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Synthesis of new flexible diamine for applications in transparent poly (amide-imide) thin films with low residual stress

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ABSTRACT

A method to improve the optical properties of transparent poly(amide-imide) (PAI) by incorporating a new flexible diamine is demonstrated. The new diamine-incorporated PAI films show a lower glass transition temperature, yellow index, residual stress than neat PAIs irrespective of their structure. The DSC results show that the new diamine increases the flexibility of the polymer matrix indicating the poor packing of the matrix. However, the light transmittance reduces from 89.73 to 88.58%. This discrepancy can be clarified by measuring the residual stress of the PAI films. The results confirm that PAI has high elasticity and flexibility at low and high temperatures. Thus, flexible diamines can be added to PAI films for transparent materials owing to their good optical properties such as a transmittance of over 87%, yellow index lower than 2.8 and low residual stress < 20 MPa. Moreover, such diamines eliminate the occurrence of cracks in the substrate.

1. Introduction

Aromatic polyimides (PIs) are important engineering plastics and superior polymers and have been widely used owing to their high thermo-oxidative stability, chemical resistance and mechanical properties [1]. With the continued growth of the electronic industry, PIs are being widely used in semiconductors and integrated circuits. However, PIs have a conjugated rigid backbone and charge transfer complex (CTC) owing to their aromatic structure. This leads to high residual stress, poor workability and strong color [2]. Optical clarity is the most important aspect of transparent flexible display and coating materials and colorless films should be used for industrial applications [3].

A high residual stress between a polymer and a substrate leads to an instable state which causes delamination and cracking. Therefore, the residual stress is related to the reliability of a product and should be carefully controlled [4]. Since the polymer chain structure is a key factor affecting the residual stress, it is necessary to synthesize new monomers to reduce the stress between a polymer and a substrate [5]. Poly(amide-imide) (PAI) with new monomers can offer a transparent membrane with low residual stress, good optical properties and good reliability. Researchers have tried reducing the CTC and removing the color of PIs both electronically (by introducing electron withdrawing and donating groups in the polymer matrix) and physically (by introducing a kink structure in the polymer matrix) [6,7].

In this study, a flexible new monomer was synthesized to act as an extra electron donating group (EDG) in the polymer matrix. The new diamine was added into the PAI matrix to reduce its residual stress and to improve its optical properties. The resulting low-crack transparent polymer films showed the potential to be used in display and coating materials.

2. Experimental

2.1. Materials

α,α′-dibromo-*m*-xylene 97.0%, 3-nitrophenol 98.0%, palladium 10% on carbon, 4,4′-(hexafluoro isopropylidene) diphthalic anhydride (6FDA) 99.0%, isophthalic dihydrazide 95.0% and dodecanedioic dihydrazide 98.0% were purchased from Tokyo Chemical Industry Co. Potassium carbonate anhydrous, *N,N*-dimethyl formamide(DMF), *N,N*-dimethyl acetamide (DMAc) and ethanol were purchased from Duksan Chemical Co., Korea. Hydrazine monohydrate was purchased from Sigma-Aldrich Co. All reagents were used without further purification.

2.2. Synthesis of the new diamine

4 mol of potassium carbonate anhydrous, 1 mol of α,α′-dibromo-*m*-xylene and 2 mol of 3-nitrophenol were dissolved in DMF and stirred for 24 h at 150 °C. The reaction mixture was filtered and the nitro powder so obtained was dried for 24 h at 80 °C. The nitro powder and catalyst

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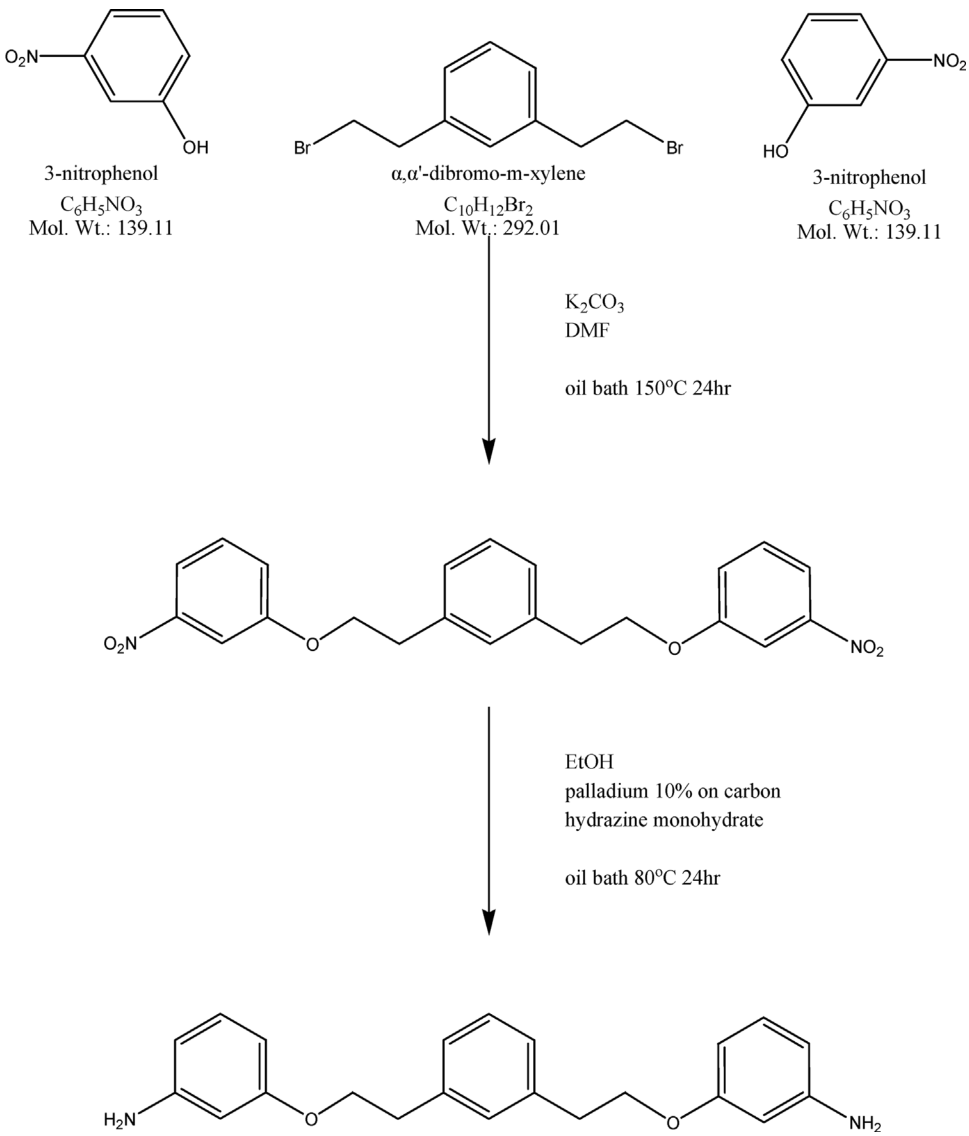

Scheme 1. Pathway for the synthesis of the new diamine.

were dissolved in ethanol and stirred for 24 h at 80 °C. Hydrazine monohydrate was added into this solution while stirring. The solution containing the diamine compounds was then filtered and the remaining solvents were removed under vacuum for 24 h at 60 °C. The pathway for the synthesis of the new diamine is illustrated in Scheme 1. The white-yellow color of monomer was prepared with 65% yield.

2.3. Preparation of the precursor solutions for PAIs with the new diamine

The PAI precursor solutions were prepared in three steps. First, isophthalic dihydrazide, dodecanedioic dihydrazide and the new diamine were dissolved in DMAc according to the molar ratios shown in Table 1. Then, 6FDA was added to the resulting solution at 20 °C. Finally, the mixture was stirred at 0 °C for 4.5 h in an ice bath and then at 20 °C for 12 h. The resulting solution contained 20 wt% solute in DMAc.

This solution was spin-coated on a glass plate to obtain 10–15 μm thick PAI films. The PAI films were then cured under the following temperature/time conditions: 100 °C/1 h, 150 °C/0.5 h, 200 °C/0.5 h, and 250 °C/2.5 h (in air). The temperature was increased at a rate of 2 °C/min. The pathway of the synthesis of the PAI samples is illustrated in Scheme 2.

Table 1
Molar ratio of the PAIs and the new diamine.

	Isophthalic dihydrazide (Iso)	Dodecane dihydrazide (D)	New diamine (NDA)	Samle name
Mole ratio	10	0	0	Iso 10 NDA 0
	9.5	0	0.5	Iso 9.5 NDA 0.5
	9	0	1	Iso 9 NDA 1
	0	10	0	D 10 NDA 0
	0	9.5	0.5	D 9.5 NDA 0.5
	0	9	1	D 9 NDA 1

2.4. Residual stress

The residual stresses of the PAI samples on a Si wafer were measured by a thin film stress analyzer(TFSA) [4]. The samples were heated at a rate of 10 °C/min from 25 to 300 °C. A Si(100) wafer (76.2 mm diameter) with one side polished was used as the substrate in this study. The residual stress was calculated from the radius of curvature obtained during the heating and cooling process using the following equation.