

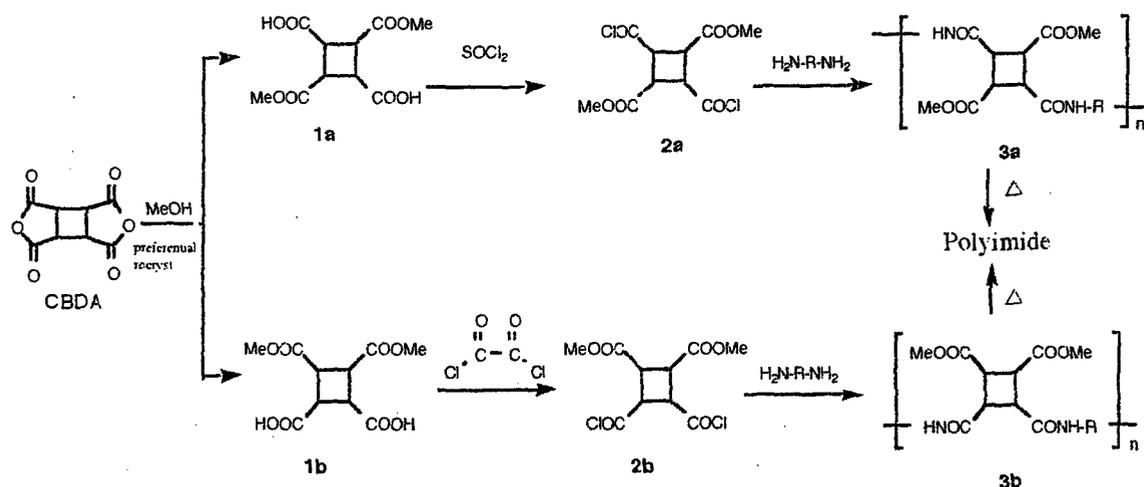
Preparation and Properties of High Molecular Weight Polyamic Ester and Polyimide having a Cyclobutane Moiety in the Main Chain

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Introduction

Cyclobutane derivative is known to be cleaved rather readily into olefin-derivatives thermally or by photoirradiation. Therefore, the polymer with cyclobutane ring in the main chain is expected to be rather susceptible to a high temperature and to prolonged photoirradiation. However, we have reported in previous papers that several cyclobutane polyamides and polyimides were remarkably heat stable.^{1,2} The result had pointed out an important possibility that these cyclobutane polyimides could be promising moiety of thermally stable "positive type" photoresist, liquid crystal or engineering plastic. After our reports of the polyimide derived from cyclobutanetetracarboxylic dianhydride (CBDA) with diamines, several papers and patents have appeared in above application fields.³⁻⁹ However, no paper has described of preparative method in detail to obtain high molecular weight of cyclobutane polyimide so far, especially for the polyimide having aliphatic diamine component.

In present study, we like to report on further work of the polyimide derived from CBDA with diamines, focusing on the preparation and properties of linear high molecular weight of polyimide containing aliphatic diamine component through two types of polyamic ester as shown below.



Scheme 1

Results and Discussion

Bis(methoxycarbonyl)cyclobutanedicarboxylic acid (**1**) was conveniently prepared from CBDA by refluxing in methanol solution. **1** consists of two regio isomers; one is 2,4-bis(methoxycarbonyl)-1,3-cyclobutanedicarboxylic acid (**1a**), with a

centrosymmetry, the other is 3,4-bis(methoxycarbonyl)-1,2-cyclobutanedicarboxylic acid (**1b**), with a plane symmetry. Separation of the mixture into each of pure **1a** and **1b** was successfully performed by fractional crystallization. The structure of first fraction is **1a**, which was determined by X-ray crystal analysis. The second fraction was necessarily assigned to **1b**. Pure **1a** was readily converted to 2,4-bis(methoxycarbonyl)-1,3-cyclobutanedicarbonyl dichloride (**2a**) by the reaction with thionyl chloride. On the other hand, 3,4-bis(methoxycarbonyl)-1,2-cyclobutanedicarbonyl dichloride (**2b**) was not obtained by the same procedure from **1b** although described in previous paper¹⁰. Then, **2b** was readily obtained from **1b** by the reaction with an excess amount of oxalyl chloride in ethyl acetate. Consequently, the mixture of isomers of **1** was successfully converted to the mixture of corresponding dichloride **2a** and **2b** in a high yield by the reaction with oxalyl chloride.

Interfacial polycondensation of dichloride with diamine afforded corresponding high molecular weight polyamic ester (**3**). Typically, benzene solution containing the dichloride was vigorously stirred with aqueous solution containing hexamethylenediamine or 4,4'-oxydianiline and acid acceptor (KOH) at 0–20 °C.

Table 1. Polymerization conditions of **2a** and **2b** with diamine

Feed (mmol)		Reaction Condition			Yield	[η]
Dichloride	Diamine	Solvent	Time (h)	Temp. (°C)	%	
Interfacial Polycondensation ^{c)}						
2a						
5.09	5.09 ^{a)}	Benzene / H ₂ O	0.50	10-20	77	0.62 ^{e)}
5.03	5.03 ^{a)}	Benzene / H ₂ O	0.50	0-15	81	0.61 ^{e)}
3.92	3.91 ^{b)}	Benzene / H ₂ O+THF	0.50	10-20	90	0.44 ^{f)}
4.85	4.85 ^{b)}	Benzene / H ₂ O+THF	0.75	5-20	97	0.52 ^{f)}
Solution Polymerization ^{d)}						
5.12	5.12 ^{a)}	DMAc	16.00	0	66	0.36 ^{e)}
Interfacial Polycondensation ^{c)}						
2b						
5.37	5.37 ^{a)}	Benzene / H ₂ O	0.50	10-20	70	0.45 ^{e)}
4.95	4.95 ^{a)}	Benzene / H ₂ O	0.50	0-15	78	0.48 ^{e)}

a) Hexamethylenediamine.

b) 4,4'-Oxydianiline.

c) Acid acceptor: KOH.

d) Acid acceptor: Et₃N.

e) in *o*-Chlorophenol at 30 °C.

f) in DMF at 30 °C.

Polymerization conditions of **2a** and **2b** with diamine are summarized in Table 1. It is obvious that compared with solution polycondensation, the interfacial polycondensation from **2a** with diamine gave higher molecular weight of polyamic ester (**3a**) having film-forming property ($[\eta] > 0.6$). And the interfacial polycondensation from **2b** afforded corresponding high-molecular-weight polyamic ester (**3b**) with film-forming property ($[\eta] \approx 0.5$).

The thermal properties of the polymers were studied by DSC/TG. The samples were measured up to 500 °C under nitrogen at a heating rate of 10 °C/min. DSC/TG curves

of polyamic esters **3a** and **3b** are shown in Figure 1 (A) and Figure 2 (A), respectively. Each polymers showed two-step weight losses corresponding to the imidization process and thermal degradation. In the range of 200-280 °C, the polymers **3a** and **3b** showed a weight loss of 16.3 and 15.7 % corresponding to the loss of methanol into the imide with endothermic broad peak at around 246 and 234 °C. From the comparison of the observed and calculated (18.8 %) weight losses, it is concluded that the methanol is eliminated to give the polyimide in a high conversion only by only heating. The following step of rigorous weight loss on the TG curves starts at temperature above 430 °C, with rigorous exo- and endo- therms, which correspond to the thermal deterioration of the polyimide. DSC/TG curves of the polyimide derived from, are illustrated in Figure 1 (B) and Figure 2 (B). Of these polyimides the endothermic peak around 246 and 234 °C completely disappeared and the thermal behavior **3a** and **3b** at higher than 350 °C is nearly identical with those of **3a** and **3b**, respectively (Figure 1 and Figure 2). The difference of imidization temperatures of **3a** and **3b** can be explained by higher T_g of **3a** caused by higher symmetry of chemical structure in **3a** than in **3b**.

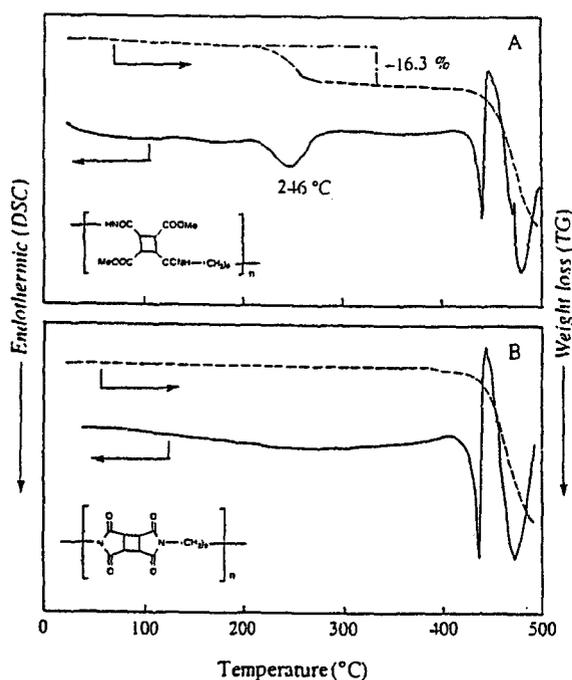


Figure 1 DSC/TG curves of (A): polyamic ester (**3a**) and (B): polyimide.

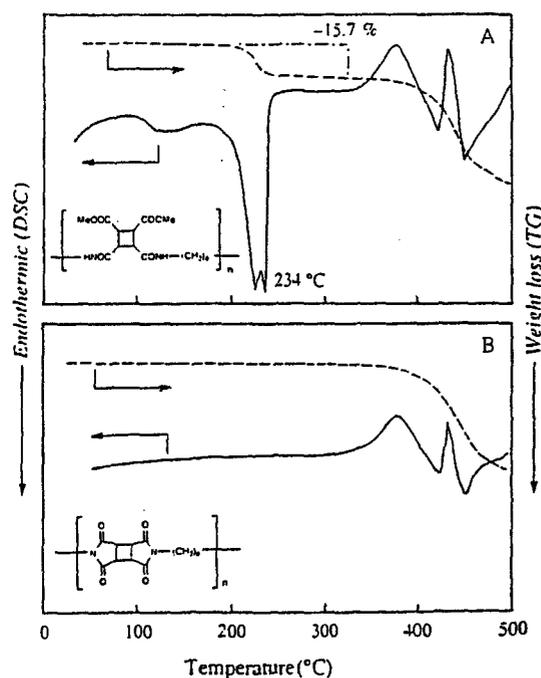
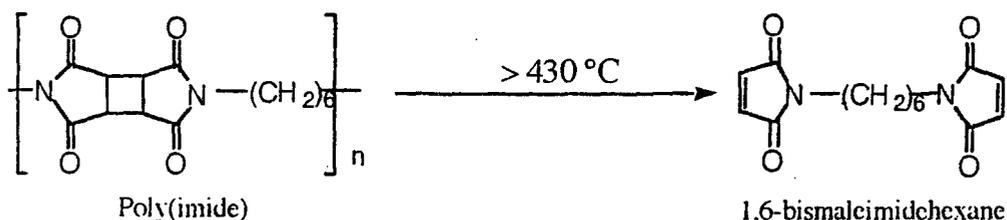


Figure 2 DSC/TG curves of (A): polyamic ester (**3b**) and (B): polyimide.

The IR spectrum of the polyamic ester shows characteristic amide absorptions at approximately 1734, 1646 and 1551 cm^{-1} due to ester carbonyl and carbonyls of amide I and II. After the heat treatment, characteristic imide absorptions newly appeared, these are the imides I and II carbonyl stretch at about 1768 and 1698 cm^{-1} , whereas the peaks of the ester carbonyl and carbonyls of amide I and II at 1734, 1646 and 1551 cm^{-1} , completely disappeared. The IR spectrum before and after the heat treatment of polyamic acid also indicates that it was nearly quantitatively converted to the polyimide during the heat treatment. Thus, from the DSC/TG and IR spectral results it is

concluded that imide ring formation occurred at around 200-280 °C and that the polyimide starts thermal degradation at 430 °C.

In the resinous substance after the degradation, a considerable amount of 1,6-bismaleimidehexane (Crude yield 60 %) was identified by ¹H NMR and crystal melting point (141 °C) in comparison with the authentic sample, as shown in Scheme 2. The observed high yield of 1,6-bismaleimidehexane strongly suggests that thermal cleavage of cyclobutane ring in **5** proceeds exclusively prior to other thermal degradation reactions. That is, thermal degradation temperature of the cyclobutane polyimide is primarily determined by the cycloreversion temperature of the cyclobutane ring.



Scheme 2

In order to compare hydrolytic stability of resulting aliphatic polycyclobutane imide with that of aromatic polypyromellitic imide, hydrolytic stability of two model compounds pyromellitic diphenylimide and cyclobutanetetracarboxylic diphenylimide was compared in aqueous sodium hydroxide at 50 °C. From the results, the cyclobutane polyimide is expected to be less stable under the hydrolytic condition, compared to polypyromellitic imide.

References

- 1 H. Takahashi, M. Sakuragi and M. Hasegawa, *J. Polymer, Sci.*, **1972**, *10*, 16.
- 2 F. Nakanishi, M. Hasegawa and H. Takahashi, *Polymer*, **1973**, *14*, 440.
- 3 H. Fukuro and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **1988**, Vol. 163, pp. 157-162.
- 4 J. A. Moore and A. N. Dasheff, *Polym. Mater. Sci. Eng.* **1988**, *59*, 999.
- 5 H. Ohkita, A. Tsuchida, M. Yamamoto, J. A. Moore and D. R. Gamble, *Macromol. Chem. Phys.* **1996**, *197*, 2493.
- 6 K. H. Chae, J. S. Park and J. S. Chung, *Bull. Korean Chem. Soc.*, **1993**, *14*, 655.
- 7 K. H. Chae, '96 Annual Meeting of the Korean Society of Photoscience, Abstr, pp. 41 (June, 1996, Kyongju, Korea).
- 8 U. S. Patent 81-286695 810724 Standard Oil Co.
- 9 U.S. Patent 81-286696 810724 Standard Oil Co.
- 10 P. Richter and E. Fahr, *Angew. Chem. Internat. Edit.*, **1969**, *8*, 208.
- 11 M. Hasegawa, H. Miura, N. Haga, A. Hayakawa and K. Saito, *High Perform. Polym.*, **1998**, *10*, 11.