Semi-aromatic transparent polyimide

Shinsuke Inoue *, Noriyuki Kawanishi
MANAC Inc., Research Laboratory
92 Minooki-cho, Fukuyama, Hiroshima 721-0956 JAPAN

Abstract

Semi-aromatic transparent polyamide, using 4,4-oxydiphthalic anhydride (ODPA) and trans-1,4-diaminocyclohexane (CHDA), was prepared in NMP (1-methyl-2-pyrrolidone) .
Polyamic acid derived from ODPA and CHDA showed high viscosity and its polyimide film had a good transparency (T% at 400nm : 81.4%) which was almost colorless and adequate flexibility. From thermal analysis, Tg was not observed in DSC measurement. Td(5wt%) was 498.7℃。
More data for example CTE, ε, mechanical strength are necessary to characterize the polyimide film. These data will be presented at the conference held in China.

1. Introduction

Many transparent polyimides are reported[1] which have either alicyclic diamine or anhydride unit. But (ODPA/CHDA)polyimide presented here has not been shown so far. Hasegawa et al.[2] reported that s-BPDA can react with CHDA to get flexible polyimide film with low dielectric constant and low CTE. In the (ODPA/CHDA) polyimide, the polyimide film showed better transparency compared to (s-BDPA/CHDA) polyimide film. The color of (ODPA/CHDA) polyimide film was almost colorless. (ODPA/CHDA)polyimide film prepared in this work was treated in air oven through whole process. If imidization process is carried out in nitrogen atmosphere, (ODPA/CHDA) polyimide film color should be improved better.
Thermal analytical data is not enough now. Only DSC and TGA measurement were done. Another thermal analysis (TMA for taking CTE) and ε (dielectric constant) mechanical strength are necessary to characterize (ODPA/CHDA)polyimide film.

2. Experiment

2.1 Materials

ODPA was our own company's product. CHDA(trans-1,4-cyclohexane) was purchased from TCI(Tokyo Kasei Kogyo LTD.,) and used without further purification. NMP solvent with dehydrated grade is use as received from WAKO Pure Chemical industries LTD,.

A typical polyamic acid polymerization process is as follows : CHDA was first dissolved in NMP at room temperature. After adding ODPA, reaction solution was stirred vigorously for 4hr to get constant viscosity.

The NMP solution of polyamic acid (typically 17wt%) was coated onto the Pyrex glass plate and dried at 130℃ for 10min in air oven. Then temperature was raised to 200℃ and cooled

to room temperature. The polyimide film was peeled off from glass plate, followed by setting stainless frame. The frame was placed in air oven which temperature was raised from 200℃ to 300℃ to remove residual stress. After the temperature reached to 300℃, Polyimide film was taken out to cool down to room temperature for analysis.

2.2 Measurement

Viscosity : viscosity of polyamic acid was taken at 25℃ using B type rotation viscosimeter.

Transmittance : transmittance was measured using Shimadzu UV-2200 photometer

Thermal analysis : DSC and DTA measurement for PI film were conducted on a Shimadzu DSC-50 and a Shimadzu TGA-50, respectively. Both heating rate of DSC and TGA was 10℃ /min.

3. Result and Discussion

3.1. Transparency

Fig. 1 shows the transmittance of (ODPA/CHDA)polyimide film which is 20 μ in thickness, in ultraviolet – visible region, compared with other typical polyimide film (Kapton®, BPDA/CHDA, DSDA/CHDA).

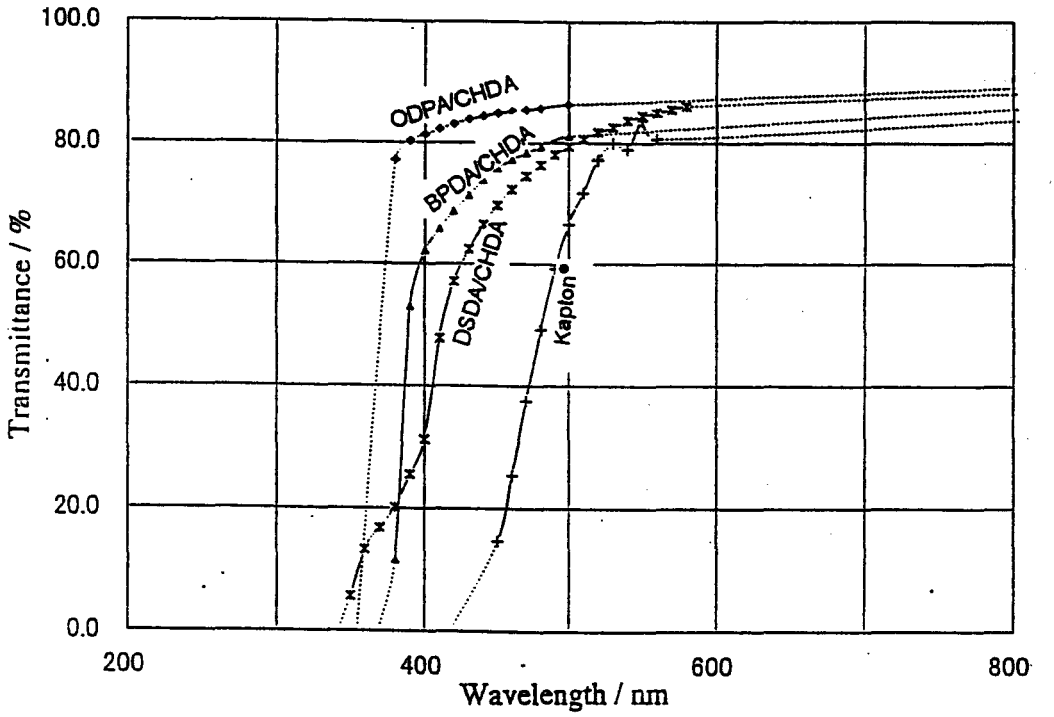

Fig. 1 Transmittance curve of 20 μ thick (ODPA/CHDA) PI film, compared with BPDA/CHDA, DSDA/CHDSA, Kapton®

Transparency of (ODPA/CHDA) PI film was much better than other PI films (T% at 400nm : 81.4%). It is assumed that CHDA units prevent the charge transfer (CT) in the PI chain to get almost colorless film. Furthermore, ether bonding of ODPA seems to contribute to get better transparence compared to biphenyl (BPDA) and sulfone (DSDA) bonding.

The difference of electron density between ground state and first excited state (356.6nm absorption) was calculated using INDO/S method (Fig.2). The dark gray regions correspond

to those with increased density, while the light gray region correspond to delete regions for the ground. Fig 2 shows the less electron transference in the chain and low absorption strength.

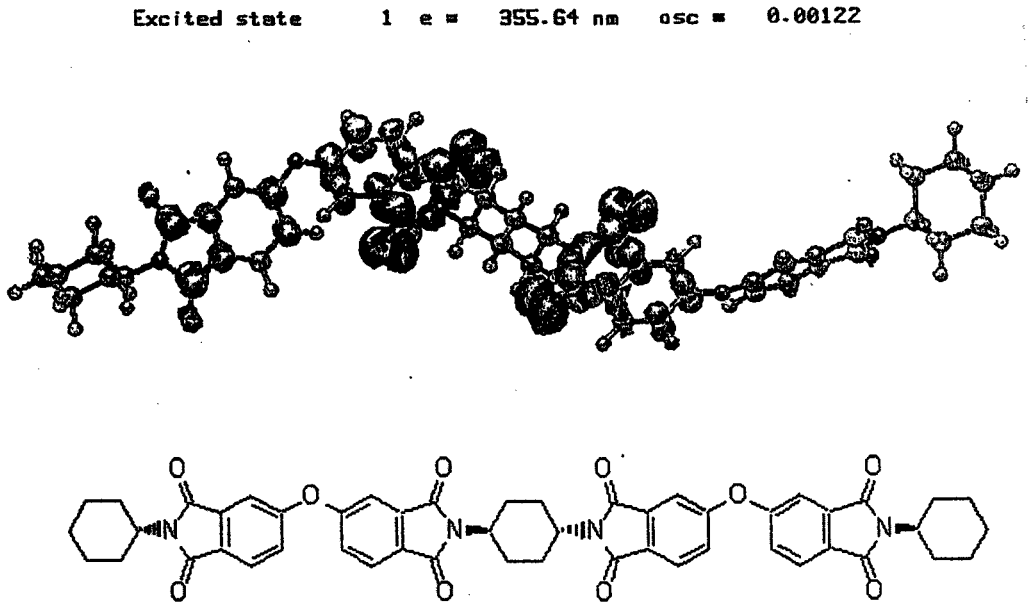

Fig 2 Model compounds of (ODPA/CHDA) PI for MO calculation

3. 2. Thermal property

DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric analysis) measurement was carried out and show in Fig 3 and Fig 4, respectively.

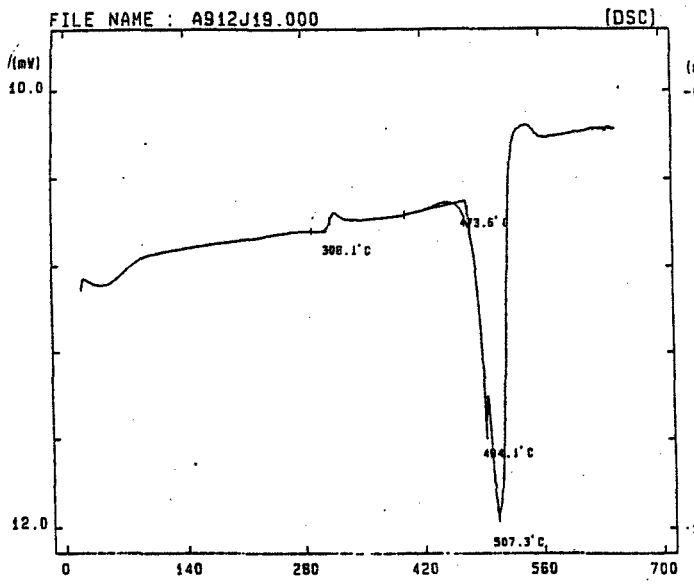

Fig 3 DSC curve of ODPA/CHDA PI film : heating rate of 10℃/min

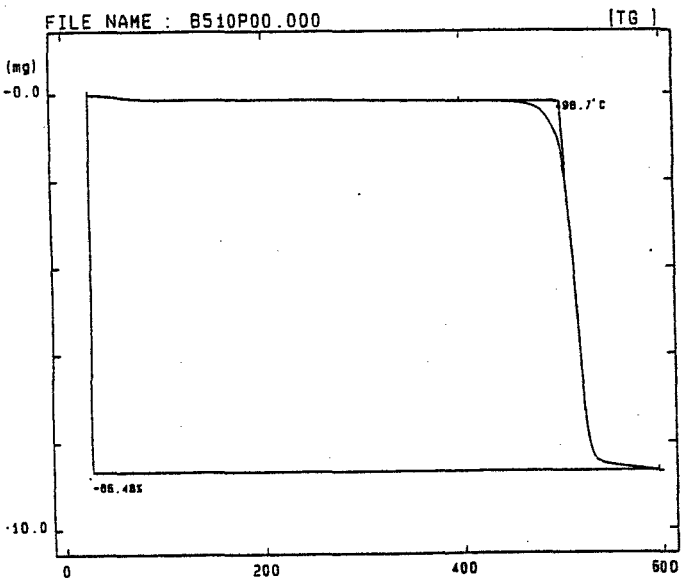

Fig 4 TGA curve of ODPA/CHDA PI film in a nitrogen atmosphere at heating rate of 10℃/min

In Fig 3, small exothermic change at 308℃ seems to be a crystallization energy, because its exothermal disappeared in the second run. Around 470℃, the (ODPA/CHDA) PI film got thermo plasticity.

The 5% wt loss temperature(T_d^5) was 498.7℃ for the (ODPA/CHDA) PI film. This indicate

the relatively low thermal stability compared the normal wholly aromatic polyimide. The relative low thermo stability seems to be due to the CHDA unit.

4. Conclusion

The goal of this work is to get high transparence PI film which has good thermo stability >300 ℃. By using semi-aromatic PI of ODPA and CHDA, the purpose was almost accomplished. PI film shown here was treated in air oven in the whole process, so the transparency should be improved if the imidization process was done in nitrogen atmosphere or Mac was used in stead of NMP.

More thermal analysis data(for example, TMA for taking CTE), dielectric constant(ε), and mechanical data are necessary to characterize ODPA/CHDA PI film used in this work. These data will be presented at conference held in China.

References

1)for example,

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- T.Matsumoto et al. *Macromolecules*, 28 5684-, (1995)
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2) M.Hasegawa *High Perform Polym.*, 13 S93-S106 (2001)