Equilibrium of One-Pot Polymerization of Polyimide

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SYNOPSIS

One-pot polymerization of polyimide from 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4′-oxydianiline (ODA) was examined. The equilibrium in the polyimide with water was examined in detail in p-chlorophenol solution during the polymerization. The equilibrium constant was expressed by $\log K = 1.50 + 1433\,(1/T)$. The polymerization reaction is exothermic. The molecular weight increased with decrease of temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have found a wide range of applications as high-performance materials in the aerospace and electronics industries, due to their excellent electrical, thermal, and high-temperature mechanical properties. Polyimide films usually are manufactured in a two-step method (Fig. 1). The first step is a polycondensation reaction between a dianhydride and diamine in a suitable solvent. This polyamic acid solution is then fabricated into a film by solvent casting and removal of the solvent. In the second step, the resulting polyamic acid film is thermally converted to the polyimide by the removal of water.

There is another method, called the one-pot method. In this method, soluble polyimides are successfully synthesized in solution by heating at 100–200°C from the combination of a dianhydride and diamine.[1-5] There are many reports regarding the mechanisms and kinetics of the formation of polyimide under homogeneous conditions.[6-12] The equilibrium between imide linkage and water has been expected to be present from the facts that polyimide formation is a dehydration reaction and imide linkage can be hydrolyzed to the amic acid group. However, there are only a few reports regarding to the

equilibrium between the imide linkage and water.[13,14] In these articles, the equilibrium constants of polyimide formation were estimated from the hydrolysis study. Consequently, there is no report that the equilibrium of the processes of polyimide formation was discussed.

In this work, we noticed the polyimide prepared from 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4′-oxydianiline (ODA), and the polymerization was carried out in p-chlorophenol solution.[15] The equilibrium between imide linkage and water is discussed and estimated under various conditions.

EXPERIMENTAL

Polymer Synthesis (Open System)

BPDA of 7.356 g (0.025 mol) and ODA of 5.006 g (0.025 mol) were incorporated into 190.65 g of p-chlorophenol. The concentration of monomers was 12 wt %. Then, the temperature of the mixture was, while being stirred in a stream of nitrogen, increased from 100 to 160°C for 1 h and then maintained at a given temperature for a period of given time in an atmosphere of nitrogen or in a stream of nitrogen.

### Polymer Synthesis (Closed System)

BPDA of 14.71 g (0.05 mol), ODA of 10.01 g (0.05 mol), and p-chlorophenol of 181.3 g were placed in

a glass reactor equipped with a cooling jacket. The concentration of monomers was 12 wt %. The content was, while being stirred under a nitrogen atmosphere, increased to the temperature of 160°C for 1 h. The polyimide solution was homogeneous and clear. The viscosity of the solution at 140°C was 1.1 Pa-s. The polyimide in the solution had a inherent viscosity of 1.02 dL/g. The polyimide solution of 11 g was placed in a glass autoclave having an inner diameter of 1.5 cm and a depth of 10 cm. Furthermore, a predetermined amount of water was introduced into the autoclave. Thereafter, the gaseous phase in the autoclave was replaced by nitrogen gas. Then, the content was heated to a given temperature for a period of given time.

Analysis

The viscosity of a polyimide solution was determined at 140°C under the condition of shear rate of 1–50 s^{-1} using a rotation viscometer (trade name VIS-METRON, supplied by Tokyo Keisoku K.K.). Inherent viscosity η_{inh} (dL/g) was determined at a temperature of 50°C on a solution of 0.5 g polymer in 100 mL of p-chlorophenol. The solution was prepared by dissolving a polyimide solution in p-chlorophenol at 150°C. Intrinsic viscosity $[\eta]$ (dL/g) was determined at 50°C using a Cannon-Ubbelohde viscometer. The amount of water in a polyimide solution was determined using a Karl Fisher moisture meter supplied by Kyoto Electronics Ltd. The polymer solution of 1 g was placed in a vessel, and, furthermore, absolute methyl alcohol of 25 mL was introduced into the vessel. The amount of water in the content was determined after stirring for 20 min. The weight-average molecular weight $(\bar{M}_w)$ was determined by an Chromatrix KMX-6 low-angle light-scattering photometer at 60°C.
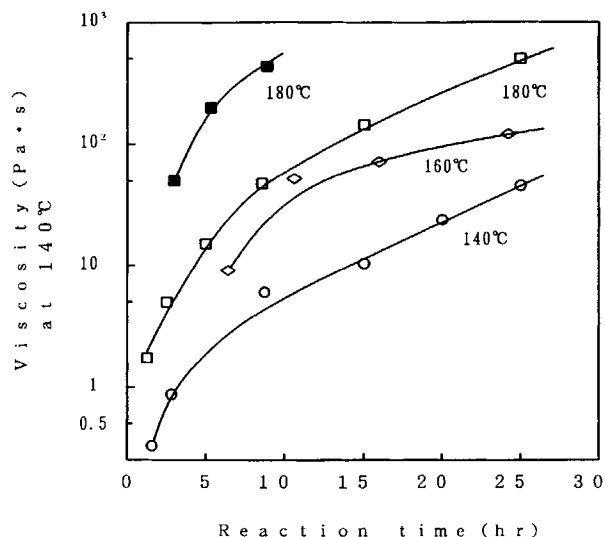

Figure 2   Change of viscosity of the polyimide solution. Polymer concentration: 12 wt %. (○, ◇, □) N_2 atmosphere; (■) N_2 flow.

RESULTS AND DISCUSSION

One-pot polymerization in p-chlorophenol was conducted at 140–180°C and the change in the viscosity of the solution followed (Fig. 2). The viscosity of the solution increases with reaction time, and the higher the temperature becomes, the faster the viscosity increases. The increase of the viscosity means increase of the degree of polymerization, and, therefore, the polymerization in p-chlorophenol proceeds smoothly.

In the case of polymerization of polyamic acid, the reaction attains equilibrium fairly rapidly; then, the increase of the viscosity levels off at a certain value. This is because water in the reaction system hydrolyzes acid dianhydride and polyamic acid. o-Dicarboxylic acid formed by the hydrolysis of acid
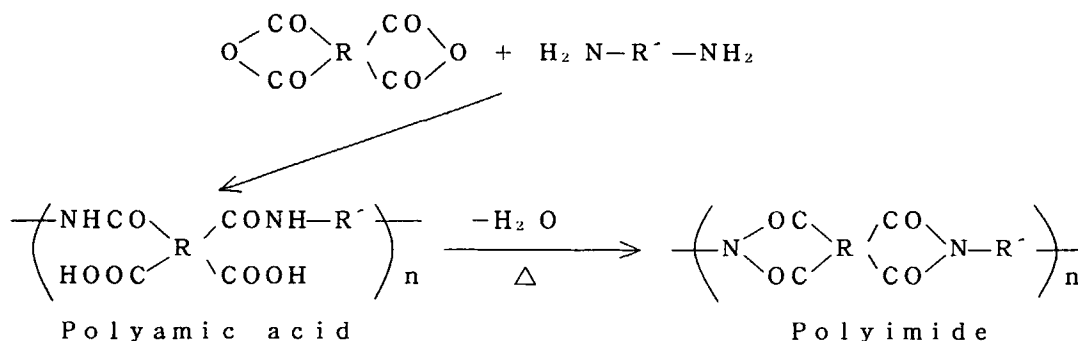
**Figure 1**   Scheme of two-step polymerization.
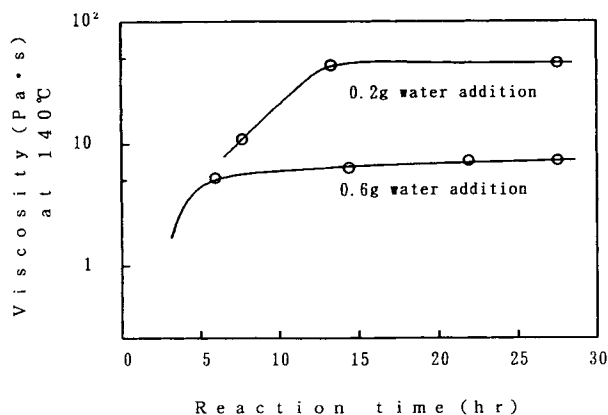
Figure 3 Influence of water content on viscosity in a closed polymerization system. Polymer concentration: 12 wt %; polymerization temperature: 180°C.

anhydride rarely reverts to the original acid anhydride at a temperature lower than 30°C. As a result of the hydrolysis, the molar ratio of acid dianhydride/diamine deviates from the equimolar ratio and the equilibrium is rapidly reached. However, in the case of one-pot polymerization, the polymerization would proceed so long as stirring is possible, since water in the reaction solution is removed as p-chlorophenol azeotrope and the o-dicarboxylic acid present in the p-chlorophenol solution reverts to acid anhydride at a temperature higher than 100°C. As shown in Figure 2, the polymerization under nitrogen gas flow proceeds faster than that under nitrogen atmosphere. For this reason, water in the reaction system could be rapidly removed out of the system by the flow of nitrogen gas. Grenier-Loustalot et al.[12] studied the ring dehydration reaction in solution in the presence of a desiccant (molecular sieve) and reported that the presence of the molecular sieve shifted the amic acid to imide. This result suggests that there is an equilibrium between water and the imide group. If there is an equilibrium between water in the solution and the imide group, the degree of polymerization could be controlled by the water content as in nylon polymerization.[16] To prepare polyimide films continuously in an industrial scale by a solution casting method, it is necessary to supply continuously a polyimide solution having a constant viscosity. If polyimide solutions different in the viscosity were supplied one by one, the film-forming conditions must be changed according to the viscosities of the respective solutions. It is actually impossible to prepare films continuously having uniform properties. Then, it is important to control the degree of polymerization. Con-

sequently, it is necessary to control the water content.

It is possible to control the water content in the solution by carrying out polymerization in a closed reaction system. Then, the polyimide solution of 16 g, having a concentration of monomers of 12 wt % and being heated to 160°C for 1 h, and water of 0.2 g or 0.6 g was placed in a glass autoclave. Then, the solution was heated to 180°C and maintained at that temperature for a period of given time. The change of the viscosity of the solution is shown in Figure 3. When 0.6 g of water was added, the solution approximately reached equilibrium in 6 h. In the case of 0.2 g, the solution approximately reached equilibrium in 14 h. The viscosity of the solution at equilibrium was higher than that in the former case. If the polymerization was carried out at 180°C in a closed system to keep the amount of water constant, the equilibrium would be reached in 20 h. The viscosity of the solution at equilibrium is dependent on the amount of water, and the larger the amount of water, the lower the viscosity of the solution.

The polymerizations in a closed system were carried out with regard to different amounts of water in order to determine the relationship between the viscosity of the solution and the amount of water. The polymerization conditions were as follows: The concentration of monomers was 12 wt %, the reaction time was 20 h, and the temperature was 180°C. Figure 4 shows the relationship between the amount of water and the viscosity of the solution. Although the experimental points are somewhat scattered, there is surely some correlation. This result suggests that there is an equilibrium between water and the imide group, and it is possible to control the degree
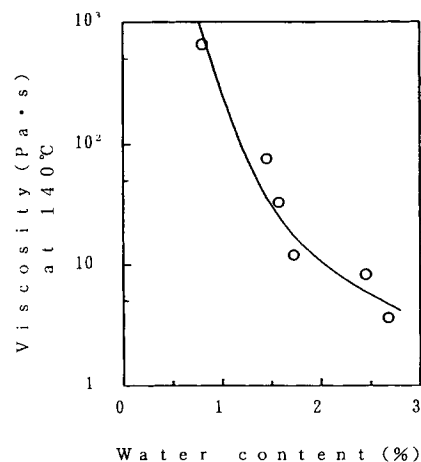
Figure 4 Relationship between amount of water and viscosity of the solution.
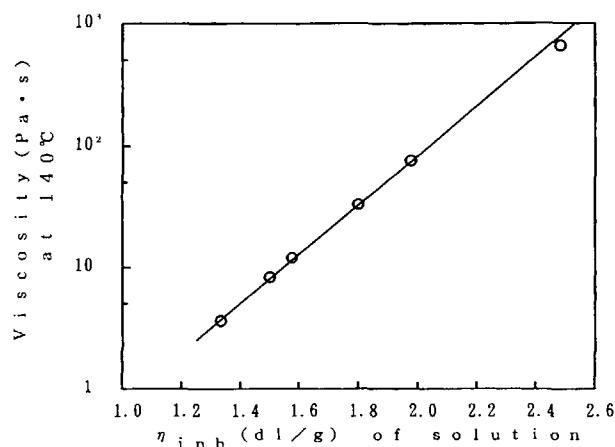
Figure 5 Relationship between η_{inh} of the solution and viscosity of the solution.

of polymerization by changing the amount of water. The relationship between inherent viscosity at equilibrium and the viscosity of the solution is shown in Figure 5. The experimental points fall on a straight line.

The equilibrium between water and the imide group was certainly confirmed with regard to the polymerization of the monomer. Further, to ascertain this equilibrium, we studied the depolymerization of polyimide. When water was added to the polyimide solution, we examined whether the molecular weight dropped. Water was added to the polyimide solution (Exp. 1), and the solution was further kept at 180°C for 16 h in a closed system. As shown in Table I, the inherent viscosities of the solutions (Exp. 2 and Exp. 3) dropped from 1.78 to 1.71 and 1.38, respectively, by addition of water. The depolymerization of polyimide by water was confirmed.

The influence of temperature on the equilibrium was studied. The higher the temperature, the lower the viscosity of the solution at equilibrium, under any given concentration of water, as shown in Figure 6.

The processes for imide formation and degradation are shown in Figure 7. A polymerization of a dianhydride with a diamine forms a polyamic acid and subsequent cyclization of the polymer forms polyimide. Anhydride and amine reappear from amic acid. The anhydride formed may hydrolyze to the acid compound, which can eventually recyclize at sufficiently high temperatures and again react with free amine groups.

Assuming that the polyimide linkage and dicarboxylic acid and amine are equilibrated, an equation for the equilibrium constant can be written as

Table I　Depolymerization of Polyimide

Polyimide Solution	Amount of Water Added (g)	Rotation Viscosity at 140°C (Pa-s)	η_{inh} (dL/g)
Exp. 1[a]	0	31.0	1.78
Exp. 2[b]	0.22	18.5	1.71
Exp. 3[b]	0.38	5.2	1.39

[a] Solution: polyimide solution of 12 wt % prepared by polymerizing at 180°C for 10 h in a closed system.

[b] Water was added to the Exp. 1 solution of 11 g and kept at 180°C for 16 h.

$$K_1 = \frac{[\text{imide group}][H_2O]^2}{[\text{dicarboxyl group}][\text{amino group}]} \quad (1)$$

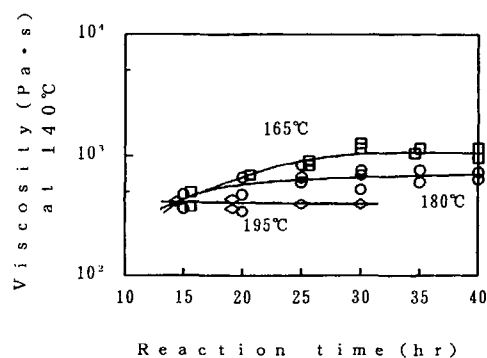Each species is represented by the following formulas:

$$[\text{dicarboxyl group}] = C \times \frac{1}{Pn}$$

$$[\text{amino group}] = C \times \frac{1}{Pn}$$

$$[\text{imide group}] = C \times \left(1 - \frac{1}{Pn}\right)$$

$$K_1 = \frac{[H_2O]^2 \times Pn(Pn - 1)}{C} \quad (2)$$

C (mol/kg) is the concentration of monomers and Pn is the polymerization number. $[H_2O]$ (mol/kg) is the concentration of water in the solution. The Pn at equilibrium was obtained from the number-

Figure 6 Influence of temperature on viscosity of the solution. Water content: 0.78% (165°C); 0.82% (165°C); 0.68% (195°C).
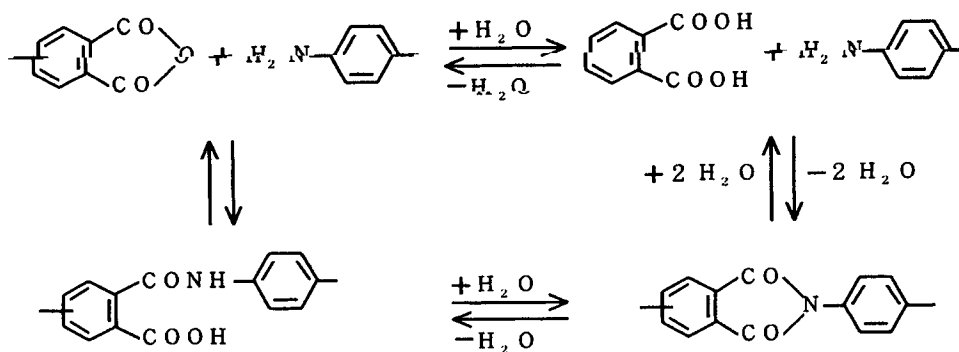
Figure 7 Processes of polyimide formation and degradation.

average molecular weight $(\bar{M}_n)$. The relation be-tween intrinsic viscosity and weight-average molecular weight $(\bar{M}_w)$ was obtained as shown in Figure 8 and is expressed by following equation:

$$\bar{M}_w = 3.954 \times 10^4 [\eta]^{0.989} \tag{3}$$

We assumed the theoretical polydispersity of 2.0:

$$\bar{M}_n = \bar{M}_w/2 \tag{4}$$

The values of the equilibrium constant (K_1) are given in Table II. The values are considerably scattered and increase with water content. Then, we assumed that there is an equilibrium between the polyimide linkage and anhydride and amine. Thus, the equilibrium of hydrolysis of anhydride would be negligible and the dicarboxyl group would be rarely present. If this idea is correct, the equilibrium constant written by the following equation would be constant:

Figure 8 Relationship between molecular weight and $[\eta]$.

$$K_2 = \frac{[\text{imide group}][H_2O]}{[\text{anhydride group}][\text{amino group}]} \tag{5}$$

$$K_2 = \frac{[H_2O] \times Pn(Pn - 1)}{C} \tag{6}$$

The values of the equilibrium constant (K_2) are shown in Table II. These values are approximately constant. This result proves that the equilibrium constant of the hydrolysis of anhydride is negligible under our polymerization conditions.

Vinogradova et al.[13] studied the hydrolysis of the polyimide from 9,9-bis(4-aminophenyl)fluorene and 3,3',4,4'-tetracarboxy diphenyloxide in a N-methyl-pyrrolidone solution containing 0.03% water and reported that the equilibrium constants have a strong temperature dependence and drop by more than a factor of 10 in a 50°C range. They pointed out that the equilibrium was attained in 2.5–3 h, but that the equilibrium could not be attained in such a short time in the case of 115°C. Then, the equilibrium constants at lower temperatures will become larger than the predicted value. Our values are much larger than are the values reported by Vinogradova et al. The equilibrium constant by Vinogradova et al. at 160°C was 0.31 × 10⁴, while the constant at 165°C by us was 5.91 × 10⁴. Heacock[14] noticed the hydrolysis of polyimide film and reported that an equilibrium was established under high humidities after a long period of experiment. In his study, the temperature was 70–100°C. The equilibrium constants were smaller than those reported by Vinogradova et al. The constant at 100°C reported by Heacock was 2.84 × 10⁴, while the constant at 115°C reported by Vinogradova et al. was 5.31 × 10⁴. These differences may be due to the difference of the solvents as well as to the difference in the chemical nature of the polyimides.
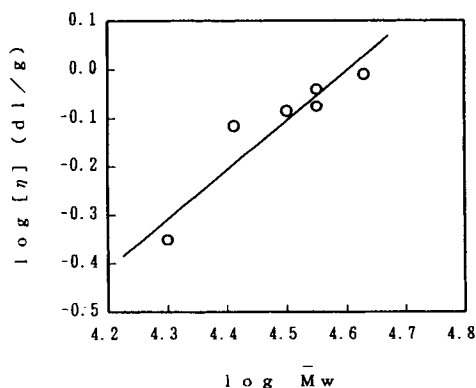
Table II Equilibrium Constants

Polymerization Temperature (°C)	Water Content (%)	Water Content Mol/kg	$[\eta]$ (dL/g)	$\bar{M}_n \times 10^{-4}$	$K_1 \times 10^{-4}$	$K_2 \times 10^{-4}$
165	0.78	0.433	3.03	5.92	2.56	5.91
180	0.82	0.444	2.70	5.29	2.14	4.82
180	1.45	0.806	2.18	4.26	4.56	5.66
180	1.57	0.872	1.98	3.89	4.45	5.11
180	1.72	0.956	1.74	3.42	4.15	4.34
180	2.45	1.361	1.64	3.22	7.46	5.48
180	2.68	1.489	1.45	2.86	6.98	4.69
195	0.68	0.378	2.56	5.01	1.40	3.70

A linear relationship was obtained by plotting the log K_2 against the reciprocal of the absolute temperature as shown in Figure 9 and is expressed by the following experimental formula:

$$\log K_2 = 1.50 + 1433/T \tag{7}$$

Thus, the heat of condensation polymerization is given as follows:

$$\Delta H = -6.5 \text{ kcal mol}^{-1} \tag{8}$$

This value is within the range of the one reported by Heacock[14] and by Fukumoto.[16] Thus, the polymerization reaction is exothermic and the molecular weight increases with decrease of temperature.
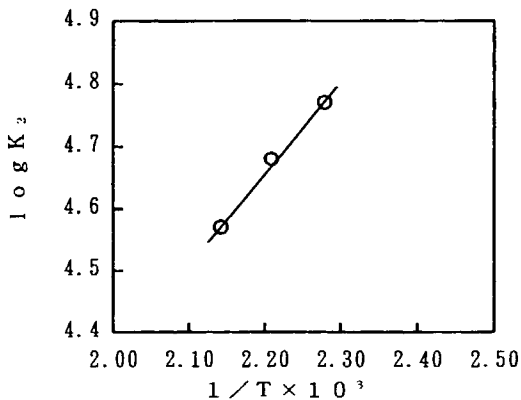
CONCLUSIONS

One-pot polymerization of polyimide from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and

Figure 9 Relationship between log K_2 and $(1/T)$.

4,4'-oxydianiline (ODA) was examined. The equilibrium in the p-chlorophenol solution was studied during the polymerization of the polyimide and the equilibrium between imide linkage and water was discussed. The experimental result could be explained by assuming that there was an equilibrium between the polyimide linkage and anhydride and amine. The equilibrium constant of the polymerization is expressed by log $K = 1.50 + 1433(1/T)$. The polymerization reaction is exothermic and the molecular weight increased with decrease of temperature.

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