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# Preparation and properties of new polyamides from 1,6-diaminodiamantane and aromatic diacid chlorides

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## Summary

New polyamides were prepared by the solution polycondensation and interfacial polycondensation starting from 1,6-diaminodiamantane and aromatic diacid chlorides. The polyamides had inherent viscosities of 0.15-0.45 dL/g. The temperatures at 5% weight loss for the polyamides were between 435-475℃ in nitrogen. The glass transition temperatures of the polyamides determined by DSC ranged from 245℃ to 300℃. The crystallinity of the resultant polyamides was influenced by the method of polycondensation and various monomers.

## Introduction

Because aromatic polyamide has good heat stability, good chemical resistance properties, and good mechanical properties, it is therefore applied in many industries. But some aromatic polyamides contain intermolecular hydrogen bonds and some polyamides crystallize easily. Due to these factors some polyamides can not be dissolved in most organic solvents, and are difficult to process. Therefore much research focuses on the modification of hard processing, attempting to maintain considerable heat stability and to modify its dissolving properties. These studies (1-11) include: (1) to introduce rather soft segments into the main chain; (2) to break its symmetry and regularity, making crystallization impossible; (3) to introduce the bulky side groups to exempt from the crystallization; (4) to form 3-dimensional structure without sharing the same surface; (5) to destroy the hydrogen-bonding by N-substitution with certain groups such as methyl, etc. The most popular method for synthesis of aramids is the one starting from diamine-diacid chloride monomer pairs by low-temperature solution polycondensation. Interfacial polycondensation has also been used to prepare polyamides. Method of interfacial polycondensation can be applied to prepare composite membranes as well. It provides high selectivity without severely reducing membrane flux (12-15). In previous studies, we discussed the interfacial polycondensation to prepare polyimide and composite membranes (16-19). In a recent study, we reported that the polyimides derived from 1,6-diaminodiamantane and aromatic tetracarboxylic dianhydrides had high glass transition temperature and good thermal stability (20). Based on these results, the polycyclic aliphatic

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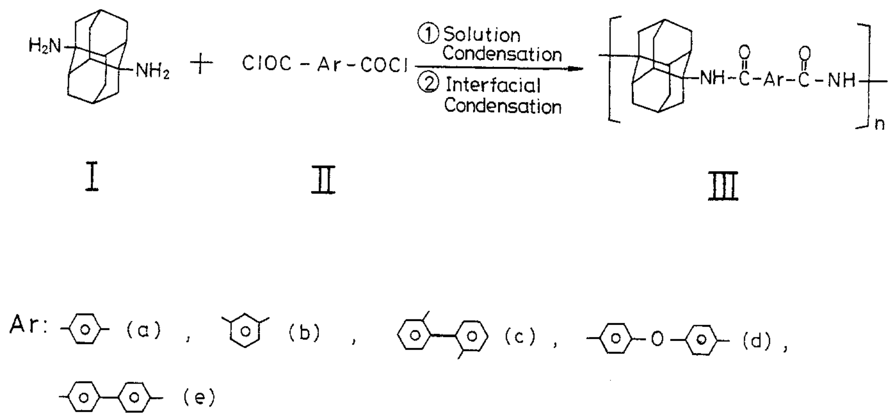

Scheme I

diamine, 1,6-diaminodiamantane, is a potential monomer for the preparation of composite membrane. In this article we describe the synthesis of novel polyamides containing diamantyl unit by the polymerization of 1,6-diaminodiamantane with aromatic diacid chlorides through conventional solution polycondensation and interfacial polycondensation techniques (Scheme I ). The characteristics of polyamides such as solubility and thermal properties are also discussed.

## Experimental

### *Materials*

1,6-Diaminodiamantane( I ) was synthesized according to our previous research (21). 2,2´-Bibenzoyl chloride (IIc) was prepared by reacting 2,2´-bibenzoic acid with thionyl chloride, and was purified by two repeated distillations before use. mp: 92-93℃ (lit. (22) mp 92-93℃); IR(KBr)cm$^{-1}$: 1775(C=O); Anal.Calcd for $C_{14}H_8O_2Cl_2$: C,60.22%; H,2.87%. Found: C,60.96%; H,2.80%. Terephthaloyl chloride (IIa), isophthaloyl chloride (IIb), 4,4´-oxydibenzoyl chloride (IId), and 4,4´-biphenyldicarbonyl chloride (IIe) were purified by vacuum distillation. N-Methyl-2-pyrrolidone (NMP) was vacuum distilled over calcium hydride before use. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150℃ for 6 h and at 180℃ for 10 h.

### *Polymer Synthesis*

The typical examples of the polycondensation are given below.

*Polyamide IIId by Solution Polycondensation of I and IId*

A 1.09 g (5.0 mmol) portion of I and 15 ml of NMP containing 5 (w/v)% LiCl were placed into a three-necked flask. The mixture was cooled in an ice-acetone bath under nitrogen. To this partially frozen liquid, 1.475 g (5.0 mmol) of solid 4,4´-oxydibenzoyl chloride (Ⅱd) was added all at once. The polymerization proceeded as these solids dissolved. After stirring at 15℃ for 6 h, the reaction solution was poured into methanol. The precipitated polymer was collected, washed thoroughly with methanol, and dried at 100℃ in a vacuum oven. The yield was 1.87 g (85%). The inherent viscosity of the polymer in NMP containing 5 (w/v)% LiCl was 0.45 dL/g, measured at a concentration of 0.5 g/dL at 30℃. The IR spectrum exhibited absorptions at 3357 cm$^{-1}$ (NH) and 1644 cm$^{-1}$ (C=O), showing the characteristics of amide group. ANAL.Calcd for $(C_{28}H_{28}N_2O_3)_n$: C,76.32%; H,6.36%; N,6.36%. Found: C,75.75%; H,6.17%; N,5.97%.

### *Polyamide Ⅲd by Unstirred Interfacial Polycondensation of I and Ⅱd*

We prepared 0.01 M of Ⅱd in dichloromethane, and 0.01 M of I in distilled water containing 0.002 M of $Na_2CO_3$. We used a 50 ml graduated cylinder to take 40 ml of the dichloromethane solution and placed it on the bottom of a beaker with a diameter of 9 cm. Next, we used a 50 ml syringe to take 40 ml of the I solution and injected it onto the surface of the dichloromethane solution along the lining wall of the beaker. Then we carried out the interfacial polycondensation at 15℃ for 30 minutes. The film formed was rinsed with 0.001 N of aqueous NaOH, and then rinsed with methanol until no more dissolved substances appeared. Then the film was vacuum-dried at 100℃. The inherent viscosity of the polymer in NMP containing 5 (w/v)% LiCl was 0.36 dL/g, measured at a concentration of 0.5 g/dL at 30℃. The IR spectrum showed absorptions at 3318 cm$^{-1}$ (NH) and 1646 cm$^{-1}$ (C=O), indicative of amide group.

### *Characterization*

A Bio-Rad FTS-40 FTIR spectrophotometer was used to record spectra of the KBr pellets. In a typical experiment, an average of 20 scans per sample was made. A Perkin-Elmer 240C elemental analyzer was used for elemental analysis. Qualitative solubility was determined using 0.01 g of polymer in 2 ml of solvent. A Du Pont 9900 differential scanning calorimeter (DSC) and a Du Pont 9900 thermogravimetic analyzer (TG) were employed to study the transition data and thermal decomposition temperature. The wide-angle X-ray diffraction (WAXD) measurements were performed on a Philips PW 1730-10 X-ray diffractometer using CuK$\alpha$ radiation.

## Results and Discussion

Table 1 Synthesis of Polyamides by low-temperature solution polycondensation

| Polymer | yield(%) | $\eta_{inh}$(dL/g)[a] | Remark[d] |
|---|---|---|---|
| Ⅲa | 80 | 0.42(0.19[c])[b] | S |
| Ⅲb | 78 | 0.34(0.15[c]) | S |
| Ⅲc | 65 | 0.22( - ) | S |
| Ⅲd | 85 | 0.45(0.36) | S |
| Ⅲe | 75 | 0.28(0.25[c]) | S |

[a] Measured at 30℃ at a concentration of 0.5 (g/dL) in NMP containing 5 (w/v)% LiCl. [b] The values in parentheses were those of the polyamides obtained by the interfacial polycondensation. [c] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30℃. [d] Apperance of the polymerization mixture: S, turbid suspension solution.

### *Polymer Synthesis*

New diamantane-containing polyamides were prepared by two different methods, i.e., low temperature solution polycondensation and interfacial polycondensation. The results of the polycondensation are listed in Table 1. The polyamides had inherent viscosities of 0.15-0.45 dL/g. The inherent viscosities of the polyamides prepared by solution polycondensation were not high. This is probably due to the fact that when the alicyclic diamine was used, the solubility of the polyamides in aprotic solvents was lower than that of polyamides with aromatic diamines. All the reactions proceeded in turbid suspension without forming high-molecular-weight polyamides because of their poor solubility.

Also, the polyamides with high inherent viscosities were not obtained by the unstirred interfacial polycondensation, probably due to the dense interfacial films formed during the very early stages of the polycondensation. Due to the hindrance of the films, the polycondensation stopped (17,23). Polyamide IIIc was not obtained by the interfacial polycondensation, probably due to the highly steric hindrance of IIc. Moreover, polyamide IIIc prepared by the solution polycondensation had relatively low inherent viscosity, possibly caused by the highly steric hindrance of IIc. We also attempted to synthesize these polyamides according to the direct polycondensation procedure of Yamazmki et al. (24,25), which gave unsatisfactory results by the polycondensation of I with the aromatic diacids in NMP containing lithium chloride using triphenyl phosphite and pyridine as condensing agents. This was due to the fact that the precipitation occurred during the first course of the polycondensation. The FTIR spectra of the polyamides showed characteristic amide bands at 3318-3358 and 1638-1648 $cm^{-1}$.

### *Characterization of Polymers*

The structural characterization of the "as prepared" powders was made by the X-ray diffraction study. Polymers IIIa - IIId prepared by the solution polycondensation were essentially amorphous in powder form, as shown in Figure 1. Polymer IIIe prepared by the solution polycondensation showed rather sharp diffraction peaks at $2\theta$ of 17° (d=5.2 Å), 25 ° (d=3.6 Å), and 27 ° (d=3.3 Å). Polyamides III prepared by the interfacial polycondensation showed weak diffraction peaks which indicated the presence of a small fraction of crystalline materials, as shown in Figure 2. Enkelmann and Wegner (23) studied the interfacial polycondensation between sebacoyl chloride and hexamethylenediamine. They found that the polymer chains are mainly oriented perpendicularly to the interface in the direction of membrane growth. Referring to Figures 1 and 2, polyamides IIIa and IIId prepared by the interfacial polycondensation had a greater tendency to form crystal than those by the solution polycondensation. However, polyamide IIIe prepared by the solution polycondensation had a greater tendency to form crystal than that by the interfacial polycondensation. Thus, the crystallinity of the resultant polyamides is influenced by the method of polycondensation and various monomers. It is recongnized that additional work is needed to characterize the structures more specifically. The solubility of the polyamides obtained by the two different methods was studied qualitatively, and the results are shown in Table 2. Polyamides IIIb, IIIc, and IIId prepared by the solution polycondensation dissolved in organic solvents such as pyridine, NMP, N,N-dimethylacetamide (DMAc), and N,N-dimethylforamide (DMF). The introduction of rigid p-phenylene groups into the polymer backbone, such as IIIa and IIIe, caused the decrease in polymer solubility. The polyamides, except IIIe, prepared by the solution polycondensation have better solubility than those prepared by the interfacial polycondensation. The polyamides prepared by the interfacial polycondensation dissolved only in concentrated sulfuric acid. The difference in solubility of the polyamides obtained by the two different methods can be ascribed to the

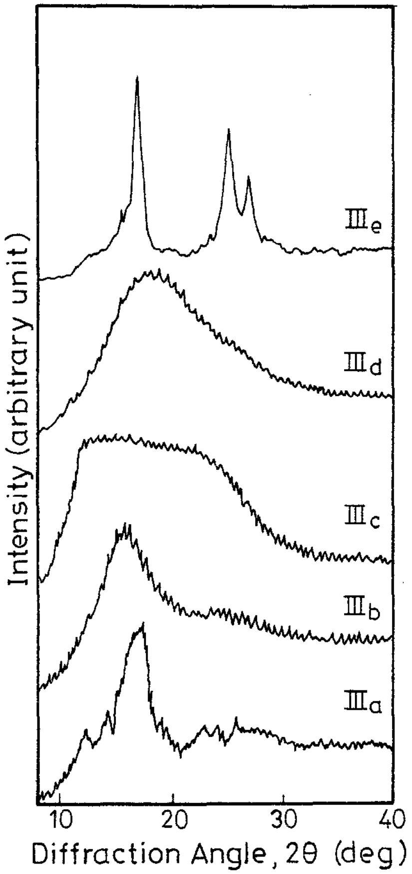

Figure 1: X-ray diffraction diagrams for polyamides prepared by the solution polycondensation.

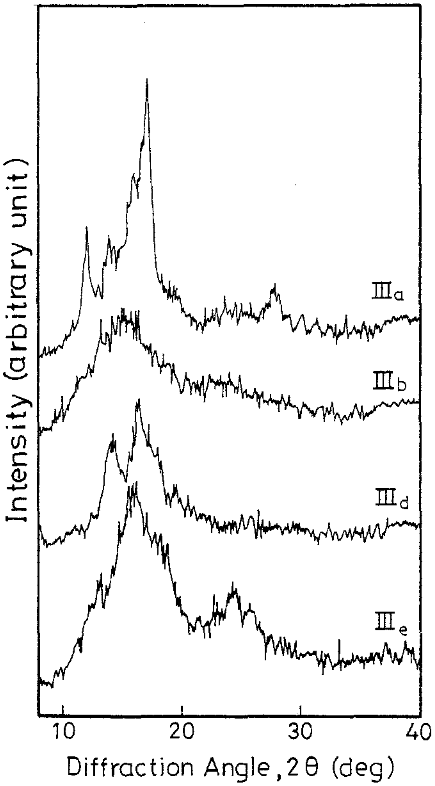

Figure 2: X-ray diffraction diagrams for polyamides prepared by the interfacial polycondensation.

Table 2 Solubility of Polyamides

| | Method of | Solvent[a] | | | | | |
|---|---|---|---|---|---|---|---|
| Polymer | Preparation | conc. $H_2SO_4$ | NMP | DMAc | DMF | Nitrobenene | Pyridine |
| Ⅲa | Interfacial | ++ | - | - | - | - | - |
| | Solution | ++ | +- | +- | +- | - | +- |
| Ⅲb | Interfacial | ++ | - | - | - | - | - |
| | Solution | ++ | ++ | ++ | +- | - | +- |
| Ⅲc | Interfacial | | | | | | |
| | Solution | ++ | ++ | ++ | ++ | +- | +- |
| Ⅲd | Interfacial | ++ | - | - | - | - | - |
| | Solution | ++ | ++ | ++ | ++ | + | ++ |
| Ⅲe | Interfacial | ++ | - | - | - | - | - |
| | Solution | ++ | - | - | - | - | - |

[a] Key: ++, soluble at room temperature; +, soluble on heating at 60 ℃ ; +-, partial soluble; -, insoluble.

Table 3 Thermal Behavior of Polyamides

| Polymer | $T_g$[a] (℃) | Decomposition[b] Temperature(℃) in Air | Decomposition[b] Temperature(℃) in $N_2$ |
|---|---|---|---|
| Ⅲa | 290 | 447 | 465 |
| Ⅲb | 250 | 455 | 475 |
| Ⅲc | 250 | 432 | 450 |
| Ⅲd | 245 | 418 | 435 |
| Ⅲe | 300 | 450 | 470 |

[a] Determined by DSC at a heating rate of 20 ℃/min in introgen. [b] Temperature at which 5% weight loss recorded by TG at a heating of 20 ℃/min.

morphological difference of the polymers.

The thermal behavior of these polyamides was evaluated by means of TG and DSC. The thermal properties of the polymers are summarized in Table 3. The representative TG and DSC curves for these polymers are shown in Figure 3. Their temperatures at 5% weight loss were between 435-475 ℃ in nitrogen, and 418-455 ℃ in air. The glass transition temperatures (Tg) and other thermal properties were evaluated by DSC of the second heating. The Tg of the polyamides ranged from 245 to 300℃. Polymer Ⅲe showed a glass-transition temperature of about 300 ℃ and a melt-transition followed by decomposition with endothermic peaks at approximately 420℃ (shown in Figure 3). No observation of melting endothermic peaks in the DSC charts of the other polyamides was found due to amorphous nature of the polymers.

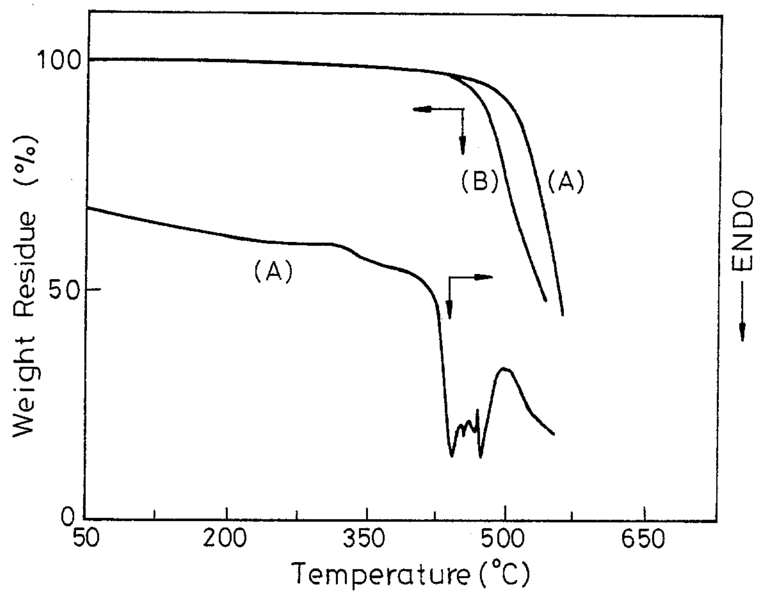

Figure 3: DSC and TG curves for polyamide Ⅲe prepared by the solution polycondensation at a heating rate 20℃/min: (A) in nitrogen, (B) in air.

## Conclusions

The diamantyl-containing polyamides were successfully prepared from 1,6-diaminodiamantane( I ) by solution polycondensation and interfacial polycondensation. The introduction of diamantyl unit into the polyamides backbone resulted in high Tg and good thermal stability. The crystallinity of resultant polyamides was influenced by the method of polycondensation and various monomers. The polyamides, except $\text{III}_e$, prepared by the solution polycondensation had better solubility compared with those prepared by the interfacial polycondensation. The difference in solubility of the polyamides obtained by the two different methods can be ascribed to the morphological difference of the polymers.

## Acknowledgements

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## References

1. Jeong HJ, Kakimoto MA, Imai Y (1991) J. Polym. Sci. Polym. Chem., 29: 767
2. Cimecioglu AL, Weiss RA (1992) J. Polym. Sci. Polym. Chem., 30: 1051
3. Yang CP, Lin JH (1994) J. Polym. Sci. Polym. Chem., 32: 423
4. Yang CP, Chen WT (1993) Makromol. Chem., 194: 1595
5. Jeong HJ, Oishi Y, Kakimoto MA, Imai Y (1990) J. Polym. Sci. Polym. Chem., 28: 3293
6. Korshak VV, Rusanov AL, Tugishi DS, Cherkasova GM (1972) Macromolecules, 5:807
7. Akutsu F, Kataoka T, Naruchi K, Miura M,Nagakubo K (1987) Polymer, 28: 1787
8. Imai Y, Malder NN,Kakimoto M (1985) J .Polym. Sci. Polym. Chem. Ed., 23: 797
9. Jadhav JY, Preston J, Wrigbaum WR (1989) J. Polym. Sci. Polym. Chem. Ed., 23: 1175
10. Delaviz Y, Gungor A, Mcgrath JE,Gibson HW (1993) Polymer, 34: 210
11. Takayanagi M, Katayose T (1981) J. Polym. Sci. Polym. Chem. Ed., 19: 1133
12. Cadotte JE, King RS, Majerle RJ, Petersen RJ (1981) J. Macromol. Sci. Chem., A15(5): 727
13. Stengnard FF (1988) J. Membrane Sci., 36: 257
14. Lonsdal HK (1985) Polym. Eng. Sci., 25: 1074
15. Chai GY,Krantz WB (1994) J. Membrane Sci., 93: 175
16. Chern YT, Chen LW (1991) J. Appl .Polym. Sci., 42: 2535
17. Chern YT, Chen LW (1991) J. Appl. Polym. Sci., 42: 2543
18. Chern YT, Chen LW (1991) J. Macromol. Sci. Chem., A28(1): 105
19. Chern YT, Chen LW (1992) J. Appl. Polym. Sci., 44: 1087
20. Chern YT, submitted.
21. Chern YT, Wang JJ, submitted.
22. Lious GS, Oishi Y, Kakimoto M, Imai Y (1991) J. Polym. Sci .Polym. Chem., 29: 995
23. Enkelmann V, Wegner G (1976) Makromol. Chem., 177: 3177
24. Yamazaki N,Higashi F, Kawabata J (1974) J. Polym. Sci. Polym. Chem. Ed., 12: 2149
25. Yamazaki N,Matsumoto M, Higashi F (1975) J. Polym. Sci. Polym. Chem. Ed., 13: 1373