Synthesis of Heat Curable Soluble Polyimides Utilizing Pendant Phenylethynyl Group

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A diamine, 2,4-diaminophenylethynylbenzene (DAPEB), that have pendant phenylethynyl group, was synthesized. Utilizing DAPEB as one component, a novel soluble polyimide (PI), Solpit-T, that can be thermally cured was synthesized. Solpit-T is soluble prior to curing, but became insoluble in organic solvents after curing, showing improvement in chemical resistance. In addition, cured Solpit-T films revealed largeelongation at break; 8% and 39% at 33 mol% and 8 mol% DAPEB in total diamine, respectively, showing that cured Solpit-T has outstanding toughness for thermosetting PI. Cured Solpit-T films have T\textsubscript{g}s as high as above 400 °C from the DMA measurement, which is the same as the Solpit-S and PI(PMDA/ODA). Thermogravimetric analyses revealed that 5 % weight loss temperatures were higher than 450 °C.

Keywords: polyimide / soluble / phenylethynyl / crosslink

1. Introduction

Polyimide (PI) has excellent electrical properties and mechanical strength as well as high heat resistance [1]. From the excellent properties, it is used, for example, in the field of microelectronics and aerospace field. However, demand has also been subdivided in accordance with the intended application, and higher performance is required. Typical PI such as PI(PMDA/ODA) is infusible and insoluble in organic solvents. Therefore, it is fabricated at the state of poly(amide acid) (PAA), which is soluble in organic solvents. PAA is converted to PI usually by thermal imidization (Scheme 1).

However, PAA has low storage stability, and also evolves water during the imidization process, which may cause voids. As a result, typical PI is used only as films. Therefore, in recent years, the study of soluble PIs has been developed. Soluble PIs have excellent storage stability, and have advantage in that the molded product can be produced only by removing organic solvent. However, conventional soluble PI tends to have low heat resistance.

Recently, a series of novel soluble PI, Solpit-S, was developed based on the molecular design quite different from the molecular design of traditional soluble PIs [2]. Solpit-S, a soluble block copolyimide, is synthesized by precisely
controlling the sequence of monomers by the multi-stage polymerization reaction. This block copolyimide, Solpit-S, is soluble while maintaining a high heat resistance equivalent to that of the conventional typical PIs such as Kapton and Upilex. However, soluble PI has a disadvantage in that the product dissolves in organic solvents, resulting in poor chemical resistance.

An effective method to improve the chemical resistance of soluble PI is to introduce crosslink sites, and form three-dimensional network structures. Various crosslink sites have been examined including nadic end-cap, acetylene end-cap, and so on. To have excellent thermal properties after crosslinking, crosslink site that give aromatic structure is favorable. For example, the combination of internal acetylene and biphenylene end-cap was shown to give thermally stable phenanthrene [3,4]. Recently, phenylethynyl group is introduced into oligoimides, and the cured PI was shown to have excellent thermo-mechanical properties [5,6]. In this study, by introducing pendant phenylethynyl groups into the side chain of Solpit-S, thermally curable soluble PI (Solpit-T) was synthesized.

2. Experimental

2.1. Reagents

Triethylamine, 1,3-dinitro-4-bromobenzene, phenylacetylene, bis(triphenylphosphine)palladium dichloride, copper iodide, triphenylphosphine, tin chloride dihydrate, 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), pyromellitic dianhydride (PMDA), 4,4'-oxydianiline (ODA), N-methyl-2-pyrrolidone (NMP), 2,4-diaminotoluene (DAT), and γ-valerolactone were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and were used as received.

2.2. Synthesis of 1,3-dinitro-4-phenylethynylbenzene (DNPEB) and 1,3-diamino-4-phenylethynylbenzene (DAPEB)

The Sonogashira coupling using phenylacetylene (1.42 g, 14 mmol) and 1,3-dinitro-4-bromobenzene (2.50 g, 10 mmol) gave 1,3-dinitro-4-phenylethynylbenzene (DNPEB) (2.63 g, 9.8 mmol) as brown powder in 98 % yield.

DNPEB was reduced using concentrated hydrochloric acid and tin chloride dihydrate, and then converted to free amine by using sodium hydroxide solution, affording 1,3-diamino-4-phenylethynylbenzene (DAPEB).

2.3. Synthesis of Solpit-T

Solpit-T was prepared from PMDA, s-BPDA, ODA, DAT, and DAPEB as follows. Into a separable flask equipped with nitrogen inlet and mechanical stirrer, ODA (0.800 g, 4 mmol) and NMP (8.0 g) were added. The mixture was kept stirring until clear solution was obtained. s-BPDA (0.588 g, 2 mmol) was added to the solution and the wall of the flask was washed with a mixture of toluene (4.0 g) and NMP (8.0 g) containing pyridine (0.32 g) and γ-valerolactone (0.40 g). The reaction mixture was stirred for 1 h at 180 °C to give a transparent dark-red imide oligomer solution.

After cooling down to room temperature, in the second step, PMDA (1.75 g, 8 mmol), DAT (0.489 g, 4 mmol) and NMP (16 g) were added, and stirred for 30 minutes at room temperature. Finally, in the third step, s-BPDA (0.588 g, 2 mmol), DAPEB (0.833 g, 4 mmol) and NMP (15 g) were added, and stirred for 6 h at 180 °C to give a transparent dark brown Solpit-T solution. The Solpit-T solution was added dropwise into methanol to precipitate Solpit-T. The precipitate was filtered and dried 65 °C for 3 h to give Solpit-T33 that contains 33 mol% of DAPEB, as yellow powder.

Another Solpit-T that contains 8 mol% of DAPEB, Solpit-T08, was prepared using 1 mmol of DAPEB and 3 mmol of DAT.

2.4. Measurements

IR spectra were obtained using a Jasco FT/IR-420 spectrophotometer. 1H-NMR spectra were obtained using VarianMercury300 (frequency 300 MHz) in dimethyl sulfoxide-d6. Molecular weights were measured by a gel permeation chromatography (GPC) in NMP using a Tosoh HLC-8320 GPC system and polystyrene standards for calibration. Thermogravimetric analysis (TGA) was performed with a Rigaku Thermo Plus TG8120 at a heating rate of 5 °C/min under argon. Differential scanning calorimeter (DSC) was performed with a Rigaku Thermo Plus DSC8230 at a heating rate of 10 °C/min under nitrogen. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm/min using films of 2 cm long. The tensile properties of each sample were determined from an average of at least 15
Dynamic mechanical analysis (DMA) was conducted on a Seiko Instruments model EXSTAR DMS6100 at 1 Hz at a heating rate of 5 °C/min.

3. Results and Discussion

3.1. Synthesis of Solpit-T

DAPEB, a diamine having a phenylethynyl group, was synthesized according to Scheme 2. DNPEB was obtained as brown powder in 98 % yield. DAPEB was obtained as tan-colored powder in 50 % yield.

![Scheme 2. Synthesis of DAPEB.](image)

1H-NMR spectra of DNPEB (Fig. 1) and DAPEB (Fig. 2) agreed well with the structures. IR spectra also agreed with the structure of DNPEB and DAPEB (Fig. 3). The absorption at 2200 cm⁻¹ is due to the C≡C stretching vibration, at 1340 cm⁻¹ and 1525 cm⁻¹ are NO₂ stretching vibration (Fig. 3a), and at 1620 cm⁻¹ is NH₂ bending vibration (Fig. 3b).

Then we synthesized two types of Solpit-T, Solpit-T08 and Solpit-T33, which account for 8 mol% and 33 mol% of DAPEB in the total diamine, respectively. The procedure for the synthesis of Solpit-T33 is shown in Scheme 3. The structure of Solpit-T was confirmed by IR (Fig. 4). Molecular weight was measured by GPC. The weight average molecular weight of Solpit-T33 and Solpit-T08 was 54000 and 94000, respectively.

![Fig. 1. 1H-NMR spectrum of DNPEB.](image)

![Fig. 2. 1H-NMR spectrum of DAPEB.](image)

![Fig. 3. IR spectra of a) DNPEB and b) DAPEB.](image)
Scheme 3. Synthesis of Solpit-T33.
3.2. Preparation of cured Solpit-T films

By dissolving PI powder in NMP, 10 wt% PI solution was prepared. The PI solution was cast on glass plate, and heat-treated at 50 °C for 16 h, and then at 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, and 370 °C for 1 h each to give thermosetting film. Thermosetting film was brown, transparent, and flexible. Completion of curing reaction by the heat treatment at 370 °C was confirmed by DSC. Solpit-T film that was heat-treated at 200 °C (before crosslinking) was soluble in NMP. After thermal curing at 370 °C (after crosslinking), the films became insoluble in NMP, showing that chemical resistance was improved.

3.3. Physical properties of the cured films

The cured films were tough. From the tensile test, elongation at break was 39 % for Solpit-T08 and 8 % for Solpit-T33 (Fig. 5 and Table 1). These values are extremely high as thermosets. The viscoelastic measurements revealed that both of the Solpit-T hold high T_g above 400 °C (Fig. 6). TGA measurement of Solpit-T confirmed high heat resistance equal to Solpit-S (Fig. 7 and Table 1).

It was reported previously that internal acetylene groups introduced into the backbone of PI gives crosslinked PI by heat treatment, giving aromatic structure as shown in Scheme 4a [7], thus affording crosslinked PI having excellent thermal properties [8-11]. We propose here the reaction shown in Scheme 4b as the reaction mechanism of pendant phenylethynyl group in Silpit-T, which is quite similar to the reaction of internal acetylene shown in Scheme 4a [7]. The proposed mechanism (Scheme 4b) explains not only the excellent physical and thermal properties of Solpit-T, but also the reaction of terminal

![Fig. 4. IR spectrum of Solpit-T33.](image)

![Fig. 5. Stress-strain curves of PI films.](image)

![Fig. 6. DMA of PIs. ○PI(PMDA/ODA), △Solpit-S, □Solpit-T08, ●Solpit-T33.](image)

| Sample       | Tensile properties | Thermal properties |
|--------------|--------------------|--------------------|
|              | Modulus (GPa)      | Tensile Strength (MPa) | Elongation at break (%) | T_5 (°C) | T_10 (°C) | Weight residue at 850°C (%) |
| Solpit-T33   | 2.7                | 81                 | 8                    | 473      | 534      | 50                      |
| Solpit-T08   | 2.8                | 108                | 39                   | 462      | 523      | 47                      |
| Solpit-S     | 2.9                | 137                | 80                   | 502      | 539      | 49                      |
| PI(PMDA/ODA) | 2.6                | 196                | 79                   | 537      | 565      | 46                      |
phenylethynyl groups in PETI-5 [5] and TriA-PI [6] that is considered to proceed by chain extension mechanism.

4. Conclusions

Heat-curable novel soluble PI, Solpit-T, was synthesized using diamine having phenylethynyl groups. Solpit-T was soluble before crosslinking, and became insoluble after crosslinking in organic solvents. Cured Solpit-T was tough, and had excellent physical and thermal properties.

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