.16 (C<sub>4'</sub>), 114.03 (C<sub>2'</sub>), 116.89 (C<sub>3'</sub>), 120.13 (C<sub>4</sub>), 121.26 (C<sub>5</sub>), 137.02 (C<sub>1'</sub>), 147.15 (C<sub>2</sub>), 168.73 (C=O). FTIR (KBr): 3418 (N–H, stretching), 3063 (C–H, stretching), 1666 (C=O, stretching), 1611, 1551, 1503, 1419 (Ar, stretching). Anal. calcd for C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C 63.15, H 4.42, N 18.41, O 14.02; found: C 63.13, H 4.43, 18.39, O 14.05.

### Synthesis of 5,5'-Bis [(4-amino) phenoxy]-2,2'-Bipyrimidine (6)

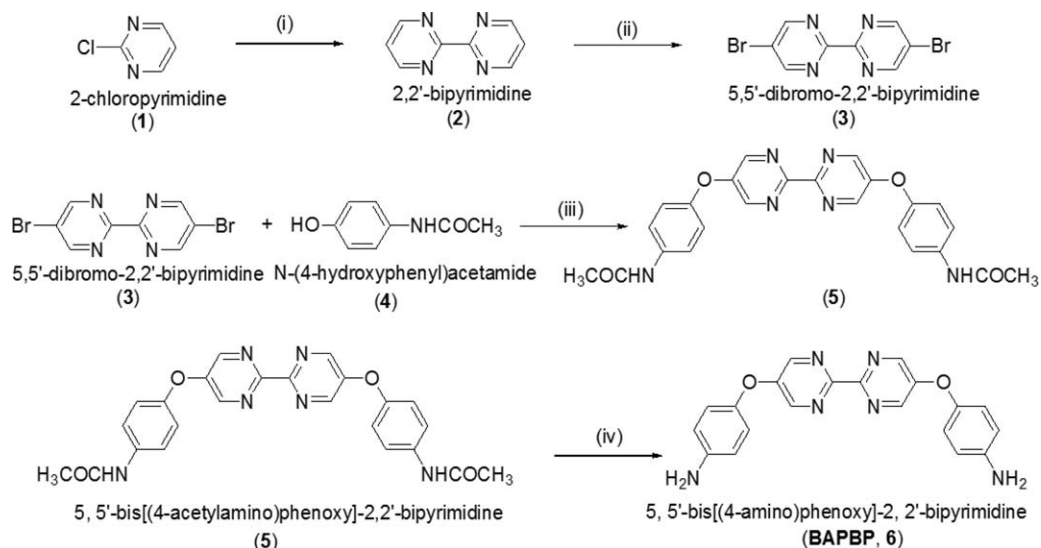
5,5'-Bis[(4-acetylamino)phenoxy]-2,2'-bipyrimidine (5, 9.12 g, 0.02 mol) was added to 20 wt % sulfuric acid solution, and heated at 80°C for 8 h. After cooling, pH of solution was adjusted to 7.0 with ammonia water. The precipitated solid was filtered, and then recrystallized from DMF/ethanol. After dried in vacuum at 60°C for 12 h, the white solid product 5,5'-bis [(4-amino) phenoxy]-2,2'-bipyrimidine (BAPBP) was obtained. 5,5'-Bis [(4-amino) phenoxy]-2,2'-bipyrimidine 32 g (85%), m.p. 298–299°C. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, δ): 5.16 (s, 4H), 6.65 (d, 4H), 6.96 (d, 4H), 8.56 (s, 4H). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ): 115.40 (C<sub>3'</sub>), 121.16 (C<sub>2'</sub>), 144.56 (C<sub>4</sub>), 146.01 (C<sub>4'</sub>), 147.01 (C<sub>1'</sub>), 153.50 (C<sub>5</sub>), 156.33 (C<sub>2</sub>). FTIR (KBr): 3446, 3333 (N–H, stretching), 1627, 1575, 1546, 1507 (Ar, stretching). Anal. calcd for C<sub>20</sub>H<sub>16</sub>N<sub>6</sub>O<sub>2</sub>: C 64.51, H 4.33, N 22.57, O 8.59; found: C 64.46, H 4.31, N 22.58, O 8.66.

### Preparation of Polyimide Containing Bipyrimidine (PI, 9)

PI containing bipyrimidine units was prepared from the diamine (BAPBP, 6) and biphenyl dianhydride (BPDA, 7) via a two-step method. In a round bottom flask, BAPBP (4.14 g, 0.01 mol) and BPDA (2.94 g, 0.01 mol) were added to 63.7 g of DMAc and the mixture was reacted for 12 h at room temperature. The resulting polyamic acid (PAA, 8) solution with 10 wt % was diluted into 5 wt % with DMAc and casted into PAA films. The PAA films was imidized into PI (9) in a high-temperature furnace according to the following protocol: (1) heating to 160°C at a rate of 10°C/min and annealing at 160°C for 2 h to remove the residual solvent, (2) heating at a rate of 10°C/min and annealing at 250°C for 15 min, (3) heating at a rate of 5°C/min and annealing at 350°C for 2 h to complete the imidization process.

### Measurements

Proton and carbon (<sup>1</sup>H- and <sup>13</sup>C-NMR) nuclear magnetic resonance spectra were measured at 400 MHz and 10<sup>5</sup> Hz, respectively, on a Bruker Avance-400 spectrometers. FTIR spectra were obtained with Perkin–Elmer SP one FTIR. Elemental analyses were determined by a Perkin–Elmer model 2400 CHN analyses. The inherent viscosities were measured (Ubbelohde viscometer) in DMAc at 25°C. Thermal gravimetric analysis (TGA) was performed with ~6–8 mg film samples with a Perkin–Elmer Pyris 1 TGA in nitrogen (40 cm<sup>3</sup>/min) at a heating rate of 10°C/min. A Perkin–Elmer Diamond DMA instrument was used to determine the glass transition temperatures. During the test, a load of 10 g (stress, 0.125 MPa) and a heating rate of 10°C/min in air were applied. Tensile tests of polymer films were performed using SANS CMT8012 (Shenzhen, China) instrument at 5 mm/



**Figure 1.** Synthesis of BAPBP. The reagents and conditions are described as follows: (i)  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ , Zn powder, RT, 30 min; add substrate, 1 h at RT, heating to  $50^\circ\text{C}$  for 50 h; (ii)  $\text{Br}_2$  (liquid),  $150^\circ\text{C}$ , 15 h; (iii)  $\text{K}_2\text{CO}_3$ , DMF,  $140^\circ\text{C}$  for 10 h; (iv) 20 wt %  $\text{H}_2\text{SO}_4$ ,  $80^\circ\text{C}$  for 8 h.

min on strips (0.5 cm wide, 2 cm long, and about 0.05 mm thick). The dielectric properties were measured on an HP 4276A LCR electrometer at different frequencies.

## RESULTS AND DISCUSSION

### Synthesis of 5,5'-Bis [(4-amino)]-2,2'-Bipyrimidine

Figure 1 shows the preparation of BAPBP. The synthesis process includes four steps. Firstly, the 2-chloropyrimidine (1) undergoes catalytic ( $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ , Zn powder) homo-coupling to give 2,2'-bipyrimidine (2), which is brominated in the second step using liquid  $\text{Br}_2$  to give 5,5'-dibromo-2,2'-bipyrimidine (3). In the third step, 4-acetaminophenol (4) was reacted with 5,5'-dibromo-2,2'-bipyrimidine (3) in DMF to provide 5,5'-bis[(4-acetylamino)phenoxy]-2,2'-bipyrimidine (5). In the fourth step, 5,5'-bis[(4-acetylamino)phenoxy]-2,2'-bipyrimidine (5) undergoes hydrolysis reaction under mild acidic conditions to provide the diamine monomer (BAPBP, 6). All the molecules were characterized by the elemental analysis, FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopic techniques and complete data is presented in the experimental section. The  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra of important compounds (5) and (6) are given in the Supporting Information (Figures S1–S4). Detailed assignments of protons and carbons are given in the figures, confirming the molecular structure.

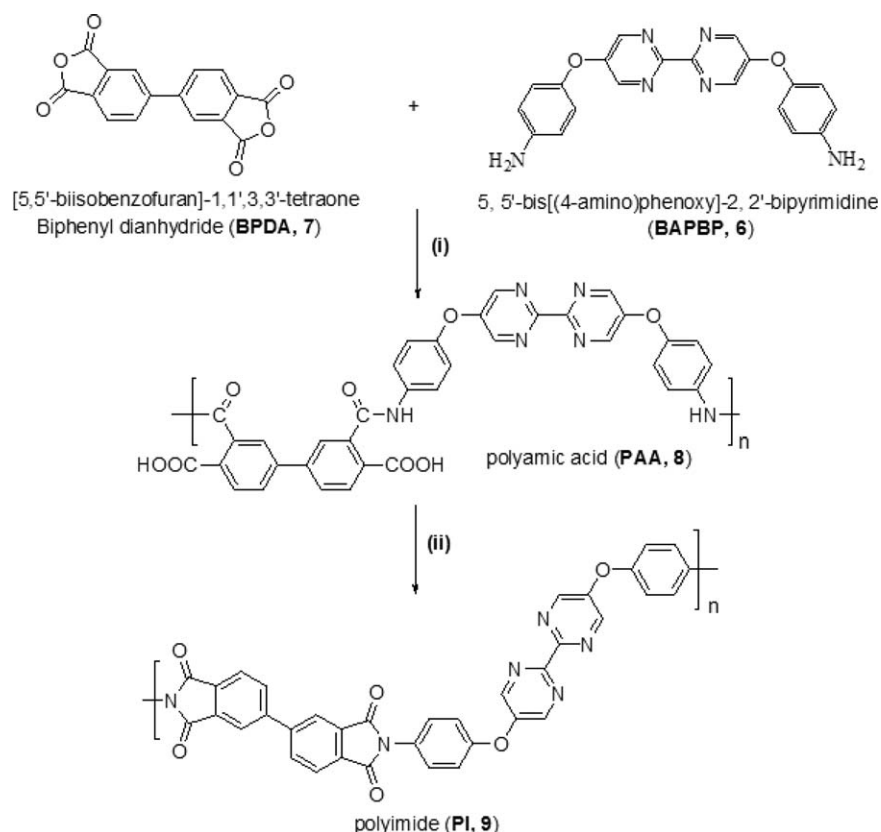
### Polymerization

Figure 2 shows the synthesis of PI. The novel PI (9, Figure 2) was prepared by reacting the BAPBP (6) and BPDA (7) via a two-step method. The mixture was allowed to react in the solvent DMAc for 12 h at room temperature and the as-synthesized PI precursor solution (PAA, 8) was used to prepare PI thin films by solution casting and heating process for the imidization. The inherent viscosity of the precursor (PAA, 8) is 1.5 dL/g. The high intrinsic viscosity corresponds to a high molecular weight, which is helpful for making high performance PI films with good mechanical properties. Figure 3 is the FTIR

spectra of the PAA and PI. The characteristic peaks of PAA appears at the big absorption bands from  $2500$  to  $3600\text{ cm}^{-1}$  ( $\text{O-H}$  in the group  $-\text{COOH}$  and  $\text{N-H}$  in the group  $-\text{CONH-}$ ), at  $1708\text{ cm}^{-1}$  ( $\text{C=O}$  stretching in the group  $-\text{COOH}$ ),  $1660\text{ cm}^{-1}$  (amide I) and  $1546\text{ cm}^{-1}$  (amide II). After imidization, the above characteristic peaks of PAA disappear completely, and new absorption peaks of PI appear at  $1774$  and  $1720\text{ cm}^{-1}$  (typical of imide carbonyl asymmetric and symmetric stretching),  $1374\text{ cm}^{-1}$  ( $\text{C-N}$  stretching),  $1117$  and  $740\text{ cm}^{-1}$  (imide ring deformation), which confirms the complete conversion (imidization) from PAA to PI.

### Dielectric Properties

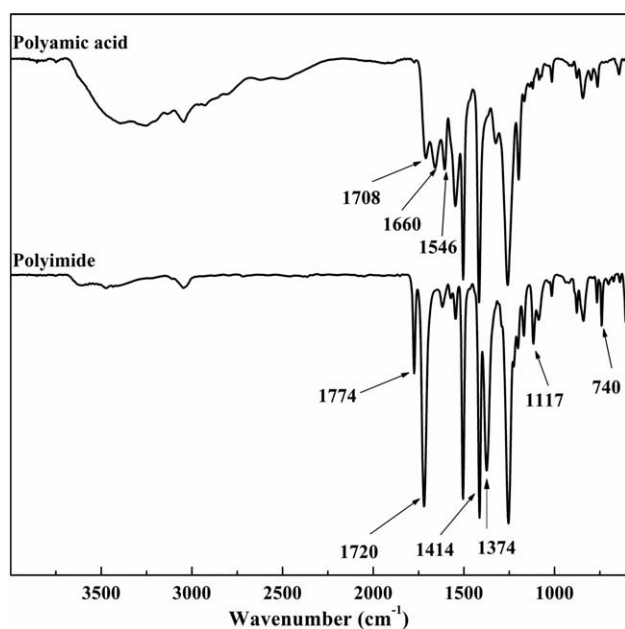
Depending on the exact chemical structure, PIs have different dielectric constant. As reported by Lee et al.,<sup>23</sup> PIs based on PMDA-ODA, BPDA-ODA, and 6FDA-ODA have dielectric constants of 2.95, 3.10, and 2.78 at 1000 Hz, respectively. In our studies, the prepared PI based on bipyrimidine-contained diamines shows much higher dielectric constant (7.12–6.71, 100–100,000 Hz, Figure 4). In the meantime, quite low dielectric loss (below 0.04, Figure 4) with frequency ranging from 100 Hz to  $10^5$  Hz was also observed from the bipyrimidine-contained PI. The high dielectric constant originates from the chemical structure, and the strong polarity of nitrogen atoms. It is well known that the dielectric constant of a polymer is dependent upon the ability of the polarizable units. There are many bipyrimidine units in the PI molecule and in every bipyrimidine unit there are four lone electron pairs in a conjugated system, which are provided by four nitrogen atoms of two pyrimidine rings. Such impressive dielectric performance was related to strong polarity of nitrogen atoms and the high electron mobility. When a higher frequency up to  $10^5$  Hz was applied, the dielectric constant of the PI presents a small decrease but still at a high level. Such special dielectric properties of PI-containing bipyrimidine is due to the electron hopping among the imide rings, benzene rings, and pyrimidine rings.<sup>29,30</sup>



**Figure 2.** Synthesis of PI. The reagents and conditions are described as follows: (i) DMAc, room temperature for 12 h; (ii) heating to 160°C at a rate of 10°C/min, annealing for 2 h to remove the residual solvent, then heating at a rate of 10°C/min and annealing at 250°C for 15 min, finally heating at a rate of 5°C/min and annealing at 350°C for 2 h.

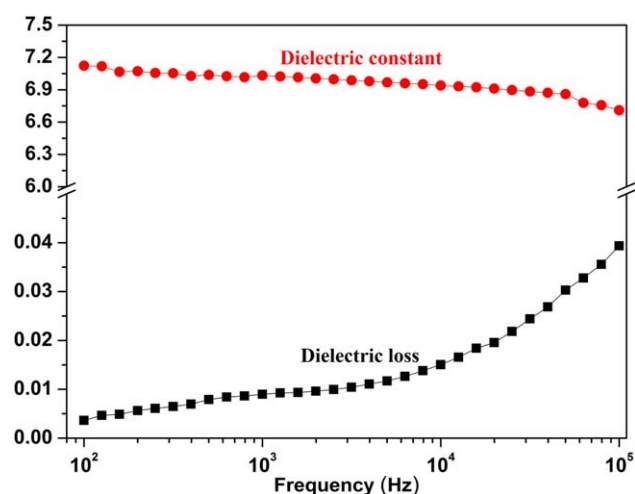
### Thermal Properties

The thermal properties of the PIs were investigated by TGA (Figure 5) and dynamic mechanical analysis (DMA, Figure 6).



**Figure 3.** FTIR spectra of the PAA and the PI.

The thermal stability of the PI can be evaluated from TGA measurements under nitrogen atmosphere, which showed a high onset decomposition temperature,  $T_d = 506^\circ\text{C}$ , 5% weight loss at 498°C, and 10% weight loss at 542°C. The char yield of the PI was 56% at 800°C under nitrogen atmosphere. The PI exhibited a high glass transition temperature ( $T_g = 291^\circ\text{C}$ , Figure 6). The incorporation of rigid bipyrimidine units into the



**Figure 4.** Dielectric properties of the synthesized PI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

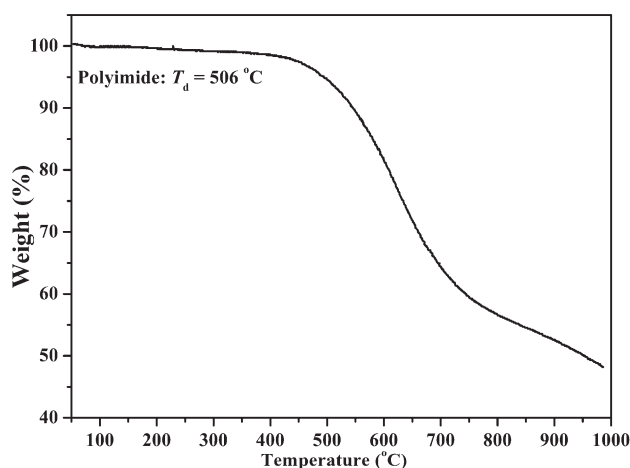


Figure 5. TGA curves of the PI at a scan rate of 10°C/min.

polymer backbone and the strong intermolecular interaction can be attributed for the high  $T_g$  and excellent thermal stability.

### Mechanical Properties

Stress–strain curves of the PI film are shown in Figure 7. The PIs can be processed into transparent, flexible, and tough films. The four stress–strain curves with similar mechanical strength and strain demonstrate that the prepared PI film is very homogeneous without defects inside. The PI has a tensile strength of 200 MPa and an elongation at break of 20%. We believe that the multiple ether bonds and the strong polarity of nitrogen atoms, present in the novel PI macromolecule, are respectively responsible for the good flexibility and excellent mechanical properties.

### CONCLUSIONS

A novel bipyrimidine-contained PI was successfully synthesized via a two-step method with a newly synthesized diamine monomer (BAPBP) and BPDA. The molecular structures of the synthesized monomer and polymer were confirmed by NMR, FTIR, and elemental analyses. The prepared PI had high thermal stability with decomposition temperature of up to 506°C

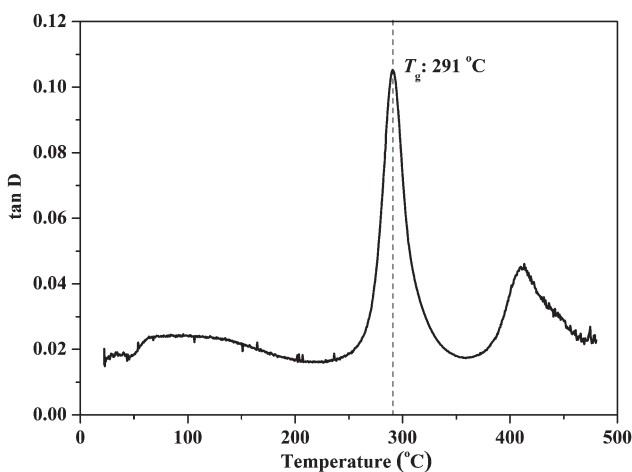


Figure 6. Dynamic mechanical analysis curves at a heating rate of 5 °C/min.

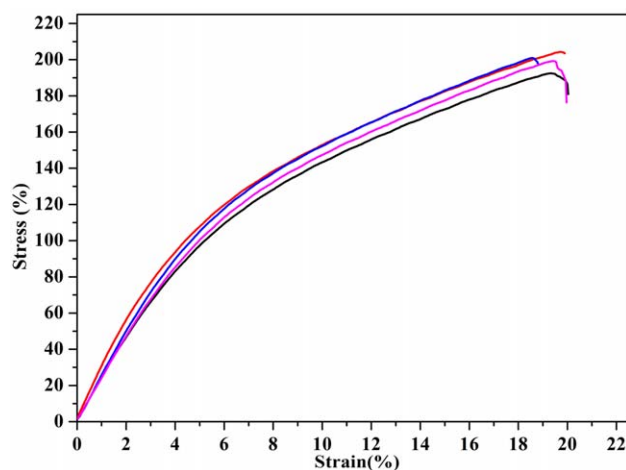


Figure 7. Stress–strain curves of PI film with four times' measurements. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and high glass transition temperature of 291°C. The PI film had excellent mechanical properties with a tensile strength of 200 MPa and elongation at break of 20%. The PI also had high dielectric constant (7.12–6.71 and low dielectric loss (below 0.04) at the frequency ranged from 100 to 100,000 Hz. The excellent properties were attributed to the introduction of rigid and polar bipyrimidine moieties in the PI macromolecular chains. Such PI has a promising future for the application in high energy density capacitors.

### ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (Grants No.: 21174058), the important science and technology special project of Jiangxi province, China (Grants No.:20114ABF05100).

### REFERENCES

- Shen, Z.-Y.; Hu, Q.-G.; Li, Y.-M.; Wang, Z.-M.; Luo, W.-Q.; Hong, Y.; Xie, Z.-X.; Liao, R.-H. *J. Am. Ceram. Soc.* **2013**, *96*, 2551.
- Nalwa, H. S. *Handbook of Low and High Dielectric Constant Materials and Their Applications*, 2 Volumes; Academic Press: London, **1999**.
- Kar, S. K.; Kumar, P. *J. Phys. Chem. Solids* **2013**, *74*, 1408.
- Amaral, F.; Rubinger, C. P. L.; Valente, M. A.; Costa, L. C.; Moreira, R. L. *J. Appl. Phys.* **2009**, *105*, 034109.
- Wang, Y.; Zhou, X.; Chen, Q.; Baojin, C.; Zhang, Q. *IEEE Trans. Dielectric. Electric. Insul.* **2010**, *17*, 1036.
- Mathai, C. J.; Saravanan, S.; Anantharaman, M. R.; Venkitachalam, S. *J. Phys. D Appl. Phys.* **2002**, *35*, 240.
- Tjong, S. C.; Liang, G. D.; Bao, S. P. *Scripta Mater.* **2007**, *57*, 461.
- He, F.; Lau, S.; Chan, H. L.; Fan, J. *Adv. Mater.* **2009**, *21*, 710.

9. Derouiche, H.; Mohamed, A. B. *Thin Solid Films* **2012**, *526*, 274.
10. Rahaman, M.; Chaki, T. K.; Khastgir, D. *Eur. Polym. J.* **2012**, *48*, 1241.
11. Huang, C.; Zhang, Q. *Adv. Funct. Mater.* **2004**, *14*, 501.
12. Chu, L.; Xue, Q.; Sun, J.; Xia, F.; Xing, W.; Xia, D.; Dong, M. *Compos. Sci. Technol.* **2013**, *86*, 70.
13. Wang, X.; Li, W.; Luo, L.; Fang, Z.; Zhang, J.; Zhu, Y. *J. Appl. Polym. Sci.* **2012**, *125*, 2711.
14. Dang, Z. M.; Wang, L.; Yin, Y.; Zhang, Q.; Lei, Q. Q. *Adv. Mater.* **2007**, *19*, 852.
15. Deng, Y.; Zhang, Y.; Wang, Y.; Li, M.; Yuan, J.; Bai, J. *Compos. A* **2012**, *43*, 842.
16. Arbatti, M.; Shan, X.; Cheng, Z. Y. *Adv. Mater.* **2007**, *19*, 1369.
17. Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laisus, L. A. *Polyimides-Thermally Stable Polymers*; Consultants Bureau: New York, **1987**.
18. Kricheldorf, H. R.; Carter, K. *Progress in Polyimide Chemistry: II*; Springer: Berlin, **1999**.
19. Mittal, K. L. *Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications*; CRC Press: Cleveland, OH, **2005**.
20. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications*; CRC Press: Cleveland, OH, **1996**.
21. Ding, M. *Prog. Polym. Sci.* **2007**, *32*, 623.
22. Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3.
23. Lee, C.; Shul, Y.; Han, H. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40*, 2190.
24. Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1984**, *1984*, 736.
25. Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, *67*, 443.
26. Ziessel, R.; Stroh, C. *Tetrahedron Lett.* **2004**, *45*, 4051.
27. Romero, F. M.; Ziessel, R. *Tetrahedron Lett.* **1995**, *36*, 6471.
28. Bouilly, L.; Turck, A.; Plé, N.; Darabantu, M. *J. Heterocycl. Chem.* **2005**, *42*, 1423.
29. Muruganand, S.; Narayandass, S. K.; Mangalaraj, D.; Vijayan, T. M. *Polym. Int.* **2001**, *50*, 1089.
30. Deligöz, H.; Yalcinyuva, T.; Özgümüş, S.; Yildirim, S. *J. Appl. Polym. Sci.* **2006**, *100*, 810.