Synthesis and Characterization of Polyimide Films for Flexible Display Substrates

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Abstract

A series novel films of polyimide (PI) and co-polyimide (Co-PI) containing fluorine with colorless, flexible properties was prepared by a two-step process from various commercial aromatic monomers such as 4,4'-(Hexafluoro iso propylidene) diphthalic anhydride (6FDA), 2,2'–Bis(Trifluoromethyl) benzidine (TFDB), 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (AH6FP) and Bis(4-(3-aminophenoxy)phenyl)sulfone (BAS). Furthermore, these obtained transparent and flexible Co-PI films exhibited excellent thermal stability with the decomposition temperature (at 5% weight loss) around of 500°C and the glass transition temperature (T_g) in the range of 275-350°C.

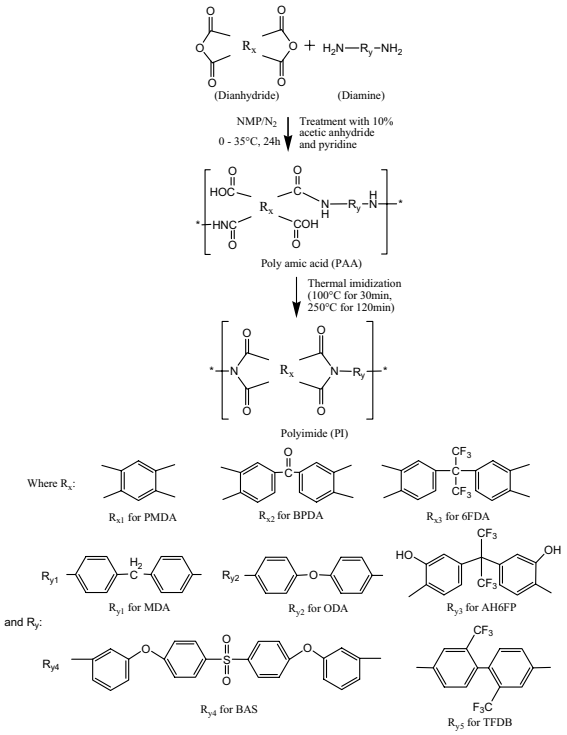
1. Introduction

Polyimide films have been used widely in the electronic industry due to their good mechanical properties, chemical resistance and thermal stability [1-3]. Although there have been many research reports related to the novel synthesis of polyimide, its application to the substrate for organic light-emitting diodes (OLEDs) were limited due to yellow color and stiffness of the film. The aim of this research was to make new polyimide films which could be applied to the flexible OLED substrate.

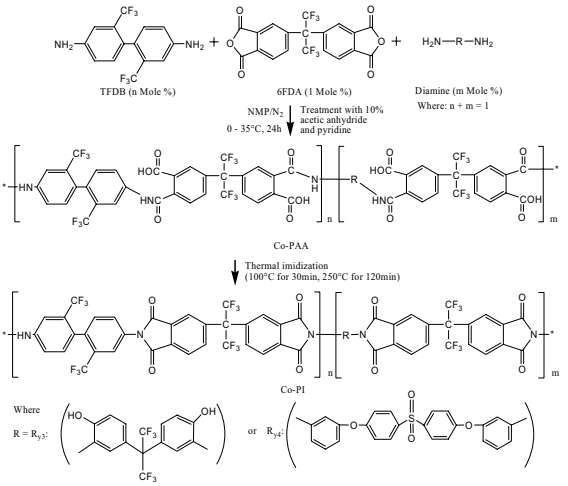
2. Experimental

Synthesis Poly Amic Acid (PAA) and Co-poly Amic Acid (Co-PAA)

PAAs and Co-PAAs were synthesized via the process shown in Scheme 1 and Scheme 2. First, aromatic diamine monomer was dissolved in NMP solvent in a three-neck round bottomed flask equipped with a nitrogen inlet and outlet and stirrer. The solution was cooled at 0°C and the aromatic dianhydride monomer was added and stirred at the temperature of ice-water bath till it became clear. The solid content of mixture monomer was 15 wt%. Reaction mixture was then reacted for 24 hours at 35°C under nitrogen atmosphere. The mixture was subsequently treated with 10 mol% acetic anhydride and pyridine solution for 150 min, respectively. The obtained PAAs and Co-PAAs were precipitated twice in distilled water, filtered and dried at ambient temperature in the vacuum oven for 12h [2, 3].



Scheme 1. Synthesis of poly amic acids and conversion to polyimide films



Scheme 2. Synthesis of Co-polyamic acids and conversion to Co-polyimide films

Films Making

Polyamic acids were converted into polyimide films by the thermal imidization method. PAAs and Co-PAAs were dissolved in N,N-dimethylacetamide (DMAC) solvent to make 35wt% solutions. PI and Co-PI films were obtained by coating the corresponding PAAs and Co-PAAs solutions onto clean and dry glass by Automatic Film-Coating Apparatus (Comate^{TM} 3000V) and subjecting to thermal imidization process in IR oven. Film thickness was controlled from 40 to 140μm by the bar diameter.

The imidization process was performed according to the two-step method. The first was pre-baking at 100°C for 30min, and the second baking at 250°C for 120min [4-6]. After thermal treatment, films were removed from the glass substrate by immersing into hot water, washed by methanol and dried in IR oven.

3. Results and Discussion

Effects of Solvent on the Synthesis of PAAs

We used three different solvents such as NMP, DMAc and DMF for the synthesis of PAAs as shown in Table 1. The results showed that the highest reaction yields as well as the best PAA colors were obtained when using NMP as solvent. Therefore we used NMP for synthesis of all PAAs and Co-PAAs.

Table 1. Effect of solvent on the PAA synthesis

PAA name	R_x	R_y	Solvent	Yield (%)	Color
PAA.1	R_{x1}	R_{y1}	NMP	87.0	Yellow
PAA.1	R_{x1}	R_{y1}	DMAc	67.7	Yellow
PAA.1	R_{x1}	R_{y1}	DMF	78.0	Yellow
PAA.2	R_{x1}	R_{y2}	NMP	85.0	Milky
PAA.2	R_{x1}	R_{y2}	DMAc	81.5	Milky
PAA.2	R_{x1}	R_{y2}	DMF	80.0	Brown

Optical and Film Forming Properties

List of PIs and Co-PIs films synthesized according to the Scheme 1 and Scheme 2 are shown in Table 2 and Table 3. The result showed that all homopolyimide films except PI.6 had dark yellow color and stiff film property. Color of Co-PI films was improved much better than that of homopolymer PI films. These results might be due to the stacking phenomena of benzene rings. By making copolyimides and also introducing bulky group like CF_3 in the polymer backbone, the Co-PI films exhibited almost no yellow color and good film forming property. As shown in Table 3, Co-PI films especially CoPIF-85:15 and CoPIS-85:15 exhibited best film forming property and optical clarity. It was noted that the yellow indexes of CoPIF-85:15 and CoPIS-85:15 were 6.91 and 7.54 respectively which were quite low compared to much stiff homopolyimide film (PI.6, yellow index 24.88)

Table 2. Physical properties of homopolymer PI films

PI name	R_x	R_y	Yield (%)	Thickness (μm)	PI color
PI.1	R_{x1}	R_{y1}	87.0	≤20μm	Dark Yellow
PI.2	R_{x1}	R_{y2}	85.0	≤20μm	Dark Yellow
PI.3	R_{x2}	R_{y3}	40.0	≤20μm	Dark Yellow
PI.4	R_{x2}	R_{y4}	81.0	≤20μm	Dark Yellow
PI.5	R_{x3}	R_{y3}	82.0	≤40μm	Dark Yellow
PI.6	R_{x3}	R_{y5}	92.0	80μm	Yellow

The Degree of Imidization

The degree of imidization (ID) from the polyamic acid to polyimide was checked with the FT-IR spectrometer (Jasco FT/IR-620) according to the following equation (1)

$$ID\ (\%) = (A_{C\text{-}N}/A_{C=C})/(A_{C\text{-}N}/A_{C=C})_{fullyimidization} \times 100 \quad (1)$$

Where: $A_{C\text{-}N}$, $A_{C=C}$ are absorbance of imide C-N bond at 1385 cm^{-1} and aromatic C-C bond at 1523 cm^{-1} in the polyimide structure respectively [7].

A typical FT-IR spectrum of PI.5 homopolyimide film is shown in Fig. 1. The degree of imidization was followed both according to the imidization temperature (under constant time of 40 min) and to the heat treating time (at constant temperature of 250°C). As shown in Fig. 2, high degree of imidization (ID = 94%) was obtained under the condition of baking at 250°C for 120 min after pre-baking at 100°C for 30 min.

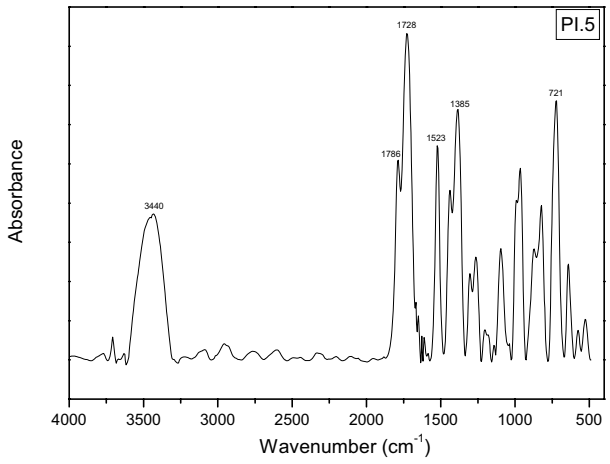


Fig. 1. FT-IR spectra of PI.5

Transmittance and Thermal Properties

In order to be used as flexible substrate of OLED devices, the polyimide film needs to be highly transparent in the visible region with low yellow index and also to be thermally stable. The thermal stability of the Co-PI films with low yellow index was checked with TGA and DSC. The TGA thermograms of Co-PI films (CoPIF-95:05 and CoPIS-80:20) exhibited 5% weight loss at about 503°C and 497°C, respectively as shown in Fig. 3. The glass transition temperatures (T_g) of CoPIF-95:05 and CoPIS-80:20 films were 352°C and 277°C, respectively from the DSC measurement. The transmittance of the Co-PI films was measurement with UV-Vis spectrometer (Jasco V-650 Spectrometer). As shown in Table 3, the CoPIF-85:15 film exhibited average transmittance of 92.65% in the 380-700 nm region and 64.07% at 400 nm. These values were comparable to those of optical films used in the display devices.

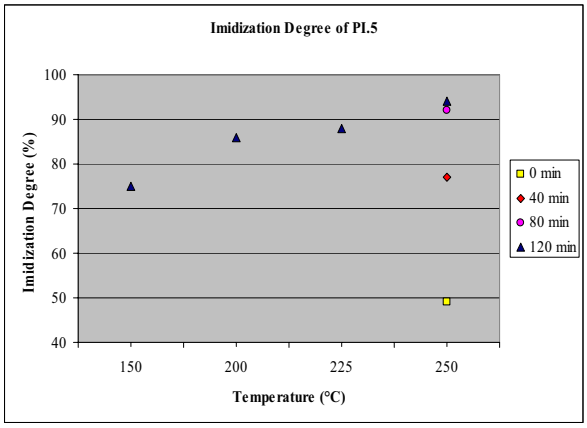


Fig. 2. Imidization degree of PI.5

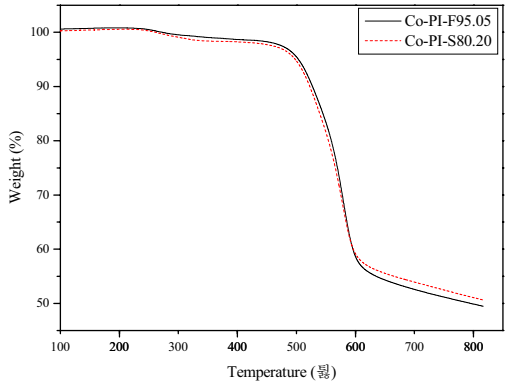


Fig.3. TGA curves of Co-PIs films

4. Summary

PIs and Co-PIs films were obtained with high yield. The Co-PI samples exhibited good film forming property (80μm thickness) with low yellow index. Co-PI films especially CoPIF-85:15 and CoPIS-85:15 exhibited good thermal property and high transmittance in the visible region. These results suggest that the synthesized Co-PIs films have the potential to be used as flexible OLED substrate.

Table 3. Physical and optical properties of PIs and Co-PIs films

No	Sample	R	n (Mole %)	m (Mole %)	Thick-ness (μm)	Yellow Index (b-value)	T_g/T_d^5 (DSC/ TGA)	Ave-Trans (%, 380 ~700nm)	Trans (%, 400nm)	Yield (%)
1	CoPIF-80:20	R_{y3}	80.0	20.0	80 μm	15.67		88.00	54.59	92.3
2	CoPIF-85:15	R_{y3}	85.0	15.0	80 μm	6.91		92.65	64.07	91.5
3	CoPIF-90:10	R_{y3}	90.0	10.0	80 μm	7.46		92.17	65.39	90.7
4	CoPIF-95:05	R_{y3}	95.0	5.0	80 μm	8.88	352°C /503°C	92.21	66.20	93.1
5	CoPIS-60:40	R_{y4}	60.0	40.0	80 μm	26.98		82.34	33.53	94.4
6	CoPIS-70:30	R_{y4}	70.0	30.0	80 μm	20.96		83.57	39.05	95.8
7	CoPIS-80:20	R_{y4}	80.0	20.0	80 μm	15.55	277°C /497°C	86.18	49.00	93.7
8	CoPIS-85:15	R_{y4}	85.0	15.0	80 μm	7.54		87.63	50.81	94.5
9	CoPIS-90:10	R_{y4}	90.0	10.0	80 μm	23.24		83.21	41.46	95.3
10	PI.5				≤40 μm	ND		ND	ND	92.1
11	PI.6				80 μm	24.88		86.50	53.83	82.0

ND: Not determined; Td^5: the decomposition temperature at 5% weight loss

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5. References

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