# Synthesis and Characteristic of A New Polyimides From 2,3,3',4'- Diphenylether tetracarboxylic dianhydride and 4,4'-Diaminodiphenylether

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**Abstract:**·

The new polyimide was synthesized from 2,3,3',4'-diphenylether tetracarboxylic dianhydride (a-ODPA) and 4,4'-diaminodiphenylether (ODA) by polymerization in dimethylacetamide (DMAc) using chemical imidization. It was molded under high temperature and pressure. This new polyimide exhibits better thermal properties than the polyimide from 3,4,3',4'-diphenylether tetracarboxylic dianhydride (s-ODPA) and 4,4'-diaminodiphenylether (ODA) made by Shanghai Research Institute of Synthesis Resins (YS-20). It shows good mechanical properties and thermal resistance. It is soluble in some organic solvents such as N-methylpyrrolidone (NMP), dimethylformamide (DMF), γ-butyrolactone etc. The thermal properties of polyimides were studied by TGA, DSC and DMA. Its melting viscosity and molecular weight were determined. It exhibits good processability. This polyimide could be applied in astronautics, aircraft, automobile and microelectronics fields.

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**Keyword:** Polyimide, 2,3,3',4'-Diphenylether tetracarboxylic dianhydride (a-ODPA), 4,4'-Diaminodiphenylether (ODA), Soluble, Processability, Thermal resistance

## Introduction

Polyimides exhibit excellent comprehensive physical properties. They have been used in astronautics, aircraft and microelectronics fields. Because most of them are insoluble in ordinary organic solvents and can not be melted by heating, we usually use their precursor polyamic acids, which are soluble in polar solvents, to form film by casting. Their molding compounds were usually produced under high temperature and high pressure. Therefore their applications were limited. In order to improve the processability of polyimides, it has been reported that soluble and thermoplastic polyimides can be obtained by introducing bulky side groups, fluorine atoms, and destroying conjugation with some free aromatic structures. However, up till now, only thermoplastic polyetherimide "Ultem" of Sabic (GE) and polyimide "Aurum" of Mitsui Chemicals are commercially available. Asymmetric aromatic tetracarboxylic dianhydrides were studied in late 90's. It was found that they exhibit special properties in Tg and processability. It was noticeable because the contradiction of thermal resistance and processability could be resolved. At first Yokota et[1,2] exploited "TriA-PI" using a-BPDA to get a new addition type of polyimide which exhibits high Tg, low viscosity and toughness. He[3-6] reported the new polyimide film from a-ODPA and ODA, this film can be melting-bonded to each other at 280°C for several seconds too. It has been applied to solar sail successfully this May in Japan. Hasegawa et[7] used a-ODPA to synthesize PI ink. Chuang[8] of NASA reported the low viscosity of PI oligomer using a-ODPA too. After that the researchers were interested in symmetric monomers to obtain polyimide exhibiting high thermal resistance and good processability. We try to improve the thermal

properties and processability of YS-20 made from s-ODPA and ODA by Shanghai Research Institute of Synthesis Resins for increasing processing efficiency. At first, we synthesized a-ODPA successfully then tried to get a new thermoplastic polyimide by using it. The better results were obtained and goal was achieved. We report it in this paper.

## Experimental

Materials.

s-ODPA, a-ODPA were obtained from Shanghai Research Institute of Synthetic Resins. Their purities are more than 99%. ODA and all solvents were used without further purification.

Polymerization.

ODA, ODPA (equivalent molar to ODA) and DMAc were introduced into a flask with a stirrer, thermometer, and nitrogen inlet. The reaction temperature was kept at room temperature for 4 hours. Then acetic anhydride and catalyst were added to PAA solution under room temperature and high stirring for chemical imidization. The polyimide powders were precipitated then filtered, washed and dried.

Measurements

Infrared spectra (IR) was measured on films used a FTIR system of Nicolet 460. TGA, DSC and DMA were performed with a TGA Q50, DSC Q10 and DMA Q800 of TA's thermal analysis instrument at a rate of 20°C/min and 5°C/min in $N_2$ and air atmosphere respectively. Shimadzu Autographs AG-50KNE was used for testing mechanical properties of molding compounds by GB standard. The molecular weights of polyimides were determined by GPC of on a JASCO PU-2080 Plus with two polystyrene gel columns (TSK GELS $GMH_{HR}$-M). *N,N*-Dimethylformamide (DMF) containing 0.01 M LiBr as an eluent at a flow rate of 1.0 $mL \cdot min^{-1}$ calibrated by polystyrene standard samples. Rheological properties were measured by TAAR 2000 rheometer at a rate of 4°C/min in $N_2$ and 1Hz between 300°C and 450°C.

Molding

The polyimide powder was added in a mold then molded under high temperature and pressure.

## Results and Discussion

At first, the polyimides were characterized by IR. It was found that the peaks appear near 1780$cm^{-1}$ in IR from Fig.1. It means there are imide rings in these polymers.

We used two methods of thermal and chemical imidization for polyimide from a-ODPA and ODA. It was found that polyimide obtained by chemical imidization exhibited high viscosity. However it was not stable to get high viscosity polyimide by thermal imidization. It is possible that cyclo-oligomer formed in thermal imidization because of a-ODPA configuration. So we used chemical imidization to obtain polyimide powder for molding. The viscosity of polyimide can be controlled by changing the condition of chemical imidization. The range of PI viscosity is from 0.4dl/g to 1.2dl/g.

The solubility of polyimide was investigated in several organic solvents. We found this PI is soluble in polar solvents. The results are shown in Table 1. Its solubility is more than 10% in DMAc, NMP, DMF, DMSO and γ-butyrolactone. But it is not soluble in THF, cyclohexanone, dioxane. It is because regularity and crystalline of this PI could be damaged by a-ODPA configuration, the solubility is increased.

**Table 1 The solubility of polyimides in organic solvents**

| PI | DMF | DMAc | NMP | DMSO | γ-BTL | THF | DIOX | CHXON |
|---|---|---|---|---|---|---|---|---|
| **a**-ODPA/ODA | ◎ | ◎ | ◎ | ◎ | ◎ | × | × | × |
| s-ODPA/ODA | △ | △ | △ | △ | × | × | × | × |

Note: DIOX, Dioxane; CHXON, Cyclohexanone, γ-BTL, γ-butyrolactone

◎, soluble; △, partly soluble; ×, insoluble.

The molecular weights of polyimides were determined by GPC. It was found that the molecular weight of polyimides obtained by chemical imidization is higher than that of thermal imidization. PI molecular weight decreases because PAA molecular weight could decrease by heating. Their ratios of Mn and Mw are about 2. This is similar to the theory of condensation polymer. The results are shown in Table 2.

**Table 2 The molecular weight of polyimide (GPC)**

| PI (a-ODPA/ODA) | η(ml/g) | Mn | Mw | Mw/Mn | Imidization |
|---|---|---|---|---|---|
| No. 1 | 81.96 | 36000 | 68800 | 1.91 | Chemical |
| No .2 | 52.72 | 29700 | 58300 | 1.96 | Chemical |
| No. 3 | 27.25 | 16100 | 34200 | 2.13 | Thermal |

Note: Thermal imidization is one step heating method in DMAc.

The thermal properties of PI were determined by TGA, DSC and DMA. The results are shown in Table 3. It was found that the Tg of PI (a-ODPA/ODA) is about 10°C higher than that of PI (s-ODPA/ODA) by DSC and DMA. This is the same result reported by Yokota. But the thermal stability of this PI (s-ODPA/ODA) determined by TGA in air is better than that of PI (a-ODPA/ODA).

Table 3 The thermal properties of polyimides

| | $T_5$ (°C) | $T_{10}$ (°C) | Tg (°C) | | |
|---|---|---|---|---|---|
| | TGA in air | | DSC | DMA* | |
| | | | | E' | tanδ |
| PI (a-ODPA/ODA) | 551 | 567 | 277 | 261.6 | 289.7 |
| PI (s-ODPA/ODA) | 561 | 576 | 266 | 247.7 | 277.5 |

* 3-Point bending at 1Hz

The melting viscosity of polyimide was determined. The results are shown in Fig.2 to Fig.4. We found that the melting viscosity of PI (a-ODPA/ODA) is lower than that of PI (s-ODPA/ODA). The former is 7000 Pa·s but the latter is 60000Pa·s at 380°C. The melting viscosity of PI increased with rising of inherent viscosity. The van der Waals' force decreased between molecules by symmetric molecule structure, therefore leading to the lower melting viscosity. It is similar to the reason of solubility in solvents.

We obtained the molding compound of PI (a-ODPA/ODA) under 310°C and 150kg/cm$^2$. The mechanical properties were determined at room temperature and 220°C. Comparing PI (a-ODPA/ODA) with PI (s-ODPA/ODA), we found at high temperature the properties of PI (a-ODPA/ODA) are better than that of PI (s-ODPA/ODA). The modulus of PI (a-ODPA/ODA) increased at 220°C about 20% more than that of PI (s-ODPA/ODA) molded under 380°C and 400kg/cm$^2$. The temperature and pressure of molding of PI (a-ODPA/ODA) were lower. The results are shown in Table 4. Because a-ODPA has asymmetric

configuration, the crystalline is damaged and the melting viscosity decreases. The result is shown in Fig.5. But the rotation energy is higher than that of the symmetric PI (s-ODPA/ODA), Tg of PI (a-ODPA/ODA) is about 10°C higher than that of PI (s-ODPA/ODA). The impact strength increased at the same time.

Conclusion

We synthesized a-ODPA and polyimide from a-ODPA and ODA. This polyimide exhibits good mechanical and thermal properties, processability. Comparing the properties of PI (a-ODPA/ODA) and PI (s-ODPA/ODA), we found the former exhibits better thermal properties than the latter. This PI is very soluble in some polar organic solvents. It can be applied in astronautics, aircraft, automobile and microelectronics fields.

Table 4 The properties of polyimide molding compounds

| | Tensile Strength | Compression Modulus | Compression Strength | Bending Modulus | Bending Strength | Impact Izod Modulus | Impact Izod Strength | Elongation |
|---|---|---|---|---|---|---|---|---|
| | MPa | GPa | MPa | GPa | MPa | GPa | $KJ/m^2$ J/m | % |
| RT | | | | | | | | |
| YS-20A | 119 | 2.96 | 160 | 1.39 | 168 | 3.22 | 250 94 | 21 |
| YS-20 | 119 | 3.18 | 178 | 1.49 | 167 | 3.17 | 300 | 34 |
| 220℃ | | | | | | | | |
| YS-20A | 44 | | 60.4 | 1.06 | 73.7 | 2.08 | | |
| YS-20 | 29 | | 40.7 | 0.85 | 52.5 | 1.58 | | |

Note: YS-20A (a-ODPA/ODA); YS-20 (s-ODPA/ODA)

The mechanical properties were determined by GB Chinese standard.

Reference

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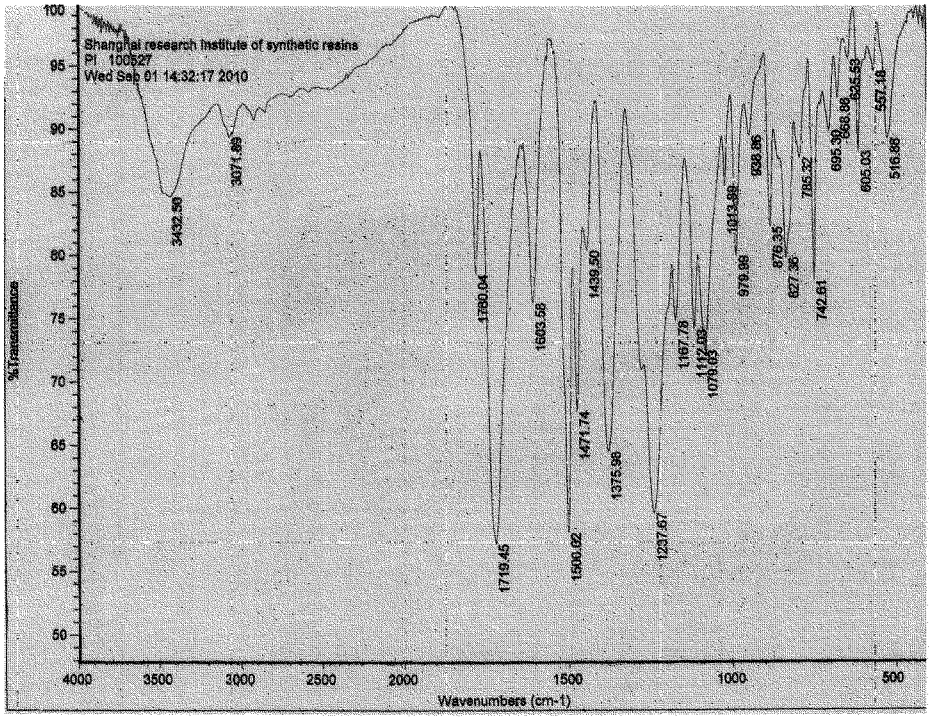


Fig. 1 IR of Polyimide (a-ODPA/ODA)

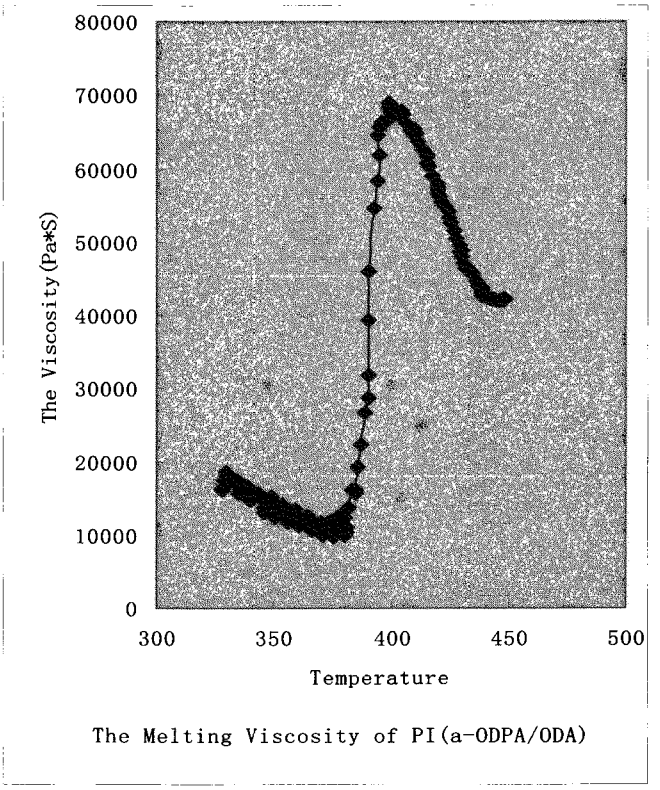


Fig. 2 The Melting Viscosity of PI (a-ODPA) $\eta$ :99.88ml/g

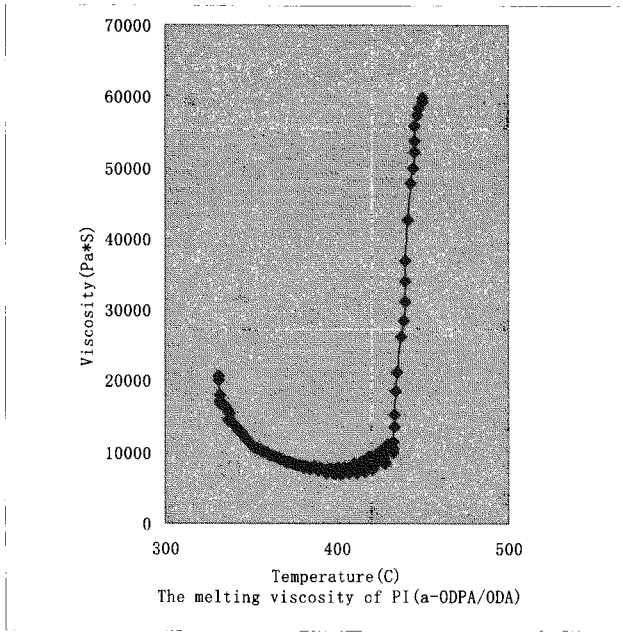


Fig. 3 The Melting Viscosity of PI (a-ODPA) $\eta$ :67.84ml/g

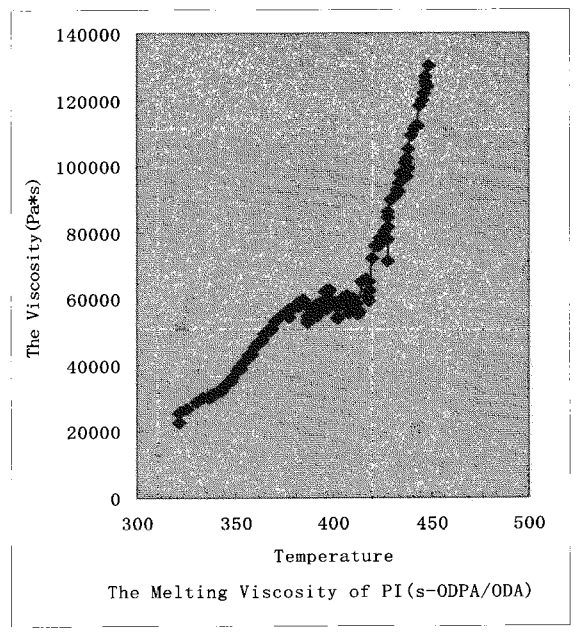


Fig. 4 The Melting Viscosity of PI (s-ODPA)

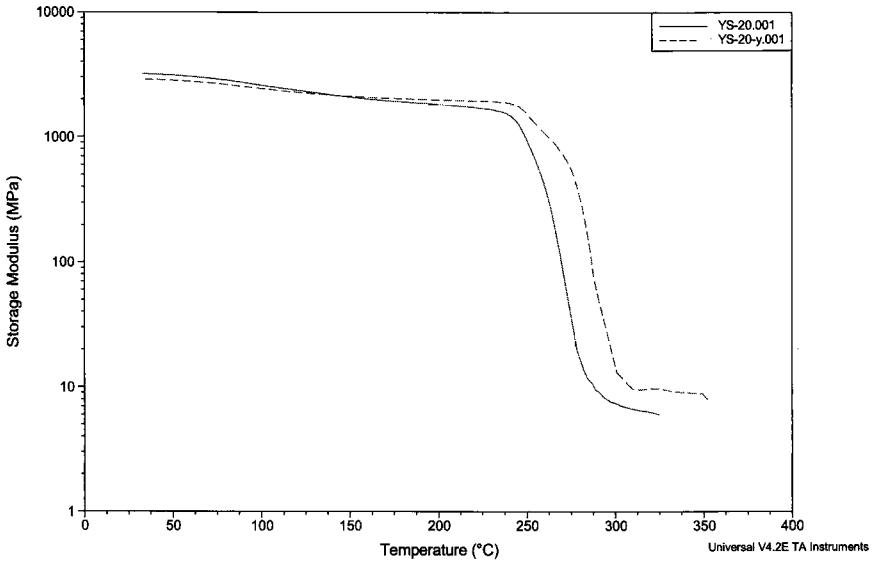


Fig. 5 DMA of Polyimides (a-ODPA/ODA and s-ODPA/ODA)

YS-20 (s-ODPA/ODA); YS-20 (a-ODPA/ODA)