Soluble wholly aromatic polyamides containing unsymmetrical pyridyl ether linkages

Insik In, Sang Youl Kim *

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, 373-1, Guseonng-dong, Yuseong-gu, Daejeon 305-701, South Korea

Abstract

Wholly aromatic polyamides were synthesized from the amidation reaction between unsymmetrical diamine containing a pyridyl ether linkage and aromatic dicarboxylic acid chloride. The resulting polyamides containing pyridyl ether linkages showed high thermal stability ($T_{d5} = 467\ ^\circ\text{C}$) and enhanced solubility in organic solvents compared with the analogous polyamides having phenyl ether linkages. Substitution of just a single atom in a repeating unit was effective to disrupt the strong inter-chain interaction of parent aramid polymers.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: High performance polymers; Polyamide; Step-growth polymerization

1. Introduction

Wholly aromatic polyamides (aramids) are high performance polymeric materials with outstanding mechanical properties and excellent thermal and chemical stabilities due to chain stiffness and intermolecular hydrogen bonding of amide groups [1,2]. However, the poor solubility and high softening or melting temperature caused by the high crystallinity of the aramid backbones lead to difficult processing of these materials. For the practical use in various recent applications, new aromatic polyamides possessing both high thermal stability and solubility in common organic solvents have been required. Incorporation of pendent groups [3–6] or molecular asymmetry [7,8] or flexible linkages [9–11] into the backbone is a typical approach to improve solubility and processability while maintaining the high thermal stability of aromatic polyamides. Generally, it is more convenient to synthesize the modified aramids via the structural modification of diamine monomers, followed by the polycondensation reaction with available aromatic dicarboxylic acids or their derivatives. The most popular diamine monomer with a flexible linkage

is 4,4′-oxydianiline (ODA) [12–14]. Although the resulting aromatic polyamide, which is produced by the polyamidation reaction with terephthaloyl chloride, has flexible ether linkages along the main chain, it is still insoluble in organic solvents such as NMP or DMSO without lithium chloride.

Recently, we have been interested in the effects of the minimal structural modification on the physical properties of various step-growth polymers. In this study, we incorporate unsymmetrical pyridyl ether linkages instead of phenyl ether linkages into the main chain of ODA-based aramid polymers (Fig. 1). Unsymmetrical pyridyl ether containing aramids are structurally different in the aspect that only single carbon atom of the repeating unit of the corresponding ODA-containing aramid is changed by a nitrogen atom (Fig. 1). This change in a single atom is the least structural modification to the parent ODA based aramid polymers and the modified aramid polymers are isoelectric compared with the parent aramid polymers. It is interesting to investigate how much of the physical and chemical properties are affected with such a minimal structural modification in the repeating unit of polymers. Also, it is well known that aramids containing heterocyclic units in the main chain possess excellent thermal stabilities [15,16]. Therefore, incorporation of pyridyl ether linkages may induce the least detrimental effect on the thermal properties of the polymer.

* Corresponding author. Tel.: +82 42 869 2834; fax: +82 42 869 2810.
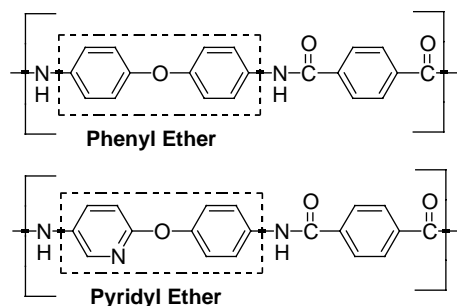 *E-mail address:* kimsy@kaist.ac.kr (S.Y. Kim).

Fig. 1. Structures of aromatic polyamides containing phenyl or pyridyl-ether linkages.

2. Experimental

2.1. Materials

2-Chloro-5-nitropyridine, 4-nitrophenol, benzoyl chloride, palladium (5 wt% on activated carbon), and potassium carbonate (K_2CO_3) were purchased from Aldrich Chemical Company and used as received. Toluene, triethylamine (TEA), N-methyl-2-pyrrolidinone (NMP), and N,N-dimethylacetamide (DMAc) were dried over calcium hydride for 24 h and distilled under reduced pressure. Terephthaloyl chloride (TPC) and isophthaloyl chloride (ITC) (from Aldrich) were purified by recrystallization in hexane.

2.2. Characterization

FT-IR spectra of the compounds were obtained with a Brucker EQUINOX-55 spectrophotometer using KBr pellet. NMR spectra of the synthesized compounds were recorded on Brucker Fourier Transform AVANCE 300 spectrometers. High-resolution mass (HRMS) spectra of the monomers and model compounds were obtained with a Jeol JMS-SX-102 mass spectrometer. Inherent viscosity data were obtained in NMP with a Canon-Ubbelohde type viscometer at a concentration of 0.5 g/dL at 30 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system at a heating rate of 10 °C/min in nitrogen. Molecular model was obtained by molecular mechanics (MM+) by means of the Chem 3D Ultra® program (Molecular Modeling System, Version 6.0, 2000; Cambridge Scientific Computing, Inc.).

2.3. Monomer synthesis

2.3.1. 5-Nitro-2-(4-nitrophenoxy)-pyridine (1) [17]

2-Chloro-5-nitropyridine (25.40 g, 160.2 mmol), 4-nitrophenol (22.30 g, 160.3 mmol), and K_2CO_3 (22.15 g, 160.3 mmol) were added to a mixture of 210 mL of DMAc and 20 mL of toluene in nitrogen. The solution was heated to 100 °C with the azeotropic distillation of toluene for 14 h. The dark brown solution was cooled and poured into 500 mL of distilled water. The precipitated solid was collected by filtration and dried in vacuo at 60 °C for 12 h. The crude product was used without further purification. Yield: 92%.

FT-IR (KBr): 1606 (C=C and C=N band), 1511, 1354 (NO_2), 1264 cm^{-1} (C–O–C stretching).

^{1}H NMR (DMSO-d_6, 300 MHz, δ): 9.03 (d, 1H), 8.69 (dd, 1H), 8.33 (d, 2H), 7.52 (d, 2H), 7.42 (d, 1H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 165.2, 157.8, 144.6, 144.5, 141.1, 136.2, 125.6, 122.5, 112.6.

FAB-MS (m/e) 261.0388, Calcd 261.0386 for $C_{11}H_7N_3O_5$.

2.3.2. 5-Amino-2-(4-aminophenoxy)-pyridine (2) [18]

Dinitro compound 1 (5.00 g, 19.1 mmol) and 5 wt% palladium on activated carbon (0.638 g) were added to 250 mL of anhydrous ethanol. Twenty millilitres of hydrazine monohydrate was added dropwise to this mixture at 50 °C for 1.5 h. After an additional reflux for 1.5 h, the catalyst was removed by hot filtration and the solvent was removed from filtrate by rotary evaporation. The remaining oily mixture was added into 300 mL of distilled water and the resulting solid was collected by filtration. Recrystallization from ethyl acetate gave the desired 2 as white crystalline solid. Yield: 65%. MP: 172 °C.

FT-IR (KBr): 3473, 3384 (N–H), 1617 (N–H out-of-plane bending), 1512 (N–H bending and C–N stretching), 1240 cm^{-1} (C–O–C stretching).

^{1}H NMR (DMSO-d_6, 300 MHz, δ): 7.49 (d, 1H), 7.03 (dd, 1H), 6.69 (d, 2H), 6.59 (d, 1H), 6.55 (d, 2H), 4.91 (s, NH_2, 2H), 4.80 (s, NH_2, 2H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 155.4, 145.8, 144.7, 140.8, 132.1, 125.4, 120.7, 114.5, 111.1.

FAB-MS (m/e) 201.0911, Calcd 201.0902 for $C_{11}H_{11}N_3O$.

2.4. Model reaction

2.4.1. 5-Benzamido-2-(4-benzamidophenoxy)-pyridine (3)

Diamine monomer 2 (0.5000 g, 2.485 mmol) and benzoyl chloride (0.6986 g, 4.970 mmol) were dissolved in 11 mL of NMP at 0 °C. After stirring for 3 h, 0.7 mL of triethylamine was added to the solution. The reaction mixture was allowed to warm up to room temperature gradually for 1 h and stirring was continued for 12 h. The reaction mixture was poured into 300 mL of distilled water and the precipitate solid was collected by filtration and dried in vacuo at 80 °C. Yield = 94%.

FT-IR (KBr,): 3294 (N–H), 1647 (C=O), 1543 (N–H bending and C–N stretching), 1237 cm^{-1} (C–O–C stretching).

^{1}H NMR (DMSO-d_6, 300 MHz, δ): 10.4 (s, –CONH–, 1H), 10.3 (s, –CONH–, 1H), 8,51 (d, 1H), 8.24 (dd, 1H), 7.97 (m, 4H), 7.82 (d, 2H), 7.60 (m, 6H), 7.14 (d, 2H), 7.07 (d, 1H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 165.6, 165.4, 159.2, 150.1, 139.4, 135.5, 134.9, 134.3, 132.7, 131.8, 131.7, 131.5, 128.5, 128.4, 127.6, 127.5, 121.7, 120.9, 111.1.
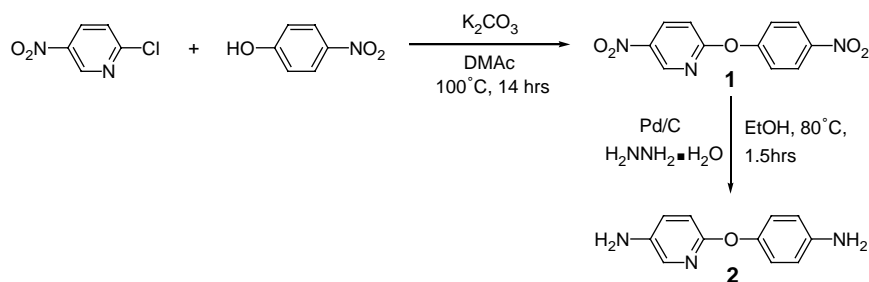
Scheme 1. Synthesis of the diamine monomer **2**.

FAB-MS (*m/e*) 409.1426, Calcd 409.1426 for $C_{25}H_{19}N_3O_3$.

2.5. Polymerization

2.5.1. P1

Diamine monomer **2** (0.5000 g, 2.485 mmol) and TPC (0.5045 g, 2.485 mmol) were dissolved in 10 mL of ice-cold NMP. The solution was stirred mechanically at 0 °C for 3 h and 0.7 mL of triethylamine was added to the solution. The reaction mixture was allowed to warm up to room temperature gradually for 1 h and stirring was continued for 12 h. The viscous polymerization mixture was poured into 300 mL of distilled water and the fibrous solid was collected by filtration and dried in vacuo at 120 °C. Yield: 98%. η_{inh}: 0.94 dL/g.

FT-IR (KBr): 3300 (N–H), 1645 (C=O), 1537 (N–H bending and C–N stretching), 1268 cm^{-1} (C–O–C stretching).

^{1}H NMR (DMSO-d_6, 300 MHz, δ): 10.59 (s, –CONH–, 1H), 10.47 (d, –CONH–, 1H), 8.54 (s, 1H), 8.22 (b and m, 5H), 7.85 (d, 2H), 7.13 (m, 3H).

2.5.2. P2

The above procedure was repeated with **2** (0.4985 g, 2.477 mmol) and IPC (0.3820 g, 2.477 mmol). Yield: 96%. η_{inh}: 0.70 dL/g. T_g: 206 °C.

FT-IR (KBr,): 3297 (N–H), 1655 (C=O), 1536 (N–H bending and C–N stretching), 1245 cm^{-1} (C–O–C stretching).

^{1}H NMR (DMSO-d_6, 300 MHz, δ): 10.60 (s, –CONH–, 1H), 10.48 (d, –CONH–, 1H), 8.55 (s, 2H), 8.22 (b and m, 3H), 7.82 (d, 2H), 7.71 (b, 1H), 7.16 (d, 2H), 7.06 (d, 1H).

2.5.3. Polyamide from ODA and TPA

The above procedure was repeated with ODA (1.0000 g, 4.994 mmol), TPC (1.0139 g, 4.994 mmol), and LiCl (0.4000 g, 9.436 mmol). Yield: 98%. η_{inh}: 1.08 dL/g (with 2 wt% LiCl).

FT-IR (KBr,): 3261 (N–H), 1653 (C=O), 1225 cm^{-1} (C–O–C stretching).

3. Results and discussion

The pyridine-containing diamine monomer, 5-amino-2-(4-aminophenoxy)-pyridine (**2**) was synthesized via 2 step

procedures presented in Scheme 1. In the first step, 5-nitro-2-(4-nitrophenoxy)-pyridine (**1**) was synthesized by nucleophilic aromatic substitution reaction of 2-chloro-5-nitropyridine with 4-nitrophenol using potassium carbonate as a base in DMAc. In the second step, dinitro compound **1** was reduced to **2** with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol. Both structures of the dinitro compound **1** and diamino monomer **2** were confirmed by FT-IR and NMR spectroscopies. Because of the unsymmetrical structure of **2**, two amines show different proton resonance peaks at 4.91 and 4.80 ppm in ^{1}H NMR spectrum, respectively (Fig. 2). Due to the electro-deficient characteristic of pyridine ring, amine in the pyridine ring shows resonance peak in the more downfield region ($\delta =$ 4.91 ppm).

To investigate the feasibility of polymerization, model reaction was conducted with benzoyl chloride. The diamine monomer **2** was reacted with two equivalents of benzoyl chloride in the presence of triethylamine as an acid acceptor at a concentration of 10 wt% in NMP from 0 °C to room temperature (Scheme 2). Between two amine groups of the monomer, the amine attached to the pyridine ring is
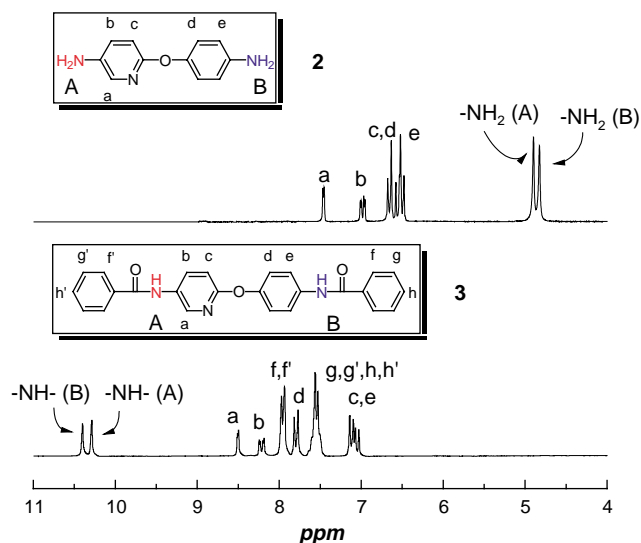
Fig. 2. ^{1}H NMR spectra of the monomer **2** and the model compound **3**.
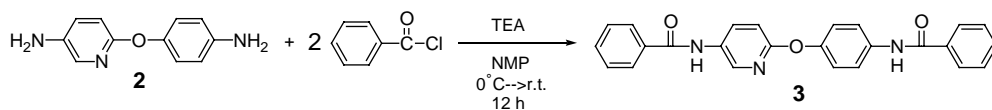
Scheme 2. Model reaction of the monomer **2** with benzoyl chloride.
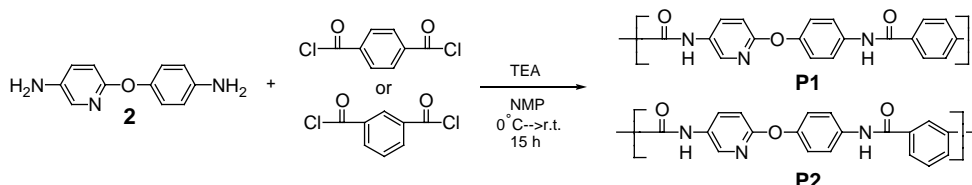
Scheme 3. Syntheses of polymers, **P1** and **P2**.

expected to have less nucleophilicity than the amine attached to the phenyl ring, but the reactivity difference of two diamine groups did not affect the model reaction. The model reaction proceeds quantitatively and the structure of model compound **3** was confirmed by FT-IR and NMR spectroscopies (Fig. 2).

The successful results of the model reaction prompted us to perform the polymerization. The polymerizations were carried out by reacting stoichiometric amounts of the diamine monomer **2** with terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC) (Scheme 3). All other conditions were same with the model reaction. The inherent viscosity values over 0.7 dL/g and the absence of detectable end groups in the ^{1}H NMR spectrum support the formation of high molecular weight polymers.

The pyridyl ether containing aramids, **P1** and **P2** could be solvent-cast from NMP solution into transparent, flexible, and tough films. The formation of aramid polymers was confirmed with the spectroscopic data. The FT-IR spectra of the polymers showed the absorption bands around 3300 and 1650 cm^{-1} corresponding to the N–H and C=O stretching of amide group, respectively. ^{1}H NMR spectra of the polymers prepared from the unsymmetrical diamines showed two amide proton peaks at 10.51 and 10.45 ppm (Fig. 3).

To confirm the solubility enhancement effect of pyridyl ether linkage, the polymerization of ODA and TPC was conducted by using the similar method [19]. But in this case, precipitation occurred during the polymerization in NMP without LiCl. Pyridyl ether containing **P1** was soluble in NMP and DMSO without LiCl. The improved solubility of **P1** is originated from the different monomer structures of ODA and **2**. The diamine containing pyridyl ether has more twisted structure than the corresponding ODA and inter-chain interaction of amide linkages is reduced. Fig. 4 shows the computer modeling of the structures of two ether linkages. The lone pair interaction between oxygen and nitrogen forces the pyridyl ether linkage to have more

twisted structure. In addition, pyridine-containing diamine is unsymmetrical and produces several constitutional isomers along the polymer main chain. Also, pyridine ring has higher polarity than the phenyl ring. All of these characteristics of the pyridyl ether linkage can enhance the solubility of aromatic polyamides in aprotic polar solvents, such as NMP and DMSO.

Thermal analysis reveals that the pyridine containing aramids have high thermal stability. The DSC curves of the synthesized polymers are shown in Fig. 5. Meta-linked polyamide **P2** showed T_g at 206 °C and para-linked **P1** did not show any transition up to 400 °C. Both polymers did not show any melting transition up to 400 °C, indicating that the pyridyl either linkage is effective in disturbing the inter-chain interaction of aromatic polyamides. The TGA results indicate that all the polymers are stable up to around 400 °C in
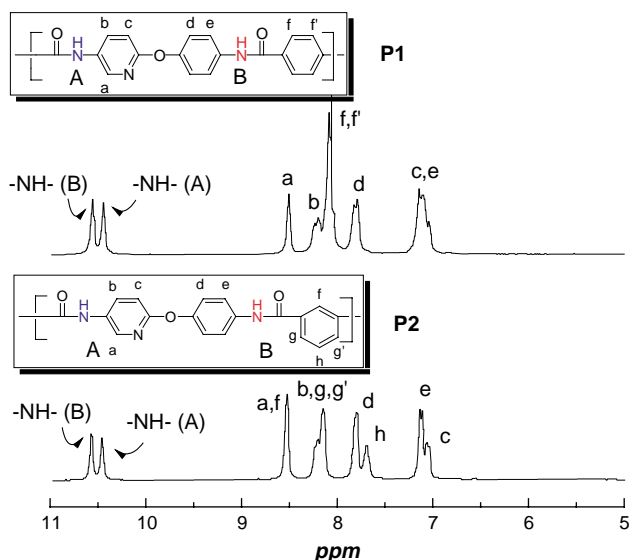
Fig. 3. ^{1}H NMR spectrum of polymers, **P1** and **P2**.
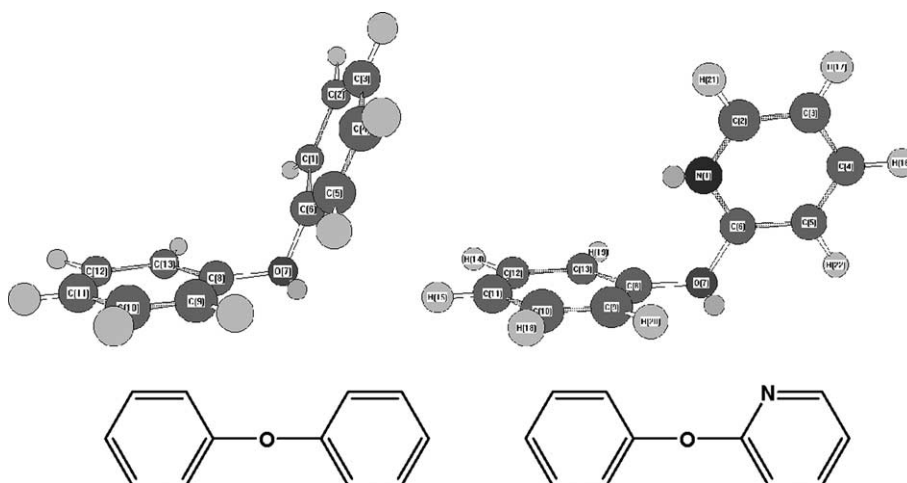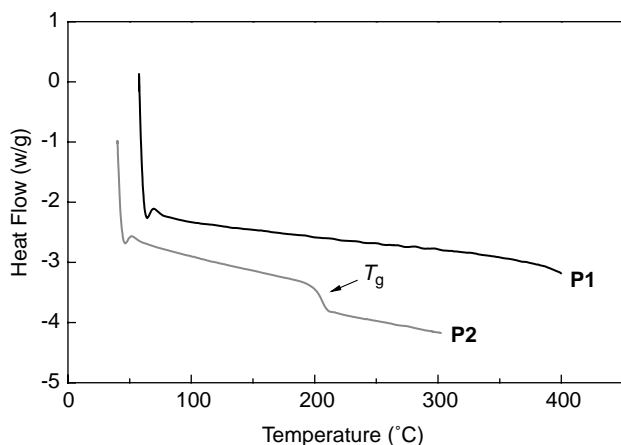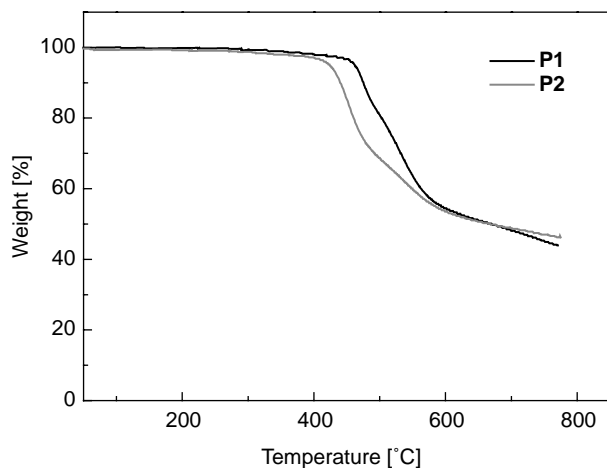
Fig. 4. Optimized geometry of phenyl ether linkage and pyridyl ether linkage.

Fig. 5. DSC curves of the polymers, **P1** and **P2**.

Fig. 6. TGA curves of the polymers, **P1** and **P2**.

nitrogen (Fig. 6). The 5% decomposition temperature (T_{d5}) of para-linked polyamide **P1** was higher (467 °C) than the corresponding meta-linked polymer **P2** (425 °C) and almost similar to the T_d value of ODA based polyamide (460 °C [19]) (Table 1). The incorporation of pyridyl ether linkage induced no detrimental effect on the high thermal stability of aramids.

4. Conclusion

New soluble aromatic polyamides were synthesized from novel pyridine containing diamine monomer. The improved solubility of these aramid polymers was originated from the incorporated unsymmetrical pyridyl ether linkage along the polymer main chain. Thermal stability of polymers was essentially not decreased compared with the corresponding phenyl ether containing aramid polymers. These results support that such a minimal modification of the polymer structure can be used as an effective strategy for enhancing the

Table 1
Polymerization results and properties of polymers

Polymer	Yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_{d5}[c] (°C)	T_{d10}[c] (°C)	Residue[d] (wt%)
P1	98 (98)[e]	0.94 (1.08)[e]	n.d. (n.d.)[e]	467 (460)[e]	477 (482)[e]	44 (37)[e]
P2	96	0.70 (1.20)[f]	206	425	443 (450)[f]	46

[a] Measured at a concentration of 0.5 g/dL in NMP at 30 °C.
[b] Measured by second scan of DSC with a heating rate of 10 °C/min.
[c] A 5 or 10% weight-loss temperature measured by TGA with a heating rate of 10 °C/min.
[d] Weight residue measured by TGA with a heating rate of 10 °C/min at 800 °C.
[e] Data shown in the parenthesis is that of the analogous polyamides based on ODA and TPC [19].
[f] Data shown in the parenthesis is that of the analogous polyamides based on ODA and IPC [20].

processability of aramids based high-performance polymers, while maintaining the high thermal stability.

Acknowledgements

References

[1] Frazer AH. High-temperature resistant polymers. 1st ed. New York: Wiley; 1968.

[2] Lin J, Sherrington DC. Adv Polym Sci 1994;111:177.

[3] Sakaguchi Y, Harris FW. Polym J 1992;24:1147.

[4] Jeong HJ, Oishi Y, Kakimoto MA, Imai Y. J Polym Sci, Part A: Polym Chem 1990;28:3293.

[5] Spiliopoulos IK, Mikroyannidis J. Macromolecules 1998;31:515.

[6] Rogers HG, Gaudiana RA, Hollinsed WC, Kalyanaraman PS, Manello JS, McGowam C, et al. Macromolecules 1985;18:1058.

[7] Cheng L, Jian XG, Mao SZ. J Polym Sci, Part A: Polym Chem 2002;40:3489.

[8] Yang C-P, Chen R-S, Chen C-D. J Polym Sci, Part A: Polym Chem 2001; 39:775.

[9] Johnson RA, Mathias LJ. Macromolecules 1995;28:79.

[10] Zhang Y, Tebby JC, Wheeler JW. J Polym Sci, Part A: Polym Chem 1996;34:1561.

[11] Liaw DJ, Liaw BY. J Polym Sci, Part A: Polym Chem 1998;36: 1075.

[12] Yang CP, Oishi Y, Kakimoto M, Imai Y. J Polym Sci, Part A: Polym Chem 1989;27:3895.

[13] Liou GS, Oishi Y, Kakimoto M, Imai Y. J Polym Sci, Part A: Polym Chem 1991;29:995.

[14] Idage SB, Idage BB, Verneker SP. J Appl Polym Sci 1989;38: 2057.

[15] Tamami B, Yeganeh H. Polymer 2001;42:415.

[16] Yu SC, Hou S, Chan WK. Macromolecules 2000;33:3259.

[17] Hwang KJ, Park SK. Synth Commun 1990;20:949.

[18] Ozawa S. Kyoto Daigaku Kekkaku-Kenkyusho Nempo 1956;4: 284.

[19] Butta E, de Petris S, Frosini V, Pasquini M. Eur Polym J 1971;7: 387.

[20] Ueda M, Aizawa T, Imai Y. J Polym Sci, Part A: Polym Chem 1977;15: 2739.