

방향족 이미드의 특성관계 : 2. 고분자량의 폴리아믹산과 폴리이미드 합성을 위한 최적조건

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(1994년 4월 18일 접수)

Structure-Property Relationships in Aromatic Polyimide: 2. Optimum Conditions for High Molecular Weight Poly(amic acids) and Polyimides

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(Received April 18, 1994)

요약 : 방향족 dianhydride [PMDA(pyromellitic dianhydride), ODPA(4,4'-oxydiphthalic anhydride)]와 방향족 diamine[3,3'-DDSO₂(3,3'-diamino diphenyl sulfone), 4,4'-DDSO₂(4,4'-diamino diphenyl sulfone), DDM(4,4'-diamino diphenyl methane)]를 공용매 DMAc(N,N'-dimethyl acetamide)에 용해시켜 용액 중합반응으로 폴리아믹산을 제조한 후, 축합반응으로 고내열성 방향족 폴리이미드를 합성하였다. 폴리아믹산의 대수 및 고유점도와 분자량 측정으로 (1) 고분자량을 위한 중합 최적조건과 (2) 단량체의 순도와 제조형상(필름 및 분말)이 분자량에 미치는 영향 등을 조사하였다. 경화온도에 따른 이미드화도를 FT-IR 분석으로, DSC와 DMA를 이용하여 유리전이온도를, 그리고 극성 및 비극성 용매에 대한 용해도 등을 조사하였다. TGA에 의한 열안정성은 정제된 단량체로 제조된 폴리이미드가 보다 높은 열안정성을 보여 열안정성의 분자량 의존도가 관찰되었는데, 이는 GPC 분석을 통한 분자량 조사에서도 확인되었다.

Abstract : Poly(amic acids)(PAAs) prepared from the mixtures of aromatic dianhydrides [PMDA(pyromellitic dianhydride) and ODPA(4,4'-oxydiphthalic anhydride)] with aromatic diamines [3,3'-DDSO₂(3,3'-diamino diphenyl sulfone), 4,4'-DDSO₂(4,4'-diamino diphenyl sulfone), and DDM(4,4'-diamino diphenyl methane)] in cosolvent, DMAc (N,N'-dimethyl acetamide), were thermally cured to convert polyimides (PIs). (1) The optimum condition of polymerization, (2) the effect of monomer purity and the type of PAAs (film or powder) on the molecular weight were investigated by measuring the intrinsic and inherent viscosity and molecular weight of the PAAs. The degree of imidization was obtained using FT-IR and the glass transition temperatures were measured using DSC or DMA. Solubilities of the fully imidized PIs were tested in polar and non-polar solvents. Thermal analysis using TGA revealed that thermal stabilities of the PIs depend on their molecular weights and the shape of PAAs as well.

Keywords : aromatic polyimide, structure-property.

INTRODUCTION

Recently a novel class of polymer has successfully prepared to be useful for a wide variety of applications requiring high temperature materials.¹ Above all, polyimides are mainly used in film form, as coatings and composite matrix resins, which are characterized by high thermal stability, electrical resistance and modulus, as well as outstanding chemical resistance. In spite of their wide uses and various patents about the formation of aromatic polyamic acid and polyimide, commercial development has resulted a little.² The papers reported recently are concerned with the preparation and properties of the polyimides consisting other connecting groups between rings, and the effects of these groups upon physical properties and thermal stability.³

In this work, we have studied the optimum condition of the polymerization for high molecular weight of PI for film formation, and the relationships between molecular weight and physical and thermal properties using the PAAs and PIs formed from PMDA(pyromellitic dianhydride) and ODPA(4,4'-oxydiphthalic anhydride) with various diamines consisting of 3,3'-DDSO₂ (3,3'-diamino diphenyl sulfone), 4,4'-DDSO₂ (4,4'-diamino diphenyl sulfone) and DDM(4,4'-diamino diphenyl methane). These monomers were chosen for commercial purposes in terms of material resources, cost and applicability. In particular, the effect of monomer purity on molecular weight was studied by measuring the inherent and intrinsic viscosity as well as the secondary molecular weight measurement by GPC using THF as a mobile phase.

EXPERIMENTAL

Materials. The aromatic dianhydride and diamine monomers used in this study are shown in Fig. 1. Pyromellitic dianhydride(PMDA: Chriskev Co. Kansas, USA) was purified by subli-

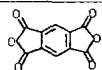
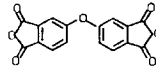
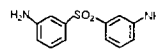
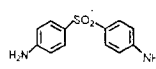
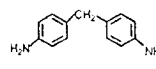
Structure & Nomenclature	Mol.Wt	M.P.°C
 PMDA : pyromellitic dianhydride	218.12	285.8
 ODPA : 4,4'-oxydiphthalic anhydride	310.2	227
 3,3'-DDSO ₂ : 3,3'-diamino diphenyl sulfone	248.3	170
 4,4'-DDSO ₂ : 4,4'-diamino diphenyl sulfone	248.3	176
 DDM : 4,4'-diamino diphenyl methane	195.3	92

Fig. 1. Chemical structure of dianhydrides and diamines used in this study.

mation⁴ and 4,4'-oxydiphthalic dianhydride(ODPA: Chriskev Co. Kansas, USA) was recrystallized from methyl ethyl ketone(MEK) before sublimed.⁵ 3,3'-diamino diphenyl sulfone(3,3'-DDSO₂) and 4,4'-diamino diphenyl sulfone (4,4'-DDSO₂) obtained from Chriskev Company, and 4,4'-diamino diphenyl methane (DDM) from Hodogaya Company, Japan, were recrystallized from ethanol.⁵

N,N'-dimethyl acetamide(DMAc:Janssen Co. Belgium) used as a solvent for polymerization was distilled at room temperature with CaH₂ and used for viscosity measurements. N,N'-dimethyl formamide(DMF), N-methyl-2-pyrrolidinone(NMP) and chloroform obtained by commercial sources were directly used as received for solubility test. HPLC grade THF used for GPC mobile phase was obtained from EM Science, Gibbstown, New Jersey, U.S.A.

Preparation of Polyamic acid and Polyimide. Polyamic acid solutions were prepared according to the procedures described in published literatures.^{6,8} Using a three-neck reactor equipped with an overhead stirrer and nitrogen

outlets, diamine solutions were prepared at a constant solid concentration in DMAc. After adding dianhydride powder into diamine solution in a stoichiometric ratio, the solution was slowly stirred at a constant temperature for 5~30hr.

In order to determine the optimum condition of polymerization for polyamic acid, the effects of monomer purity, various monomer concentration(5~30%) and reaction temperature(5°C, 25°C, and 65°C) were investigated by measuring the viscosity of polymerizing medium at given time intervals.

Two different types of PAA sample were prepared and studied in terms of the effect of viscosity; (1) poly(amic acid)(PAA) film was cast on a glass plate and, DMAc was removed at 70°C for 24hr. (2) PAA powder was obtained by dropping PAA solution into distilled water as a non-solvent, followed by isolating it for drying at 70°C in a vacuum oven. Later, two sorts of PAAs were dissolved in DMAc for viscosity measurements.

PAA film or powder was then thermally cured at desired temperature to convert to a PI medium, and then to convert to a corresponding PI at fully imidizing temperature, which is 20°C higher than the T_g for 2 hours in a vacuum oven.³

Solubility of the prepared PAAs or PIs were tested at room temperature in such solvents as N,N'-dimethyl acetamide(DMAc), N,N'-dimethyl formamide(DMF), tetrahydrofuran(THF) and chloroform.

Instrumentation. Fourier Transform Infrared(FT-IRs) spectra were recorded with Bruker IFS48 using 16 scans at a resolution of 2cm^{-1} for the measurement of polymerization and the degree of imidization.

The glass transition temperature of ODPAA based polyimides, which was taken as a midpoint of the transition, was measured on a Perkin-Elmer DSC-7 with a heating rate of 20°C/min under nitrogen atmosphere. Dynamic

mechanical analysis was performed on a DuPont DMA 983 at 1 Hz with a heating rate of 3°C/min for the measurement of damping factor $\tan\delta$ or E'' of PMDA based polyimides.

A Perkin-Elmer TGA-7 was used to evaluate a weight residue of the PIs up to 900°C and a temperature of 5% weight loss (taken as the decomposition temperature, T_d) of PIs at a heating rate of 20°C/min under nitrogen purge.

Viscosity of PAA solution(0.5wt%) taken from the reaction(polymerization) bottle in a given time interval was measured to study the reaction time dependence on viscosity by using an Ubbelohde suspended level viscometer. In addition, relative viscosity of a dilute PAA solution prepared by dissolving the PAA film or powder in DMAc was measured to obtain inherent, reduced and intrinsic viscosity at 35°C and averaged in five measurements. The values in each measurement was reproducible within 0.05% error.

For molecular weight and distribution of molecular weight, the PAA powder or film was dissolved in THF and experiments were performed by a Waters 510 GPC with a refractive index detector using THF as a mobile phase at 1 ml/min. Calibration of molecular weights was performed by using monodisperse polystyrene standard sample with ultrastaygel columns connected in series, 500, 10^3 , 10^4 , 10^5\AA .

RESULTS AND DISCUSSION

The degree of imidization. In FT-IR spectra studies of polyimides, an internal standard peak is the most important factor as to how sensitive it is to the various changes involved in the curing of polyimides. Ginsberg and Susko⁸ suggested that 1776cm^{-1} carbonyl absorbance was fairly well isolated from the rest of the spectrum and resulted in a good reproducibility. Navarre⁹ found that the FT-IR bands at 1780cm^{-1} (symmetric carbonyl stretching band) and 720cm^{-1} (deformation or carbonyl stretching of

imide ring) were insensitive in high temperature stage of reaction. Pyride¹⁰ suggested that the absorption near 1500cm^{-1} attributed to the ring breathing modes of the aromatic moieties appeared to be the most satisfactory as internal standards.

In this study, the technique employed for the degree of imidization was the method of comparing band ratio,^{8,10} i.e., the area of the characteristic bands of imide ring at the 1780cm^{-1} , 1370cm^{-1} (C-N stretching), and 720cm^{-1} was compared with the absorption band at 1720cm^{-1} or 1480cm^{-1} which was chosen as internal standards. Thus, the degree of imidization based on 1720cm^{-1} internal peak for the PMDA/3,3'-DDSO₂ system is compared with the one based on 1480cm^{-1} peak in Fig. 2 and 3, respectively; as a result, normalized at $720\text{cm}^{-1}/1480\text{cm}^{-1}$ is rather reliable than the others. The degree of imidization was calculated in this method during the performance of this project and the values at various curing temperature is described in Table 2.

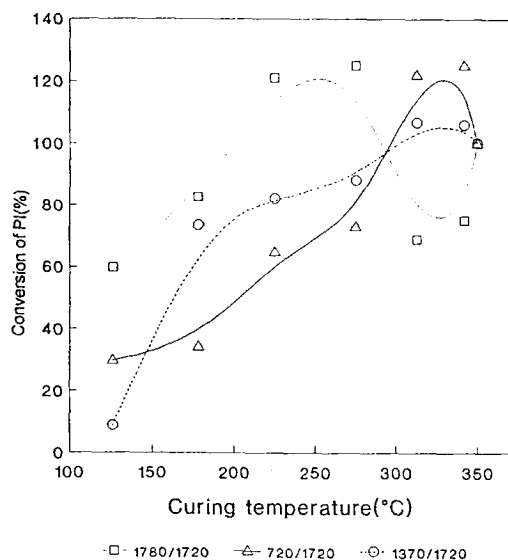


Fig. 2. Conversion of PI(PMDA/3,3'-DDSO₂) as a function of curing temperature by using the 1729cm^{-1} internal standard peak.

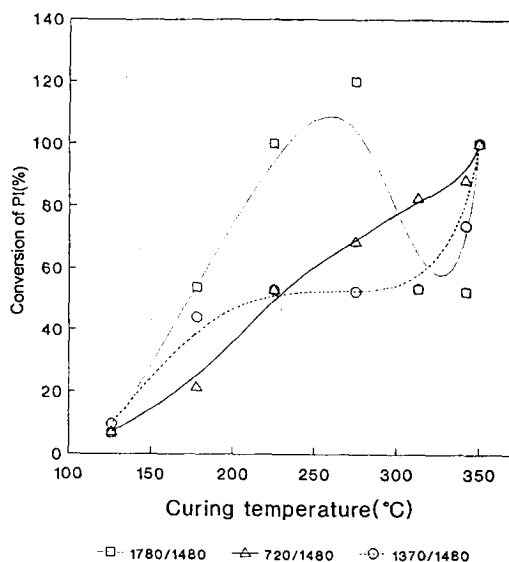


Fig. 3. Conversion of PI(PMDA/3,3'-DDSO₂) as a function of curing temperature by using the 1480cm^{-1} internal standard peak.

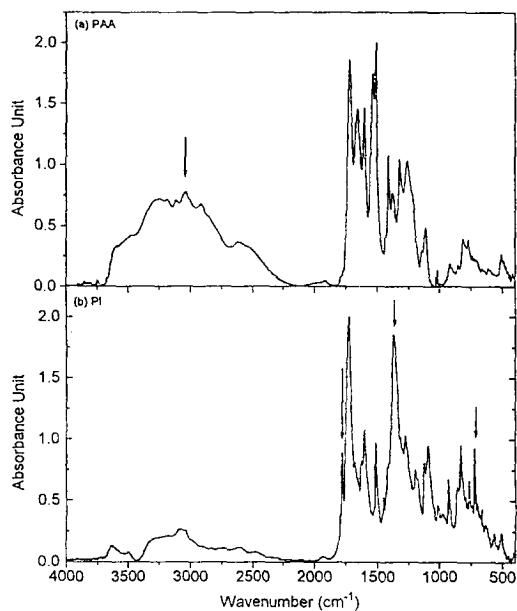


Fig. 4. FT-IR spectra of PMDA/DDM in $4000\text{--}400\text{cm}^{-1}$ (a) poly(amic acid) (b) fully imidized polyimide.

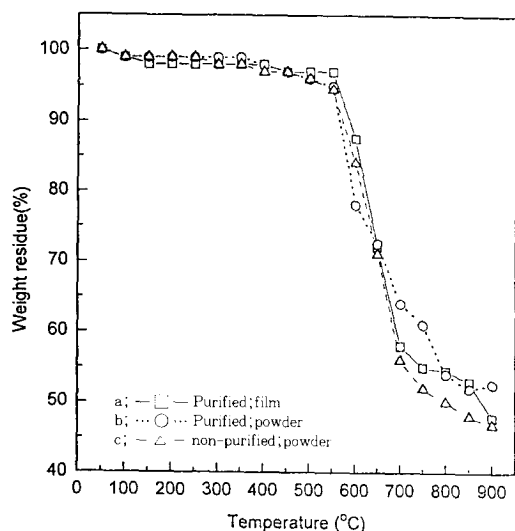


Fig. 5. TGA thermograms of PMDA/3,3'-DDSO₂ in various sample forms (heating rate of 20 °C/min under N₂ gas).

The representative FT-IR spectra between PAA and PI after fully imidized (the condition for fully imidization is curing the PAA at 20°C higher than its T_g for 2 hrs³) are respectively shown in Fig. 4(a) and 4(b) in ODA/4,4'-DDSO₂ system. In fully imidized PI films, no evidence of DMAc peak was observed at 1650cm⁻¹.

Thermal stability. In Fig. 5, the thermal stabilities of PMDA/3,3'-DDSO₂ produced by purified (Fig. 5(a) and (b)) and non-purified (Fig. 5(c)) monomers were compared in terms of sample forms in film or powder. As seen in this figure, the thermal stability of PI synthesized from purified monomer is relatively enhanced. The TGA thermograms of the various PI powder formed from the purified monomers are plotted in Fig. 6. The weight residue between 500°C and 900°C was higher in PMDA based system than in ODA based one, and in all system, a slight weight loss is observed at between 100°C and 150°C. The former behavior may arise from the chain stiffness of the PMDA and the latter may result from a volatile such

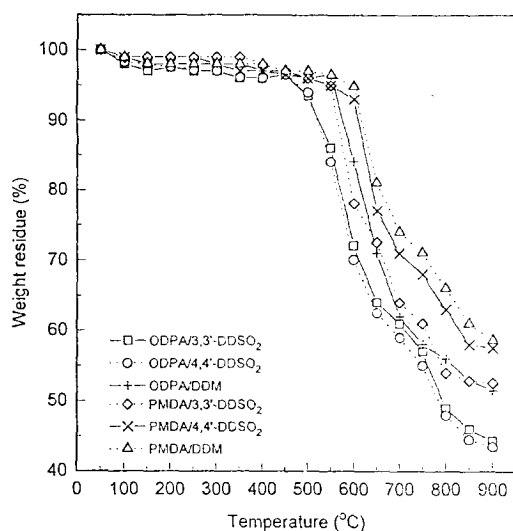


Fig. 6. TGA thermograms of various PI powder synthesized from purified monomer (heating rate of 20 °C/min under N₂ gas).

as moisture uptake during experiment. Decomposition temperature, T_d , defined as 5% weight loss of the PI in Table 1 shows higher value in PMDA based PIs than in ODA based PIs, where describes the higher thermal stability in PMDA than in ODA.

Glass Transition Temperature (T_g). DSC thermograms of the ODA based polyimides are drawn in Fig. 7. In this figure, relatively flexible structure (ODA/3,3'-DDSO₂, in Fig. 7(a)) shows lower T_g (246°C) than the one (262°C) of rigid structure (ODA/4,4'-DDSO₂, in Fig. 7(b)). This is the same result as in the previous report,³ of which the meta-substituted moiety has a bigger steric hindrance than the para-substituted one. PMDA/3,3'-DDSO₂, which apparently has a bigger steric hindrance showed its T_g at 327°C (in Fig. 7(d)). However, the rest of the PIs synthesized with PMDA was not traced its T_g by DSC. This may be the same case as the PMDA/ODA system of which the T_g was not observed on DSC, but was observed at 399 °C on DMA. Thereby, the T_g of PMDA/DDM

Table 1. Physical and Thermal Properties of Various PAA/PI Systems

System		PAA			PI			
		\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n	IV ^a	T _g (°C)	T _d (°C)	Wt. residue(%)	Solubility ^b
A	non-purified	12,900	1.20	0.58	-	-	-	-
	purified	63,000	1.30	0.66	246	522	44.3	P.S
B	non-purified	12,000	1.22	0.56	-	-	-	-
	purified	59,000	1.30	0.60	262	530	43.5	P.S
C	non-purified	22,900	1.18	0.67	-	-	-	-
	purified	80,000	1.30	0.82	271	575	51.7	P.S
D	non-purified	2,900	1.21	0.17	-	-	-	I
	purified	12,000	1.13	0.25	327	554	52.6	I
E	non-purified	-	-	0.07	-	-	-	-
	purified	-	-	0.18	>350 ^c	554	57.5	I
F	non-purified	-	-	0.79	-	-	-	-
	purified	-	-	1.34	345	582	58.6	I

A:ODPA/3,3'-DDSO₂ B:ODPA/4,4'-DDSO₂ C:ODPA/DDM D:PMDA/3,3'-DDSO₂ E:PMDA/4,4'-DDSO₂ F:PMDA/-DDM

^aIntrinsic viscosity:0.5wt% solution(powder) in DMAc(dℓ/g), ^b5wt% in DMAc(with fully imidized PI), P.S;Partially soluble, I; Insoluble, ^cUnknown T_g(assumption:300~400°C)

Table 2. Solubility of PAA and PI's Cured at Various Temperature

System	Curing Temp.(°C)	DMAc	DMF	THF	CHCl ₃	System	Curing Temp.(°C)	DMAc	DMF	THF	CHCl ₃
(I)	PAA	S	S	S	I	(II)	PAA	S	S	S	I
	128°C (24%)	S	S	S	I		128°C (27%)	S	S	S	I
	158°C (31%)	S	S	S	I		158°C (45%)	S	S	S	I
	198°C (42%)	S	S	S	I		198°C (51%)	S	S	S	I
	220°C (84%)	S	S	I	I		220°C (89%)	S	S	I	I
	240°C (91%)	S	S	I	I		260°C (97%)	S	S	I	I
Fully imidized PI		P.S	P.S	I	I	Fully imidized PI		P.S	P.S	I	I
(III)	PAA	S	S	S	I	(IV)	PAA	S	S	S	I
	128°C (20%)	S	S	S	I		178°C (21%)	S	S	S	I
	158°C (40%)	S	S	S	I		225°C (53%)	SW	SW	SW	I
	216°C (74%)	S	S	S	I		275°C (68%)	SW	SW	SW	I
	230°C (84%)	S	S	I	I		313°C (87%)	I	I	I	I
	260°C (93%)	S	S	I	I		332°C (93%)	I	I	I	I
Fully imidized PI		P.S	P.S	I	I	Fully imidized PI		I	I	I	I
(V)	PAA	S	S	I	I	(VI)	PAA	S	S	I	I
	178°C (27%)	S	S	I	I		178°C (24%)	S	S	I	I
	225°C (45%)	SW	S	I	I		225°C (31%)	S	P.S	I	I
	275°C (51%)	SW	SW	I	I		275°C (42%)	I	I	I	I
	320°C (89%)	I	I	I	I		313°C (84%)	I	I	I	I
	340°C (97%)	I	I	I	I		332°C (91%)	I	I	I	I
Fully imidized PI		I	I	I	I	Fully imidized PI		I	I	I	I

(I) ODPA/3,3'-DDSO₂ (II) ODPA/4,4'-DDSO₂ (III) ODPA/DDM (IV) PMDA/3,3'-DDSO₂ (V) PMDA/4,4'-DDSO₂ (VI) PMDA/DDM (S; Soluble, P.S; Partially soluble, I;Insoluble)

^aT_g by DSC, ^bDegree of imidization by calculation of peak area 720/1480cm⁻¹, ^cT_g-Assumption, ^dT_g by DMA

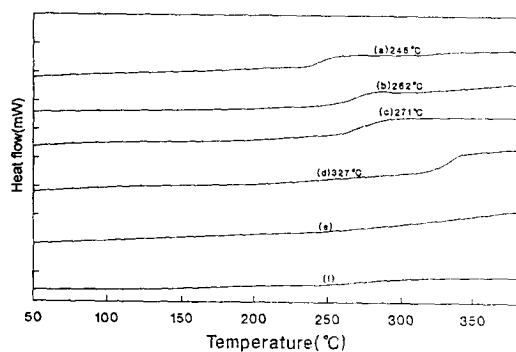


Fig. 7. DSC thermograms of polyimides powder (heating rate of 20°C/min under N₂ gas).

- (a) ODP/3,3'-DDSO₂ (b) ODP/4,4'-DDSO₂
 (c) ODP/DDM (d) PMDA/3,3'-DDSO₂
 (e) PMDA/4,4'-DDSO₂ (f) PMDA/DDM

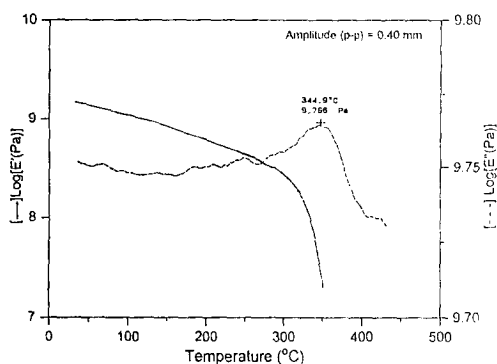


Fig. 8. DMA thermogram of PMDA/DDM polyimides (heating rate of 3°C/min in air).

measured by DMA was shown at 345°C by E'' (in Fig. 8) with small amplitude of the peak. For the entire system except PMDA/3,3'-DDSO₂, the film formation from purified monomer was available with 15wt% solution. We believe that the technique for film formation is needed for further development.

Solubility. The solubility of PAAs and PIs cured at various temperature was investigated and the results are listed in Table 2. ODP/3,3'-DDSO₂ based PIs show better solubility than PMDA based PIs. In addition, fully imidized PIs based

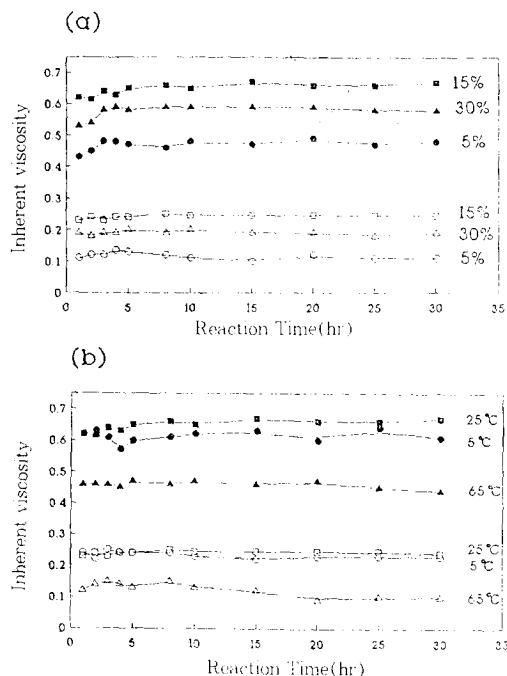


Fig. 9. Inherent viscosity of PAA vs. reaction time in various reaction (a) concentration (b) temperature. Solid symbol; ODP/3,3'-DDSO₂. Open symbol; PMDA/3,3'-DDSO₂.

ODP are partially soluble in DMAc or DMF which is a polar solvent. Solubilities of the PIs are correlated with the chemical structure, thermal stability or the glass transition temperature. Thus, the more flexible structure, the lower thermal stability and T_g , and the higher solubility are observed.

Viscosity. The reaction concentration and reaction temperature dependency on the inherent viscosity of PAAs in PMDA/3,3'-DDSO₂ and ODP/3,3'-DDSO₂ formed from purified monomers were measured and plotted as a function of reaction time in Fig. 9(a) and Fig. 9(b). ODP system showed higher viscosity than PMDA system. 15 wt% solution shows higher viscosity than the one measured at 5wt% or 30wt% in concentration. In addition, the inherent viscosity, measured at 25°C was relatively

higher than that at 5°C or at 65°C. Thus, the maximum condition for high molecular weight was a reaction of 15wt% in concentration at 25 °C for at least 5 hours. In comparison, inherent viscosity of the ODPA system(A, B and C in Table 1) shows approximately four times higher than that of PMDA system(D and F in Table 1). Molecular weight of the ODPA system is as well. In addition, electron affinity of PMDA and ODPA is 1.9 eV and 1.3 eV, respectively.⁸ The difference in electron affinity may induce a formation of high molecular weight PAA such as in ODPA system than PMDA system. We will come to this again in the later section.

Dilute PAA solution for the measurement of inherent and reduced viscosity was prepared from the once precipitated powder or film. The intrinsic viscosity of the above PAA is obtained by extrapolation at zero concentration from the inherent viscosity. In Fig. 10, the inherent and reduced viscosity of the purified PMDA/4,4'-DDSO₂ system was increased with lower concentration and as a result, the intrinsic viscosity at the zero concentration is 0.22dL/g for film (Fig.10-(a)) and 0.18dL/g (Fig. 10-(b)) for powder. The difference in intrinsic viscosity may arise from the original sample form(film or powder) or polyelectrolyte effect of DMAc. As will be discussed later, extrapolation of the inherent viscosity at zero concentration was performed without considering the polyelectrolyte effect which was significantly observed in this experiment(arrows in Fig. 10). As in Fig. 10-(a) and (b), the upturn behavior in viscosity at low concentration is what we believe to be arisen from the polyelectrolyte effect of the polar solvent, DMAc. Thus we suggest that the exact intrinsic viscosity may vary. The values of inherent and reduced viscosities were also used to calculate $[\eta]$ in Huggins and Kraemers equation. In contrast, the calculated inherent and reduced viscosities of the PMDA/4,4'-DDSO₂ system synthesized by non-purified monomers were 0.09dL/g in film form and 0.07dL/g

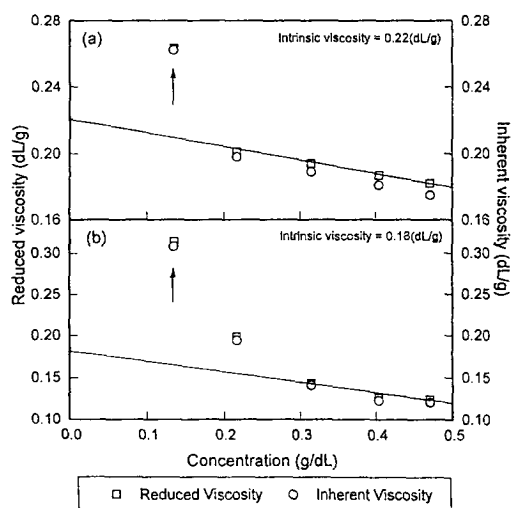


Fig. 10. Intrinsic viscosity extrapolation of PAA (PMDA/4,4'-DDSO₂) synthesized in various forms (a) Purified film (b) Purified powder.

g in powder, which are concurrently decreased with lower concentration and extremely low value. Precipitating PAA solution in water is reported to give rise to a reduced molar mass. This behavior also induces that the intrinsic viscosity of non-purified system is lower than that in purified system and that the molecular weight of PMDA system is relatively lower than ODPA system. This is the similar result as Wallach¹¹ reported.

Average molecular weight. The number average molecular weight (\bar{M}_n) and polydispersity (\bar{M}_w/\bar{M}_n) by GPC are listed in Table 1 for the system studied. It has not been often to report the molecular weight of polyimide because of poor solubility. We have approached to measure molecular weight of PAA powder dissolved in THF using GPC with a mobile phase, THF. For the purified ODPA system, the observed number average molecular weight is 59,000~80,000. This is fairly reasonable data compared to the non-purified ODPA system in which (\bar{M}_n) is 13,000~23,000. The latter is relatively four times lower than the purified one

and this correlates to the viscosity difference in two different systems.

PMDA/3,3'-DDSO₂ system shows extremely low value of molecular weight and the trend is similar to the intrinsic viscosity. Molecular weight of the PMDA/4,4'-DDSO₂ and PMDA/DDM systems was not available due to poor solubility in THF. From the above observation, we believe that molecular weight of PAAs using THF is not influenced by the polyelectrolyte effect of the solvent. However, DMAc or DMF as a mobile phase is believed to give a severe polyelectrolyte effect by polarity or impurity (amine group). Polyelectrolyte effect of polar solvent on molar mass is under investigation and will be disclosed shortly.

CONCLUSIONS

Using the purified and non-purified monomers (dianhydride and diamine), the polyamic acid and polyimide were synthesized and they are dependent on the purity of monomer, reaction temperature, and monomer-solvent concentration. In this reaction, the reactivity of electrophilic dianhydride may be correlated with its electron affinity, while the reactivity of nucleophilic diamine may be correlate with its basicity. The structural changes in diamine affect the reaction rate more than changes in dianhydride. Optimum conditions for high molecular weight PAAs measured by the viscosity and GPC technique are resulted in a reaction with purified monomer at 25°C, with 15wt% concentration for 5 hours. Less flexible PI moiety shows high T_g and an enhancement in thermal property. Molecular weight of PI was also influenced by monomer purity as well as the polyelectrolyte effect induced by impurity of sol-

vent.

Acknowledgment. This work was supported by the Ministry of Education Research Fund for Advanced Materials in 1991~1992, and partially supported by the Dong-Sung Chemical Industry Co. Ltd.. S. Choe is particularly grateful to the president, Jung-Ho Paek and the former vice-president, Byung-Kwon Choi, of the Dong-Sung Chemical Ind. Co., Ltd., for their continual support in performing research and in purchasing GPC instrument.

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