

N-Methyl Carbazole-3,6-Diamine과 Diacid Chloride 로 부터 방향족 폴리아미드의 합성

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Synthesis of Aromatic Polyamide from N-Methyl Carbazole-3,6-Diamine and Diacid Chloride

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Abstract : N-methylcarbazole - 3, 6-diamine was synthesized from the carbazole by N-methylation, nitration and reduction of nitro groups. Aromatic polyamides containing carbazole unit were synthesized by the solution polycondensation of N-methylcarbazole-3, 6-diamine with terephthaloyl and isophthaloyl chloride at the low temperature. The monomer and polymers synthesized were identified by means of IR, NMR and MS. The optimum polymerization conditions were as follows; Reactants concentration: 0.12 mole/l for N-methylcarbazoleterephthalamide (NMCTA) and 0.32 mole/l for N-methylcarbazole isophthalamide (NMCIA). Polymerization temperature: 25°C, Solvent: NMP+5% LiCl. NMCTA and NMCIA did not melt but decomposed above 420°C. The weight loss of NMCTA was 10% at 475°C and 50% at 670°C. On the whole, NMCTA showed better thermal stability than NMCIA.

1. INTRODUCTION

Since 1958 when Maget¹ first synthesized

wholly aromatic polyamides in which amide groups are directly linked to the aromatic rings, numerous papers on the ordered aro-

matic polyamides have been published out. Due to their superior properties such as good chemical resistance, excellent thermal stability and high physical strengths, they have vast application as a high-performance polymers, e.g. protection clothes, ropes and conveyor belts for hot materials. Nowadays, they become more important in the fields of military and aerospace industries as well. In general, since a high melting point, high chain stiffness and good dimensional stability are essential to achieve an excellent heat resistance², aromatic polyamides, polyheterocyclic amides³, polyimides⁴, polyamideimides and metal chelated polymers have been developed for the purpose of high performance polymers.

It has been recognized that thermal stability of polymer increased markedly by introducing double strand heterocycles. Ueda⁵ has prepared a polyamide containing phenoxathiin unit and they reported that the polymer had a better thermal stability than the polymer with open chain ether linkage. Heterocyclic polyamides including phosphorus⁶ had a good solvent resistance and were hardly degraded even at 400°C.

But, there have been only a little studies on the heterocyclic polyamides. Carbazole is one of heterocyclic compounds which has a three ring system and it was reported⁷ that carbazole based polymers exhibit an excellent thermal and dielectric properties, so the authors studied on the synthesis and thermal properties of N-methylcarbazole-terephthalamide (NMCTA) and N-methylcarbazole-isophthalamide (NMCIA).

There are two methods⁸ to prepare high molecular weight aromatic polyamides (Ar-

amids). One is interfacial polymerization and the other is solution polymerization, but it has been suggested that the latter is more effective method for obtaining high molecular weight polymers. First, we tried to protect the reactivity of N-H group of carbazole, so N-methylation was performed and then it was nitrated and reduced. Polyamide was prepared by low temperature solution polycondensation of N-methylcarbazole-3,6-diamine (CDA) with terephthaloyl chloride (TCl) or isophthaloyl chloride (ICl) in dimethyl acetamide (DMAc) solvent containing 5% dissolved lithium chloride (LiCl). To establish the optimum conditions of giving high molecular weight polyamides, several factors such as reactants concentration, salt concentration, polymerization temperature and solvent system were intensively investigated.

2. EXPERIMENTS

2-1. Materials and Reagents

2-1-1. Materials

Carbazole was recrystallized from ethyl alcohol. TCl and ICl was purified by vacuum distillation under nitrogen atmosphere to avoid hydrolysis of acid chloride. Equimolar quantity of diamine and diacid chloride was weighted in nitrogen atmosphere and stored in desiccator with silica gel.

2-1-2. Reagents

DMAc, hexamethyl phosphoramide (HMPA) N-methyl 2-pyrrolidone (NMP) was dehydrated by calcium hydride. Pyridine was stored over molecular sieve to remove water. Lithium chloride was dried in vacuum oven at 150°C with phosphorus pentoxide. Potassium hydroxide, dimethyl sulfate, tin

power and the other solvents were GR grade and used without further purification.

2-2. Synthesis of N-methylcarbazole-3,6-diamine (CDA)

2-2-1. Synthesis of N-methylcarbazole

5g of crystallized carbazole was dissolved in 100ml of acetone, and then 5g of KOH dissolved in 25ml of water was added. Its color was readily changed to yellow solution forming N-potassium salt of carbazole.

The solution was stirred vigorously for 30 min. and then 10ml of dimethyl sulfate was added. The pale yellow solid of N-methylcarbazole was readily precipitated. The reaction mixtures were stirred for 30min, and poured into 2l of water and then filtered. Obtained N-methylcarbazole was washed 5times with water and vacuum dried at 30°C for 12hrs. After drying N-methylcarbazole was purified by vacuum distillation under the nitrogen atmosphere. 4.5g of very pure N-methylcarbazole solid was obtained (Scheme 1).

Fig. 1 shows the IR spectrum of N-methylcarbazole. Two strong bands at 1,260 and 1,330 cm^{-1} show the N-C aromatic stretching vibration of N-CH₃ and the band at 2,910 cm^{-1} shows the aliphatic C-H stretching vibration.

Elementary analysis data are as follow.

Calculated C; 86.18 H; 6.08 N; 7.73
Found C; 86.18 H; 6.20 N; 7.47

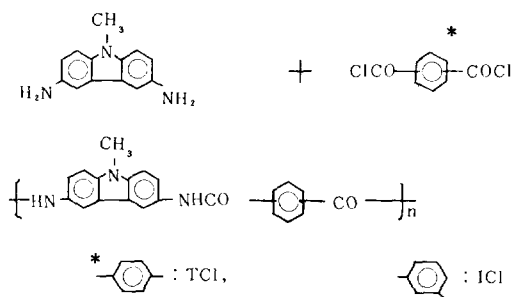
2-2-2. Synthesis of 3,6-dinitro-N-methylcarbazole

In a 300ml of three necked flask, 4.5g of N-methylcarbazole was dissolved in 80ml of 1,2-dichloro ethane and then 20ml of glacial acetic acid was added.

A nitrating agent (20ml of concentrated HNO₃ and 20ml of glacial acetic acid) was added dropwise at room temperature and agitated moderately by mechanical stirrer.

When 20ml of nitrating agent was added,

Scheme 2. Synthesis of polyamide.



Scheme 1. Synthesis of N-methylcarbazole-3,6-diamine.

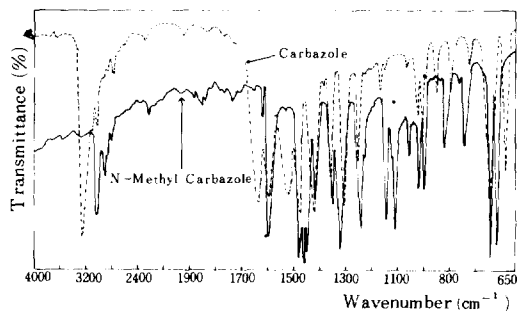
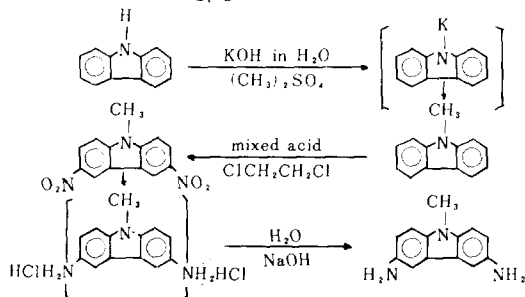


Fig. 1. IR spectra of carbazole and N-methylcarbazole.

dark yellow compound of 3,6-dinitro-N-methylcarbazole was precipitated. As dropping was completed total content was heated to 70°C for 5 hrs. with moderate stirring, and then kept over night at room temperature. After separation of solid compound, it was poured into cold ethanol with vigorous stirring and filtered. Dinitro compound was washed 4 times in ethanol and dried. 5g of 3,6-dinitro-N-methylcarbazole was obtained.

Fig. 2 shows the IR spectrum of dinitro compound. The strong absorption bands at 1510cm^{-1} and $1,330\text{cm}^{-1}$ shows.

asymmetric and symmetric stretching vibration of C-NO₂ group respectively.

Following data are the elementary analysis results.

Calculated	C; 57.56	H; 3.32	N; 15.50
	C; 23.62		
Found	C; 58.04	H; 3.34	N; 15.43
	O; 23.19		

2-2-3. Synthesis of N-methylcarbazole-3,6-diamine

5g of 3,6 dinitro-N-methylcarbazole was mixed with 10g of tin powder in an 150ml

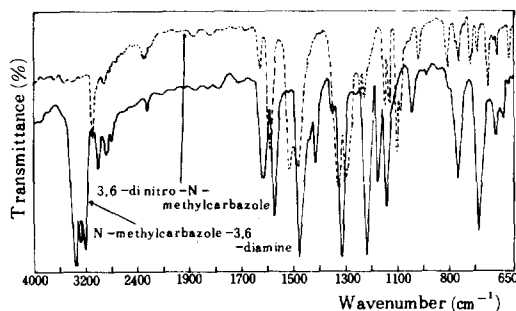


Fig. 2. IR spectra of 3,6-dinitro-N-methylcarbazole and CDA.

of round flask equipped with a condenser and mechanical stirrer and 60ml of conc. HCl was added. The reaction mixture was refluxed at 110°C in oil bath for 3hrs. And then, the reaction mixture was cooled to room temperature. The reaction mixtures were poured into 1,000ml of water. White compound of CDA·HCl salt was dissolved in water, and filtered through the micro filter paper to remove the unreacted nitro compound and tin. Filtrate was collected and then basified with 10% NaOH solution. Bright yellow compound precipitated and then filtered. This compound was washed 5 times with water and dried in nitrogen charged vacuum oven at room temperature. It was purified by vacuum distillation under the nitrogen atmosphere. As shown in Fig. 2, $34,000\text{cm}^{-1}$ and $3,310\text{cm}^{-1}$ indicates aromatic stretching vibration for -NH₂. Elemental analysis data shows that diamine monomer is synthesized correctly.

Calculated	C; 73.93	H; 6.16	N; 19.90
Found	C; 73.82	H; 6.27	H; 19.45

Fig. 3 shows the mass spectrum of CDA. Mass of 196 indicates the departure of methyl group and we can see that methyl group is weakly attached to the nitrogen of carbazole.

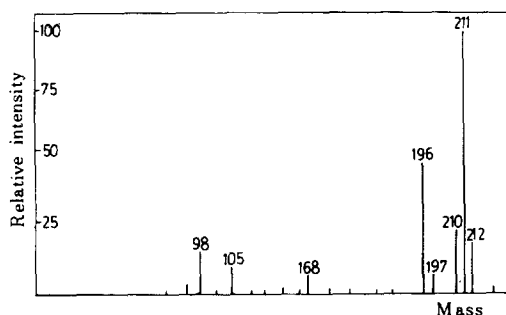


Fig. 3. Mass spectrum of CDA.

2-3. Polymerization

In a 300ml round flask equipped with N_2 gas inlet, 6.5g (0.26mol) of CDA was dissolved in 120ml of DMAc containing 5% LiCl. 15ml of pyridine as acid acceptor was added. Total content was completely dissolved at room temperature. 6.25g (0.26 mol) of TCl was added at once with vigorous stirring. Reaction mixture was immediately gelatinized with temperature rising of about $35^\circ C$. Stirring was continued for 30min and then kept over night. Reaction mixture was poured into water with vigorous stirring. After washing 3 times with water additional washing with acetone was carried out 3-times. Greenish yellow compound of poly N-methylcarbazole terephthalamide (N

MCTA) was obtained in powder form (Scheme 2).

2-4. Instrumental analysis

IR spectra were obtained by IR spectrophotometer (JASCO A-102).

Proton NMR spectra were obtained by JNM-MH-100 NMR spectrometer (100MHz). D_6 -DMSO was used for CDA and D_2SO_4 for polyamide as solvent. Mass spectra (Shimadzu GC-MS LKB 9,000) were used to analyze molecular weight of CDA. Crystalline CDA obtained by sublimation was used.

The elementary analyses were carried out by CHN-corder analyzer (YANACO MT-2 Japan).

DTA and TGA (Shimadzu DT-2 Japan)

Table 1. The Polymerization of Condition of CDA with Acid Chloride

Code	CDA (g)	Acid	Chloride (g)	LiCl (g)	Temp. ($^\circ C$)	Solvent (120ml)	mole/l
1-1	1.5	Tcl	1.44	6	25	DMAc	0.06
1-2	3.0	Tcl	2.88	6	25	DMAc	0.12
1-3	4.8	Tcl	4.62	6	25	DMAc	0.19
1-4	8.6	Tcl	8.30	6	25	DMAc	0.35
2-1	3.0	Icl	2.88	6	25	DMAc	0.12
2-2	4.0	Icl	3.85	6	25	DMAc	0.16
2-3	8.0	Icl	7.69	6	25	DMAc	0.32
2-4	12	Icl	11.54	6	25	DMAc	0.47
3-1	6.5	Tcl	6.25	6	25	HMPA-NMP	0.26
3-2	6.5	Tcl	6.25	6	25	HMPA-DMAc	0.26
3-3	6.5	Tcl	6.25	6	25	HMPA	0.26
3-4	6.5	Tcl	6.25	6	25	NMP	0.26
3-5	6.5	Tcl	6.25	6	25	DMF	0.26
3-6	6.5	Tcl	6.25	6	25	DMSO	0.26
4-1	6.5	Tcl	6.25	1.2	25	DMAc	0.26
4-2	6.5	Tcl	6.25	2.4	25	DMAc	0.26
4-3	6.5	Tcl	6.25	4.2	25	DMAc	0.26
5-1	6.5	Tcl	6.25	6	0	DMAc	0.26
5-2	6.5	Tcl	6.25	6	40	DMAc	0.26
5-3	6.5	Tcl	6.25	6	60	DMAc	0.26

were used to investigate the thermal properties of polyamide. Sample of about 25mg was used and heating rate was 10°C/min.

2-5. Viscosity measurement

Inherent viscosity of polyamides were determined by an Ubbelohde viscometer in 0.5% H₂SO₄ (96%) solution at 30 ± 0.02°C. Samples were completely dissolved at room temperature over night. Table 1 shows the various experimental conditions which affects the inherent viscosity of polymer. The reaction conditions were controlled to study about factors affecting the molecular weight (concentration, salt, temperature, and solvent).

3. RESULTS DISCUSSION

3-1. Synthesis of monomer

The oxidation of CDA is fatal for polymerization. Morgan⁹ has reported that air oxidation of some diamines in the presence of alkali is a problem. So it is desirable that CDA is treated in neutral condition. We tried some methods to purify the CDA. One is recrystallization method. CDA was recrystallized in CHCl₃, C₆H₆ and methanol-water mixture.

Recrystallization in CHCl₃ gave a bright yellow needle type CDA but it was oxidized during drying. Benzene and methanol-water mixed solvent gave better yield than CHCl₃ but it was more easily oxidized during drying in nitrogen charged vacuum oven.

Y. Hayashi et al.¹⁰ reported that 3,6-diamino-9-ethyl carbazole is very sensitive to light and air in polar organic media, so they recrystallized it from ligroin to obtain a pure diamine. But we purified the CDA by vacuum distillation in the nitrogen atmo-

sphere, we could obtain a very pure CDA in powder form, and then it was stored in dark desiccator.

There are many factors for low temperature polycondensation to yield a high molecular weight polymer and the monomer purity is one of the most important factor. Heinz Herlinger¹³ et al. reported that monomer whose purity must be at least 99.95% are needed to obtain a high molecular weight polymer.

3-2. Synthesis of polymer

Carbazole based polyamides were synthesized through low temperature polycondensation. Fig. 4 shows a IR spectrum of N-methylcarbazole terephthalamide (NMCTA). The absorption bands at 3,400 cm⁻¹ and 3,310 cm⁻¹ indicate the N-H stretching vibration for -NHCO- and the peak at 650 cm⁻¹ shows the C=O vibration and the absorption band at 1,520 cm⁻¹ indicates the bending vibration for -NHCO-.

Fig. 5 shows a NMR spectrum of NMCTA. A sharp hydrogen peak of -NHCO- appeared at 11.3 ppm, and a phenylic hydrogen and 2,3,7,8-aromatic hydrogen of carbazole appeared at 8.8 ppm with broad peak. An aliphatic hydrogen peak of CH₃-N showed at 4.2 ppm and 4,5-aromatic hydrogen of

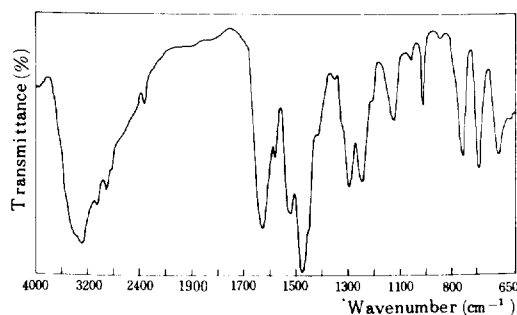


Fig. 4. IR spectrum of NMCTA.

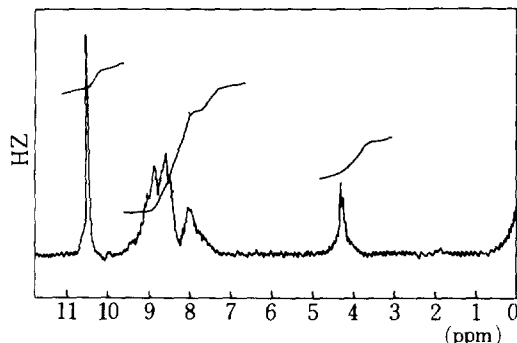


Fig. 5. NMR spectrum of NMCTA.

carbazole at 8.1ppm. The hydrogen ratio of polymer was 2:8:2:3. From IR and NMR spectra, we could confirm that NMCTA was synthesized correctly.

Synthesis of polyamide was a exothermic reaction, so there was a mild exotherm to 35°C during the addition of terephthaloyl chloride. The solution became viscous and greenish yellow in color. High speed stirring were needed to protect the aggregation which cause a precipitation resulting in a low molecular weight polymer. So terephthaloyl chloride was added at one portion, at the same time, vigorous stirring was carried out.

3-3. Factors affecting molecular weight

There are a little study on the heterocycle containing polyamide and we wish to inspect the proper condition yielding high molecular weight polymer. There are some factors¹¹ which affect formation of polyamide. Purity of intermediates and solvent, equivalence of reactants, solubility of intermediates and polymer, mixing, side reaction, temperature concentration were major factors.

First, we have synthesized the polyamide at various mole condition. Fig. 6 shows the results that TCl and ICl have different

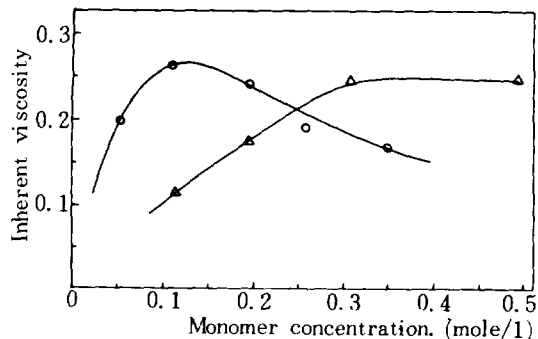
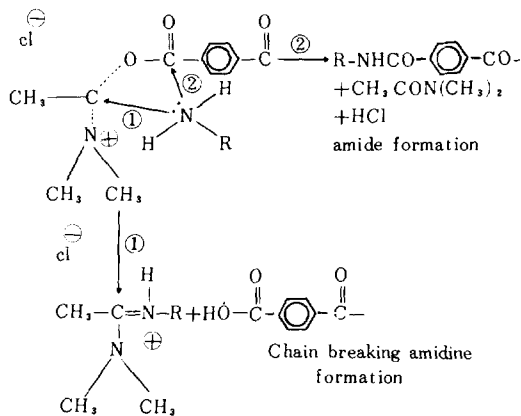


Fig. 6. Inherent viscosity according to monomer concentration.

○ : N-methylcarbazole-terephthalamide
△ : N-methylcarbazole-isophthalamide



patters. NMCTA have a optimum concentration at about 0.125mole/liter and the inherent viscosity was decreased above this concentration but NMCTA doesn't decreased above the 0.35mole/l. Preston¹² has reported that a higher ratio of solvent to diacid chloride produce the low molecular weight polymer owing to occur the chain terminating reaction dominantly in low concentration of monomer. According to the mechanism reported by Herlinger¹³, DMAc is acylated at the carbonyl oxygen, so the complex of DMAc and acid chloride have two nucleophilic centers resulting a chain breaking amidine formation or amide formation by the attack of diamine.

Therefore, we could expect that chain termination reaction easily obtained in the case of large amount of solvent. But the decrease of molecular weight by side reaction due to the solvent is small. It is reported that the rate of side reaction is second order whereas the rate of amide formation is 10^{-2} sec. order. The main factor affecting to the molecular weight at lower concentration of monomer is statistical effect. This effect could be explained by the fact that the polymerization reaction is completed at short time. So it is necessary that diamine component should be reacted with diacid chloride component effectively. But the chance of amide formation reaction is small at lower concentration of monomer resulting low molecular weight polymer. This fact fits the result above. On the other hand, at higher concentration, inherent viscosity of NMCTA was decreased. One possible explanation is reduced reactant mobility due to the gelation before high inherent viscosity could be reached. Another reason is an increase in the rate of side reaction as a result of greater heat generation at higher concentration. We thought that both aspect affect to the polymerization. As indicated in Fig. 6 NMCTA doesn't show above phenomenon. This is explained by effective volume of rod-like polymer. NMCTA is more rod-like than NMCTA resulting large effective volume of solvent. As indicated above, NMCTA immediately gelatinized when TCl is poured into CDA but NMCTA doesn't.

The effect of LiCl concentration in the polymerization was showed in Fig. 7. The inherent viscosity of NMCTA was increase

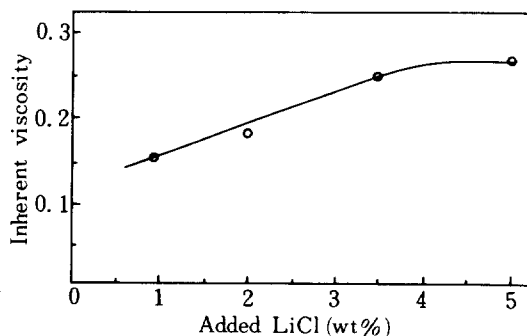


Fig. 7. Inherent viscosity of NMCTA according to the concentration of LiCl in DMAC.

according to the increasing of LiCl concentration, but above the 5wt % of LiCl concentration, there was no difference of inherent viscosity. Scheffgen et al.¹⁴ reported that the role of salt is to complex with the amide type solvent. When the salt is added to the amide type solvent the salt combines with the solvent causing Cl^- ion. The solvent which makes complex with salt have a higher polarity than uncomplexed solvent causing effective solvation of polymer. The mechanism of solvation by polarized solvent is that the solvent easily attacks the hydrogen bond of polymer. Morgan⁹ pointed out that at lower concentration of salt, high speed stirring is needed in order to obtain maximum mixing and uniform reaction before the polymer precipitates resulting low molecular weight polymer. But the decrease of molecular weight according to the low salt concentration was small.

In general it is well known that 1 : 2 ratio of HMPA to NMP is most powerful solvent system. Federov⁸ et al. Speculates that this is why a complex exists between these solvent in a molar ratio of 3 : 1. Such complex can be visualized by the fact that

NMP exists one methyl group coordinated to the nitrogen atom of HMPA. This combination represents the optimum basicity of solvent which results the lowest degree of reactivity of solvent with diacid chloride monomer. But we could not obtain a high molecular weight polymer at this solvent system. HMPA and NMP gave a moderately good solvating system yielding a inherent viscosity of 0.25 and 0.28 respectively. We could not obtain a polymer in DMSO and DMF solvent system. Preston⁸ have reported that these solvent easily reacted with acid chloride resulting in side reaction. Table 2 shows the relation between the solvent and inherent viscosity of NMCTA and above aspect could be confirmed through Table 2.

Polymerization was carried out at various temperature. As the temperature rose, the molecular weight of polymer was decreased. This can be explained by the fact that DM Ac · HCl salt dissociates into acetyl chloride and dimethyl amine hydrochloride which is chain terminating agent. Fig. 8 shows this results. It is generally known that diamine component easily oxidized above 25 °C, so it is recommended that the reaction system is cooled below this point. But at lower reaction temperature, there was a

Table 2. I. V. and Yield of Polymer at Several Solvent System

Solvent	Yield (%)	η_{inh} (dl/g)
HMPA-NMP (1/2)	97	0.2
HMPA-DMAc (3/2)	100	0.22
HMPA	100	0.25
NMP	100	0.28
DMSO	—	—
DMF	—	—

slight decrease of inherent viscosity. This was thought that the polymer was easily gelatinized due to the poor solvation power of solvent at the beginning of polymerization reaction.

3-4. Thermal properties

Fig. 9 shows the DTA curves of polyamides. Mild exothermic curve was observed at about 400°C but we could not identify whether it was melting curve or not. As pointed out at some paper³, we thought that the polymer melt with decomposition. As shown in Fig. 10, NMCTA and NMCIA had an initial decomposition temperature of 420°C. NMCTA had a decomposition temperature of 475°C at which the weight loss was

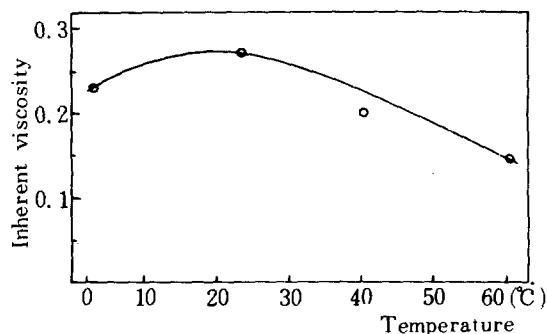


Fig. 8. Inherent viscosity of NMCTA according to polymerization temperature in DMac.

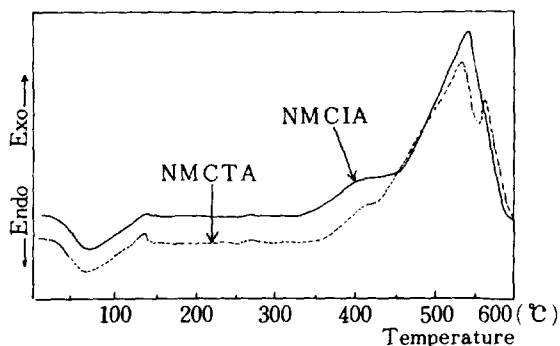


Fig. 9. DTA curve for polyamides (in air).

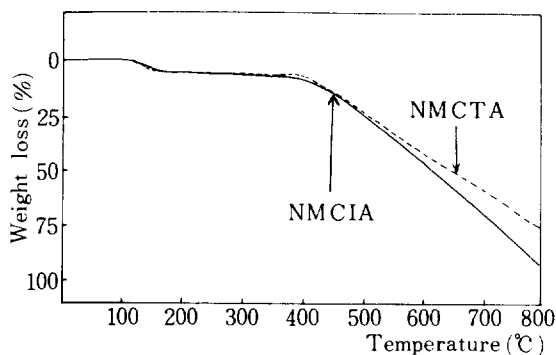


Fig. 10. TGA curve for polyamide (in air).

approximately 10% of the original weight after correction for loss of absorbed water¹⁵. NMCTA lost 50% of its weight at about 680°C. From the Fig. 10, we could see that NMCTA was more heat resistant than NMClA.

4. CONCLUSIONS

Aromatic polyamides of moderate molecular weight were synthesized from CDA and aromatic dicarboxylic acid chloride by low temperature solution polymerization. The polymers obtained were identified by means of IR and NMR spectrometers, and their thermal properties were measured by TGA and DTA.

The optimum polymerization conditions were as follows;

Reactants concentration : 0.12 mole/l for N-methylcarbazole-terephthalamide and 0.32 mole/l for N-methylcarbazole-isophthalamide.

Polymerization temperature : 25°C.

Solvent : NMP + 5% LiCl.

NMCTA and NMClA did not melt but decomposed above 420°C.

The weight loss of NMCTA was 10% at 475

°C and 50% at 670°C.

On the whole, NMCTA showed better thermal stability than NMClA.

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