Thermal Conversion of Polyamic Acid Gel to Polyimide Solution Having Amino Group Sidechains

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Deformation of a polyamic acid gel was observed upon heating. The gel prepared from 1,1-bis[4-(aminophenoxy)phenyl]-1-[4-(4-amino-2-trifluoromethylphenoxy)phenyl]ethane (triamine-CF₃), 4,4'-oxydianiline (ODA) and benzzenonetetraacarboxylic dianhydride (BTDA) in N-methyl-2-pyrrolidone (NMP) at 20 °C was heated to 180 °C. The swelling became weak upon increasing the temperature, and the gel turned into a solution that could be stirred easily above 80 °C. The solution heated to 180 °C did not return to the gel state even upon cooling to 20 °C. IR measurements of the heated gel showed that the deformation was due to an amide exchange reaction, which proceeded through scission of the amide linkage into anhydride and amine end groups. The viscosity barely changed upon heating. The amide exchange and imidation reactions proceeded simultaneously upon heating the polyamic acid gel, and formed a soluble polyimide containing amino sidechains.

Keywords: Deformation of polyamic acid gel, Amino group sidechains, Triamine-CF₃, Amide exchange, Imidation reaction

1. Introduction
Polyimide-silica hybrid materials have been prepared by a sol-gel process involving tetraethoxysilane in a polyamic acid solution, followed by thermal treatment [1-3]. Transparent and tough hybrid films with high silica contents were prepared using polyamic acid by conjugation to silica [4-5]. We prepared the polyamic acid containing amino group sidechains from BTDA, 4,4'-ODA, and triamine-CF₃. The amino group reacted with 3-(triethoxysilyl)propyl succinic anhydride (TESSA) to introduce ethoxysilyl moieties that allowed for the conjugation to silica. The polyimide-silica hybrid films were prepared by sol-gel reaction with tetraethoxysilane in the polyamic acid solution, and thermal imidation. These hybrid films were more transparent than those prepared without TESSA [6]. In the preparation of polyamic acid, the 4-amino-2-trifluoromethylphenoxy group in triamine-CF₃ was expected to react slower with the anhydride than the 4-aminophenoxy group in triamine-CF₃ due to the electron-withdrawing effect of the trifluoromethyl group. This would lead to a polyamic acid containing amino group sidechains [6]. However, gelation was also observed. The gel became a solution upon heating and could be reacted with TESSA to introduce the ethoxysilyl moiety.

In this study, the change of the chemical structure during heating of the polyamic acid gel as it changed into a solution was evaluated.

2. Experimental
2.1. Preparation of polyamic acid gel from triamine-CF₃
In a three-necked flask, 1.128 g (3.5 mmol) of BTDA was added to a solution of 0.324g (0.5 mmol) of triamine-CF₃ and 0.601 g (3.0 mmol) of ODA in 30.0 mL of NMP at 20 °C. The mixture was stirred at 20 °C under nitrogen. The solution became more viscous as BTDA was dissolved and formed a gel.

The gel was heated at a rate 2 °C/min to 180 °C. It became a solution above 80 °C. Upon cooling to 20 °C, this sample remained in the solution state.
2.2. Preparation of polyamic acid gel from 2,4,4'-triaminodiphenyl ether [7]

In a three-necked flask, 1.128 g (3.5 mmol) of BTDA was added to a solution of 0.108 g (0.5 mmol) of 2,4,4'-triaminodiphenyl ether and 0.601 g (3.0 mmol) of ODA in 30.0 mL of NMP at 20 °C. The mixture was stirred at 20 °C under nitrogen. The solution became more viscous as BTDA was dissolved and gelation occurred.

The gel was heated at a rate 2 °C/min to 180 °C. It did not become a solution even at 180 °C.

2.3. Measurements

IR measurements were carried out using a SHIMADZU IR 435 spectro-photometer with the films prepared by drying the gel or solution at 70 °C. Viscosity measurements were carried out at a concentration of 0.5 g dL⁻¹ in NMP at 30 °C using an Ostwald viscometer.

3. Results and discussion

3.1. Deformation of polyamic acid gel and imidation

Deformation of polyamic acid gel was observed by heating. The gel prepared from triamine-CF₃, ODA and BTDA in NMP at 20 °C was heated to 180 °C. The gel changed as shown in Fig. 1. The swelling became weak with increasing temperature, and the gel became a solution which could be stirred easily above 80 °C. The solution heated to 180 °C did not return to a gel even if cooled to 20 °C.

Fig. 1. Reaction between BTDA, ODA and triamine-CF₃, and the change by heating.

The formation of a polyamic acid is an exothermic reaction, which involves an equilibrium [8-10]. The equilibrium constant K is very large, and the concentration of amic acid is very high in the equilibrium. When the polyamic acid solution is heated, the reverse reaction, which is caused by chain scission into amine and anhydride groups, proceeded at an early stage. However, the forward reaction, reformation of polyamic acid, proceeds later since the concentration of amic acid is lower due to thermal imidation during heating of polyamic acid solution [11-12].

Figure 2 shows IR spectra of the films prepared from the gel at 20 °C, and the solutions at 80 °C, 150 °C, and 180 °C. The IR absorption peak due to carbonyl stretching of the amide group appeared at about 1650 cm⁻¹ in the film from the gel at 20 °C. Additional absorption peaks appeared at 1850 cm⁻¹ (↑), 1780 cm⁻¹, 1720 cm⁻¹, and 730 cm⁻¹ in the film formed from the solution at 80 °C. The 1850 cm⁻¹ band is attributed to asymmetric stretching of the carbonyl groups in the anhydride moiety [13], 1780 cm⁻¹ and 1720 cm⁻¹ bands are attributed to the symmetric and asymmetric stretching of the carbonyl groups in the imide group, respectively, and the 730 cm⁻¹ band is attributed to deformation of the imide ring [13-14]. The anhydride peak at 1850 cm⁻¹ suggests that chain scission into amine and anhydride groups occurred. The intensity of the imide peaks at 1780 cm⁻¹, 1720 cm⁻¹ and 730 cm⁻¹ were higher in the films formed from the solution at higher temperatures and reached a maximum in the film from the solution at 180 °C at 3 h. The percent imidation [13,15] calculated from the absorbance ratio of the characteristic absorption due to imide groups at 1720 cm⁻¹ to that due to aromatic groups at 1500 cm⁻¹ was 95%. As for the calculation, a value of the previously prepared polyimide film produced by heating the polyamic acid film at 100 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1 h under vacuum was performed as 100% [6]. The polyimide was not precipitated during heating in spite of the high percent imidation. Polyimide was reported to be prepared by heating anhydride-terminated amic acid oligomer, 2, 4-diaminotoluene, and 3,3',4,4'-biphenyltetraacarboxylic dianhydride in NMP at 180 °C for 3 h [16].

The relationship between the inherent viscosity (η_inh) and temperature of the heating solution is shown in Fig. 3. An initial decrease followed by an increase in the viscosity were observed at 80-120 °C and 140-180 °C, respectively. The decrease at 80-120 °C is thought to be correlated with the generation of anhydrides by chain scission, and the increase at 140-180 °C is thought to be correlated with the reformation of polyamic acid and the imidation reaction. η_inh barely changed during heating, nor did water formed during the imidation have a great influence on η_inh due to the small amount present.
Crosslinking to form a gel occurred by the reaction of all amino groups in triamine-CF$_3$ with anhydride groups. The transformation of the gel to a solution is proposed to occur as shown in Fig. 4. The crosslinking is broken by the scission of amic acid into amine and anhydride groups. Next, a reaction causing reformation of the amic acid is followed by imidation. In the reformation of amic acid, the 4-aminophenoxy group (○) and the 4-amino-2-trifluoromethylphenoxy group (×) could both react with anhydride groups. The 4-amino-2-trifluoromethylphenoxy group (×) was expected to react slower than the 4-aminophenoxy group (○) due to the electron-withdrawing effect of the trifluoromethyl group. Since the equilibrium process of scission and recombination (amide exchange reaction) [17-18] occurred sufficiently, the number of crosslinking sites was reduced.
Such reactivity of amino group was reported to influence the storage time of polyamic acid / polyamic acid solutions before becoming random copolyimide [19]. For example, the storage time of the pyromellitic dianhydride (PMDA)-p-phenylenediamine (PPD)/ PMDA-2,2-bis(4-aminophenyl) hexafluoropropane (6F) blend was much longer than that of PMDA-PPD/ PMDA-ODA due to the electron-withdrawing character of the hexafluoroisopropylidene group in 6F. The gel prepared from 2,4,4'-triaminodiphenyl ether without a trifluoromethyl group, ODA and BTDA in NMP did not become a solution even upon heating to 180°C but remained in the gel state (Fig. 5) [20].

3.2. Preparation of polyimide-silica hybrid films from polyimide solution having amino group sidechain

The polyamic acid gel prepared from triamine-CF₃ changed to a soluble polyimide containing amino sidechains by heating to 180°C. The amino group could then be reacted with TESSA to introduce ethoxysilyl moieties that allow for conjugation to silica. The sol-gel reaction of tetraethoxysilane was carried out in the polyimide solution, followed by thermal imidation of the amic acid generated from TESSA, and polyimide-silica hybrid films were prepared as shown in Fig. 6. For comparison, the polyimide-silica hybrid film was also prepared without TESSA (Fig. 7). The fractured surfaces of the hybrid films containing 20 wt% silica were observed by SEM (Fig. 8). The fractured morphology of the hybrid film prepared using TESSA showed smooth surface. On the other hand, silica particles were clearly observed as beads having diameter 1.0-2.0 µm in the hybrid film.
prepare without TESSA. It was suggested that TESSA acted as conjugation between the polyimide and silica.

**Fig. 6.** Preparation of polyimide-silica hybrid film from polyimide solution using TESSA.

**Fig. 7.** Preparation of polyimide-silica hybrid film from polyimide solution without TESSA.
4. Conclusion
During heating of a polyamic acid gel to 180°C, equilibrium processes involving the scission and recombination of amic acid occurred, followed by imidation, which change the gel into a soluble polyimide containing amino group sidechains.

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