Synthesis and Properties of Novel Polyimides Derived from 2,2′,3,3′-Benzophenonetetracarboxylic Dianhydride

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ABSTRACT: A new synthetic route to 2,2′,3,3′-BTDA (where BTDA is benzophenonetetracarboxylic dianhydride), an isomer of 2,3′,3′,4′-BTDA and 3,3′,4,4′-BTDA, is described. Single-crystal X-ray diffraction analysis of 2,2′,3,3′-BTDA has shown that this dianhydride has a bent and noncoplanar structure. The polymerizations of 2,2′,3,3′-BTDA with 4,4′-oxydianiline (ODA) and 4,4′-bis(4-aminophenoxy)benzene (TPEQ) have been investigated with a conventional two-step process. A trend of cyclic oligomers forming in the reaction of 2,2′,3,3′-BTDA and ODA has been found and characterized with IR, NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, and elemental analyses. Films based on 2,2′,3,3′-BTDA/TPEQ can only be obtained from corresponding polyimide (PI) solutions prepared by chemical imidization because those from their polyamic acids by thermal imidization are brittle. PIs from 2,2′,3,3′-BTDA have lower inherent viscosities and worse thermal and mechanical properties than the corresponding 2,3′,3′,4′-BTDA- and 3,3′,4,4′-BTDA-based PIs. PIs from 2,2′,3,3′-BTDA and 2,3′,3′,4′-BTDA are amorphous, whereas those from 3,3′,4,4′-BTDA have some crystallinity, according to wide-angle X-ray diffraction. Furthermore, PIs from 2,2′,3,3′-BTDA have better solubility, higher glass-transition temperatures, and higher melt viscosity than those from 2,3′,3′,4′-BTDA and 3,3′,4,4′-BTDA. Model compounds have been prepared to explain the order of the glass-transition temperatures found in the isomeric PI series. The isomer effects on the PI properties are discussed. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2130 –2144, 2004

Keywords: 2,2′,3,3′-benzophenonetetracarboxylic dianhydride (2,2′,3,3′-BTDA); cyclic oligomers; polyimides; model compounds; isomer effects on polyimide properties; structure-property relations; rheology

INTRODUCTION

Polyimides (PIs) are a class of thermally stable polymers that are often prepared from dianhydride and diamine monomers.1–4 The subtle variations in the structures of the dianhydride and diamine components have a tremendous effect on the properties of the final PIs.5–12 Recently, PIs based on isomeric dianhydrides have attracted more attention. Researchers at General Electric Co. first reported PIs based on isomeric bis(ether anhydride)s13 and isomeric thioether dianhydrides.14,15 Gerber et al.16 reported PIs derived from isomeric 2,2′,3,3′-, 2,3′,3′-, and 3,3′,4,4′-oxydiphthalic dianhydrides. Hasegawa and co-workers17–22 found that PIs based on 2,3′,3′-biphenyltetraacarboxylic dianhydride had higher glass-transition temperatures (Tgs) and better solubility and melt processability than the corresponding 3,3′,4,4′-biphenyltetraacarboxylic dianhydride based PIs. Previously, we have reported PIs based on various isomeric dianhydrides.23–30

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The relationships between the structure and properties of isomeric PIs have become a novel area for investigations of the chemistry and processing in the pursuit of high-performance materials.

It is well known that PIs from 3,3',4,4'-BTDA (where BTDA is benzophenonetetracarboxylic dianhydride) have excellent thermal and mechanical properties, and they have been extensively used as matrix resins for advanced composites, such as PMR-15. Very recently, we reported on PIs derived from 2,3,3',4'-BTDA. However, 2,2',3,3'-BTDA (3; Fig. 1), an isomer of 2,3',3',4'-BTDA and 3,3',4,4'-BTDA, has not received any attention until now. To the best of our knowledge, no reports on PIs derived from 2,2',3,3'-BTDA have appeared in the literature.

As part of our continuing study of isomeric PIs, in this article we describe a new synthetic route to 2,2',3,3'-BTDA and the polymerization behaviors of this new dianhydride in polycondensation reactions with 4,4'-oxydianiline (ODA) and 4,4'-bis(4-aminophenoxy)benzene (TPEQ). Furthermore, the properties of PIs derived from 2,2',3,3'-BTDA have been characterized, and they are compared with those of PIs from 2,3',3',4'-BTDA and 3,3',4,4'-BTDA.

EXPERIMENTAL

Materials

1,8,9-Anthracemetriol (dithranol) was purchased from Linear Scientific, Inc., and used as received. 2,3-Dimethylaniline was purchased from Merck Co. and was distilled under reduced pressure before use. All the other reagents were from Shanghai Chemical Reagent Co. and were analytical-grade. Anhydrous methanol was purified by distillation over magnesium chips before it was used. N,N-Dimethylacetamide (DMAc) was purified by distillation over phosphorus pentoxide and stored over 4 Å molecular sieves. Acetic anhydride and triethylamine were used after distillation in the presence of magnesium and calcium hydride, respectively. Aniline (AN) was distilled under reduced pressure. 3,3',4,4'-BTDA, cis-5-norbornene-endo-2,3-dicarboxylic anhydride, and ODA were purified by sublimation in vacuo. 4,4'-Methylenedianiline was recrystallized from ethanol before use. TPEQ was prepared from hydroquinone and p-chloronitrobenzene in the presence of K2CO3 in DMAc, was then reduced by Pd/C—H2, and was finally recrystallized from ethanol before use.

Characterization

IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. 1H and 13C NMR spectra were recorded on Bruker spectrometers at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard. Elemental analyses were performed on an Elemental Analyses MOD-1106 (Italyd). Mass spectra were obtained on a Finnigan LCQ mass spectrometer with an electrospray voltage of 5.0 kV and a capillary temperature of 200 °C. The inherent viscosities were determined at 30 °C with an Ostwald viscometer, and the concentrations were 0.5 g/dL in DMAc. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (Rheometric Scientific, Inc., United States) in a tension mode at a heating rate of 5 °C/min and at a frequency of 1 Hz from room temperature to 450 °C. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min in air with a PerkinElmer TGA-2 thermo-
gravimetric analyzer. The differential scanning calorimetry (DSC) experiments were carried out on a PerkinElmer DSC-7 system at a heating rate of 10 °C/min under a nitrogen atmosphere. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku X-ray diffractometer with Cu Kα radiation (40 kV, 200 mA) at a scanning rate of 2°/min. The tensile measurements were carried out on an Instron model 1122 at room temperature.

Melt viscosity measurements were performed on a Physica MCR-300 mechanical spectrometer (Germany) at a ramp rate of 4 °C/min in air. Sample specimen discs 25 mm in diameter and 1 mm thick were prepared by the press molding of the powderlike imide oligomers at 80 °C under high pressure. The melt viscosity (or complex viscosity as a function of time) was measured from 200 to 400 °C.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Biflex mass spectrometer equipped with delayed extraction. A 337-nm nitrogen laser producing 3-ns pulses was used, and the instrument was operated in the positive reflection mode with an accelerating potential of 20 kV and an extraction delay of 50 ns. Samples were prepared by the mixing of 10 μL of tetrahydrofuran (THF) of the oligomer sample (2 g L⁻¹) with 50 μL of a solution of 15 g L⁻¹ dithranol (dithranol) in THF.

Single-crystal X-ray diffraction data were collected at 293(2) K on a Rigaku R-Axis rapid diffractometer (λ = 0.71073 Å). The structure was solved by the direct method with the SHELX-97 system and was refined by full-matrix least squares on F² with all reflections.

**Monomer Synthesis**

**4,4’-Diamo-2,2’,3,3’-tetramethyldiphenylmethane**

Water (50 mL) and concentrated hydrochloric acid (12.5 mL) were added to a 250-mL, three-necked flask equipped with a reflux condenser, a dropping funnel, and a mechanical stirrer. 2,3-Dimethylaniline (19 mL, 0.15 mol) was added, and the mixture was heated to 60 °C; this was followed by the addition of 6 mL (0.075 mol) of a 38 wt % aqueous formaldehyde solution. The mixture was stirred for 4 h and was gradually elevated to 90 °C for another 4 h. After cooling, the reaction mixture was carefully neutralized to pH 8 with a 20% aqueous NaOH solution. After the product was collected by filtration and washed with warm water, it was recrystallized from an aqueous ethanol solution to give 16.4 g (86%) of white crystals.

mp: 134–135 °C. IR (KBr): 3407, 3335, 3011, 2910, 2857, 1623, 1597, 1481, 1384, 1286, 825, 782, 712 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 6.61 (d, J = 11.6 Hz, 1H), 6.53 (d, J = 12 Hz, 1H), 3.83 (s, 1H), 3.53 (s, 2H), 2.20 (s, 3H), 2.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 141.62, 136.04, 130.88, 127.70, 122.59, 114.07, 37.92, 16.17, 13.86. Mass spectrometry (MS) Calcd. for C₁₇H₂₂N₂: 254.37. Found [M + H]⁺: 255.43. ELEM. ANAL. Calcd. for C₁₇H₂₂N₂: C, 80.27%; H, 8.72%; N, 11.01%. Found: C, 80.65%; H, 8.36%; N, 10.48%.

**2,2’,3,3’-Tetramethyldiphenylmethane**

To a 250-mL, three-necked, round-bottom flask were added water (50 mL) and concentrated hydrochloric acid (5 mL). The mixture was mechanically stirred and heated to 90 °C, and this was followed by the addition of 4,4’-diamino-2,2’,3,3’-tetramethyldiphenylmethane (5.08 g, 0.02 mol). After cooling to room temperature, the mixture was added to another portion of concentrated hydrochloric acid (5 mL). The solution was cooled to −2 °C, and a solution of NaNO₂ (3.10 g, 0.045 mol) in water (10 mL) was added dropwise until a test paper of KI starch became blue. After being added to a 60-mL hyrophosphorous solution (30%) and remaining in a refrigerator overnight and then at room temperature for 2 days, the mixture was extracted with 80 mL of benzene three times. The extract was dried over anhydrous magnesium sulfate overnight. After filtration, the filtrate was concentrated on a rotary evaporator, and the residue was distilled at 140–150 °C (1 mmHg) to give a white product, which was recrystallized from ligroin to yield 2.40 g (54%) of white crystals.

mp: 72–73 °C. IR (KBr): 3063, 2967, 2908, 1926, 1584, 1464, 1381, 1089, 785, 734 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.06–6.98 (m, 12H), 6.73 (d, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.23 (s, 3H), 2.17 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 138.97, 137.04, 135.46, 128.36, 127.53, 125.84, 125.04, 121.10, 15.60. MS Calcd. for C₁₇H₂₀N₂: 255.43. Found [M + H]⁺: 255.43. ELEM. ANAL. Calcd. for C₁₇H₂₀N₂: C, 80.27%; H, 8.72%; N, 11.01%. Found: C, 80.65%; H, 8.36%; N, 10.48%.
2,2′,3,3′-Benzenophenonetetra-carboxylic Acid (1)

2,2′,3,3′-Tetramethyldiphenylmethane (30 g, 0.134 mol), pyridine (1000 mL), and water (500 mL) were added to a 3-L, three-necked, round-bottom flask equipped with a reflux condenser and a mechanical stirrer. The solution was heated until slight refluxing, and then 130 g (0.784 mol) of solid potassium permanganate was added in portions to the mixture over a period of 8 h. After stirring overnight, white solids were obtained by filtration, and the filtrates were dried to give a residue. The residue was carefully acidified to pH 1 with concentrated hydrochloric acid to ensure that the temperature was not in excess of 50 °C. After cooling to room temperature, the mixture was filtered, and manganese dioxide was extracted twice with pyridine/water (2:1 v/v). The combined filtrates were concentrated on a rotary evaporator to 500 mL. The residue was carefully acidified to pH 1 with concentrated hydrochloric acid to ensure the complete reaction. Then, acetic anhydride (5 mL) and triethylamine (3 mL) were added to the mixture over a period of 8 h. After the addition, the mixture was kept at 260 °C for 4 h (82% yield).

A single crystal of 3 was obtained by slow sublimation at 260 °C in vacuo and was selected with dimensions of 0.55 mm × 0.34 mm × 0.30 mm. The crystal data for 3 are as follows: C_{17}H_{6}O_{7}, colorless, fw = 322.23, monoclinic, C2/C, a = 17.413(4) Å, b = 5.620(6) Å, c = 13.406(2) Å, α = 90.00 °, β = 94.55(4) °, γ = 90.00 °, V = 1307.9(4) Å³, Z = 2, T = 293(2) K, R$_{1}$/I > 2σ(I) = 0.0542, ωR$_{2}$ (all data) = 0.0711, GOF = 0.907. The molecular structure of 2,2′,3,3′-BTDA is shown later in Figure 3.

Synthesis of Model Compounds Derived from Isomeric BTDA and AN

For the preparation of the PI model compounds, isomeric BTDA and stoichiometric amounts of AN were stirred in DMAc at room temperature for 3 h; subsequently, the solutions were chemically cyclodehydrated with acetic anhydride and triethylamine and were stirred at room temperature for 24 h. The mixtures were then diluted by the addition of large amounts of water. The crude products obtained by filtration were recrystallized twice from toluene for model compounds 2,2′,3,3′-BTDA/AN and 2,3,3′,4′-BTDA/AN and from DMAc for model compound 3,3′,4,4′-BTDA/AN.

Synthesis of Imide Cyclic Oligomers Derived from 2,2′,3,3′-BTDA and ODA

A solution of 2,2′,3,3′-BTDA (0.8581 g, 2.66 mmol) in DMAc (40 mL) and a solution of ODA (0.5332 g, 2.66 mmol) in DMAc (40 mL) were added to a mechanically stirred flask containing 120 mL of DMAc over a 2-h period. After the addition, the mixture was stirred for another 2 h to ensure the complete reaction. Then, acetic anhydride (5 mL) and triethylamine (3 mL) were added. The temperature was gradually raised to 50 °C. After 24 h of reaction, the solution was

(continued)
concentrated to about 20 mL by distillation under reduced pressure and was poured into methanol. The precipitate was filtered off and extracted in a Soxhlet extractor with methanol for 12 h. The product, a light yellow solid, was dried in a vacuum oven at 120 °C for 24 h with a yield of 0.64 g (68% yield).

IR (KBr): 1782 (imide C==O asymmetric stretching), 1720 (imide C==O symmetric stretching), 1668 (diaryl ketone C==O stretching), 1379 (C—N stretching), 723 cm⁻¹ (C==O bending). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.12–8.05 (m, 2H), 7.94–7.90 (t, 1H), 7.21–7.19 (m, 2H), 7.08–7.05 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 193.06, 166.27, 165.51, 137.17, 135.14, 134.48, 133.57, 132.03, 130.55, 128.61, 128.12, 126.57, 123.91, 122.24, 121.56, 120.33, 119.43, 118.27.

**Synthesis of PIs Derived from 2,2',3,3'-BTDA and TPEQ**

**Polymer 3b**

TPEQ (0.8744 g, 2.99 mmol) and DMAc (6 mL) were charged into a 50-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and a dry nitrogen gas inlet. After the dissolution of TPEQ, 2,2',3,3'-BTDA (0.9638 g, 2.99 mmol) and DMAc (6 mL) was added as a solid to the flask over 0.5 h. After 12 h of stirring at room temperature, polyamic acid (PAA) was formed in the viscous solution. The viscosity increasing, DMAc (9 mL) was gradually added to the PAA solution. Then, acetic anhydride (4 mL) and triethylamine (2 mL) were added to the PAA solution, as the reaction progressed for 24 h, to make the solution viscous. The solution was poured slowly into 200 mL of methanol with stirring. The precipitate was collected by filtration and extracted with methanol in a Soxhlet extractor for 6 h and was dried in vacuo; this yielded a PI powder of 3b. Dissolving the PI powder in DMAc produced a polymer solution, which was cast onto a glass plate and dried at 80 °C for 18 h; this was followed by heating at 300 °C (1 h) to afford a PI film. The film was used for DMTA and tensile measurements.

Yield: 0.82 g (95%). IR (KBr): 1784 (imide C==O asymmetric stretching), 1722 (imide C==O symmetric stretching), 1668 (diaryl ketone C==O stretching), 1377 (C—N stretching), 727 cm⁻¹ (C==O bending). ELEM. ANAL. Calcd. for (C₃₅H₄₈O₇N₂)ₙ: C, 72.66%; H, 3.14%; N, 4.84%. Found: C, 71.38%; H, 3.72%; N, 4.96%.

**Synthesis of PMR-15-Type PI Resins Derived from Isomeric BTDAs**

The synthetic procedure for PMR-15-type isomeric PI resins was reported previously, except that a new monomer (2,2',3,3'-BTDA) was used.

**RESULTS AND DISCUSSIONS**

**Monomer Synthesis**

To date, no reports on the synthesis of 2,2',3,3'-BTDA have appeared in the literature, except for one patent. In this patent, only mixtures of 2,2',3,3'-BTDA and 2 are described from the oxidation of 2,2',3,3'-tetramethyl-diphenylmethane in the liquid phase and the subsequent heating of 1. The synthesis of 2,2',3,3'-tetramethyl-diphenylmethane and the method of acquisition of pure 2,2',3,3'-BTDA are not reported in the patent.

As shown in Scheme 1, the synthesis of 2,2',3,3'-BTDA was performed in four steps from 2,3-dimethylaniline as a starting material in a high yield. 4,4'-Diamino-2,2',3,3'-tetramethyl-diphenylmethanediame was easily prepared through the condensation of 2,3-dimethylaniline with formaldehyde. The subsequent steps involved a deamination reaction with hypophosphorus acid, followed by oxidation with potassium permanganate/pyridine/ether, acidification, and dehydration with acetic anhydride. It is known that compounds bearing a 2,2'-benzophenonedicarboxylic acid structure can be easily converted into corresponding bislactones.

We found that lactone 2 and tetraacid 1 could be obtained by careful control of the acidification. When the carboxylic salt was treated with concentrated hydrochloric acid to pH 1 and heated to reflux for 2 h, 2 was obtained as the only product. However, when the acidified solution was kept below 50 °C, a mixture of 1 and various salts of the tetraacid was obtained. The sublimation of the mixture in vacuo at 260 °C produced 3 (18%). However, this route suffered from a tedious workup and a poor yield. Furthermore, the direct sublimation of 2 in vacuo at 280 °C produced a mixture of 2 and 3 (2/3 = 3:1, as determined by ¹H NMR).

We developed a method in our laboratory to obtain pure 2,3,2',3'-BTDA in a reasonable yield. 2 was directly transformed into 3 in a good yield (82%) via refluxing in acetic anhydride for 4 h.
The progress of the transformation reaction was monitored with Fourier transform infrared (FTIR). As shown in Figure 2, 2 shows strong bands at 1712 (aromatic carboxylic acid C=O stretching) and 1805 cm$^{-1}$ (lactone C=O stretching), and 3 shows bands at 1857 and 1776 (aro-
matic dianhydride C—O stretching) and 1674 cm\(^{-1}\) (diaryl ketone C—O stretching). However, no transformation took place in refluxing xylene at the same temperature, even for 24 h. This suggests that acetic acid plays an important role in the conversion of 2 to 3. As shown in Scheme 2, it is believed that an acid-catalyzed dehydration reaction occurred during the conversion of 2 to 3.

The chemical structure of 3 was confirmed by means of elemental analysis, IR, and NMR, and the results were in good agreement with the proposed structure. Its structural features were further detailed by single-crystal X-ray diffraction. As shown in Figure 3, the molecular structure of 2,2',3,3'-BTDA showed that this dianhydride had a bent and noncoplanar structure. The dihedral angle of two phthalic anhydride planes in 2,2',3,3'-BTDA is 74°, which is greater than that of 2,2',3,3'-biphenyltetraarboxylic dianhydride (62.9°).\(^{26}\)

Cyclic Oligomers Derived from 2,2',3,3'-BTDA and ODA

When the conventional two-step process was used for the synthesis of PI 2,2',3,3'-BTDA/ODA (3a), high-molecular-weight polymers could not be obtained. In view of the trend of forming cyclic oligomers for this kind of configuration of dianhydrides,\(^{30,37}\) pseudo-high-dilution techniques were used to obtain cyclic oligomer 3a (Scheme 3). The MALDI-TOF MS spectrum (Fig. 4) gives the correct protonated molecular ion peaks from cyclodimer (\(n = 2\)) to cycloheptamer (\(n = 7\)). The expanded scale of the MS spectrum shows three signals for each oligomer. For example, signals for the cyclic trimer are located at 1459, 1481, and 1497 Da. The signal at 1459 Da corresponds to the protonated molecular ion peak, that at 1481 Da is due to the adduct of the cyclic trimer with a sodium cation, and that at 1497 Da is due to the adduct with a potassium cation. The FTIR spectrum (Fig. 5) of 3a shows absorption bands at 1782 (asymmetric C—O stretching), 1720 (symmetric C—O stretching), 1379 (C—N stretching), and 723 cm\(^{-1}\) (imide ring deformation), corresponding to the characteristics of imide rings. Furthermore, the \(^1\)H NMR spectrum and elemental analysis are also in agreement with the cyclic structures of 3a.
Scheme 3. Synthesis of oligoimides and PIs from 3.

Figure 4. MALDI-TOF-MS spectrum of cyclic oligomer 3a with 1,8,9-anthracemtriol as a matrix.
The high propensity of the bent dianhydride to form cyclic oligoimides is presumably due to the rigidity of the dianhydride coupled with the orientation angle of the ortho-bridged dianhydride functionalities. This rigidity and orientation increase the probability of an end-to-end encounter with the functionalities of ODA and thereby facilitates cyclic formation.

Polymer Synthesis

From these results, it is apparent that a diamine (e.g., ODA) has a tendency to form cyclic oligomers with 2,2',3,3'-BTDA. High-molecular-weight polymers based on 2,3',3',4'-BTDA/ODA and 3,3',4,4'-BTDA/ODA (the inherent viscosities were 0.92 and 1.37 dL/g, respectively) could be obtained. This is attributed to the conformational structure of 2,2',3,3'-BTDA being more bent than those of 2,3',3',4'-BTDA and 3,3',4,4'-BTDA. We suspect that a diamine (e.g., TPEQ) with a longer, more flexible chain can suppress the formation of cyclics, and so a high-molecular-weight PI based on 2,2',3,3'-BTDA could be obtained. Furthermore, because the monomer concentration has an effect on the molecular weights of PAAs, increasing the monomer concentration favors high-molecular-weight products. As shown in Scheme 3, the PI powders were synthesized in two steps, by the polycondensation reaction of 2,2',3,3'-BTDA with TPEQ at a higher solid concentration (ca. 25%), to form PAAs in the beginning, and subsequently diluted to 10% with the viscosity increasing, and by chemical imidization.

The films based on 2,2',3,3'-BTDA/TPEQ (3b) could only be obtained from corresponding PI solutions prepared by chemical imidization because those from their PAAs by thermal imidization were brittle. One likely reason is the unfavorable conformations of PAA from 3b during the later stages of thermal imidization, producing a final PI of lower molecular weight. The other is that the generated cyclic oligomers are more stable than the linear ones in the reversion process of PAA from 3b during thermal imidization. In contrast, polymers 2,3',3',4'-BTDA/TPEQ (4b) and 3,3',4,4'-BTDA/TPEQ (5b) with higher molecular weights could be easily obtained from their PAAs by thermal or chemical imidization.
Table 1. Properties of the Isomeric Polyimides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>η (dL/g)a</th>
<th>Tg (°C)b</th>
<th>T3% (°C)c</th>
<th>Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
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<tr>
<td>3b</td>
<td>0.52</td>
<td>0.34</td>
<td>278</td>
<td>464</td>
<td>1320</td>
<td>56</td>
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<tr>
<td>4b</td>
<td>2.28</td>
<td>1.75</td>
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<td>2525</td>
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<tr>
<td>5b</td>
<td>2.38</td>
<td>—</td>
<td>255</td>
<td>504</td>
<td>2546</td>
<td>122</td>
</tr>
</tbody>
</table>

a Inherent viscosity measured with 0.5 g/dL in DMAc at 30 °C.
b Obtained from DMTA at a heating rate of 5 °C/min at 1 Hz.
c 5% weight loss in air obtained from TGA at a heating rate of 10 °C/min.

Polymer Characterization

The properties of the isomeric PIs are listed in Table 1. The inherent viscosities of the polymers were in the range of 0.34–2.38 dL/g in DMAc at 30 °C. The molecular weight increased for the isomeric PIs according to the dianhydride: 2,2’,3,3’-BTDA < 2,3’,3’,4’-BTDA < 3,3’,4,4’-BTDA. The order is in good agreement with the isomeric biphenyltetra carboxylic dianhydrides.26,37 The relatively lower inherent viscosity of polymer 3b in comparison with those of PIs 4b and 5b may be attributed to the more bent conformational structure of the dianhydride monomer (2,2’,3,3’-BTDA), which favors the formation of cyclics.37

The complete imidization of the polymers was confirmed by IR spectra. All the polymers showed the characteristic absorption bands of the imide ring near 1780 (asymmetric C==O stretching), 1720 (symmetric C==O stretching), 1668 (diaryl ketone C==O stretching), 1380 (C==N stretching), and 725 cm⁻¹ (imide ring deformation). There were no amide groups near 3363 (N—H stretching) and 1674 cm⁻¹ (amide C==O stretching), and this indicated that the polymers had been fully imidized. In addition to the IR spectra, the elemental analysis values of the polymers generally agreed well with the calculated values for the proposed structures.

Table 1 shows that Tg’s of the isomeric PIs decreased in the following order: 3b > 4b > 5b. Figure 6 shows the dynamic storage modulus (E’), and tan δ as functions of temperature for polymer 3b. With the peak temperature in the tan δ curves considered to be Tg, 3b showed the highest Tg at 278 °C, whereas polymers 4b and 5b had Tg’s at 268 and 255 °C, respectively. This could be explained in terms of the different restricted rotations around the bond between the bridged carbonyl and the carbon in phthalimide.17,29,37,41,42

The 2,2’,3,3’-BTDA-based PIs had more restricted rotations around the bond than the 2,3,3’,4’-BTDA-based PIs, and the latter had more restricted rotations than the 3,3’,4,4’-BTDA-based PIs. This phenomenon should be a general rule for the PIs based on isomeric dianhydrides.17–22,26,27,29,30,37

The DMTA curve (Fig. 6) shows that the E’ curve of polymer 3b increased above its Tg. Figure 7 provides the WAXD measurements for polymer films of 3b and 3b’ (after 3b was measured in a DMTA analyzer). Polymer 3b showed an amorphous pattern, however, an ordered structure was found for 3b’. The factors possibly responsible for the significant changes in the E’ curves are a decrease in the amorphous fraction due to crystallization and crystal-like local ordering.17

The thermal stability of the isomeric PIs was evaluated by TGA, and the thermal analysis data are listed in Table 1. The temperatures for 5% weight loss for these isomeric PIs were around 500 °C in air, except for polymer 3b (464 °C), probably because of the relatively lower molecular weight (the inherent viscosity was 0.34 dL/g) or the existence of cyclic oligomers. Furthermore, as shown in Table 1, the three isomeric polymers were cast into transparent, flexible, and tough films. However, polymer 3b showed mechanical properties inferior to those of polymers 4b and 5b. This probably resulted from the relatively lower molecular weight of 3b.

The solubility of the isomeric PIs is shown in Table 2. In comparison with PIs 4b and 5b, PI 3b exhibited good solubility not only in polar aprotic solvents such as DMAC, DMSO, and N-methylpyrrolidinone (NMP) but also in 1,1,2,2-tetrachloroethane (TCE), CHCl₃, and THF. The difference in the solubilities may be attributed to the more bent chain for PIs from 2,2’,3,3’-BTDA. A possible explanation is that the 2- and 2’-positions of the dianhydride monomer are occupied by...
imide groups, creating a steric hindrance effect and enhancing solubility. Furthermore, the non-linear and noncoplanar imide groups inhabit chain interactions and chain packing, thus increasing solubility. This result is also consistent with the results previously reported for PIs based on other isomeric dianhydrides. The WAXD patterns of these isomeric PI powders prepared by chemical imidization showed overall amorphous humps, except for polymer 5b, which showed a little crystalline order, as shown in Figure 8. This probably resulted from 3,3',4,4'-BTDA-based PIs having a more regular and ordered chain structure than 2,2',3,3'-BTDA- and 2,3',3',4'-BTDA-based PIs.

As shown in Figure 9, PMR-15-type imide oligomers based on 2,2',3,3'-BTDA displayed the highest melt viscosity over a narrower range of temperatures, whereas those based on 2,3',3',4'-BTDA showed the lowest melt viscosity over a broader range of temperatures, in comparison with those based on 3,3',4,4'-BTDA. The difference in the melt viscosity was presumably a result of the different structures provided by isomeric BTDA s due to the catenation of the dianhydride. The new PI resins based on 2,3',3',4'-BTDA exhibited the best processability and promising potential as matrix resins for advanced composite materials because of the irregular structure provided by 2,3,3',4'-BTDA.

Model Compounds

Model compounds were prepared by the conventional two-step method to probe the order of Tg's found in the isomeric PIs. From the literature, it is known that the melting temperatures (Tm's) of pyromellitic dianhydride-type model compounds have a tendency to increase with increasing Tg's of the corresponding PIs. This empirical relation leads to the expectation that the Tm's decrease in the following order: M(2,2',3,3'-BTDA/AN) > M(2,3,3',4'-BTDA/AN) > M(3,3',4,4'-BTDA/AN). Additionally, we predicted first that M(2,2',3,3'-BTDA/AN) would have lower enthalpy of melting (ΔHm) than M(2,3,3',4'-BTDA/AN) and the latter would show lower ΔSm and lower ΔHm values than M(3,3',4,4'-BTDA/AN) from the assumptions mentioned previously. First, the rotational motion around the bond between the
bridged carbonyl and the carbon in phthalimide is suppressed in the following order: \(2,2'\),\(3,3'\)-BTDA unit \(> 2,3,3',4'-\)BTDA unit \(> 3,3',4,4'-\)BTDA unit. Second, the intermolecular interactions are increasingly enhanced in the following order: \(2,2',3,3'\)-BTDA systems \(< 2,3',3',4'-\)BTDA systems \(< 3,3',4,4'-\)BTDA systems. Interestingly, as shown in Table 3, the values of \(T_m, \Delta H_m, \) and \(\Delta S_m\) for the three model compounds were quite consistent with our first expectation, except that M(3,3',4,4'-BTDA/AN) showed the highest \(T_m\). A possible explanation is the higher symmetry of M(3,3',4,4'-BTDA/AN), which favors more packing for the molecules.

### CONCLUSIONS

Pure 2,2',3,3'-BTDA, starting from 2,3-dimethylaniline, has been synthesized by a novel facile procedure and effectively transformed from the byproduct of the spirolactone diacid in a relatively high yield. It is believed that an acid-catalyzed dehydration reaction occurs during the conversion of lactone to dianhydride. A single-crystal X-ray diffraction analysis of 2,2',3,3'-BTDA has shown its bent and noncoplanar structure. The dihedral angle of two phthalic anhydride planes is 74°.

The trend of cyclic oligomers forming in the reaction of 2,2',3,3'-BTDA with ODA has been

### Table 2. Solubility of the Isomeric Polyimides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHCl₃</th>
<th>TCE</th>
<th>THF</th>
<th>DMAc</th>
<th>DMSO</th>
<th>NMP</th>
<th>m-Cresol</th>
<th>p-Chlorophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>4b</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>5b</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>±</td>
</tr>
</tbody>
</table>

* + = fully soluble at room temperature; ± = partially soluble on heating; − = insoluble on heating.*
attributed to the rigidity of the monomers coupled with the orientation angles of the ortho-bridged dianhydride functionalities and the diamine functionalities. $T_g$'s decrease for the PIs based on isomeric dianhydride in the following order: $2,2',3,3'$-BTDA > $2,3',3',4'$-BTDA > $3,3',4,4'$-BTDA. This can be explained in terms of the different restricted rotations around the bond be-

Figure 8. WAXD curves for isomeric PI powders of 3b, 4b, and 5b.

Figure 9. Dynamic rheological behavior of PMR-15-type isomeric PI resins based on (△) $2,2',3,3'$-BTDA, (◇) $2,3',3',4'$-BTDA, and (○) $3,3',4,4'$-BTDA. A Physica MCR-300 mechanical spectrometer was used at a ramp rate of 4 °C/min in air.
between bridged carbonyl and the carbon in phthalimide. The order of $T_m$'s found in the isomeric PIs can also be explained by model compounds. PIs from 2,2',3,3'-BTDA have excellent solubilities but worse thermal and mechanical properties than those from 2,3',3',4'-BTDA and 3,3',4,4'-BTDA; this is mainly due to the lower inherent viscosity and weaker chain interactions for PIs from 2,2'-BTDA. The PIs from 2,2',3,3'-BTDA and 2,3',3',4'-BTDA are amorphous, whereas those from 3,3',4,4'-BTDA have some crystallinity. Furthermore, PMR-15-type PI resins based on 2,2',3,3'-BTDA have the highest melt viscosity, whereas those based on 2,3',3',4'-BTDA show the lowest melt viscosity, over a broader range of temperatures than those based on 3,3',4,4'-BTDA.

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REFERENCES AND NOTES

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Table 3. $T_m$, $\Delta H_m$, and $\Delta S_m$ Values Obtained by DSC Measurements (10 °C min$^{-1}$) in N$_2$ for PI Model Compounds M(2,2',3,3'-BTDA/AN), M(2,3,3',4'-BTDA/AN), and M(3,3',4,4'-BTDA/AN)

<table>
<thead>
<tr>
<th>Model Compound</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_m$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(2,2',3,3'-BTDA/AN)</td>
<td>285</td>
<td>31.6</td>
<td>56.6</td>
</tr>
<tr>
<td>M(2,3,3',4'-BTDA/AN)</td>
<td>277</td>
<td>34.8</td>
<td>63.3</td>
</tr>
<tr>
<td>M(3,3',4,4'-BTDA/AN)</td>
<td>373</td>
<td>58.0</td>
<td>89.8</td>
</tr>
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</table>

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