## The Synthesis and Characteristic of A New Soluble Polyimides

# He Feifeng\*, Lv Jue\* and Qiu Ziixue\*\* \*Technology Research Institute of Shanghai Hua Yi(Group) Company \*\*Shanghai Research Institute of Synthesis Resins 36 Cao Bao Road, Shanghai, China, 200235

## Abstract:

The new soluble polyimides were synthesized from various aromatic dianhydrides and 3,3'-dimethyl-4,4'-diamino-5,5'-diethyldiphenylmethane (DMEPMA) by one step polymerization in N-methylpyrrolidone (NMP). The polyimides are soluble in organic solvents e.g. tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), methylene chloride, and cylcohexanone (CHXON). The films can be formed by casting their solutions. The films exhibit good mechanical properties and thermal resistance. The polyimides exhibit better resistance to alkali than Kapton film. The thermal resistance of polyimides was studied by TGA and DMA. These kinds of polymiides could be applied in microelectronic fields.

Keyword: Soluble, Polyimide, 3,3'-dimethyl-4,4'-diamino-5,5'-diethyl-diphenylmethane (DMEPMA)

## Introduction

Polyimides exhibit excellent comprehensive physical properties. They have been used in astronautics, aircraft and microelectronics fields. Because they 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 processibility of polyimides, it has been reported that soluble and thermoplastic polyimides can be obtained by introducing bulky side groups, fluorine atoms, and destroying conjungation with some free aromatic structures. However, up till now, only thermoplastic polyetherimide "Ultem" of GE and polyimide "Aurum" of Mitsui Chemicals are commercially available. In addition, the microelectronic industry is developing rapidly the new trend of developments is miniaturisation, high integration, multiple stratification. The new flexible printed circuit board (FPC) is non-adhesive type for decreasing thinness and increasing heat resistance. The soluble polyimides have been attracted attentions for FPC application. 2,2'-substituted 4,4'-diphenylmethanediamine (i.e., 2,2'-substituted benzidine) have been used as diamine monomer for improving solubility and optical transparency.<sup>[1-6]</sup> Polyimides from various dianhydrides and 3,3'5,5'-tetramethylbenzidine used as diamine have been studied as gas separation membranes.<sup>[7, 8]</sup> Their property-structure relationships have been reported.

3,3'-dimethyl-4,4'-diamino-5,5'-diethyl-diphenylmethane (DMEPMA) has been reported as diamine to synthesis polyimides.<sup>[9-11]</sup> They were used for coating <sup>[9,10]</sup> and film.<sup>[11]</sup> At first, polyamic acids were synthesized in NMP then they were imidized by heating and chemical method. But their molecular weights were not reported. We selected it as diamine to synthesize

soluble polyimides with various aromatic dianhydrides in a high boiling solvent, such as NMP by using isoquinoline as catalyst, by one step method. <sup>[12]</sup> They exhibit high molecular weight and good solubility in THF, DMAc, NMP, cyclohexanone, dichloromethane and thermoplastic properties except those obtained from PMDA and DMEPMA. We are interest in their solubility, processibility and other properties. We are trying to obtain a new type of polyimide that exhibit good thermal resistance until 250°C, can be cast into film from polyimide solution, and can be compressed for molding at the same time.

### **Experimental**

### Materials.

BPDA was purchased from Ube Chemical Industry Ltd. Co., ODPA, BSAA, PMDA were obtained from Shanghai Research Institute of Synthetic Resins. BTDA was purchased from Daicel Chemical Co.. All the dianhydrides were used directly without purification. DMEPMA was got from Ihara Chemical Industry Co. Ltd, and it was recrystallized with ethanol before use. All solvents and isoquinoline were used without purification.

## Polymerization.

DMEPMA, dianhydride (equivalent molar to DMEPMA) and NMP were introduced into a flask with a stirrer, thermometer, nitrogen inlet and Dean-Stark trap. Isoquinoline and xylene were used as a catalyst and azeotrope former. The reaction temperature was rose up  $160^{\circ}$ C and kept for 3 hours for moving water, then heated again to distillate out xylene and reacted at 190-200°C for several hours. After cooling, the polymer solution was precipitated in ethanol by high speed stirring. The polyimide powder was obtained by filter, washing and dry.

The polyimide films were directly prepared by casting the NMP or other solutions of polyimides and heating up 250°C for removing the solvent. The films were characterized by UV, IR, TGA, and DMA. The polyimide powders were soluble in various solvents as THF, DMAc, NMP, cyclohexanone and methylene chloride etc. in solubility test. The molding compounds were obtained by compression under high temperature and pressure.

#### Measurements

Infrared spectra (IR) and ultra violet spectra (UV) were measured on films used a FTIR system of Nicolet 460 and Shimadzu UV-240 respectively. TGA and DMA were performed with a TGA Q50 and DMA Q800 of TA's thermal analysis instrument at a rate of 20°C/min and 5°C/min in N<sub>2</sub> and air atmosphere respectively. Shimadzu Autographs AG-50KNE was used for testing mechanical properties of film by GB standard. The molecular weights of polyimides were determined by GPC of Waters

#### **Results and Discussion**

At first, the polyimides were characterized by IR. It was found that the peaks were appearance near 1778cm<sup>-1</sup>, 1727 cm<sup>-1</sup>, 1372 cm<sup>-1</sup>, 731 cm<sup>-1</sup> in IR from Fig.1. It means there are imide ring in these polymers. We also found that DMEPMA has lower activity than ODA because the steric hindrance of methyl and ethyl groups at ortho position affecting the reactive activity of amino group in between. Hence, we can not obtain high molecular weight polymer in common polar

solvents at room temperature, but the high molecular weight of polyimide can be obtained in NMP at 190-200°C by one step method. The molecular weight of polyimide can be determined because the polyimides are soluble in THF. The effects of reaction time and catalyst have been studied. It was found the molecular weight linearly increased with increasing of reaction time from Fig.2 (PMDA/DMEPMA) and Fig.3 (ODPA/DMEPMA). The effect of catalyst was showed in Fig,4 (BPDA/DMEPMA) and Fig.5 (PMDA/DMEPMA). We found the molecular weight increased with increasing of catalyst, but its effect was not evident in the case of using BPDA. Maybe it relates to the reactivity of dianhydride. So we can control the molecular weight of polyimide by adjusting reaction conditions. We obtained higher than 200000 (Mw) of the soluble polyimides.

We tested the solubility of polyimides in various organic solvents. The results were shown in Table 1. It is interesting to find cyclohexanone, methylene chloride were good solvents for these polyimides. So we can easily obtain films from the above solutions of polyimides by casting. Color of polyimide film derived from BSAA and DMEPMA is the lightest among all other polyimides used DMEPMA as diamine. Its cut spectrum is near 310 nm at the ultraviolet region. This is because  $\pi$  conjungation structure is destroyed by methyl and ethyl side groups in benzidine and isopropyl in BSAA. It is slightly yellowish and has good transparency. It was found that the structure of the polyimide changed during heating up 320°C. The mechanism was studied by using IR and TGA. A new peak was appeared in 1650cm<sup>-1</sup> at 300℃ and disappeared at 350℃ from Fig.6. This peak appears in the type of polyimides from various dianhydrides and DMEPMA. So we think there could be some structure changes in DMEPMA. This peak is characteristic to the styrene structure. It may be assumed that ethyl group was dehydrogenated in benzene and formed styrene structures. Then the double bond of styrene structure was open and cross-linked by thermal initiation at 350°C. After the thermal treatment at 320°C, the polyimide film was no longer soluble in DMAc and the color became yellow with the rise of the heating temperature. The result of TGA is in agreement with our hypothesis. The weigh loss was 0.478% at 320% for one hour under  $N_2$  in polyimide from PMDA and DMEPMA. The weigh loss of dehydrogenation is 0.542% in theoretical calculation and maybe the dehydrogenation of ethyl group was not completed.

PI	m-cresol	DMAc	NMP	THF	CH <sub>2</sub> Cl <sub>2</sub>	CHXON	
PMDA	Ø	×	Ø	$\triangle$	Ø	Ø	
BPDA	Ø	Ø	Ø	O	Ø	O	
BTDA	Ø	Ø	Ø	Ø	Ø	O	
ODPA	O	Ø	O	Ø	Ø	Ø	
BSAA	Ø	Ø	Ø	0	Ø	Ø	

Table 1 The solubility of polyimides in various solvents

Note: DMEPMA was used as diamine. Inherent viscosity was determined in DMAc at 30°C. Soluble;  $\triangle$ , partly soluble;  $\times$ , insoluble.

The film was formed by casting solution of polyimide. Cyclohexanone was better than other solvents because solubility of polyimide is high in it and its water absorption is very low. The properties of polyimides were showed in Table2. We found the tensile strengths and elongation at break of films were 93.1-131MPa and 7.6-12% respectively. It can be found T<sub>5</sub> and T<sub>10</sub> (5% and 10% weight loss temperatures) were 446-495°C and 510-538°C in N<sub>2</sub>, but they were 428-473°C in air respectively. It is evident that stability is better in N<sub>2</sub> than that of air. It is BPDA>ODPA,

BSAA>BTDA>PMDA in order of stability for thermal weight loss. Because of dehydrogenated in benzene the radio of weight loss is bigger in polyimide made from PMDA and DMEPMA than that of others. This is one reason that temperature of weight loss is lower in case of PMDA. Tg of polyimides are changed from 244°C to 322°C by various dianhydrides except PMDA, because it can not be determined by DSC. The properties of polyimide made from BPDA and DMEPMA is the highest than others.

The DMA results of polyimides derived from PMDA/DMEPMA, BPDA/DMEPMA and BSAA/DMEPMA were shown in Fig.7. The storage modulus E' decreased rapidly from 2000 MPa at room temperature to 5 MPa around 300°C for BSAA/DMEPMA. The E' of BPDA/DMEPMA decreased from 2000 MPa to 40MPa at room temperature to 400°C. But the change of E' was from 2000 MPa to 600 MPa at the same temperatures in the case of PMDA/DMEPMA. It means they exhibit good processbility for BPDA/DMEPDA and BSAA/DMEPMA, but its processbility is poor for PMDA/DMEPMA. The molding compound of polyimide from PMDA/DMEPMA was obtained by compression molding under 400°C and 4MPa. It was brown and transparent and difference from "Vespel" made in Du pont from PMDA and ODA. It became dark brown and opacity after 400°C under nitrogen, but shape and size were not changed. The molding compounds of BPDA/DMEPMA and BSAA/DMEPMA can be obtained at 370°C and 280°C under 4 MPa respectively. The result is consistent with the DMA analysis. We found their processbility are better than that of polyimides from ODA.

1able 2 The physical properties of polyimide films								
Dianhydride of PI	Tensile	Elongation	Tg	T₅℃		T <sub>10</sub> ℃		Water Absorption
	MPa	%	°C	N2	air	N2	air	(%)
PMDA	105	8.3	ND	446	428	514	469	2.17
BTDA	120	7.6	287	477	461	510	504	1.22
BPDA	131	12	322	495	463	538	523	0.56
ODPA	115	8.2	266	493	449	514	497	1.1
BSAA	93.1	9.7	244	493	473	509	510	0.9

Diamine: DMEPMA. Film was obtained by casting NMP solution of PI.

Water absorption of polyimides were determined. We found the order of water absorption is BTDA>PMDA>BSAA>BPDA. This is related to polarity of molecular structure. The carboxyl in BTDA is polar group, so its water absorption is the highest between these polyimides. The polyimide films were drenched in 20% (wt%) of NaOH solution at room temperature for two days. We found BPDA type film exhibits the best resistance to alkali. After drenching two days, it was not any changed for weight loss and strength, but Kapton film was partly soluble in alkali solution. We tested various films from BTDA, ODPA and BSAA. It was found the order of alkali resistance is BPDA, BTDA, ODPA>BSAA>PMDA>Kapton. The result was shown in Table 3. This could be the reason that is the steric hindrance of methyl and ethyl in ortho position of amino group. The stabilities are good at room temperature for these NMP solutions of polyimides. We have not found the solutions occurred phase separation and precipitation for two years.

#### Conclusion

various dianhydrides Α new soluble polyimides were obtained from and 3,3'-dimethyl-4,4'-diamino-5,5'-diethyl-diphenylmethane (DMEPMA) used as diamine. They are soluble in organic solvents and can be cast into films and molded into compounds. It is assumed that some cross-linking reactions take place above 300°C, and makes the polyimides insoluble in solvents. These polyimides exhibit good physical properties and can be applied as electronic package material, coating, film, thermoplastic molding compound and etc.

Table 3 The resistance to alkali for polyimide films							
Туре	PMDA	BPDA	BTDA	ODPA	BSAA	Kapton	
Weigh loss (%)	18.6	0	0	0	1.5	40	
Color change	No	No	No	No	No	Fading	
Strength	Brittle	Good	Good	Good	Good	Brittle	

- - - - ---

Condition: 20% alkali solution in room temperature for two days.

## References

- 1. Becher, K.H., Schmidt, H-W., Macromolecules 25, 6784 (1992).
- 2. Bhowmik, P. K., Atkin, E. D. T., Lenz, R. W., Macromolecules 26, 440 (1993).
- 3. Schmidt, H-W., Guo D., Makmol. Chem. 189, 2029 (1988).

\_\_\_\_

- 4. Kathy C. Chuang; James D. Kinder; Diana L. Hull; David B. McConville and Wiley J. Youngs, Macromolecules 30, 7183 (1997)
- 5. J.P. 59108029 (1984)
- 6. J.P. 59232455 (1984)
- 7. Y. Kobayashi, T. Kasai, Proceeding of ICOM'90, 1407 (1990).
- 8. K. Okamoto, H. Kita, Koubunshi Kakkou (Japan) Vol.41, No.1, 16 (1992).
- 9. USP 4629777
- 10. J.P (koukai) 89-16829
- 11. J.P (koukai) 91-252478
- 12. Chinese Patent 200410053702



Fig.1 IR of PMDA/DMDEPMA













-113- ポリイミド・芳香族系高分子 最近の進歩 2007