Preparation and Properties of Crosslinking Polyimides Having Ethynyl Groups on the Side

Atsushi Morikawa* and Norihiro Sugaya

*Department of Biomolecular Functional Engineering,
Ibaraki University, Hitachi, Ibaraki 316-8511, Japan*

**atsushi.morikawa.reg@vc.ibaraki.ac.jp*

3,5-Diamino-4'-ethynylbenzanilide (**1**) was synthesized from 4-ethynylaniline and 3,5-dinitrobenzoyl chloride. Polyimides (**PI-x**) having ethynyl groups on the side were prepared from **1**, 4,4'-oxydianiline (ODA), and various dianhydrides (**x**) by the usual two-step procedure that included ring-opening polymerization leading to polyamic acid (**PAA-x**) and subsequent thermal cyclic dehydration. Since gelation was observed in the polymerization of **PAA-c** from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (**c**), the polymerization was performed in the dark. In the dynamic mechanical analysis of **PI-x**, glass transition temperatures (T_g) were observed at 262–320 °C as $\tan \delta$ peak temperatures, and the values were higher due to crosslinking of ethynyl groups at 360 °C. T_g of the film prepared from **PAA-c** solution exposed to a fluorescent lamp was higher than that of a **PI-c** film prepared in the dark, and photo-crosslinking of ethynyl groups was also observed.

Keywords: Crosslink, Ethynyl group, 3,3',4,4'-Benzophenonetetracarboxylic dianhydride, Photo-crosslink

1. Introduction

Acetylene-terminated polyimides have been developed as thermosetting polymers [1-3]. They are heated on a flame to prepare the film, and subsequently crosslinked by heating to higher temperature. The T_g is so high that rapid crosslinking occurs once T_g is exceeded, and thus oligomers having very low degree of polymerization are used as such resins. These thermosetting polyimides have high thermal stabilities and excellent mechanical properties, but their utilization has been limited due to their short gel time and low solubility in spite of the use of oligomers. To overcome these drawbacks, one approach was to use more soluble polyisoimide oligomers, which could be thermally isomerized into polyimides and subsequently crosslinked through acetylene end groups to yield polyimide networks [2-3]. Another method is the use of derivative acetylene-terminal groups. The crosslinking temperature of the phenylethynyl group is higher than that of the acetylene group, thus crosslinking

polyimide films can be prepared by pressing the melted phenylethynyl-terminated imide oligomers and curing them under pressure at higher temperature [4,5].

In this study, polyimides (**PI-x**) having ethynyl groups on the side were prepared from **1**, ODA, and various dianhydrides (**x**) by the usual two-step procedure that included ring-opening polymerization leading to polyamic acids (**PAA-x**) and subsequent thermal cyclic dehydration. **PI-x** films were annealed above T_g , the properties were compared with those of the **PI-x** films before annealing, and crosslinking of the films was examined. Such a crosslinking polyimide film had been prepared using an imide oligomer from 3,5-diamino-3'-ethynylbenzanilide, ODA and another dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride [6,7]. In this study, a high molecular weight polyamic acid was used. Photo-crosslinking of BTDA-based polyimide was also examined.

2. Experimental

2.1. Materials

4-Ethynylaniline, 3, 5-dinitrobenzoyl chloride and triethylamine were obtained commercially, and used without purification. Pyromellitic dianhydride (PMDA) (**a**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) (**b**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (**c**) and 4,4'-oxydiphthalic anhydride (ODPA) (**d**) were obtained commercially, and purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation over calcium hydride.

2.2. Monomer synthesis

2.2.1. 4'-Ethynyl-3,5-dinitrobenzanilide

To a solution of 4-ethynyl-aniline (2.34 g, 20 mmol) and trimethylamine (2.02 g, 20 mmol) in dichloromethane (30 mL) was added dropwise a solution of 3,5-dinitrobenzoyl chloride (4.61 g, 20 mmol) in dichloromethane (40 mL) at 0 °C. After stirring at 20 °C for 4 h, the mixture was poured into ice water. The organic layer was collected, and the aqueous layer was extracted twice with 50 mL of dichloromethane. The combined extract was dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was recrystallized from ethanol. Yield: 5.02 g (81%). The IR spectrum exhibited absorption bands 2110 cm⁻¹ (C≡C-), 1660 cm⁻¹ (C=O), 1520 cm⁻¹, and 1350 cm⁻¹ (NO₂).

The ¹H-NMR spectrum [δ in DMSO-d₆] showed signals at 3.80 (s, 1H, -C≡C-H), 7.35 (d, J = 8.8 Hz, 2H, aromatic at positions 2' and 6'), 7.80 (d, J = 8.8 Hz, 2H, aromatic at positions 3' and 5'), 9.10 (d, J = 1.5 Hz, 2H, aromatic at positions 2 and 6), and 9.15 (t, J = 1.5 Hz, 1H, aromatic at position 4).

2.2.2. 3,5-Diamino-4'-ethynylbenzanilide (**1**)

A mixture of 4'-ethynyl-3,5-dinitrobenzanilide (4.67 g, 15 mmol) and 10% Pd/C (0.05 g) in *N,N*-dimethylformamide (50 mL) was stirred at room temperature for 8 h under a hydrogen atmosphere. After the Pd/C was removed by filtration, the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography eluted by a mixture of dichloromethane and ethyl acetate (19:1). Yield: 3.15 g (84%). The IR spectrum exhibited absorption bands at 3450 cm⁻¹, 3380 cm⁻¹ (NH₂),

2110 cm⁻¹ (C≡C-), and 1660 cm⁻¹ (C=O).

The ¹H-NMR spectrum [δ in DMSO-d₆] showed signals at 4.10 (s, 1H, -C≡C-H), 4.83 (s, 4H, -NH₂), 5.99 (t, J = 1.5 Hz, 1H, aromatic at position 4), 6.30 (d, J = 1.5 Hz, 2H, aromatic at positions 2 and 6), 7.44 (d, J = 8.8 Hz, 2H, aromatic at positions 2' and 6'), and 7.79 (d, J = 8.8 Hz, 2H, aromatic at positions 3' and 5').

2.3. Synthesis of polyimide (PI-a)

In a three-necked flask, **a** (0.654 g, 3 mmol) was added a solution of **1** (0.15 g, 0.6 mmol) and ODA (0.48 g, 2.4 mmol) in NMP (12 mL) in one portion. The mixture was stirred at room temperature for 8 h under nitrogen. Part of the resulting viscous solution was poured into methanol (200 mL). The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of polyamic acid **PAA-a** was 1.05 dLg⁻¹ in NMP at 30 °C. The NMP solution was cast onto a glass plate and the solvent was removed at 70 °C. The thermal cyclodehydration of the polyamic acid was performed by successive heating at 100 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1 h under vacuum. The IR spectrum (film) exhibited absorption bands 1780 cm⁻¹, 1720 cm⁻¹ (C=O) and 1360 cm⁻¹ (C-N).

2.4. Preparation of photo-crosslinking film from **c**

In a three-necked flask, **c** (0.967 g, 3 mmol) was added a solution of **1** (0.15 g, 0.6 mmol) and ODA (0.48 g, 2.4 mmol) in NMP (12 mL) in one portion. The mixture was stirred at room temperature for 8 h under nitrogen in the dark. Part of the resulting viscous solution was poured into methanol (200 mL). The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of polyamic acid **PAA-c** was 0.92 dLg⁻¹ in NMP at 30 °C. The NMP solution was cast onto a glass plate, and the solution was exposed to a fluorescent lamp (illumination: 800 lx) for 1 h for gelation. After the solvent was removed at 70 °C, the thermal cyclodehydration of the polyamic acid was performed by successive heating at 100 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1 h under vacuum. The IR spectrum (film) exhibited absorption bands 1780 cm⁻¹, 1720 cm⁻¹ (C=O) and 1360 cm⁻¹ (C-N).

2.5. Measurements

Dynamic mechanical analysis (DMA) was

performed with the Advanced Rheometric Expansion System at 1.0 Hz at a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature to $500\text{ }^{\circ}\text{C}$ using film specimens (50 mm gauge length, 5 mm wide, and around $40\text{ }\mu\text{m}$ thick). The tensile tests of **PI-x** films were performed at a tensile speed of 10 mm min^{-1} on specimens of $50\text{ mm} \times 5\text{ mm} \times$ around $40\text{ }\mu\text{m}$ using a Shimadzu AGS-100G (Shimadzu Corporation, Kyoto, Japan). For thermogravimetry (TG), a Rigaku thermal analysis station TG 8110 was used and the measurements was made at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in air or nitrogen from room temperature to $800\text{ }^{\circ}\text{C}$. For differential scanning calorimetry (DSC), a Shimadzu DSC-60 was used and the measurements was made at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in nitrogen from $40\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$.

3. Results and discussion

3.1 Synthesis of 3,5-diamino-4'-ethynylbenzanilide (**1**)

Diamine **1** was synthesized from 4-ethynylaniline and 3,5-dinitrobenzoyl chloride in two steps. The reaction of 4-ethynylaniline with 3,5-dinitrobenzoyl chloride gave 4'-ethynyl-3,5-dinitrobenzanilide, and diamine **1** was obtained by hydrogenation of the dinitro compound using Pd/C as a catalyst.

Chemical structures were confirmed by IR and NMR spectroscopies. Diamine **1** showed characteristic IR absorptions 3450 and 3380 cm^{-1} for the amino group, 2110 cm^{-1} for the ethynyl group and 1660 cm^{-1} for amide carbonyl group. In the ^1H -NMR spectrum of **1**, the signal of the ethynyl proton was observed at 4.10 ppm , those of the aromatic protons on the 1,3,5-trisubstituted phenyl ring were observed at 5.99 and 6.30 ppm , and those on the 1,4-disubstituted phenyl ring were observed at 7.44 and 7.79 ppm . The obtained ratios of these protons agreed with the calculated values, and the spectra were almost the same as those of diamine **1** previously prepared by another approach [6].

3.2. Polymer synthesis

Polyimides **PI-x** having ethynyl groups on the side were synthesized by copolymerization of tetracarboxylic dianhydride (**x**), ODA, and **1** using the usual two-step procedure (Scheme 1). Tetracarboxylic dianhydride (**x**) was added to a NMP solution of **1** and ODA, and the solution was stirred, leading to the polyamic acid **PAA-x**.

The ratio of **1** and ODA was 2:8. The polymerizations except for **PAA-c** proceeded homogeneously, and viscous polyamic acid solutions were obtained. In the polymerization of **PAA-c**, gelation occurred. Since the gelation was thought to be due to crosslinking of ethynyl groups by triplet benzophenone, the polymerization of **PAA-c** was carried out in the dark, and the polymerization proceeded without gelation in the same way as the other polymerizations. The inherent viscosities were in the range of $0.88\text{--}1.05\text{ dLg}^{-1}$ (Table 1). In the second step, thermal conversion of the polyamic acid to polyimide was performed by heating the precursor polymer in the form of a film successively at $100\text{ }^{\circ}\text{C}$ for 1 h, $200\text{ }^{\circ}\text{C}$ for 1 h, and finally $300\text{ }^{\circ}\text{C}$ for 1 h under vacuum. These polyimides were obtained as tough films. The formation of polyimides was confirmed by the appearance of IR absorption bands at 1780 cm^{-1} and 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C-N) characteristic of an imide group. Crosslinking of the ethynyl groups might proceed during the imidation since the crosslinking conversion of the acetylene-terminated imide oligomer at $215\text{ }^{\circ}\text{C}$ for 1 h was reported to be about 0.7 [2].

Scheme 1. Synthesis of polyimide **PI-x**.

3.3. Polymer properties

Table 2 shows the mechanical properties of the polyimide films evaluated using tensile tests. The tensile strengths were more than 100 MPa , and the elongation-at-breaks were about 10%.

Thermal behavior of the polyimides was evaluated by DMA and TG. Glass transition temperatures (T_g) and 10% weight loss temperatures (T_{10}) are summarized in Table 3. None of the polyimides lost weight below $400\text{ }^{\circ}\text{C}$ in air and nitrogen, and T_{10} values in air and

Table 1. Synthesis of **PAA-x**.

Dianhydride	Polyamic acid	Yield / %	η_{inh}^c / dLg ⁻¹
a	PAA-a^a	98	1.05
b	PAA-b^a	97	1.02
c	PAA-c^b	97	0.92
d	PAA-d^a	98	0.88

^a Polymerization was carried out with **1** (0.6 mmol), ODA (2.4 mmol), and dianhydride (3.0 mmol) in 12 mL NMP at room temperature for 8 h.

^b Polymerization was carried out with **1** (0.6 mmol), ODA (2.4 mmol), and dianhydride **c** (3.0 mmol) in 12 mL NMP at room temperature for 8 h in the dark.

^c Measured at 0.5 g dL⁻¹ in NMP at 30 °C.

Table 2. Mechanical properties of **PI-x**.

Polyimide	Tensile strength (MPa)	Elongation at break (%)	Tensile Modulus (GPa)
PI-a	122 (118) ^a	11 (7) ^a	2.5 (2.8) ^a
PI-b	115 (108) ^a	9 (5) ^a	3.1 (3.8) ^a
PI-c	105 (104) ^a	10 (6) ^a	2.2 (2.8) ^a
PI-d	102 (96) ^a	14 (10) ^a	1.8 (2.2) ^a

^a Mechanical properties of **PI-x** annealed at 360 °C for 1 h.

nitrogen were in the range of 445–455 °C and 483–490 °C, respectively.

Figure 1 shows the dynamic mechanical behavior of the polyimides **PI-x** by continuous line. T_g was observed as $\tan \delta$ peak temperatures at 262–320 °C. In the temperature dependence of the storage modulus, a high modulus glassy region was followed by a decrease in modulus around T_g in spite of the imidation at 300 °C. The modulus of **PI-x** increased at about 340 °C. DSC curve of **PI-d** shows T_g around 260 °C followed by broad exothermic peak above about 280 °C (Fig. 2). The peak was smaller in the second heating. Thus, the exothermic peak is considered to be due to the more crosslinking of the ethynyl groups, which caused the increase of the modulus. The **PI-x** films were annealed at 360 °C for 1 h. The dynamic mechanical behavior of the annealed **PI-x** films is shown by broken line (Fig. 1). T_g values ($\tan \delta$ peak temperature) were higher (Table 3), storage moduli were larger and the decrements of storage modulus at the glass transition were smaller than the **PI-x** film, thus showing the effect of crosslinking. The tensile strengths of the polyimide films annealed at 360 °C were almost the same as those of **PI-x** films before annealing, and the elongation-at-breaks were lower (Table 2).

Fig. 1. Comparison of dynamic mechanical behavior of **PI-x** films. Continuous line: **PI-x** film. Broken line: **PI-x** film annealed at 360 °C for 1 h.

Fig. 2. DSC curves of **PI-d**.Table 3. Thermal properties of **PI-x**.

Polyimide	T_g^a / °C	T_{10}^c / °C	T_{10}^d / °C
PI-a	320 (360) ^b	452	488
PI-b	270 (320) ^b	455	490
PI-c	280 (320) ^b	445	485
PI-d	262 (300) ^b	445	483

^a Determined by dynamic mechanical analysis ($\tan \delta$) at a heating rate of 5 °C·min⁻¹.

^b T_g value of polyimide film annealed at 360 °C for 1 h.

^c Temperature at which 10% weight loss was recorded by TG at a heating rate of 10 °C·min⁻¹ in air.

^d Temperature at which 10% weight loss was recorded by TG at a heating rate of 10 °C·min⁻¹ in N₂.

In the polymerization for **PAA-c** in the light, gelation occurred. We investigated crosslinking the polyimide film by using this gelation, and the polyimide film was prepared from **PAA-c** solution as follows. The **PAA-c** solution cast on a glass plate was exposed to a fluorescent lamp for 1 h for gelation, then the solvent was removed at 70 °C, and thermal conversion to polyimide was performed. Figure 2 shows the dynamic mechanical behavior of the polyimide film. The T_g value ($\tan \delta$ peak temperature) was higher (368 °C), and the decrement of storage modulus at the glass transition was smaller than the **PI-c** film, thus confirming photo-crosslinking of the ethynyl groups. Some polyimides from BTDA were crosslinked by photo-polymerization of pendant acrylate groups [8-14], but a photoinitiator was used in the crosslinking. Photo-crosslinking proceeded in the **PAA-c** solution without a photoinitiator. Photo-crosslinking were also observed in the polyimide from BTDA and bis(4-amino-3-methylcyclohexyl)methane (DMDHM) [15]. Triplet benzophenone abstracts a hydrogen, and benzophenone ketyl

radical was formed. The crosslinking were thought to be due to coupling between the ketyl radical and an alkyl radical generated by hydrogen abstraction. In this study, radical polymerization of the side ethynyl groups by the triplet benzophenone moiety might occur in **PAA-c** solution.

Fig. 3. Comparison of dynamic mechanical behavior. Continuous line: **PI-c** film. Broken line: the film prepared from **PAA-c** solution exposed to a fluorescent lamp.

4. Conclusion

Crosslinking polyimides films having ethynyl groups on the side could be prepared from 3,5-diamino-4'-ethynylbenzanilide (**1**), 4,4'-oxydianiline and various dianhydrides by the usual two-step procedure. Crosslinking of the ethynyl groups proceeded by annealing the polyimide film at 360 °C, whereupon the T_g values were higher and the decrements of storage modulus were smaller. In polyimide film from 3,3',4,4'-benzophenonetetracarboxylic dianhydride, photo-crosslinking by exposing the polyamic acid solution to a fluorescent lamp was also observed.

References

1. S. J. Havens and P. M. Hergenrother, *J. Polym. Sci., Part A., Polym. Chem.*, **22** (1984) 3011.
2. W. X. Hung and S. L. Wunder, *J. Polym. Sci., Part B., Polym. Phys.*, **32** (1994) 2005.
3. R. H. Pater and T. Va, US005306784A.
4. M. Miyauchi, Y. Ishida, T. Ogasawara, and R. Yokota, *Polym. J.*, **45** (2013) 594.
5. M. Ogino, T. Ohashi, H. Yoshida, D. Nagayama, T. Kubota, A. Morikawa, and K. Ono, *J. Photopolym. Sci. Technol.*, **27** (2014) 155.
6. M. Nakayama, JP5207801.
7. A. Imakuni, M. Yagihara, M. Nakayama, Y.

- Nakai, and O. Uchida, PCT/JP2009/051988.
8. R. Stephen Davidson, A. Dias Aylvin, and D. Illsley, *Eur. Coat. J.*, (1994) 193.
 9. R. Stephen Davidson, A. Dias Aylvin, and D. Illsley, *Eur. Coat. J.*, (1994) 198.
 10. R. Stephen Davidson, A. Dias Aylvin, and D. Illsley, *J. Photochem. Photobiol., A: Chem.*, **89** (1995) 75.
 11. H. Tojo, A. Kameyama, and T. Nishikubo, *J. Photopolym. Sci. Technol.*, **12** (1999) 223.
 12. M. Meledyn, R. Paszkiewicz, and B. Masiulonis, *J. Appl. Polym. Sci.*, **91** (2004) 971.
 13. C-H. Ho, S. Chang, and Y-D. Lee, *J. Appl. Polym. Sci.*, **114** (2009) 2395.
 14. Q. Jin, T. Yamashita, and K. Horie, *J. Polym. Sci., Part A., Polym. Chem.*, **32** (1994) 503.
 15. K. Murakami and S. Ando, *J. Photopolym. Sci. Technol.*, **24** (2011) 277.