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Novel polyimides derived from 2,3,3′,4′-benzophenonetetracarboxylic dianhydride

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Abstract

A series of polyimides (PIs) based on 2,3,3′,4′-benzophenonetetracarboxylic dianhydride (2,3,3′,4′-BTDA) and 3,3′,4,4′-BTDA were prepared by the conventional two-step process. The properties of the 2,3,3′,4′-BTDA based polyimides were compared with those of polyimides prepared from 3,3′,4,4′-BTDA. It was found that PIs from 2,3,3′,4′-BTDA have higher glass transition temperature and better solubility without sacrificing their thermal properties. Furthermore the rheological properties of PMR-15 type polyimide resins based on 2,3,3′,4′-BTDA showed lower melt viscosity and wider melt flow region (flow window) compared with those from 3,3′,4,4′-BTDA. The structure–property relations resulted from isomerism were discussed.

Keywords: 2,3,3′,4′-BTDA; Isomeric polyimides; Structure–property relations

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1. Introduction

Aromatic polyimides are a class of high performance polymers that have excellent thermal, electrical and mechanical properties [1,2]. However, aromatic polyimides are usually difficult to process because of their poor solubility in organic solvents and high melting temperature. Many attempts have been made to improve the processability (melt processing properties and/or solubility in organic solvent) of polyimides while maintaining the excellent thermal and mechanical properties [3–8]. Recently, one of the attractive methods for the enhanced processability was incorporation geometrically asymmetric unit by altering catenation patterns of dianhydride in polyimide chain structure. Gerber and the coworkers first reported polyimides derived from isomeric 2,2′,3,3′-, 2,3,3′,4′-, and 3,3′,4,4′-oxydiphthalic dianhydrides (ODPA) and found that the polyimide from more asymmetric 2,3,3′,4′-ODPA is more soluble than that from less asymmetric 3,4,3′,4′-ODPA [9]. It was also found that polyimides based on 2,3,3′,4′-biphenyltetracarboxylic dianhydride (BPDA) have higher glass transition temperature (T_g), better solubility and melt-processability than the corresponding 3,3′,4,4′-BPDA based polyimides [10–18]. Very recently, we have reported polyimides based on various isomeric dianhydrides [17–20]. The relationships between the structure and the property of isomeric polyimides have become a novel area for the investigation in chemistry and fabrication to pursue the materials that possess high performances both in application and processing.

It is well known that polyimides from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) have excellent thermal and mechanical properties and have been extensively used as matrix resin for advanced composites, such as PMR-15 [21–23]. However, polyimides derived from 3,3′,4,4′-BTDA usually exhibited poor solubility and processibility [24]. To our best knowledge, no reports on the polyimides from 2,3,3′,4′-BTDA have appeared in the literature.

In this paper, we present the comparative study on the properties of polyimides derived from 2,3,3′,4′-BTDA and 3,3′,4,4′-BTDA. The excellent properties exhibited in 2,3,3′,4′-BTDA based PIs demonstrate a promising potential for future advanced materials.

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2. Experimental

2.1. Materials

2,3,3′,4′-Benzophenonetetracarboxylic acid, which is a byproduct of 3,3′,4,4′-benzophenonetetracarboxylic acid, was supplied from Beijing Coking & Chemical Co. The corresponding dianhydride (2,3,3′,4′-BTDA, mp: 213–214 °C) was obtained by sublimating tetra acid under vacuum at 230 °C. The single crystal for 2,3,3′,4′-BTDA was grown during sublimation and selected with dimensions of $0.54 \times 0.33 \times 0.15$ mm^3. Crystal data for 2,3,3′,4′-BTDA: $C_{17}H_6O_7$, colorless, fw = 322.22, monoclinic, $P21\backslash n, a = 5.681(0)$ Å, $b = 10.266(6)$ Å, $c = 22.735(4)$ Å, $\alpha = 90.00°$, $\beta = 94.265(9)°$, $\gamma = 90.00°$, $V = 1322.42(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, $R_1(I > 2\sigma(I)) = 0.0307$, ωR_2(all data) = 0.0772, GOF = 0.683. The molecular structure of 2,3,3′,4′-BTDA is shown in Fig. 1.

All of other reagents were from the Shanghai Chemical Reagent Co. and were of analytical grade. Anhydrous methanol was purified by distillation over magnesium chips before use. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation over phosphorus pentoxide and stored over 4-Å molecular sieves. Acetic anhydride and triethylamine (TEA) were used after distillation in the presence of magnesium and calcium hydride, respectively. *p*-Chlorophenol was distilled under reduced pressure before use. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (3,3′,4,4′-BTDA), *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA) and 4,4′-oxydianiline (ODA) were purified by sublimation. 4,4′-Methylenedianiline (MDA) was recrystallized from ethanol prior to use. 4,4′-Bis(4-aminophenoxy)benzene (TPEQ) was prepared from hydroquinone and *p*-chloronitrobenzene in the presence of K_2CO_3 in DMAc then reduced by Pd/C–H_2 and finally recrystallized from ethanol before use.

2.2. Measurements

FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Elemental analyses were performed on an Elemental Analyses MOD-1106 (Italyd). Melting points were determined on a RY-1 melting point apparatus and were uncorrected. Inherent viscosities were determined at 30 °C with an Ostward viscometer and the concentration was 0.5 g/dl in DMAc or *p*-chlorophenol. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical thermal analyzer (Rheometric Scientific Inc., USA) in a tension mode at a heating rate of 5 °C/min and a frequency of 1 Hz from room temperature. Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min in air with a Perkin–Elmer TGA-2 thermogravimetric analyzer. The tensile measurements were carried out on an Instron Model 1122 at room temperature.

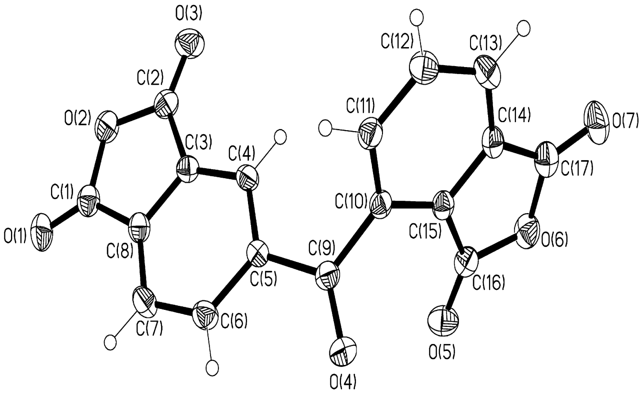


Fig. 1. Molecular structure of 2,3,3′,4′-BTDA.

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 of 25 mm diameter and 1 mm thickness were prepared by press moulding of the powder-like imide oligomers at 80 °C under high pressure. Melt viscosity (η^*, complex viscosity as a function of time) were measured from 200 to 400 °C.

Single crystal X-ray diffraction data were collected at 293(2) K on a Rigaku R-AXIS RAPID diffractometer ($\lambda = 0.71073$ Å). The structure was solved by the direct method using the SHELX-97 system and refined by a full matrix least squares on F^2 using all reflections.

2.3. Synthesis of polyimides derived from isomeric BTDAs

All polymerization reactions were carried out in dry nitrogen atmosphere with a mechanical stirrer. An equimolar amount of dianhydride and diamine monomers were used in all cases. A representative polymerization procedure is as follows: 4,4′-oxydianiline (ODA) (0.8564 g, 4.277 mmol) and DMAc (15 ml) were charged in a 50 ml three-necked, round-bottomed flask equipped with a mechanical stirrer and dry nitrogen gas inlet. After the dissolving of ODA, 2,3,3′,4′-BTDA (1.3782 g, 4.277 mmol) was delivered as a solid into the flask over 0.5 h. After stirring at room temperature for 12 h, polyamic acid (PAA) was formed in the viscous solution. An aliquot of PAA solution was taken out and cast on a glass plate and dried at 80 °C for 18 h, followed by heating at 150 °C(1 h), 200 °C(1 h), 250 °C(1 h) and 300 °C(1 h) to afford film of polyimide **1a**. The film was used for DMTA and tensile measurements. Then acetic anhydride (4 ml) and triethylamine (2 ml) were added to the reminder PAA solution, as the reaction progressed for 24 h to have a brown viscous solution. 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 dried in vacuo, to afford powder of polyimide **1a**; yield: 0.982 g (94%). IR (KBr): 1781 (imide C=O asym. stretching), 1720 (imide C=O sym. stretching), 1668 (diaryl ketone C=O stretching), 1377 (C–N stretching), 719 cm^{-1}

(C=O bending). $(C_{29}H_{14}O_6N_2)_n$ $(486.44)_n$: calcd C 71.61, H 2.90, N 5.76; found C 70.88, H 2.49, N 5.96.

2.3.1. Polyimide **2a**

Yield, 96%. IR (KBr): 1778 (imide C=O asym. stretching), 1718 (imide C=O sym. stretching), 1668 (diaryl ketone C=O stretching), 1372 (C–N stretching), 720 cm^{-1} (C=O bending). $(C_{29}H_{14}O_6N_2)_n$ $(486.44)_n$: calcd C 71.61, H 2.90, N 5.76; found C 70.94, H 2.83, N 5.91.

2.3.2. Polyimide **1b**

Yield, 94%. IR (KBr): 1781 (imide C=O asym. stretching), 1721 (imide C=O sym. stretching), 1667 (diaryl ketone C=O stretching), 1376 (C–N stretching), 718 cm^{-1} (C=O bending). $(C_{35}H_{18}O_7N_2)_n$ $(578.11)_n$: calcd C 72.65, H 3.14, N 4.84; found C 71.88, H 3.46, N 5.06.

2.3.3. Polyimide **2b**

Yield, 95%. IR (KBr): 1779 (imide C=O asym. stretching), 1720 (imide C=O sym. stretching), 1665 (diaryl ketone C=O stretching), 1372 (C–N stretching), 716 cm^{-1} (C=O bending). $(C_{35}H_{18}O_7N_2)_n$ $(578.11)_n$: calcd C 72.65, H 3.14, N 4.84; found C 70.94, H 3.51, N 5.02.

2.4. Synthesis of PMR-15 type polyimide resins derived from isomeric BTDAs

As shown in Fig. 2, PMR-15 type isomeric polyimide resins were prepared using the classic PMR-15 process according to the literature [23]. The monomers employed were the monomethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NE) (prepared by refluxing a solution of NA in anhydrous methanol), 4,4′-methylenediamine (MDA), and the dimethyl ester of benzophenonetetracarboxylic acid (BTDE) (prepared by refluxing a suspension of the corresponding dianhydride in anhydrous methanol). The mole ratios of reactants NE:BTDE:MDA were 2:2:3 which theoretically could yield oligomers with calculated molecular weights of 1500 (PMR-15).

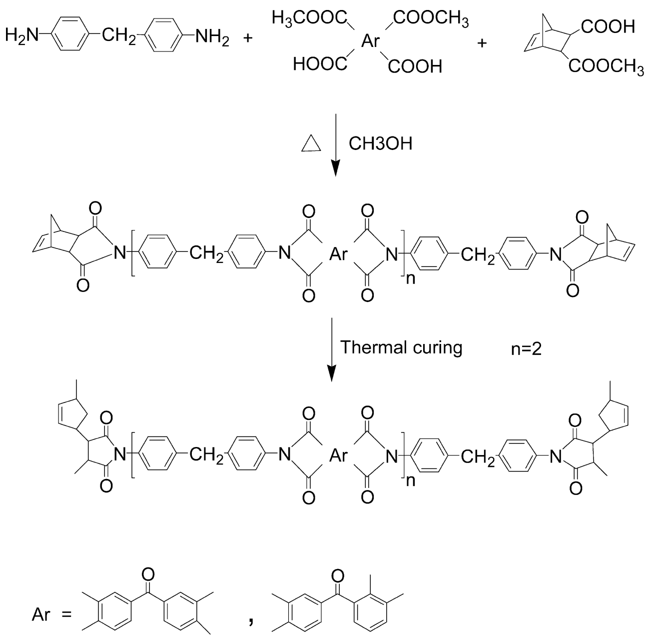


Fig. 2. Synthesis of PMR-15 type imide oligomers derived from isomeric BTDAs.

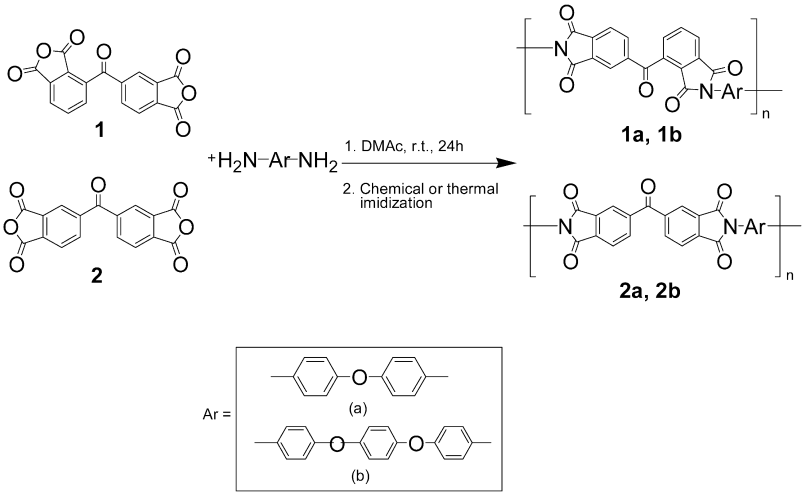
3. Results and discussion

3.1. Synthesis of polyimides derived from isomeric BTDAs

As shown in Scheme 1, all the polyimides were synthesized in two steps by the polycondensation reactions of 2,3,3′,4′-BTDA and 3,3′,4,4′-BTDA with 4,4′-oxydianiline (ODA) or 4,4′-bis(4-aminophenoxy)benzene (TPEQ) to form polyamic acid (PAA), followed by thermal or chemical imidization. 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 (asym. C=O stretching), 1720 (sym. C=O stretching), 1380 (C–N stretching), and 725 (imide ring deformation) cm^{-1}. There was no existence of the characteristic absorption bands of the amide groups near 3363 (N–H stretching) and 1674 (C=O stretching) cm^{-1}, indicating 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.

3.2. Thermal and mechanical properties of polyimides derived from isomeric BTDAs

The properties of isomeric PIs are listed in Table 1. Inherent viscosities of the polymers were in the range of 0.92–1.75 dl/g in DMAc or *p*-chlorophenol at 30 °C. The polymer films were cast from corresponding PAA solutions and cured at 150 °C/1 h + 200 °C/1 h + 250 °C/1 h + 300 °C/1 h. Fig. 3 shows the dynamic storage modulus (E') and loss tangent (tan δ) as a function of temperature for the polymer films. Regarding the peak temperature in the tan δ curves as the glass transition temperature (T_g), the polymer 2,3,3′,4′-BTDA/ODA showed an expectedly higher T_g at 343 °C than polymer 3,3′,4,4′-BTDA/ODA at 306 °C and polymer 2,3,3′,4′-BTDA/TPEQ showed an expectedly higher T_g at 268 °C than polymer 3,3′,4,4′-BTDA/TPEQ at 255 °C. This could be explained in terms of the different restricted rotation around the bond between bridge carbonyl and the carbon in phthalimide. The 2,3,3′,4′-BTDA-based polyimides had more bent chain structure and more restricted rotation around the bond than 3,3′,4,4′-BTDA-based polyimides, which could be seen from the crystal structure of 2,3,3′,4′-BTDA (Fig. 1). This result also agrees well with those obtained from polyimides based on other isomeric dianhydrides [10,12–15,19].



Scheme 1. Synthesis of polyimides from isomeric benzophenonetetracarboxylic dianhydrides.

The thermal stability of the polyimides was evaluated by TGA and the temperatures for 5% weight loss for these isomeric PIs were around 500 °C in air. As shown in Table 1, the isomeric polymers had the tensile strengths at break of 109–156 MPa, elongations at break of 8.0–11%, and initial moduli of 2.4–3.6 GPa, indicating that they could be cast into transparent, flexible and tough films.

3.3. Solubility properties of polyimides derived from isomeric BTDAs

The solubility of the isomeric polyimides is summarized in Table 2. Comparing with polyimides **2a** and **2b**, polyimides **1a** and **1b** were found to be soluble in DMAc, DMSO, NMP, and 1,1,2,2-tetrachloroethane (TCE) at room temperature. The difference in solubility may be attributed to their more bent chain for PIs from 2,3,3′,4′-BTDA. The 2- and 3′-positions of the benzophenone dianhydride are occupied by imide groups, creating a steric hindrance effect and enhancing solubility, furthermore, the imide groups inhabit interchain interaction and chain packing, thus increasing solubility. This result is also consistent with the results previously reported on the polyimides based on other isomeric dianhydrides [9,11–19]. It should be noted that polymer 2,3,3′,4′-BTDA/TPEQ could be soluble in chloroform at room temperature but insoluble at higher temperature (60 °C), which probably resulted from the strong intermolecular interactions between chloroform molecule and polymer chain at room temperature and the lowering or disappearance of the interactions at higher temperature.

3.4. Rheology properties for PMR-15 type polyimide oligomers based on isomeric BTDAs

It is known that one of the leading high temperature resin systems available today is the NASA developed PMR-15 polyimide [21–23]. Nevertheless, very problematic is the processing of PMR-15 polyimide [25,26]. Work at Rockwell [27] has shown that the characteristics of the melt flow region are dependent on both the molecular weight and molecular weight distribution. As the molecular weight is increased, the melt temperature and melt viscosity increase and the processing window decreases. Another method is the change in the aromatic diamine from MDA to other diamines, however, the thermal oxidative stability of the cured resin is lower than PMR-15 [28,29].

As shown in Fig. 4, PMR-15 type polyimide oligomer based on 2,3,3′,4′-BTDA displayed lower melt viscosity

Table 1
Properties of isomeric polyimides

Polymer	η (dl/g)		T_g^{a} (°C)	$T_{5\%}$^{b} (°C)	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
	PAA	PI					
1a	1.47^c	0.92^c	343	482	2381	109	8.2
2a	2.05^c	1.37^d	306	492	3628	156	11
1b	2.28^c	1.75^c	268	510	2525	112	9.2
2b	2.38^c	–	255	504	2546	122	8.0

[a] Obtained from DMTA at a heating rate of 5 °C/min at 1 Hz.
[b] 5% weight loss in air obtained from TGA at a heating rate of 10 °C/min.
[c] Inherent viscosity measured with 0.5 g/dl in DMAc at 30 °C.
[d] Inherent viscosity measured with 0.5 g/dl in *p*-chlorophenol at 30 °C.

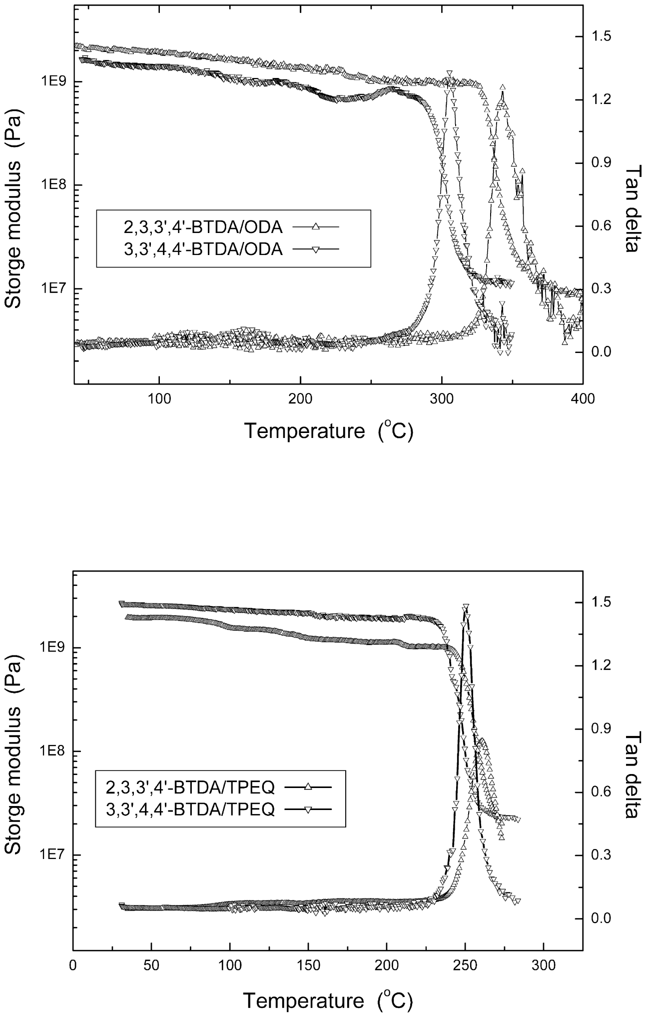


Fig. 3. Temperature dependence of mechanical storage modulus (E') and loss tangent (tan δ) at 1 Hz for isomeric polyimides **1a** (2,3,3′,4′-BTDA/ODA), **2a** (3,3′,4,4′-BTDA/ODA), **1b** (2,3,3′,4′-BTDA/TPEQ) and **2b** (3,3′,4,4′-BTDA/TPEQ).

over a broader range of temperatures as compared to those based on 3,3′,4,4′-BTDA. The lower melt viscosity was presumably a result of the irregular structure provided by 2,3,3′,4′-BTDA due to the catenation of the dianhydride. This result is in agreement with the reports on isomeric biphenyltetracarboxylic dianhydrides [14,16]. The new polyimide resin based on 2,3,3′,4′-BTDA exhibited good processability for advanced composite materials.

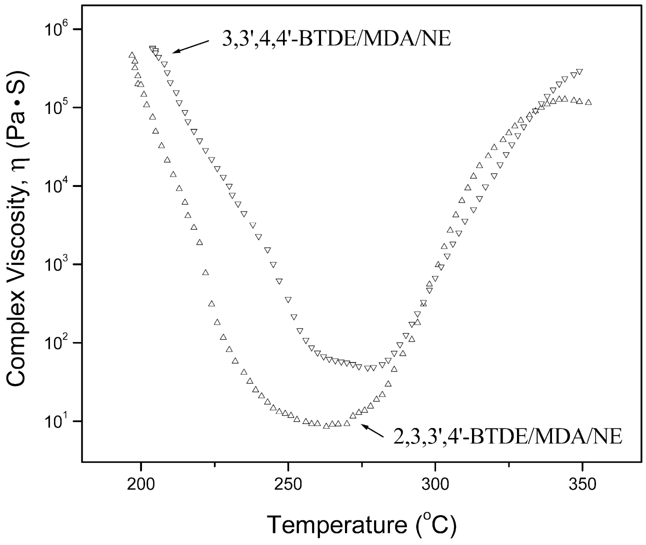


Fig. 4. The dynamic rheological behavior of PMR-15 type polyimide resins based on 2,3,3′,4′-BTDA (△) and 3,3′,4,4′-BTDA (▽) by Physica MCR-300 mechanical spectrometer at a ramp rate of 4 °C/min in air.

4. Conclusions

We found that PIs based on 2,3,3′,4′-BTDA showed excellent solubility in DMAc, DMSO, NMP and TCE. Furthermore, the PIs from 2,3,3′,4′-BTDA have higher T_gs without sacrificing their thermal properties compared with the corresponding PIs 3,3′,4,4′-BTDA. Of particular interest was that PMR-15 type polyimide resins based on 2,3,3′,4′-BTDA displayed better processing window as compared to those 3,3′,4,4′-BTDA. The dramatic effect of the catenation pattern may be attributed to the more bent chain structure of polyimides resulted from the nonlinear and asymmetric structure provided by 2,3,3′,4′-BTDA. The excellent properties exhibited in 2,3,3′,4′-BTDA based PIs demonstrate a promising potential for future applications.

Acknowledgements

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Table 2
Solubility of isomeric polyimides

Polymer	$CHCl_3$	TCE[a]	THF	DMAc	DMSO	NMP	*m*-Cresol	*p*-Chlorophenol
1a	−	+	−	+	+	+	+	+
2a	−	−	−	−	−	−	±	+
1b	+	+	−	+	+	+	+	+
2b	−	−	−	−	−	−	−	±

Key: +, fully soluble at room temperature; ±, partially soluble on heating; −, insoluble on heating.

[a] TCE = 1,1,2,2-Tetrachloroethane.

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