

Thermal imidization behavior of aromatic poly(amic dialkyl ester) precursors derived from biphenyltetracarboxylic dianhydride

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Summary

Poly(amic dialkyl ester) precursors of high performance poly(4,4'-oxydiphenylene biphenyltetracarboximide) (BPDA-ODA) and poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) were synthesized and their thermal imidizations were investigated isothermally and nonisothermally by thermogravimetry. All precursors showed a two-step imidization behavior, fast imidization at early stage and slow imidization at intermediate and later stage. Kinetic parameters were estimated from the conversion versus time plots with the first-order rate equation. The imidization behaviors observed were interpreted with considering the T_g variation, the natures of alkyl leaving group and precursor backbone, and the flexibility of polymer chain. In addition, the onset temperature of imidization and T_g of precursors were estimated from the imidization kinetic data.

Introduction

High temperature polyimides, particularly aromatic polyimides are extensively used in the microelectronic device industry as interdielectric and passivation layers owing to their excellent chemical and physical properties.¹ Most aromatic polyimides are not processable due to the insolubility and high glass transition temperature (T_g) or high melting temperature (T_m) so that they are always processed in their soluble precursors and followed by either chemical or thermal imidization. Poly(amic acid),¹ as a processable polyimide precursor, is widely used in the fabrication of devices because of its easy synthesis. However, it is in the equilibration with the constituent anhydride and amine monomer^{2,3} and, therefore is very sensitive to the temperature variation and moisture contact, causing a number of problems on the quality control and fabrication process. Another processable polyimide precursor is poly(amic dialkyl ester).⁴⁻¹⁰ It has a high hydrolytic stability due to the absence of monomer-precursor polymer equilibration, providing the processability more adequate to the device fabrication. For this reason, poly(amic dialkyl ester) has recently gained great attention from the industry.

The imidization, particularly thermal imidization of poly(amic acid)s has been well characterized.^{1,3,11-13} The imidization reaction is known to start at ca. 130°C and be completed at > 220°C, however, depending upon the reaction time. In addition to the imide-ring closure, side-reactions were proposed to include anhydride formation,¹⁴

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isoimide formation,¹⁵ and interchain imide-linkage formation.^{16,17} For these side-reactions, the thermal reaction of poly(amic acid)s is frequently called by curing reaction rather than imidization. However, during curing reaction at high temperature, the precursor is fully converted to the linear polyimide although it takes through several reaction pathways, because the imide form is most stable at the high temperature. In comparison with poly(amic acid)s, the imidization of poly(amic dialkyl ester)s has been rarely studied.^{5,7-10,13,18} In the present study, three different poly(amic dialkyl ester)s were synthesized and their thermal imidization kinetics were in detail investigated isothermally as well as nonisothermally by means of gravimetry. The results were understood with considering alkyl leaving group, backbone structure, and glass transition temperature.

Experimental

Poly(*p*-phenylene biphenyltetracarboxamic diethyl ester) (BPDA-PDA ES) was synthesized by the low temperature polymerization of sublimed *p*-phenylene diamine (PDA) and biphenyltetracarboxylic (BPDA) diethyl ester diacyl chloride in *N*-methyl-2-pyrrolidinone (NMP) as shown in Fig. 1.^{4,6-9} The polymerization was carried out at 0 - 5°C by adding a solution of BPDA diethyl ester diacyl chloride in dry ethyl acetate to a solution of PDA in dry NMP with vigorous stirring, and followed by continuous stirring for additional 20 hrs. The precursor polymer solution was precipitated in deionized water, filtered, and washed by methanol to remove the HCl byproducts. Then, the product was dried for 2 days at 50°C in a vacuum of 1×10^{-3} torr. Here, BPDA diethyl ester diacyl chloride, which was used for the polymerization, was prepared via reaction of BPDA diethyl ester dicarboxylic acid with an excess of oxalyl chloride in dry ethyl acetate at 60°C for 1 day, and followed by removal of solvent and excess oxalyl chloride under vacuum. BPDA diethyl ester dicarboxylic acid was prepared by the reaction of biphenyltetracarboxylic dianhydride (BPDA) with ethanol: BPDA sublimed was added to dry ethanol, refluxed for 5 - 8 hrs, and followed by distillation of excess ethanol under a reduced pressure. Poly(*p*-phenylene biphenyltetracarboxamic dimethyl ester) (BPDA-PDA MS) and poly(4,4'-oxydiphenylene biphenyltetracarboxamic diethyl ester) (BPDA-ODA ES) were synthesized from the respective diamine and BPDA dialkyl ester diacyl chloride in the same manner as the BPDA-PDA ES was prepared. Molecular weight measured by light scattering technique was ca. 20K \overline{M}_w for BPDA-ODA ES and ca. 30K \overline{M}_w for BPDA-PDA ES and BPDA-PDA MS.

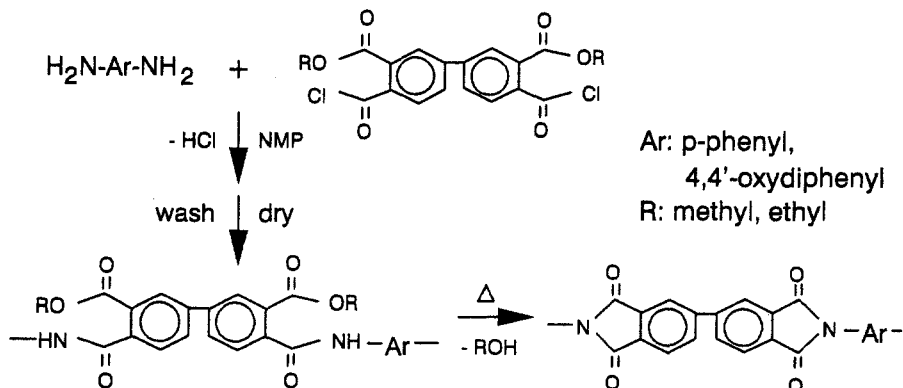


Fig.1. Synthesis scheme of poly(amic dialkyl ester)s and their polyimides.

The isothermal and nonisothermal imidization kinetics of the precursor polymers were measured over 50 - 400°C under a nitrogen gas flow using a thermogravimeter (Perkin-Elmer, TGA-7) controlled by a computer. The amount of a precursor sample was 4 - 6 mg for each measurement run. For isothermal runs, a precursor sample in the TGA sample pan was quickly heated with a ramping rate of 125 K/min to a chosen temperature and soaked isothermally at the temperature. On the other hand, nonisothermal runs were performed with various heating rates of 2.0 - 20.0 K/min.

The imidization of precursors can be expressed by the first-order reaction.^{3,12,13} The weight loss with time, which was measured during isothermal imidization, was fitted by the following first-order rate equation:^{3,12,13}

$$\ln [a / (a - x)] = k t \quad (1)$$

where a equals to 100 %, the maximum weight loss in percent for the precursor sample completely imidized at 400°C, x is the % weight loss at time t , and k is the rate constant. Here, the rate constant can be expressed by Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (2)$$

where A is the pre-exponential term, E_a is the activation energy, R is the gas constant, and T is the imidization temperature. The kinetic parameters (*i.e.*, k , E_a , and A) were estimated from TGA data with the equations above.

Results and Discussion

The nonisothermal imidization of poly(amic dialkyl ester)s were performed with various heating rates over 50 - 400°C. Typical weight loss plots with temperature are illustrated in Fig.2. On heating runs, the precursor polymers were stable up to ca.190°C and, at >190°C showed significant weight losses due to the evaporation of alcohol byproducts generated by the imide-ring formation. The imidization reaction started around 190 - 210°C and was completed at 380 - 400°C. However, the weight loss versus temperature curve was shifted into higher temperature region as heating rate increased. Onset

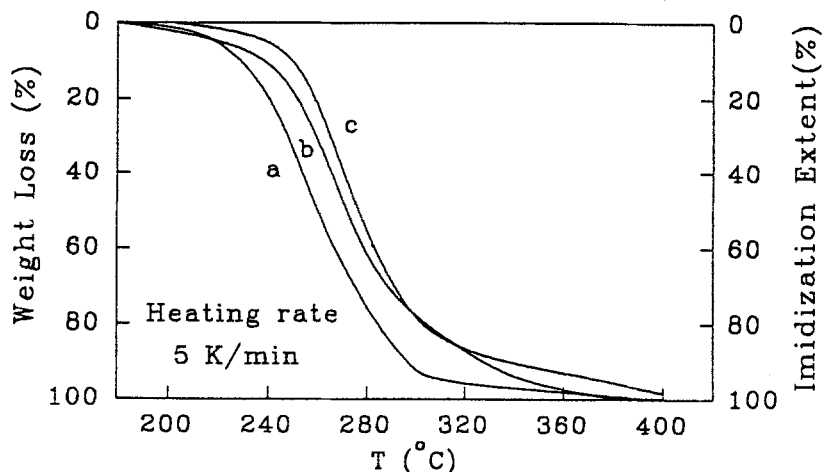


Fig.2. Weight losses of poly(amic dialkyl ester)s measured during nonisothermal imidization: a, BPDA-ODA ES; b, BPDA-PDA ES; c, BPDA-PDA MS.

temperatures of imidization were estimated from plots of weight loss versus temperature, and plotted in Fig.3 as a function of heating rate. The onset temperature (T_{onset}) was an increasing function of heating rate, regardless of the precursor polymers. The equilibrium onset temperature of imidization (T_{onset}°) was estimated by the extrapolation of T_{onset} to zero heating rate. T_{onset}° was 224°C for BPDA-ODA ES, 226°C for BPDA-PDA ES, and 232°C for BPDA-PDA MS. In comparison, BPDA-ODA ES imidizes relatively at lower temperature, whereas BPDA-PDA MS imidizes at higher temperature. BPDA-PDA ES shows intermediate imidization behavior between those of BPDA-ODA ES and BPDA-PDA MS.

The imidization behavior of the poly(amic dialkyl ester)s are quite different from that of the corresponding poly(amic acid)s. On heating runs, the imidization of the poly(amic

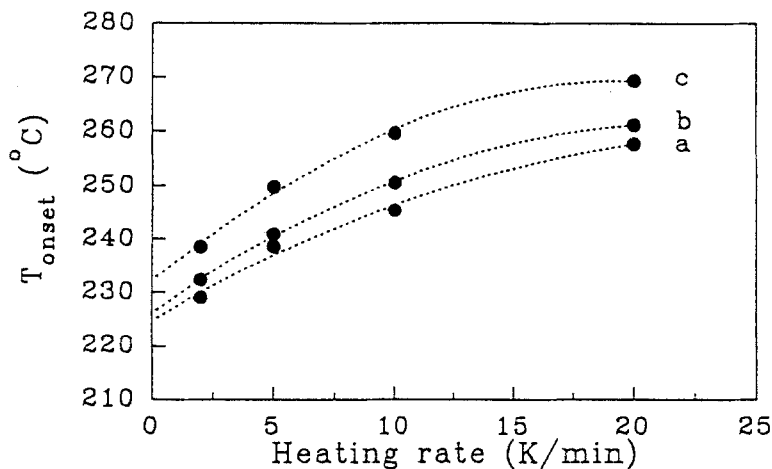


Fig.3. Variations of onset temperatures for the imidization of precursors as a function of heating rate: a, BPDA-ODA ES; b, BPDA-PDA ES; c, BPDA-PDA MS.

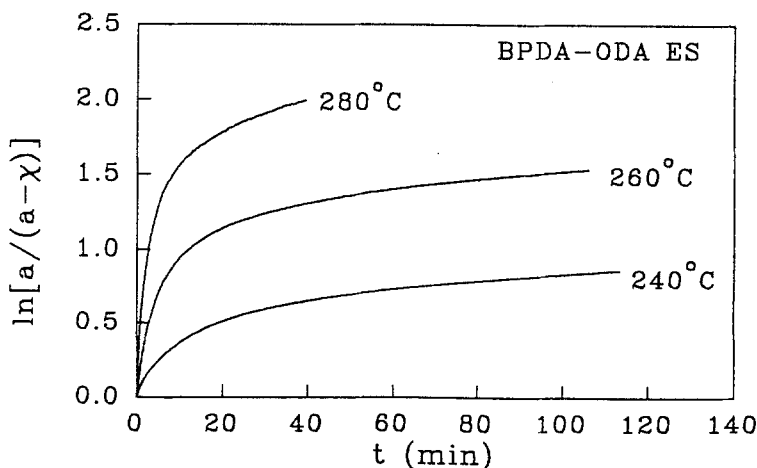


Fig.4. Logarithmic plots of weight losses in BPDA-ODA ES precursor being imidized isothermally as a function of time: $a = 100\%$ and x is the normalized weight loss in percent.

acid)s has been reported to start around 120°C,¹³ indicating that the T_{onset}° of imidization is $\leq 120^{\circ}\text{C}$. That is, the poly(amic dialkyl ester)s studied here imidize at relatively higher temperature than the corresponding poly(amic acid)s. A similar imidization behavior was observed for various dialkyl esters of poly(oxydiphenylene pyromellitic acid).^{5,7-10,13}

In addition, the imidization of poly(amic dialkyl ester)s was isothermally performed at three different temperatures, 240°C, 260°C and 280°C. During isothermal imidization at a chosen temperature, the weight losses in precursors were measured as a function of time. The weight losses were normalized to the maximum weight loss measured for its complete imidization at 400°C, and were logarithmically plotted with time in Figs.4-6. During the imidizations, all the precursors showed a typical trend that the weight loss (i.e., degree of

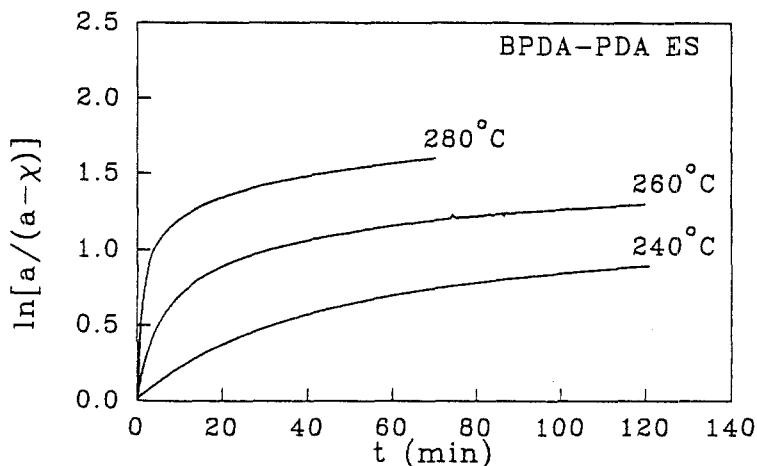


Fig.5. Logarithmic plots of weight losses in BPDA-PDA ES precursor being imidized isothermally as a function of time: $a = 100\%$ and x is the normalized weight loss in percent.

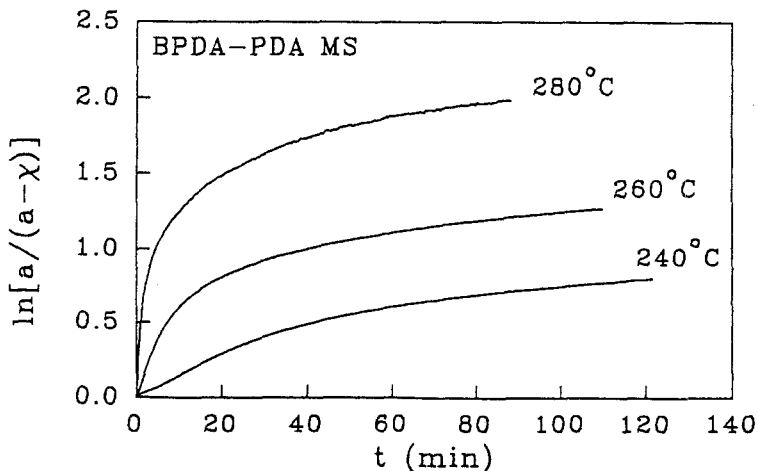


Fig.6. Logarithmic plots of weight losses in BPDA-PDA MS precursor being imidized isothermally as a function of time: $a = 100\%$ and x is the normalized weight loss in percent.

imidization) rapidly increased with time at early stage and then turned to slow increase at intermediate and later stages. That is, all the precursors showed a two-step imidization behavior, fast and slow reaction. The weight loss data were analyzed with Eqs.(1) and (2) in order to estimate kinetic parameters. The results are summarized together with the conversions accomplished on the fast and slow reactions in Table I. Overall, the rate constant increased rapidly with temperature on the fast reaction step but increased slowly with temperature on the slow reaction step.

On the fast imidization step, the rate constant k is in the increasing order BPDA-ODA ES > BPDA-PDA ES > BPDA-PDA MS. The activation energy was 27.6 kcal/mol for BPDA-ODA ES, 36.5 kcal/mol for BPDA-PDA ES and 44.4 kcal/mol for BPDA-PDA MS. These are much higher than the activation energies for the corresponding poly(amic acid)s: 16.0 kcal/mol for BPDA-ODA poly(amic acid) and 14.0 kcal/mol for BPDA-PDA poly(amic acid).¹³ In comparison with the poly(amic acid)s, the poly(amic dialkyl ester)s require relatively higher activation energy and higher temperature to imidize. This result can be explained by the imidization mechanism which was proposed by Kruez *et al.*³ The formation of an *ortho*-carboxylate anion intermediate, which can afford an easy route to imide-ring closure, favorably occurs for poly(amic acid)s.³ In contrast, the formation of an *ortho*-carboxylate anion intermediate may be very difficult for poly(amic dialkyl ester)s.

Unlike the fast imidization step, the slow imidization step showed rate constant k not

Table I. Imidization kinetic parameters of aromatic poly(amic dialkyl ester) precursors

Precursor polymer	Temperature (°C)	k ($\times 10^{-3} \text{ min}^{-1}$)	Conversion (%)	$\ln A$ (min^{-1})	E_a (kcal/mol)
BPDA-ODA ES					
(1st step)	240	47.7	21.9 (in 5 min)	24.1	27.6
	260	144	51.5 (in 5 min)		
	280	335	64.6 (in 3 min)		
(2nd step)	240	2.38	52.1 ~ (in 60 min ~)	12.2	18.7
	260	3.33	73.0 ~ (in 40 min ~)		
	280	8.91	85.7 ~ (in 30 min ~)		
BPDA-PDA ES					
(1st step)	240	23.5	11.4 (in 5 min)	32.2	36.5
	260	95.5	38.6 (in 5 min)		
	280	310	60.2 (in 3 min)		
(2nd step)	240	3.17	50.3 ~ (in 60 min ~)	~ 8.6	~15.5
	260	2.48	67.2 ~ (in 50 min ~)		
	280	4.25	76.0 ~ (in 30 min ~)		
BPDA-PDA MS					
(1st step)	240	12.7	6.6 (in 5 min)	39.3	44.4
	260	81.3	31.4 (in 5 min)		
	280	293	59.4 (in 3 min)		
(2nd step)	240	3.06	50.3 ~ (in 60 min ~)	3.0	8.9
	260	3.77	67.2 ~ (in 50 min ~)		
	280	5.71	76.0 ~ (in 30 min ~)		

to vary sensitively with temperature as well as the type of precursor. The activation energy was 18.7 kcal/mol for BPDA-ODA ES, 15.5 kcal/mol for BPDA-PDA ES and 8.9 kcal/mol for BPDA-PDA MS.

The differences in the kinetics of precursors may be correlated to the chemical natures of alkyl leaving group and amide linkage as well as the flexibility of polymer chain. Ethyl group has a relatively higher electron donor power than does methyl group. Thus, the electron density on the oxygen atom of alkyl carboxylate linkage is higher in ethyl ester precursors than methyl ester precursor. The electron density of amide nitrogen is higher in BPDA-ODA precursor than BPDA-PDA precursors, because of the relatively high electron donor ability of the ether group of ODA unit compared with PDA unit. On the chemical repeat unit, the amide nitrogen with a higher electron density can nucleophilically attack the carbon of carboxylate linkage to cyclize an imide-ring and the carboxylate oxygen with a high electron density also can nucleophilically capture the amide hydrogen to be liberated as free alcohol. Therefore, the relatively fast imidization rate in BPDA-ODA ES might result from the high electron densities of the amide nitrogen and the carboxylate oxygen provided by the ether group of ODA unit and the ethyl leaving group. On the other hand, both alkyl leaving group and backbone structure affect the flexibility of precursor chain. Ethyl group is slightly more bulky than methyl. The ODA unit has a bend conformation due to the ether group. Both ethyl group and ether bend conformation give a better flexibility on the precursor backbone, lowering T_g . Therefore, the relatively fast imidization in BPDA-ODA ES might also be contributed from the higher chain flexibility and lower T_g .

The two-step imidization behavior observed might be due to the variation of T_g in the precursor polymers being imidized. The transition of fast reaction to slow reaction might be due to vitrification. The T_g of precursors being imidized is below imidization temperatures, maybe leading fast imidization. In contrast, the T_g is very close to or above imidization temperatures, leading that the precursor being imidized is frozen so that the imidization rate be slow down very much. Thus, the slow imidization being occurred in the frozen state could not be treated by the first-order reaction.

For imidized films, T_g was measured by dynamic mechanical thermal analysis to be

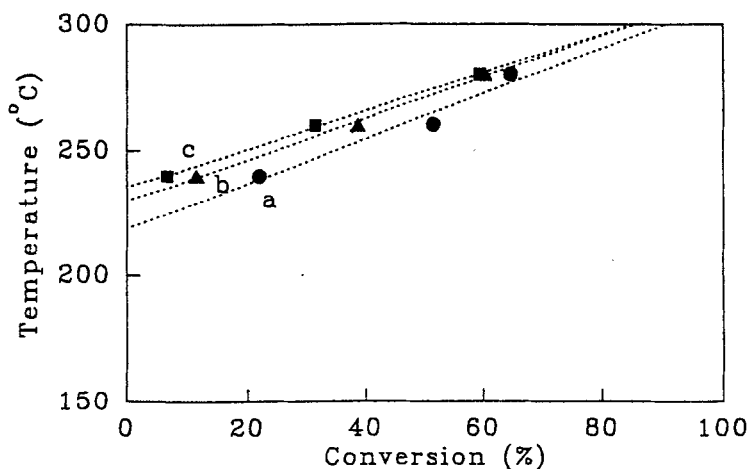


Fig.7. Plots of imidization conversions of precursors accomplished in the fast reaction step as a function of imidization temperature: a, BPDA-ODA ES; b, BPDA-PDA ES; c, BPDA-PDA MS.

352°C for BPDA-PDA and 302°C for BPDA-ODA, regardless of alkyl groups.¹⁹ However, T_g 's of the precursors have not been measured yet because of their conversion to the polyimides during measurements. In order to estimate T_g 's of the precursors, we have adopted the relationship of two-step imidization behavior and T_g discussed earlier. Additionally, we have assumed that the T_g of a precursor polymer linearly increases with the degree of imidization and finally reaches to the T_g of the resulting polyimide. For a precursor, the conversion accomplished in the fast imidization step was plotted with isothermal imidization temperature as shown in Fig.7 and extrapolated to zero conversion, giving T_g of the precursor. The T_g estimated was 219°C for BPDA-ODA ES, 230°C for BPDA-PDA ES, and 235°C for BPDA-PDA MS.

Conclusions

Poly(amic dialkyl ester)s of high performance BPDA-ODA and BPDA-PDA polyimides were synthesized. The thermal imidizations were investigated isothermally and nonisothermally by thermogravimetry. The rate constant and activation energy were estimated from the imidization kinetic data with the first-order rate equation. In addition, the onset temperature of imidization and T_g of precursors were determined. All precursors showed a two-step imidization behavior, fast imidization at early stage and slow imidization at intermediate and later stage. In comparison, the imidization rate was in the increasing order BPDA-ODA ES > BPDA-PDA ES > BPDA-PDA MS. The imidization behaviors were interpreted with considering the T_g variation, the natures of alkyl leaving group and precursor backbone, and the flexibility of polymer chains.

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