

# Comparison of One-Pot and Two-Step Polymerization of Polyimide from BPDA/ODA

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## SYNOPSIS

The one-pot method polymerization of polyimide was carried out from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) by the use of *p*-chlorophenol as the solvent. The behavior of the polymerization was compared with that of the two-step method. The imidization reaction in the one-pot method proceeds completely in this system at even a low temperature such as 100°C. In the course of the film preparation from the solution, the embrittlement occurs when the film is prepared from polyamic acid solution, while it does not occur in the case of that from the solution of the one-pot method. A molecular weight of polyimide film is almost the same as that of precursor polyimide in the solution. In the same way, that of polyimide film is almost the same as that of precursor polyamic acid. The mechanical properties of the polyimide film prepared by the one-pot method are similar to those by the two-step method. © 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 converted thermally 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.<sup>1–4</sup> This polyimide solution is fabricated into a polyimide film in a similar manner as the two-step method.

Two-step methods have been studied by many investigators. The thermal conversion of a polyamic acid precursor results in a complex mixture. Anhydride and amine starting materials reappear due to amic acid equilibration and/or hydrolysis. The imide group begins forming with the liberation of water. Additionally, the anhydride formed may hydrolyze to an acid compound, which can eventually cyclize at sufficiently high temperature and again react with the free amine groups present. Consequently, a polyamic acid undergoes an apparent reduction in molecular weight during cure before achieving its ultimate molecular weight as a polyimide.<sup>5–8</sup> Also, it is known that there is little or no difference in molecular weight between fully imidized polymer and the parent polyamic acid precursor.<sup>9,10</sup> In the two-step method, the conversion of a polyamic acid to the polyimide is commonly accomplished by thermal treatment of the polyamic acid in the solid state. The imidization in the solid state has been known to be a very complex physicochemical process, being affected by many factors.<sup>11</sup>

On the other hand, the imidization in the one-pot method proceeds in a homogeneous solution, since soluble polyimides are used. The polyimide in the solution has been considered to be completely

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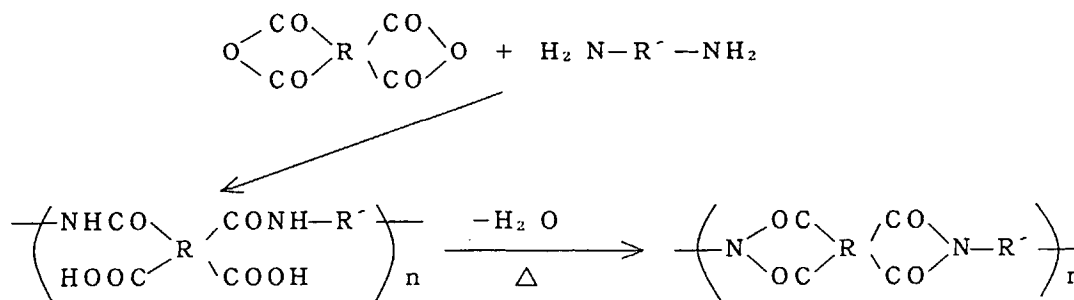


Figure 1 Scheme of two-step polymerization.

imidized at the proper condition because of the complete removal of constraints, such as a  $T_g$  increase and the existence of kinetically nonequivalent states of amic acid groups.<sup>11</sup> Since there must be some differences in the conditions of imidization between the one-pot and two-step methods, differences are expected in the molecular weights of the polyimides and the properties of the polyimide films from both methods. However, there is no literature about the same polyimide composition that is used for both the one-pot and two-step methods. The object of this report was to understand the differences in the change of molecular weight and mechanical properties throughout the entire interval of the cure and in the properties of polyimide films prepared from the two methods.

In this work, the polyimide prepared from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) was chosen and the possibility of the one-pot method was examined. The present study reports the relationship between the inherent viscosity of the polyamic acid or polyimide solution and that of the film prepared from the solution. Further, the mechanical properties of the film prepared from the one-pot method<sup>12</sup> are compared with those from the two-step method.

## EXPERIMENTAL

### Polymer Synthesis and Film Preparation (One-pot Polymerization)

Equimolar amounts of BPDA and ODA were incorporated into *p*-chlorophenol (PCP). Then, the mixture was, while being stirred in a stream of nitrogen, increased from the temperature of 100 to 180°C in 1 h and maintained at that temperature for a period of given time.

The obtained polyimide solution was cast onto a glass plate as a liquid film having a uniform thickness. The liquid film was maintained at the tem-

perature of approximately 120°C under a pressure of 1 mmHg for a period of 1 h by a vacuum dryer to evaporate PCP. Then, the film was removed from the plate and was placed on a frame. The film was gradually heated to a temperature of 300°C by using a forced-air oven to completely remove the PCP. The film thickness was about 50  $\mu\text{m}$ .

### Polymer Synthesis and Film Preparation (Two-step Polymerization)

ODA was first dissolved in *N*-methyl-2-pyrrolidone (NMP), and BPDA was added simultaneously in quantities equimolar to diamine, while being stirred in a stream of nitrogen at below 30°C. All polymerization experiments were carried out at a total solid content of 10% by weight.

The obtained polyamic acid solution was cast onto a glass plate as a liquid film of a uniform thickness. The liquid film was maintained at a temperature of approximately 120°C for 20 min in a forced-air oven. Then, the film was removed from the plate and was placed on a frame and gradually heated to the temperature of 300°C by using a forced-air oven. The film thickness was about 50  $\mu\text{m}$ .

### Analysis

The rotation viscosity of a polyimide solution was measured using a rotation viscometer (trade name VISMETRON, supplied by Tokyo Keisoku K.K.) under the condition of a shear rate of 1–50  $\text{s}^{-1}$ . The inherent viscosity,  $\eta_{\text{inh}}$  (dL/g), was determined at a temperature of 50°C in a solution of 0.5 g polymer in 100 mL of PCP. The solution was prepared by dissolving a film or a polyimide solution in PCP at 150°C. In the case of polyamic acid,  $\eta_{\text{inh}}$  was determined at a temperature of 30°C in a solution of 0.5 g polymer in 100 mL of NMP. The percent imidization of the polymer present in the PCP solution was determined by infrared spectroscopic analysis

at 60°C. An absorbance ratio of a characteristic absorption of the imide group at 720 cm<sup>-1</sup> to that of the phenol group at 1007 cm<sup>-1</sup> was applied for the determination of the percent imidization. In the case of polyamic acid, the absorption intensity at 720 cm<sup>-1</sup> was monitored with the film of about 4 μm in thickness placed in a heated cell. Tensile properties were obtained according to the ASTM method D882-67 with a Shimadzu Autograph IM-100.

## RESULTS AND DISCUSSION

### One-pot Polymerization

Various solvents were at first examined to determine the suitable solvent for one-pot polymerization of BPDA/ODA. The results are shown in Table I. In *m*-cresol, one-pot polymerization is possible. In a polymer concentration of 9.1%, the polymerization proceeded smoothly, giving a transparent polymer solution. However, it became opaque when the solution was cooled. In a polymer concentration of 12.6%, the polymer was precipitated during the polymerization. In phenol, the polymerization of a polymer concentration of 12.6% was possible. However, in the polymer concentration of 16%, the polymer adhered to a glass surface and the polymerization did not proceed smoothly. Further, when the phenol solution was cooled, it solidified and was difficult to handle. In *o,m,p*-chlorophenol, *p*-bromophenol, and 3-chloro-6-hydroxytoluene, the poly-

merization proceeded smoothly, giving a transparent polymer solution, respectively. In *o,p*-dichlorobenzene, BPDA remained unreacted, and in benzyl alcohol, the polymer precipitated.

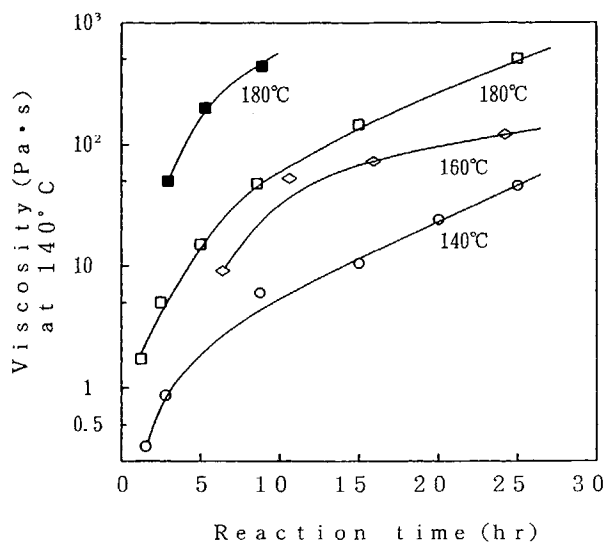
From these observations, it was found that the solvent suitable for one-pot polymerization had an OH group attached to the benzene ring. Further, halogenated phenols were preferable in terms of solubility. Among them, PCP was satisfactory due to a relatively lower melting point.

One-pot polymerization in PCP was conducted at 140–180°C and the change of the viscosity of the solution was determined (Fig. 2). The viscosity of the solution increases with the reaction time and the increase of temperature. The increase of the viscosity means that of the degree of polymerization and, therefore, the polymerization in PCP turns out to proceed smoothly.

In the case of the 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 anhydride rarely reverts to the original acid anhydride at a low temperature less than 30°C. As a result of the hydrolysis, the molar ratio of acid dianhydride/diamine deviates from an equimolar ratio, and the equilibrium is rapidly reached. However, in the case of one-pot polymerization, the polymerization would proceed so long as stirring was possible, since water in the reaction solution is removed as PCP

**Table I** One-pot Polymerization in a Variety of Solvents

Solvent	Reaction Temperature (°C)	Reaction Time (min)	Polymer Concentration	Appearance of Reaction Product
<i>m</i> -Cresol	180	60	9.1	When cooled, gelled, became opaque
	160	40	12.6	Polymer-precipitated opaque
Phenol	170	30	9.1	Opaque
	170	60	12.6	Opaque
<i>o</i> -Chlorophenol	170	40	9.1	Transparent
<i>m</i> -Chlorophenol	170	40	9.1	Transparent
<i>p</i> -Chlorophenol	170	60	9.1	Transparent
<i>p</i> -Chlorophenol	180	60	12.6	Transparent
<i>p</i> -Chlorophenol	180	60	16.0	Transparent
<i>p</i> -Bromophenol	175	60	9.1	Transparent
3-Chloro-6-hydroxytoluene	175	60	9.1	Transparent
<i>o</i> -Dichlorobenzene	170	30	9.1	<i>s</i> -BPDA remained
<i>p</i> -Dichlorobenzene	170	50	9.1	<i>s</i> -BPDA remained
Benzyl alcohol	170		9.1	Polymer precipitated at 145°C



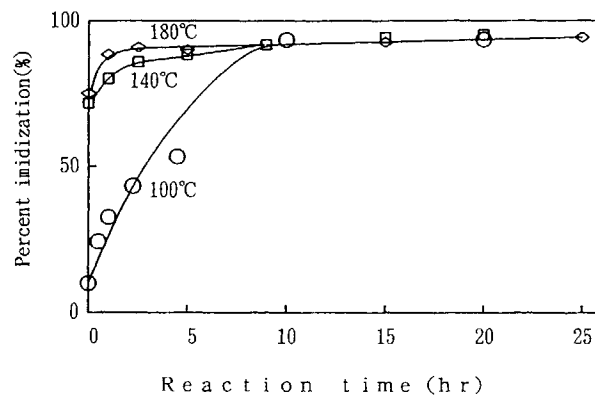
**Figure 2** Change of viscosity of polyimide solution. Polymer concentration: 12 wt %. (O,  $\diamond$ ,  $\square$ )  $N_2$  atmosphere; ( $\blacksquare$ )  $N_2$  flow.

would proceed so long as stirring was possible, since water in the reaction solution is removed as PCP azeotrope and the *o*-dicarboxylic acid present in the PCP solution reverts to acid anhydride at a higher temperature than  $100^\circ\text{C}$ . 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 from the system by a flow of nitrogen gas. This result suggests that equilibrium exists between water and the imide group.

### Percent Imidization

Next, we examined the percent imidization in one-pot polymerization. The change of percent imidization is shown in Figure 3. We examined polymerization at 50 and  $70^\circ\text{C}$ , but the absorption peak due to the imide group is not observed at  $720\text{ cm}^{-1}$  after 25 h. The imidization reaction takes place at  $100^\circ\text{C}$ . The percent imidization increases with the reaction time, and percent imidization reaches almost 100% in 10 h. However, the polymerization proceeds even for 25 h.

As shown in Figure 4, in the case of polyamic acid, the percent imidization is dependent on the temperature. When polyamic acid film is kept at  $125^\circ\text{C}$ , its percent imidization levels off at about 10% and the imidization reaction does not proceed further. In this case, imidization proceeds in a solid state, so it is necessary to heat to a higher temperature than the  $T_g$  of the polyamic acid film for fur-

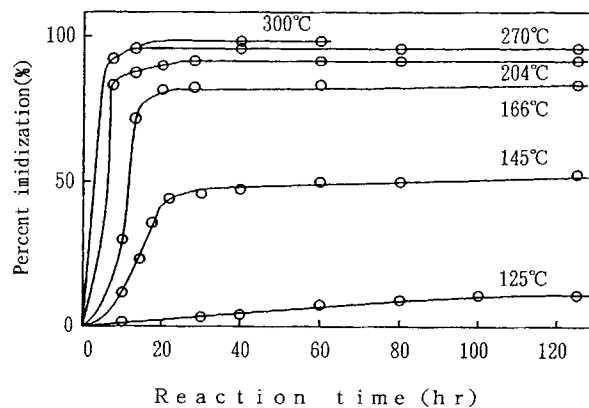


**Figure 3** Change of percent imidization by one-pot polymerization.

ther imidization.<sup>13-15</sup> On the other hand, one-pot polymerization is carried out in a solution state, so there is not the intermolecular restriction such as in the polyamic acid film. In one-pot polymerization, the percent imidization reached is not dependent on the temperature, although the rate of imidization is dependent on the temperature. The imidization of one-pot polymerization proceeds rapidly at  $180^\circ\text{C}$  and the percent imidization reaches to 75% in the process of increasing temperature.

### Relationship of $\eta_{inh}$ Between Precursor Solution and Film and Between $\eta_{inh}$ and Film Properties

We studied the relationship between the inherent viscosities and the mechanical properties of films with regard to one-pot polymerization. The films shown in Table II were prepared from the solution in the early stage of one-pot polymerization. Even the film prepared from the solution with a polymerization time of 15 min has good properties. Al-



**Figure 4** Change of percent imidization by two-step polymerization.

**Table II** Properties of Polyimide Film vs. Polymerization Conditions

Polymerization Time (min)	$\eta_{inh}$ of Polyimide Solution (dL/g) (50°C, PCP)	Properties of Polyimide Film		
		$\eta_{inh}$ (dL/g) (50°C, PCP)	Tensile Strength at Break (MPa)	Elongation at Break (%)
15	0.27	2.96	188	62
30	0.55	3.71	207	80
60	0.66	3.97	227	96
90	0.83	3.23	215	89

\* Polymerization condition: temperature, 180°C (N<sub>2</sub> flow). Polymer concentration: 10%.

<sup>b</sup> Film preparation: cure, 300°C × 1 h.

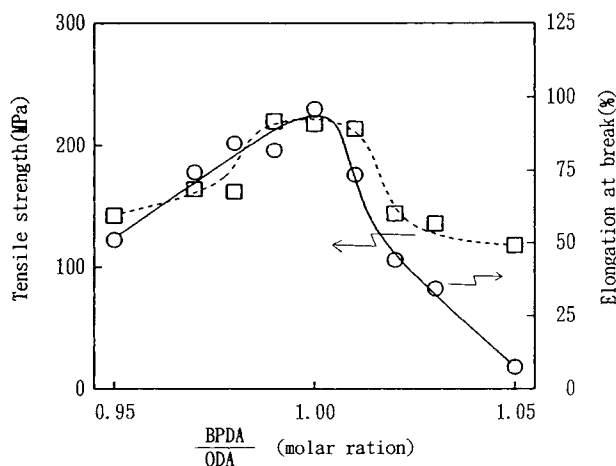
though the  $\eta_{inh}$  of the solution is 0.27, the  $\eta_{inh}$  of the film cured at 300°C increases to 2.96. The inherent viscosities of the other films shown in Table II similarly increase by curing. This result shows that the polymerization can proceed in the solid state. The  $\eta_{inh}$ 's of films are independent of the initial value of the solution, and these films have similar  $\eta_{inh}$ 's and mechanical properties. So long as BPDA and ODA are equimolar, the film having good mechanical properties could be prepared from the solution even at a short polymerization time such as 15 min.

The relationship between the molar ratio of BPDA/ODA and the mechanical properties of the films from one-pot polymerization is shown in Figure 5, and those from polyamic acid are shown in Figure 6. Both results have a similar tendency. The larger the deviation from the equimolar ratio of BPDA/ODA is, the lower the mechanical properties become.

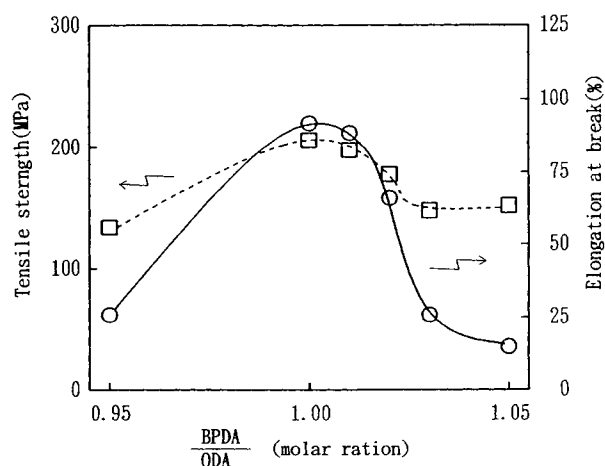
The relationship between  $\eta_{inh}$  and the mechanical properties of films from one-pot polymerization is shown in Figure 7. The film having the  $\eta_{inh}$  below

1.00 is meaningless, because the mechanical properties are not satisfiable in most practical applications, judging from the results by other investigators.<sup>16,17</sup>

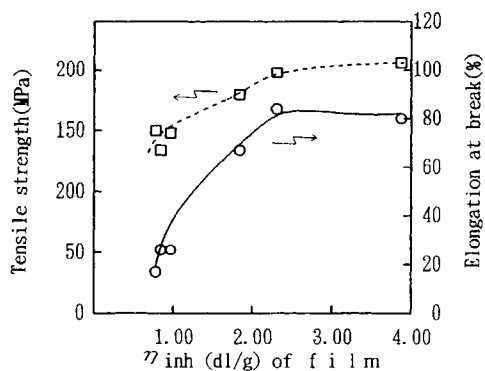
The  $\eta_{inh}$ 's of the solution and the film for one-pot polymerization in a stream of nitrogen are shown in Table III. The polymerization time is 15 h except for molar ratio of 1.00. Under these conditions, the  $\eta_{inh}$  of the solution is thought to approximately reach a maximum. Although the  $\eta_{inh}$  of the solution is 1.27 in the case of the molar ratio of 1.00, the  $\eta_{inh}$  of the film prepared from the solution by maintaining it at 300°C for 30 min increases to 3.91 as shown in Table III. Further, it increases to 4.34 on maintaining it at 350°C for 5 min. In this way, the degree of polymerization proceeds in the solid phase by heating. The  $\eta_{inh}$  of the polymer solution of the molar ratio of 0.99 is 2.31, and the  $\eta_{inh}$  of the film prepared from the solution by maintaining it at 300°C for 30 min is 2.51 and that at 350°C for 5 min is 2.47. In the case of the molar ratio of 0.99, the degree of



**Figure 5** Properties of polyimide film as a function of molar ratio of BPDA/ODA by one-pot polymerization.



**Figure 6** Properties of polyimide film as a function of molar ratio of BPDA/ODA by two-step polymerization.



**Figure 7** Mechanical properties vs.  $\eta_{inh}$  of polyimide film by one-pot polymerization.

polymerization levels off at a certain value. It is not necessarily said that both polymers in the solution and the film have the same molecular weight, even though they have almost the same  $\eta_{inh}$ . The  $\eta_{inh}$  of the film is slightly higher than that of the solution. It is thought that the cure at 300°C allows polymerization to proceed more completely and the  $\eta_{inh}$  of the film is higher than that of the solution.

The relationship of the  $\eta_{inh}$  between the polyamic acids and the films is shown in Table IV. In the measurement of the  $\eta_{inh}$ , both of the solvent and polymer of the polyamic acid solution are different from those of the film. The former is NMP and polyamic acid, while the latter is PCP and polyimide. However, the change of the  $\eta_{inh}$  with film preparation is similar to that of one-pot polymerization, and both films from the polyamic acid solution and the polyimide solution have similar  $\eta_{inh}$ . For example, both  $\eta_{inh}$ 's for the molar ratio of 1.00 are 3.85 and

3.91, respectively. With regard to the molar ratio of 1.01, both  $\eta_{inh}$ 's are 2.29 and 2.40, respectively. These results show that polyimide film having a similar molecular weight could be obtained from both precursors.

Figure 8 shows the plot of the  $\eta_{inh}$  of polyimide film in PCP vs. the  $\eta_{inh}$  of the precursor in NMP or PCP. This plot exhibits a linear relationship. This result shows that both polyamic acid and polyimide in the solution may have the same relationship between  $\eta_{inh}$ 's and molecular weights, and polyimide films having the same molecular weight are formed from both the precursors having the same  $\eta_{inh}$ . In our study, polyimide viscosities of films are about 120% of the precursor viscosities. Wallach<sup>18</sup> reported the same linear relationship with regard to the plot of polyimide inherent viscosities in concentrated sulfuric acid vs. precursor inherent viscosities in dimethylacetamide, but polyimide viscosities of films are about 80% of the polyamic acid viscosities in his study. The film was prepared by chemical imidization, followed by heating 1 h at 200°C. If the film was kept at 300°C, its inherent viscosity would be higher than that of its precursor. Young and Chang<sup>5</sup> studied soluble aromatic polyimides endcapped with a 2% molar excess of aniline and reported that the  $\eta_{inh}$  of the polyamic acid was the same as that of the polyimide cured at 325°C. In this polyamic acid and polyimide, the increase of the degree of polymerization leveled off at a certain value. The results of these studies also suggest that there is a linear relationship between the molecular weight of the precursor (polyamic acid and polyimide) and that of polyimide film, and a molecular weight of polyimide

**Table III** Properties of Polyimide Film in a Variety of BPDA/ODA Molar Ratios When One-pot Polymerization was Applied

BPDA/ODA Molar Ratio	$\eta_{inh}$ of Precursor Solution (dL/g) (50°C, PCP)	Properties of Polyimide Film		
		$\eta_{inh}$ (dL/g) (50°C, PCP)	Tensile Strength at Break (MPa)	Elongation at Break (%)
0.95			143	51
0.97			166	74
0.98	1.44	1.69	164	83
0.99	2.31	2.51	223	81
1.00	1.27	3.91	220	91
1.01	2.19	2.40	211	73
1.02	1.54	1.78	145	46
1.03			136	35
1.05			118	8

\* Film preparation: cure, 300°C × 1 h.

**Table IV** Properties of Polyimide Film in a Variety of BPDA/ODA Molar Ratios When Two-step Polymerization Was Applied

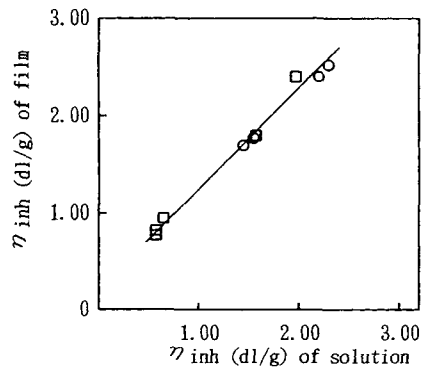
BPDA/ODA Molar Ratio	$\eta_{inh}$ of Precursor Solution (dL/g) (30°C, NMP)	Property of Polyimide Film		
		$\eta_{inh}$ (dL/g) (50°C, PCP)	Tensile Strength at Break (MPa)	Elongation at Break (%)
0.95	0.58	0.82	134	26
1.00	3.04	3.85	205	80
1.01	1.97	2.29	198	84
1.02	1.57	1.83	179	67
1.03	0.65	0.96	148	26
1.05	0.56	0.78	151	17

\* Film preparation: cure, 300°C × 1 h.

films is almost the same as that of the precursor polyamic acid.

#### Change of Mechanical Properties and $\eta_{inh}$ in the Course of Cure

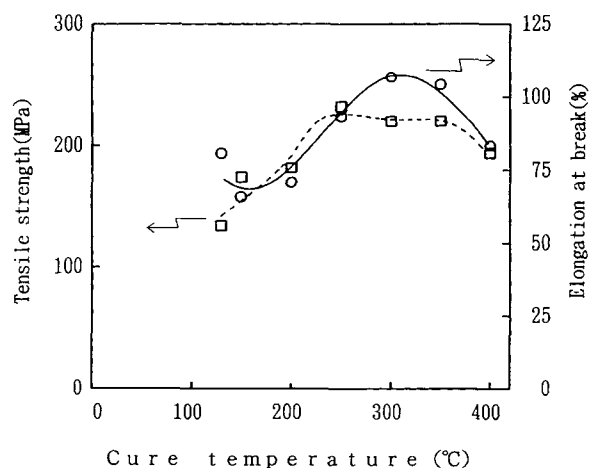
The relationships between mechanical properties and the conditions of cure with regard to one-pot polymerization are shown in Figure 9. The elongation increases from the cure temperature of 250°C and the mechanical properties reached a maximum at that between 300 and 350°C. The relationship between the cure conditions and the  $\eta_{inh}$ 's of the film is shown in Table V and Figure 10. The  $\eta_{inh}$  of the film prepared at 120°C from the solution is 3.08. This film is heated from 150 to 400°C. The  $\eta_{inh}$  of the film hardly changes on heating to 200°C. The  $\eta_{inh}$  increases from 250°C, and the increase of  $\eta_{inh}$  at 300°C is noticed. The  $\eta_{inh}$ 's are independent to heating time up to 250°C and there is little difference in the  $\eta_{inh}$  between 10 and 30 min. But at 300°C



**Figure 8**  $\eta_{inh}$  of polyimide film vs.  $\eta_{inh}$  of polymer solution: (□) polyamic acid solution; (○) polyimide solution.

there is a difference: The  $T_g$  of polyimide from BPDA/ODA is 285°C and the increase of molecular weight in the solid phase probably does not take place up to 285°C but it takes place above 285°C.<sup>5</sup> The films heated above 350°C are not dissolved in PCP at 150°C. This is thought so because of the increasing molecular weight or crosslinking or other side reactions.<sup>9</sup>

Figure 11 shows the relationships between mechanical properties and the conditions of cure in the case of the film from polyamic acid. An initial decrease in elongation at break is noted with cure temperature, reaching a minimum in 200°C and the mechanical properties increase above the cure temperature of 250°C, and the values reached a maximum between 300 and 400°C. It is known that this initial decrease is because of the decrease in molecular weight.<sup>6,7,10</sup>

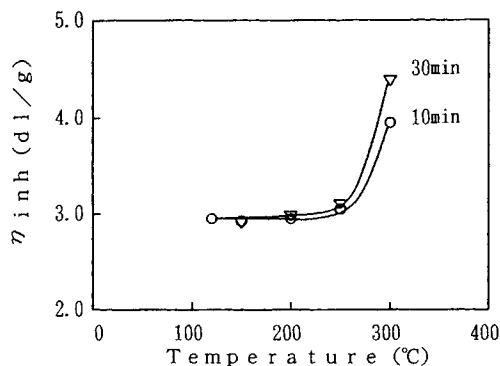


**Figure 9** Mechanical properties as a function of cure temperature for thermally staged films by one-pot polymerization.

**Table V** Properties of Polyimide Film Dependent on Curing Condition

Curing Conditions		Properties of Polyimide Film				
Temperature (°C)	Time (min)	PCP Content in Film (%)	$\eta_{inh}$ (dL/g) (50°C, PCP)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Modulus of Elasticity (GPa)
—	—	32.4	3.08	135	75	2.60
150	10	12.6	2.92	175	77	3.40
150	30	10.8	2.90	178	63	
200	10	7.2	2.94	183	71	3.50
200	30	6.3	2.98	217	60	
250	10	4.2	3.06	232	93	3.90
250	30	3.8	3.10	222	82	
300	10	0	3.96	220	107	3.70
300	30	0	4.37	204	100	
350	5	0	Insoluble	218	94	
350	10	0	Insoluble	220	104	3.70
400	5	0	Insoluble	227	116	
400	10	0	Insoluble	194	83	3.70

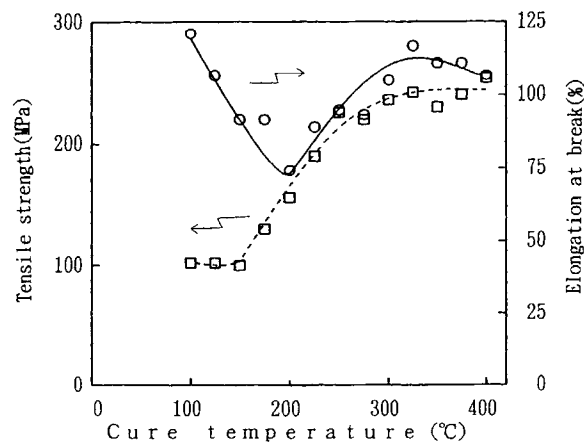
As described above, we compared one-pot and two-step polymerization. Both processes of polymerization in the solution are surely different, and both processes of film preparation are different. However, both films prepared from both processes have almost the same mechanical properties and molecular weight. The polyimide from BPDA/ODA has less crystallinity and less phase orientation; then, the structures of the polyimide from two processes are thought not to be different from each other. This same structure would bring about this result. If a polyimide had higher crystallinity and phase orientation, the properties of the polyimides from the two processes would be different from each other.



**Figure 10**  $\eta_{inh}$  as a function of cure temperature for thermally staged films by one-pot polymerization. Curing time: (O) 10 min; ( $\nabla$ ) 30 min.

## CONCLUSIONS

One-pot and two-step polymerization of polyimide was carried out from BPDA and ODA by the use of PCP as the solvent. The imidization reaction in one-pot polymerization proceeds completely in this system at even a low temperature such as 100°C. In the course of the film preparation from the solution, the embrittlement occurs when the film is prepared from the polyamic acid solution, while it did not occur in the case of that from the solution of the one-pot method. A molecular weight of polyimide film is almost the same as that of precursor poly-



**Figure 11** Mechanical properties as a function of cure temperature for thermally staged films by two-step polymerization.



imide in the solution. In the same way, that of polyimide film is almost the same as that of precursor polyamic acid. The mechanical properties of the polyimide film prepared by the one-pot method are similar to those by the two-step method.

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