

Effects of reactive end-capper on mechanical properties of chemical amplified photosensitive polyimide

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Abstract

Photosensitive polyimide (PSPI) was synthesized and characterized to replace the conventional polyimide buffer layer because direct patterning with PSPI could reduce the processing procedure to the half. Since PSPI should be dissolved in alkaline aqueous solution and have good mechanical properties after imidization, low molecular weight of PSPI was synthesized with reactive end-capper, which could extend the chain length of PSPI during imidization. Therefore norbornene end-capped PSPI precursor was synthesized with various 5-norbornene-2,3-dicarboxylic anhydride (NDA) content.

Although molecular weight of PSPI decrease with increasing NDA content, the elongation at break and the glass transition temperature (T_g) of PSPI films imidized at 300 °C increased with increasing NDA content. On the other hand, elongation at break of PSPI films imidized at 350 °C decreased but T_g of those increased with increasing NDA content. Above T_g , thermal expansion coefficient decreased dramatically by introducing NDA end-capper. From mechanical and thermal properties of PSPI, it appears that low molecular weight of PSPI can be chain-extended and crosslinked during imidization.

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1. Introduction

Polyimides have been widely used as buffer layers and dielectric layers for semiconductor devices because of their many desirable properties such as low dielectric constant, excellent thermal and mechanical properties and good planarizability [1,2]. Recently, positive type photosensitive polyimides (PSPI) have been studied to replace a conventional polyimides since direct patterning (lithography) with PSPI could reduce the processing procedure to the half in semiconductor packaging by removing the photoresist related processes [3–5]. PSPI for buffer layer have to exhibit good mechanical properties such as elongation at break and tensile strength to protect chip from the stress that is induced by thermal mismatch with the chip and fillers in epoxy molding compound [6]. To apply PSPI to semiconductor package, two conditions must be satisfied for PSPI precursor simultaneously: low viscosity and high solid

content of PSPI precursor solution. Low viscosity is required to perform easy lithography and purification. High solid content is required to achieve a film thickness over 20 μm after soft and post exposure baking with just one time of spin coating. These conditions of PSPI precursor can be achieved with low molecular weight of PSPI precursor. However, polyimide thermally imidized from precursor of low molecular weight would form brittle films [7].

In this study, novel chemical amplified positive type PSPI was synthesized and reactive end-capper, norbornene anhydride (NDA) was introduced into PSPI precursor to obtain polyimide films having good mechanical properties in spite of low molecular weight of its precursor. Norbornene end-capper have been used in thermosetting polyimides known as bisnadimide (or PMR) resin [8,9]. Mechanical and thermal properties of norbornene end-capped PSPIs were examined with various NDA content and structure of this polyimide could be speculated from these characterizations.

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2. Experimental

2.1. Materials

4,4'-Oxydiphthalic anhydride (ODPA, Daicel Co Ltd, Japan) as a dianhydride, 4,4'-oxydianiline (ODA, Wakayama Seika Kogyo Co Ltd, Japan) as a diamine, and 5-norbornene-2,3-dicarboxylic anhydride (NDA, Tokyo Kasei Kogyo Co Ltd, Japan) as a reactive end-capper were taken out of bottles in a glove box under argon atmosphere, and then used immediately without any refining. Anhydrous 1-methyl-2-pyrrolidinone (NMP, Aldrich Chemical Company Inc) was used as a solvent without further purification. Chloromethylethylether (CMEE, Tokyo Kasei Kogyo Co Ltd, Japan) was used to protect carboxylic group, and triethylamine (TEA, Tokyo Kasei Kogyo Co Ltd, Japan) was used to neutralize the hydrogen chloride produced as a by-product.

2.2. Synthesis of reactive end-capper introduced PSPI precursor

Poly(amic acid) was prepared by addition of ODPA (0.03 mol) in powder form to a mechanically stirred solution of ODA (0.04 mol) in NMP under nitrogen atmosphere. The polymerization was carried out at 10 °C for 12 h. NDA (0.02 mol) was then added to this solution and reacted further for 8 h. NDA introduced poly(amic acid) solution was cooled down to −10 °C. To protect carboxyl group, TEA (0.048 mol) and CMEE (0.050 mol) were added to this solution. The reaction proceeded for 2 h and the temperature of this solution was kept at −10 °C (Fig. 1). The resulting polymer solution was filtered to remove TEA–HCl salt and poured into a distilled water/methanol mixture. The precipitated polymer was filtered and washed with water/methanol mixture three times. This product was dried in a vacuum oven at 45 °C for 24 h. After vacuum drying, NDA

introduced PSPI precursor was dissolved in NMP. The solid content of this polymer solution was 30% by weight.

2.3. Characterization of NDA end-capped PSPI precursor

NDA introduced PSPI precursors were analyzed by H-NMR (Bruker DRX-500 spectrometer) and FT-IR (FTS-375C, Bio-Rad). DMSO- d_6 was used as a solvent in H-NMR analysis. Inherent viscosity was measured at a sample concentration of 0.2 g/dl in NMP with Ubbelohde viscometer at 30 °C.

2.4. Preparation of NDA end-capped PSPI (N-PI) film

Polyimide film was prepared for characterization. NDA introduced PSPI precursor was cast on a slide glass using a doctor blade and pre-baked at 80 °C for 30 min and thermally imidized by multi-step imidization process as follows: 150 °C/30 min, 200 °C/60 min, and 300 °C/60 min, or 150 °C/30 min, 200 °C/60 min, 300 °C/60 min, and 350 °C/30 min. The heating rate was 5 °C/min up to 200 °C and then changed to 3 °C/min above 200 °C. After delaminated in an autoclave (121 °C, 0.12 MPa), the film was dried in a vacuum oven at 100 °C for 7 h. The film thickness measured using micrometer was $30 \pm 5 \mu\text{m}$. The notations of NDA end-capped PSPI are as follows: For example, N05-PI300 represents a polyimide imidized finally at 300 °C from PSPI precursors with 0.5 of molar ratio of NDA to ODA.

2.5. Characterization of NDA end-capped PSPI (N-PI) film

Film strips of 6.4 mm width were prepared by cutting N-PI films, and mechanical properties of N-PI films were measured using an Instron 4206 universal testing machine (UTM) by tensile test mode with a testing rate of 3 mm/min (Fig. 2).

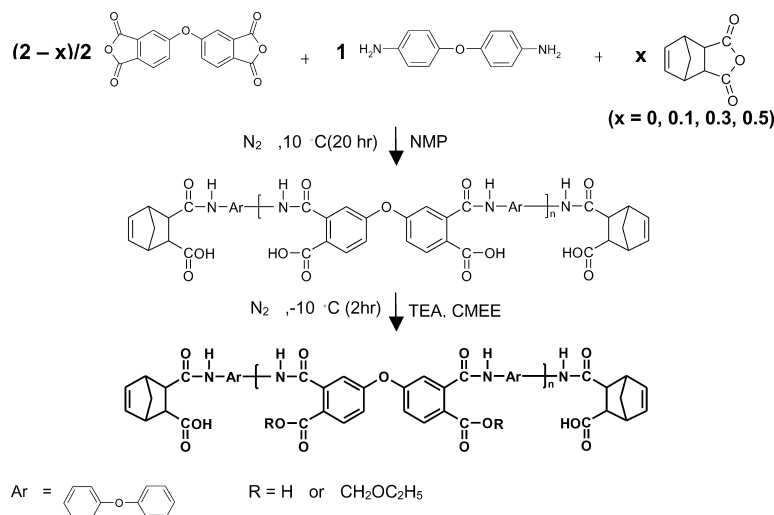


Fig. 1. Synthesis scheme of PSPI precursor.

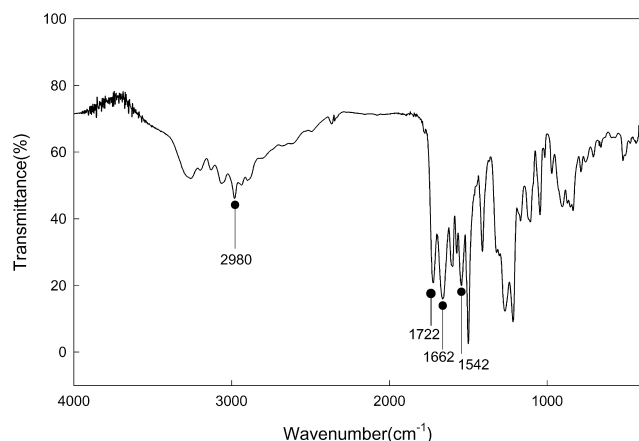


Fig. 2. FT-IR spectrum of PSPI precursor.

Dynamic mechanical properties of N-PI films were measured with a TA instruments DMA 2980 dynamic mechanical analyzer at a heating rate of 10 °C/min from 25 to 400 °C. The film tension mode was used at a frequency of 1 Hz. Thermal expansion coefficient (TEC) was also examined on the same equipment with the TMA controlled force mode at the static force of 0.1 N and a same heating condition with DMA analysis.

2.6. Photolithography of PSPI

PSPI solution was composed of NDA end-capped PSPI precursor (30.0 g), photo acid generator (4.5 g) and NMP (70 g). As a photo acid generator, novel photo acid generator (diphenyliodonium type) was synthesized [10].

PSPI solution was spin-coated on silicon wafer and pre-baked at 90 °C for 4 min. After pre-baking, UV exposure at 365 nm and post exposure baking at 130 °C for 3 min were followed. Then, PSPI film was developed in 2.38 wt% tetramethylammoniumhydroxide (TMAH) solution for 4 min at 23 °C and rinsed with deionized water several times. The thickness of patterned PSPI resist film was 12 μm after development.

3. Result and discussion

3.1. Synthesis of NDA end-capped PSPI precursor

Chemical amplified positive type PSPI was synthesized. In chemical amplified PSPI, protecting the alkaline-soluble site by the acid-labile group is necessary, i.e. this protecting group has to be removed easily when it is attacked by an acid. For protecting the alkaline-soluble site (carboxylic group), we used an ethoxymethyl esterification [11].

To obtain high mechanical properties of polyimide film thermally imidized from PSPI precursor of low molecular weight, the reactive end-capper was introduced to PSPI precursor. The molar ratio of monomers was adjusted like below to introduce the reactive end-capper at the end of

PSPI precursor chain:

$$\text{ODPA} : \text{ODA} : \text{NDA} = (2 - x)/2 : 1 : x$$

NDA content (x) was varied from 0 to 0.5.

FT-IR analysis showed the formation of ethoxymethyl ester group (2980 cm⁻¹ C–H stretching) in PSPI precursor and characteristic amide group (1662 cm⁻¹ amide C=O stretching, 1542 cm⁻¹ amide N–H bending, 1722 cm⁻¹ ester C=O stretching) of PSPI precursor also appeared. The introduction of norbornene group to PSPI precursor and the formation of ethoxymethyl group were also shown in H-NMR analysis (Fig. 3). Peak positions were 6.2 ppm (from CH=CH in norbornene group) [12,13] and 5.4 ppm (from –O–CH₂–O– in ethoxymethyl group). Protection ratio of carboxyl group was calculated from the ratio of the number of hydrogen atoms of the –O–CH₂–O– bond in ethoxymethyl group (5.4 ppm) to those of aromatic group (7–8 ppm). Protection ratio of carboxyl group was about 50–55% for all NDA content (Table 1). Therefore, the effect of the protection ratio of carboxyl group on properties of polyimide film can be excluded from our discussion.

Inherent viscosity and number average molecular weight of NDA introduced PSPI precursor decreased with increasing NDA content (Table 1) because of the increase of stoichiometric imbalance of ODPA and ODA.

3.2. Properties of N-PI film

3.2.1. Mechanical properties

Mechanical properties of N-PI films were measured by varying the NDA content at the final imidization temperatures of 300 and 350 °C (Fig 4). Elongation at break of N-PI300 did not decrease but that of N-PI350 decreased with

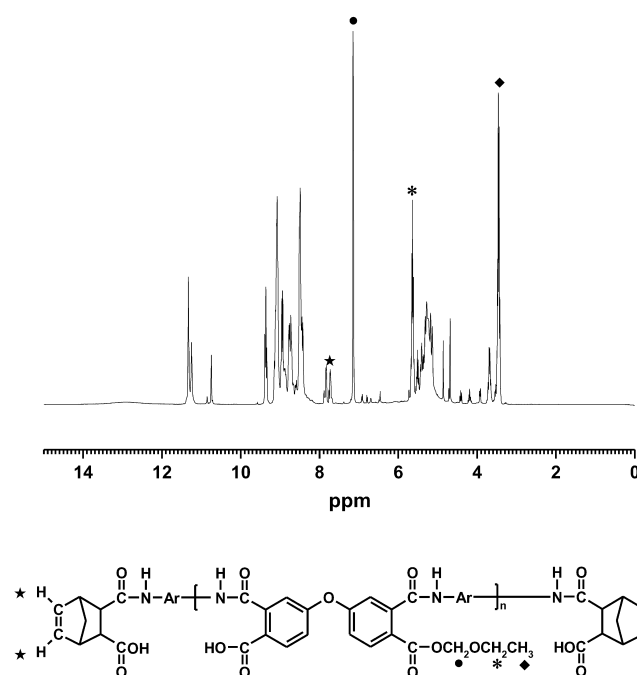


Fig. 3. H-NMR spectrum of PSPI precursor.

Table 1
Characterization of NDA introduced PSPI precursor

NDA content	Protection ratio of carboxyl group (%)	Inherent viscosity (dl/g) ^a	Number average molecular weight (g/mol) ^b
0.0	51	0.95	–
0.1	53	0.75	10,500
0.3	55	0.33	3700
0.5	50	0.26	2400

^a 0.2 g/dl in NMP at 30 °C.

^b Calculated from the modified Carothers' equation.

increasing the NDA content. Tensile strengths of N-PI300 and N-PI350 decreased with increasing the NDA content and the decrease was prominent in N-PI350.

Stress–strain curves of N-PI films were illustrated in Fig. 5. Plastic deformation was shown in N-PI300, while rigid–brittle behavior was shown in N-PI350.

Although molecular weight of precursor of N-PI was lower with higher NDA content, N-PI films imidized at

300 °C from this precursor showed good mechanical properties. It appears that NDA end-capped polyimide precursor was chain-extended. This might be attributed to the thermal reaction of norbornene group located at the end of chain.

3.2.2. Thermo-mechanical properties

It has been proposed that norbornene groups in PMR resin produce cyclopentadiene and maleic anhydride by reverse Diels–Alder reaction at elevated temperature and cyclopentadiene and maleic anhydride were linked by thermal polymerization [14]. Wong and Ritchey proposed

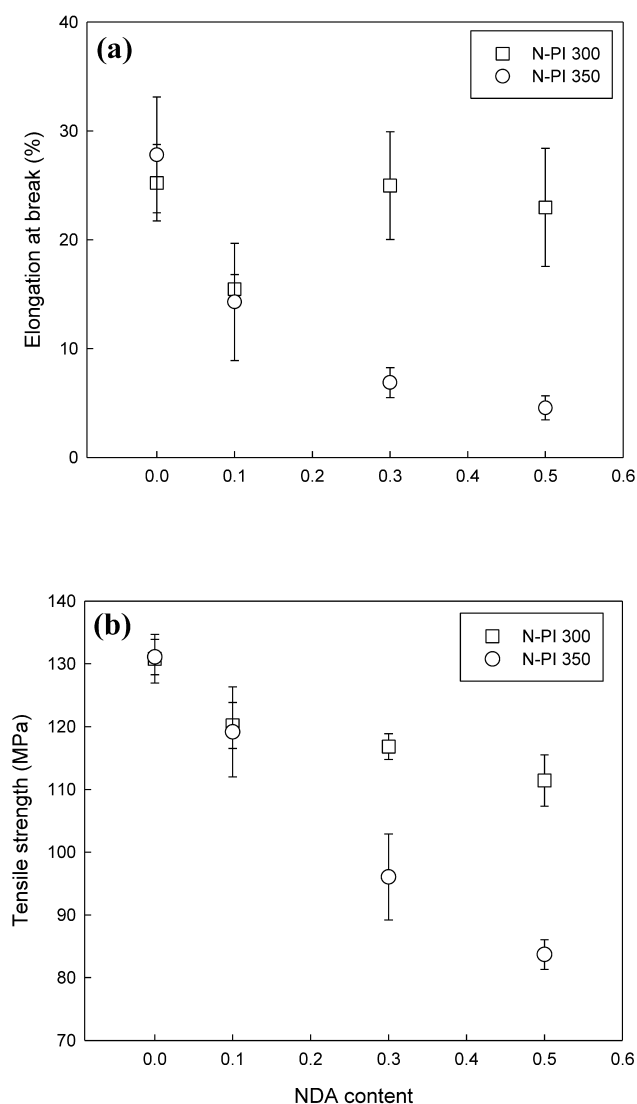


Fig. 4. Mechanical properties of N-PI300 and N-PI350 with varying NDA content: (a) elongation at break and (b) tensile strength.

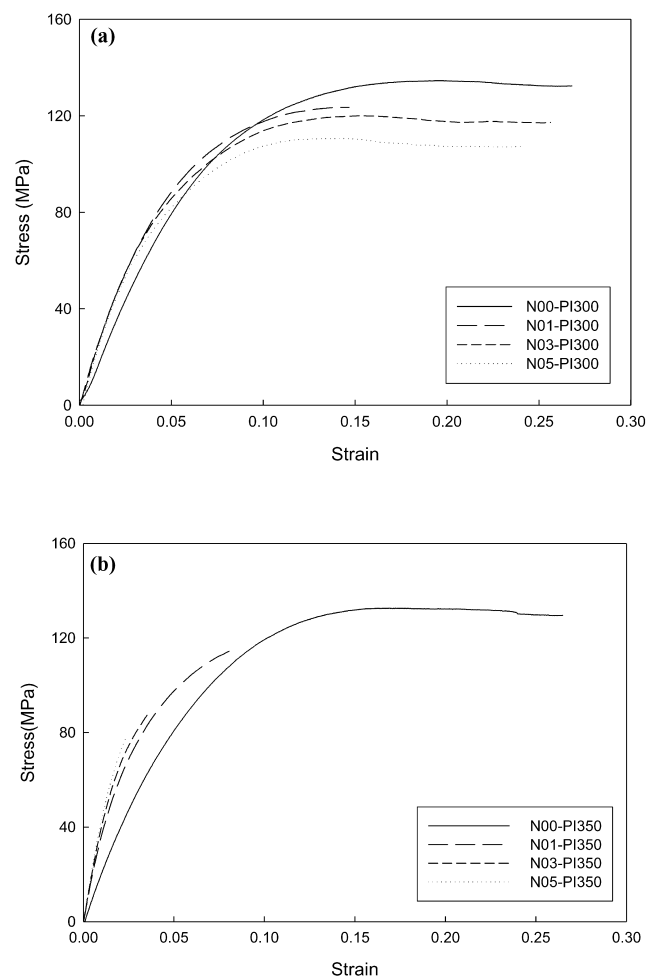


Fig. 5. Stress–strain curve of polyimide films: (a) N-PI300 and (b) N-PI350.

that double cycloadduct was formed by Diels-Alder reaction between remaining norbornene group and cyclopentadiene and cross-linking proceeds through the double bonds of norbornene group, double cycloadduct and maleic anhydride in random fashion [15]. Recently, Meador et al. reported that major product of cross-linking of norbornene end-capped polyimide, under normal cure condition, derive from olefin polymerization through double bond of norbornene group and reverse Diels-Alder reaction did not contribute to the cross-linking reaction significantly [16].

These reactions through norbornene groups would obviously result in the chain extension of polyimide molecules during imidization, whatever the proposed mechanism of cross-linking occurs (Fig. 6). Fig. 7 shows dynamic mechanical properties measured from the N-PI films. T_g increased with increasing NDA content in both N-PI300 and N-PI350 (Table 2). These phenomena indicate that the size of polyimide molecules become larger as polyimide film was formed from N-PI precursor with higher NDA content at the same imidization condition. As NDA content increased, molecular weight of precursor decreased and the number of chain end with norbornene group increased. So, the reaction through norbornene groups may occur easily and more norbornene groups participate in the reaction during imidization. As the

Table 2
Thermal properties of N-PI films

NDA content	Glass transition temperature (°C)		TEC above glass transition temperature (ppm/°C)	
	N-PI300	N-PI350	N-PI300	N-PI350
0.0	268	275	23,400	9640
0.1	295	345	5200	1620
0.3	325	365	3500	830
0.5	333	375	3540	800

consequence of high extent of reaction, the size of N-PI molecules with high NDA content would be larger than that with low NDA content.

N-PI350 exhibited higher T_g than N-PI300 at the same NDA content. This means that the thermal reaction through norbornene groups further occurred at 350 °C of final imidization temperature.

Table 2 shows a thermal expansion behavior of N-PI films. TEC above glass transition decreased with increasing NDA content both in N-PI300 and N-PI350. The decrease of TEC above glass transition was more pronounced in N-PI350 as compared with N-PI300. Interesting behavior is, in

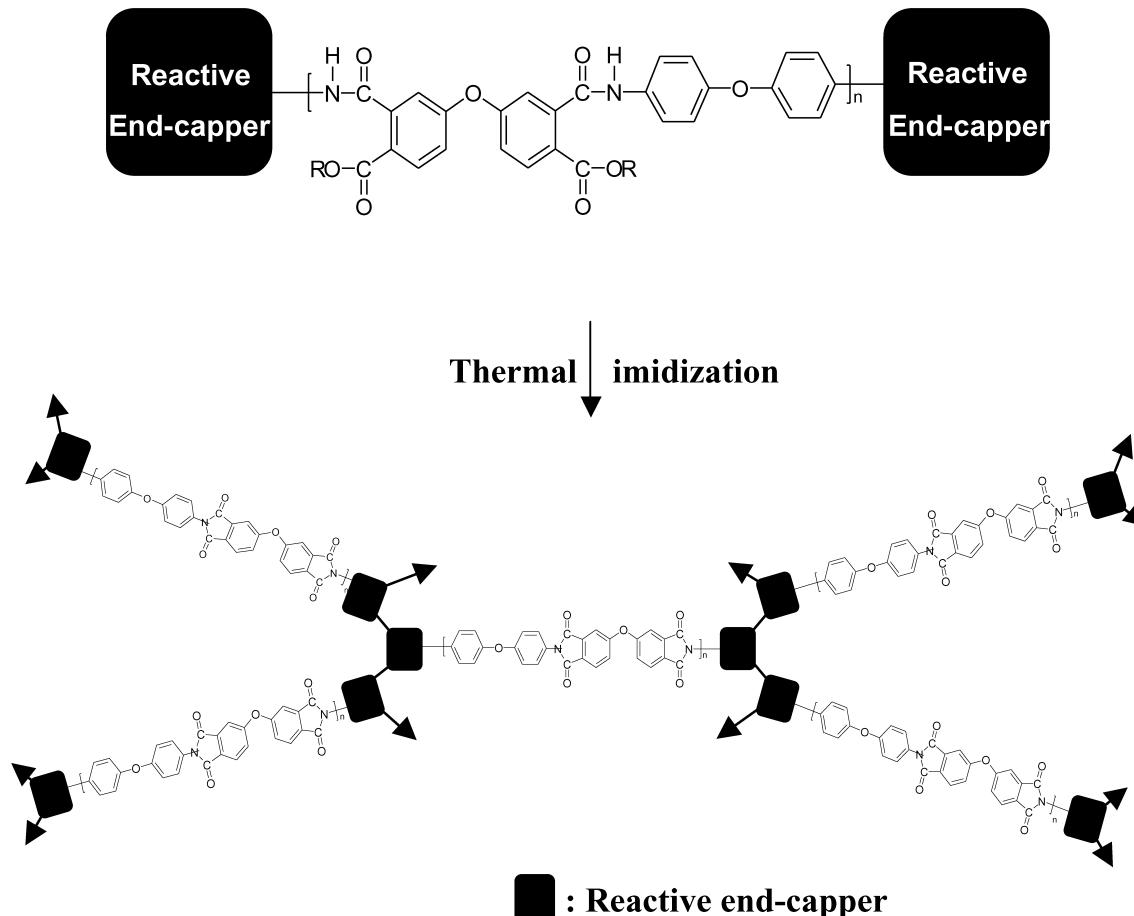


Fig. 6. Scheme of chain extension by reactive end-capper. Reactive end-capper is NDA and an arrow represents a propagation of chain extension reaction.

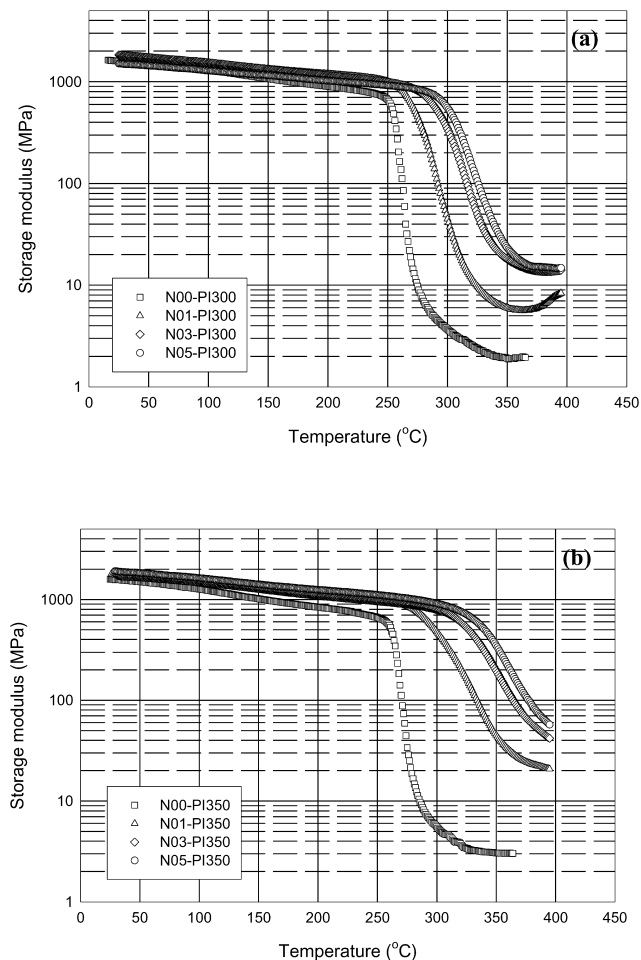


Fig. 7. Dynamic mechanical analysis of (a) N-PI300 and (b) N-PI350 with varying NDA content.

particular, that TEC above glass transition was reduced dramatically in N-PI films finally imidized at both 300 and 350 °C as compared to linear polyimide film with zero of NDA content. This means that N-PI molecules are not extended linearly during imidization and have a structure that restricts the motion of polyimide chain above glass transition. These thermal expansion behaviors of N-PI films correspond to the increase of rubbery modulus with increasing NDA content and final curing temperature in dynamic mechanical analysis (Fig. 7).

3.3. Structure of N-PI films

The structure of N-PI films can be predicted from the thermo-mechanical properties. Chain extension is carried out through $\text{CH}=\text{CH}$ in norbornene group. Therefore, N-PI molecules can be extended by forming a branched structure and a cross-linked structure. The cross-linked structure is mainly reported in the N-PI system [17–19]. In this study, however, it appears that structure of N-PI300 would be a branched and partially cross-linked structure. When N-PI300 precursor with higher NDA content was imidized,

large amount of short polymer chain would be linked through the reaction of norbornene group during imidization. The occurrence of chain extension by norbornene group was observed from the increase of T_g with increasing NDA content. This chain extension reaction could result in a highly branched structure and a partially cross-linked structure in comparison with N-PI300 precursor with lower NDA content. Therefore, the mobility of polyimide chain appeared to be restricted with the increase of NDA content.

Thermo-mechanical properties of N-PI350 showed a similar tendency to N-PI300 with NDA content. However, T_g of N-PI350 was higher than that of N-PI300 and TEC of N-PI350 was lower than that of N-PI300 at all the NDA content. In addition, rigid–brittle behavior was shown in stress–strain curves of N-PI350 films. It is thought that these behaviors are due to the development of highly cross-linked structure during imidization process at 350 °C. The higher storage modulus in the rubbery region (Fig. 7(b)) verifies the formation of highly cross-linked structure. The rubbery modulus increased with the increase of NDA content.

3.4. Photolithographic evaluation

Sensitivity of PSPI containing 15 wt% of photo acid generator to the PSPI precursor resin was determined by the exposure dose to develop the PSPI film completely. The sensitivity was 1200 mJ/cm² with the PSPI film thickness of 12 μm. Fig. 8 illustrates scanning electron micrographs of patterns from PSPI film after UV exposure at 365 nm and development. This PSPI film was capable of resolving a 5 μm feature with the film thickness of about 12 μm.

4. Conclusion

Norbornene end-capped PSPI precursor was synthesized as buffer coating layer and the effect of norbornene end-capper on the properties of polyimide films were observed. Although molecular weight of PSPI precursor decreased with increasing NDA content, the elongation at break of N-PI films imidized at 300 °C did not decrease and glass transition temperature increased with increasing NDA content. On the other hand, elongation at break of N-PI films imidized at 350 °C decreased but T_g of those increased with increasing NDA content. Above glass transition, TEC of N-PI films decreased dramatically by introducing NDA end-capper as compared with a linear polyimide. It could be deduced in this study that N-PI films imidized at 300 °C formed the branched structure and partially cross-linked structure and those imidized at 350 °C formed the cross-linked structure.

Therefore, norbornene end-capped PSPI precursor having low molecular weight showed good resolution in a

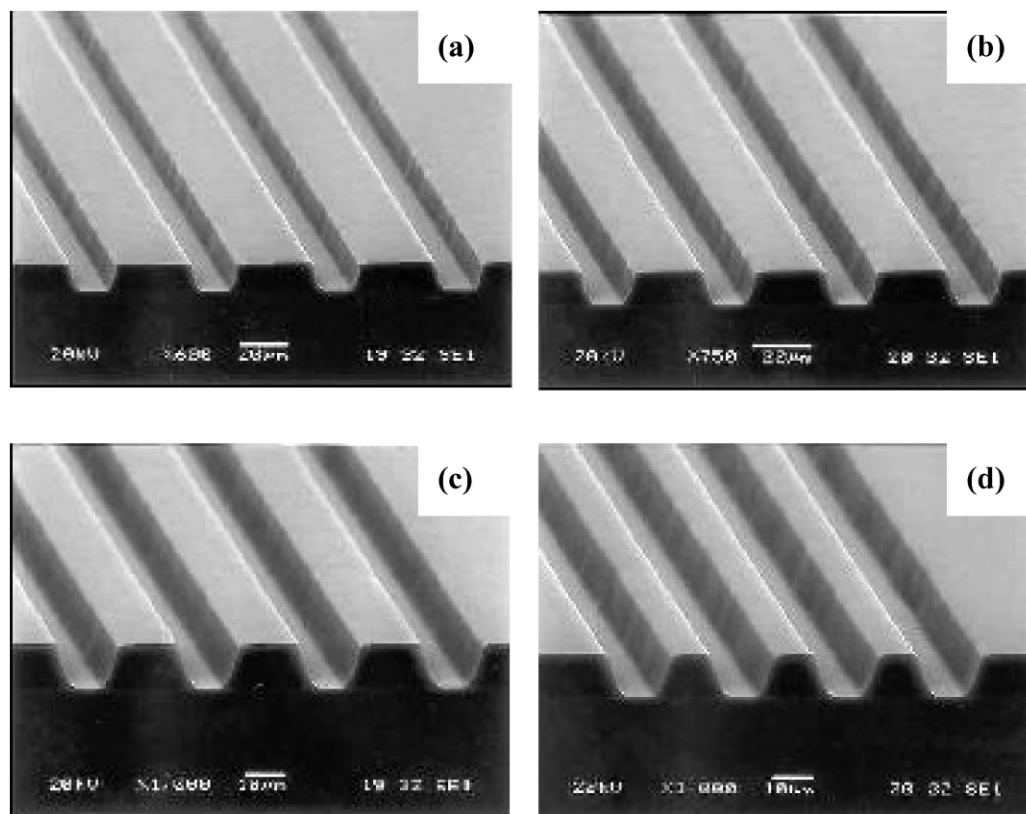


Fig. 8. Scanning electron micrograph of PSPI patterns with 365 nm stepper: (a) 10 μm space, (b) 8 μm space, (c) 6 μm space and (d) 5 μm space with film thickness of 12 μm .

lithography process and good mechanical properties after imidization.

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