J. MACROMOL. SCI.—PURE APPL. CHEM., A38(5&6), 513–525 (2001)

SYNTHESIS AND CHARACTERISTICS OF NOVEL POLYAMIDES HAVING PENDENT *N*-PHENYL IMIDE GROUPS

Sang Hyun Park,[1] Jae Wook Lee,[1] Dong Hack Suh,[2,*] and Sang Yong Ju[2]

[1]Department of Chemical Engineering, Sokang University, Shinsoo-Dong 1, Mapo-Ku, Seoul 121-742, Korea
[2]Division of Chemical Engineering College of Engineering, Hanyang University, Seoul 133-791, Korea

ABSTRACT

We have investigated a novel monomer having a pendent phenyl imide group for preparing new cycloaliphatic-aromatic polyamides. Novel polyamides were synthesized by a direct polycondensation reaction of N-phenyl-2,3-imide cyclopentane-1,4-dicarboxylic acid (PCPA) and various aromatic diamines. A direct polycondensation was carried out by a Yamazaki's direct polycondensation that is typical of using triphenyl phosphite, lithium chloride, and pyridine. Inherent viscosity of these resulting polyamides was in the range 0.47-1.05 dL/g. The glass transition temperatures of these polyamides were in the range of 190-200°C. The decomposition temperatures of them were in the range of 310-323°C in nitrogen atmosphere. The Solubility of these polyamides are good in aprotic solvents such as DMAc (N,N-Dimethylacetamide), NMP (N-Methyl-2-Pyrrolidinone) and DMF (N,N-Dimethylformamide). Transparent, flexible, and tough films were cast from DMAc solutions.

Key Words: Cycloaliphatic-aromatic polyamide; Pendent imide group.

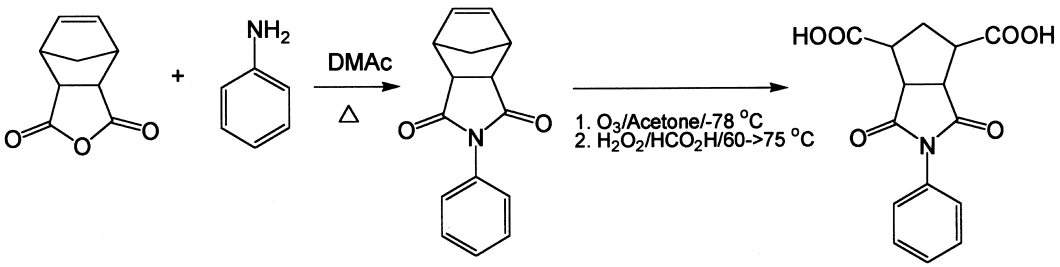
*Corresponding author. E-mail: dhsuh@email.hanyang.ac.kr

INTRODUCTION

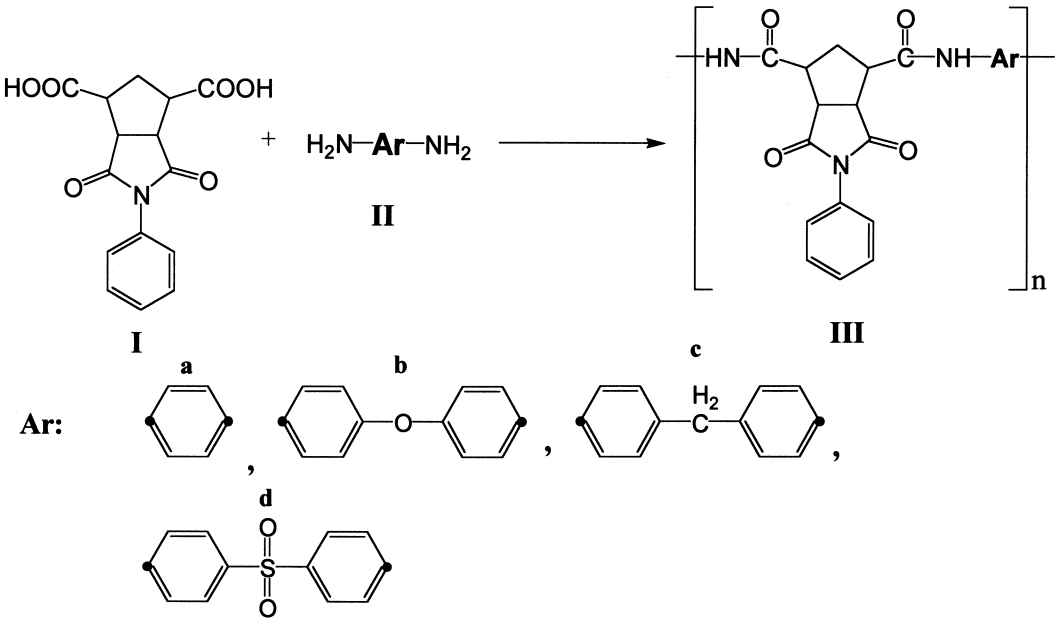
Aromatic polyamides have been widely used in industry because of excellent properties in thermal stability, good chemical resistance, and mechanical properties. But they have some disadvantages that most of aromatic polyamides were not dissolved in most organic solvents and were difficult to process due to intermolecular hydrogen bonding and their easy crystallization [1]. In order to improve solubility and processibility with maintaining thermal stability, it has been performed that some studies of introducing soft segments to the main chain of the polymers, breaking its symmetry and regularity thereby making crystallization impossible, introducing bulky groups to the side chain of the polymer breaking the hydrogen bonding through N-substitution of amide with certain groups [2–17].

In the same manner, we designed and synthesized a new monomer which is a cyclopentane derivative having two reactive carboxylic acids and a imide group. The introduction of the cyclopentane structure having a N-phenyl imide group to the polyamide could improve the solubility and excellent thermal stability, transparency, lack of color, and easily creates functionality to the polymer side chain. It was expected that high molecular cycloaliphatic-aromatic polyamides, having cyclopentane groups to the main chain and N-phenyl imide groups to the side chains, could easily be obtained by Yamazaki's polycondensation. Yamazaki and coworkers reported that polyamides were synthesized by the direct polycondensation of aliphatic dicarboxylic acids with aromatic diamines in NMP containing metal salts, triphenyl or diphenyl phosphite, and pyridine as condensing agents [18–21]. Recently, D. H. Suh *et al.* investigated the synthesis of polyarylether and polyamides from a polycondensation reaction of N,N'-substituted-2,3,5,6-diimide benzene-1,4-dicarboxylic acid [22–25].

In this article, we report a new monomer, an alicyclic diacid of N-phenyl-2,3-imide cyclopentane-1,4-dicarboxylic acid (PCPA) as shown in Scheme 1 and a new class of cycloaliphatic-aromatic polyamides prepared from them with various diamines by a Yamazaki's polycondensation as shown in Scheme 2.



Scheme 1. Synthesis of PCPA.



Scheme 2. Synthesis of polymers.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich, Junsei, and Merck Chemical companies. 1,4-phenylenediamine (p-PDA), 4,4'-oxydianiline (ODA), 4,4'-methylene dianiline (MDA) were purified by a vacuum sublimation method. 4,4'-diamino phenylsulfone was sublimed twice before use. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150°C for 6 hours. and 180°C for 10 hours. N-methyl-2-pyrrolidone (NMP) and pyridine purchased from Aldrich Co. were purified twice by distillation under reduced pressure over calcium hydride and stored over a molecular sieve 4Å.

Characterization and Equipment

For the ozonolysis, ozone was generated by electronic discharge in an oxygen stream, using a Fisher 500 ozone generator. Ozone concentration in oxygen, which was served also as a carrier gas, averaged to 4–5 g/L. The ozone concentration was determined by the percolation of the ozone-oxygen mixture through a 2% aqueous solution of potassium iodide (KI) and the subsequent titration of the liberated iodine with a 0.1N aqueous sodiumthiosulfate ($Na_2S_2O_3$) solution.

^{1}H-NMR and ^{13}C-NMR spectra were obtained by a Bruker AMX300 in DMSO-d_6 or Acetone-d_6. FT-IR spectra were taken on a Bio-Rad Digi Lab. Division FTS-165 using a potassium bromide pellet. Elemental analysis was taken on a EA 1108 Fisons. Differential scanning Calorimeter (DSC) was conducted on a TA instruments Dupont Model 910 at a heating rate of 10°C/min under nitrogen. The glass transition temperatures were determined at a midpoint of the melt transitions. Thermogravimetric analysis was performed with a TA instruments Dupont Model 951 at a heating rate of 10°C/min under nitrogen. Mass spectra recorded on a Jeol JMS-DX 303 GC/MS system using an electron impact method. Gel permeation chromatography was carried out with a Water Model 150C using μ-stage l columns with DMF as an eluent solvent. The crystallinity of the polymers was examined by X-ray diffraction diagrams using the powder method with the use of nickel-filtered Cu K_α radiation. The viscosities were measured in a 0.4 mm (i.d.) Ostwald viscometer at 30.0 ± 0.1°C with 0.5 g/dL of polymer concentration in DMAc. Transparent and tough films of polymers synthesized were obtained by casting from their DMAc solutions in a vacuum oven at 120°C overnight.

N-Phenyl-2,3-imide-5-norbornene (PINB) [26]

A 500 ml, two-neck, round-bottomed flask was equipped with a stirrer and was charged with 500 ml anhydrous DMAc, 164.16 g (1 mol) of 5-Norbornene-2,3-dicarboxylic anhydride and 94.96 g (1.01 mol) of aniline in the nitrogen atmosphere. The solution was heated up to 100°C, and kept for 4 hours. After that procedure, 25 ml of toluene was added into the solution and then a Dean-Stark trap containing 25 ml toluene. An azotropic mixture of water and toluene was removed refluxing for 5 hours. After that, the hot solution was cooled to room temperature. It was recrystallized from the DMAc solution to provide 214 g (89.5%) of white powder. The product crystallized rapidly and was filtered by a vacuum filtration system; m.p. 283°C, ^{1}H NMR (DMSO-d_6) d 1.6 (2H, 2-H), 3.3 (2H, 1-H, 3-H), 3.5 (2H, 4-H, 5-H), 6.2 (2H, 5-H, 6-H), 7.1 (2H, H-7, H-8), 7.4 (2H, H-9, H-10), 7.4 (1H, H-11); ^{13}NMR (DMSO-d_6) d 51.7 (C-2), 44.8 (C-1, C-3), 45.4 (C-4,5), 134.5 (2H, C-6,7), 176.7 (C-8,9), 128.3 (C-10), 127.1 (C-11, 12), 128.8 (C-13,14), 134.5 (C-15); Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.23; H, 5.48; N, 5.85; O,13.37. Found: C,.75.11; H, 5.43; N, 5.76; O, 13.62; EIMS m/z 239.26 (M+).

N-Phenyl-2,3-imide Cyclopentane-1,4-dicarboxylic Acid (PCPA) [27]

300 g (1.255 mmol) of N-phenyl-2,3-imide-5-norbornene was dissolved in 1 L of acetone and transferred into a 2L four-neck flask. The solution was stirred and cooled to –78°C, and then the reaction was performed by the continuous introduction of ozone. During the reaction, the gas stream was adjusted to the flow rate of 10 L/min through the reactor and contained at 0.1 mol of ozone per liter of

an O_3/O_2 mixed gas. The completion of the reaction was confirmed by the change of color in the KI trap (the change from light-yellow to light-brown due to the excess ozone and iodine) and the supply of the O_3/O_2 mixed gas was stopped and then nitrogen was purged for ca. 20 minutes to kick out the remained ozone in the reactor. Acetone was removed from the mixture by a rotary vacuum evaporator. The resulting product was dissolved in 200 ml of 90% formic acid and 100 ml of 30% hydrogen peroxide and carefully warmed to 60°C using a water bath. After the vigorous reaction was ceased, the mixture was again heated at 75°C for 6 hours. After the mixture was cooled, the excess formic acid was removed to give 250 g of the resulting diacid. It was recrystallized from formic acid to yield 298 g (78.4%) of white needles; m.p. 253°C. (The melting points of the monomers were measured by a capillary melting point apparatus). FTIR spectra of the PICA showed characteristic absorption bands of an imide group at 1780 and 1710 cm^{-1}. ^1H NMR (DMSO-d_6) d 1.9 (2H, 2-H), 3.0 (2H, 1-H, 3-H), 3.6 (2H, 4-H, 5-H), 7.2 (2H, 6-H, 7-H), 7.4 (2H, 8-H, 9-H), 7.4 (1H, 10-H), 12.6 (2H, 11-H, 12-H); ^{13}C NMR (DMSO-d_6) d 39.5 (C-2), 45.6 (C-1, C-3), 47.3 (C-4, 5), 175.7 (C-6, 7), 128.5 (C-8), 126.9 (C-9, 10), 129.0 (C-11, 12), 132.4 (C-13), 172.6 (C-14,15); IR (KBr pellet) 3491, 3060, 2980, 2945, 1780, 1760, 1725 cm^{-1}; Anal. Calcd. for

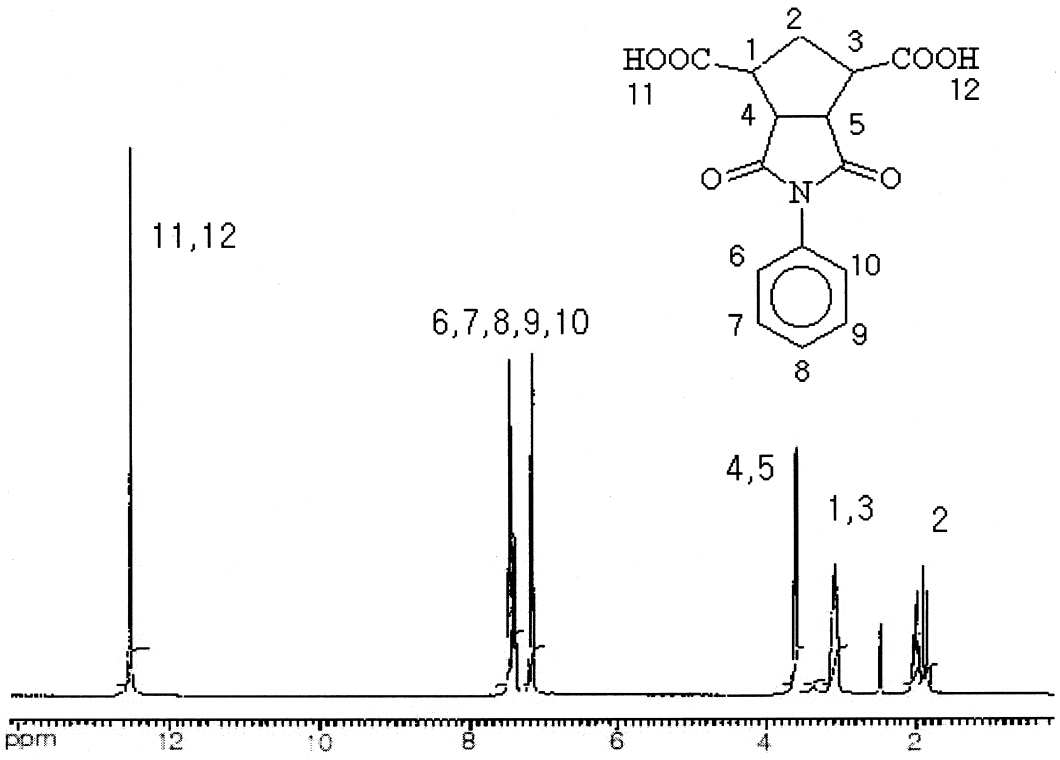


Figure 1. The ^1H NMR spectra of N-phenyl-4,5-imide-cyclopenthane-1,3 dicarboxylic acid (PCPA).

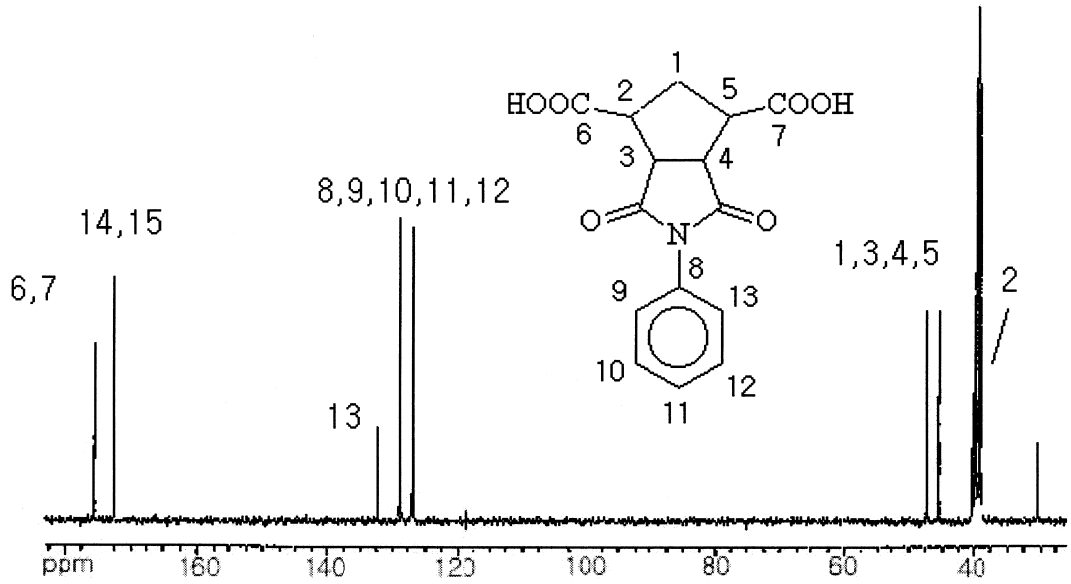


Figure 2. The ^{13}C NMR spectra of N-phenyl-4,5-imide-cyclopenthane-1,3-dicarboxylic acid (PCPA).

$C_{15}H_{13}NO_6$: C, 59.4; H, 4.3; N, 4.6; O, 31.7. Found: C, 59.2; H, 4.0; N, 4.5; O, 32.2; EIMS m/z 303 (M+).

Polymerization

A mixture of 0.303 g (1 mmol) PCPA, 0.2 g (1 mmol) ODA, 0.14 g LiCl, 0.621 g (2 mmol) triphenyl phosphite, 1 ml of pyridine, and 2 ml of NMP was stirred and heated at 105°C for 3 hours in the nitrogen atmosphere. The solution was trickled into 100 ml of methanol, and then the white fibrous precipitate was obtained. The polyamides were purified in the boiling methanol solution for 6 hours. The yield was quantitative. The inherent viscosity of polymer was 1.05 dL/g, measured at 0.5 g/dL of concentration in DMAc at 30°C.

RESULTS AND DISCUSSION

Monomer Synthesis

N-phenyl-4,5-imide-6-norbornene (PINB) was easily obtained from 5-norbornene-1,3-dicarboxylic anhydride and aniline by the equimolar imidization reaction in DMAc. N-phenyl-4,5-imide cyclopentane-1,3-dicarboxylic acid (PCPA) was synthesized by the ozonolysis reaction and followed by the further oxidation of PINB as shown in Scheme 1.

Hydrogen peroxide was used as a further oxidation reagent [29]. After the ozonolysis, resulting products was a mixture of ozonides, intermidiates of the oxidation, which were not separated and performed the next second oxidation using H_2O_2 in formic acid at 80°C.

FTIR spectra of the PICA showed characteristic absorption bands of an imide group at 1780 and 1710 cm^{-1}. The NMR spectra of the PCPA were given in Figures 1 and 2. Hydroxy protons on the carboxylic acid positioned at δ =12.6, whereas protons of a cyclopentane ring and phenyl rings on the N-substituted imide resonated at δ = 1.9, 3.0, 3.6 and δ = 7.2, 7.4, respectively. The structure was also confirmed by the ratios of integration.

Synthesis of Polymers

As shown in Scheme 2, various polyamides were prepared from PCPA with the corresponding aromatic diamines by using the most favorable conditions. Polycondensation results are listed in Table 1. All polyamides were obtained with a quantitative yield. Inherent viscosities of each polyamide are in the range of 0.47–1.05 dL/g. FTIR spectra of the polymers showed characteristic absorption bands of an amide band at 3200–3300 (N-H stretching), 1650–1670 cm^{-1} (amide band due to C=O stretching) and 1550 cm^{-1} (combination of N-H bending and C-N stretching). The NMR spectra of polymer III-c were given in Figures 3 and 4. Phenyl groups of the peak of amide protons resonated at δ =10.65, whereas the pendent imide phenyl protons of pendent unit of imide resonated at δ = 7.1–7.6 and cyclopentane protons of main chain resonated at δ = 1.7–3.7. Integration ratios confirmed the expected structure and the absence of any signals arising from end groups maybe confirmed the high polymeric nature of the product. In the case of using p-PDA as a monomer, polymer was swelled at the initial of polymerization reaction resulting in low molecular weight polymer.

The optimum condition of the polycondensation reaction is the ratio of PCPA (1 mmol) with 4,4'-oxydianiline (1 mmol), Pyridine/NMP = 1ml/3ml, LiCl = 4 wt%, and triphenyl phosphite(2 mmol) at 105°C by the various reaction condition. N. Yamazaki and F. Higashi investigated about the optimum condition of a

Table 1. Characteristics of Polyamides by the Direct Polycondensation Reaction of PICA and Various Diamines

Polymer	Yields (%)	η_{inh}[a] (dL/g)	Tg (°C)	Tm (°C)	Td (°C)	Tg/Tm (°K)
III-a	98	0.78	196.9	313.8	323	0.80
III-b	98	1.05	197.5	307.3	314	0.81
III-c	97	0.69	195.0	308.8	320	0.80
III-d	96	0.47	192.0	301.9	310	0.81

[a]Measured at concentration of 0.5 g/dL in DMAc at 30°C.

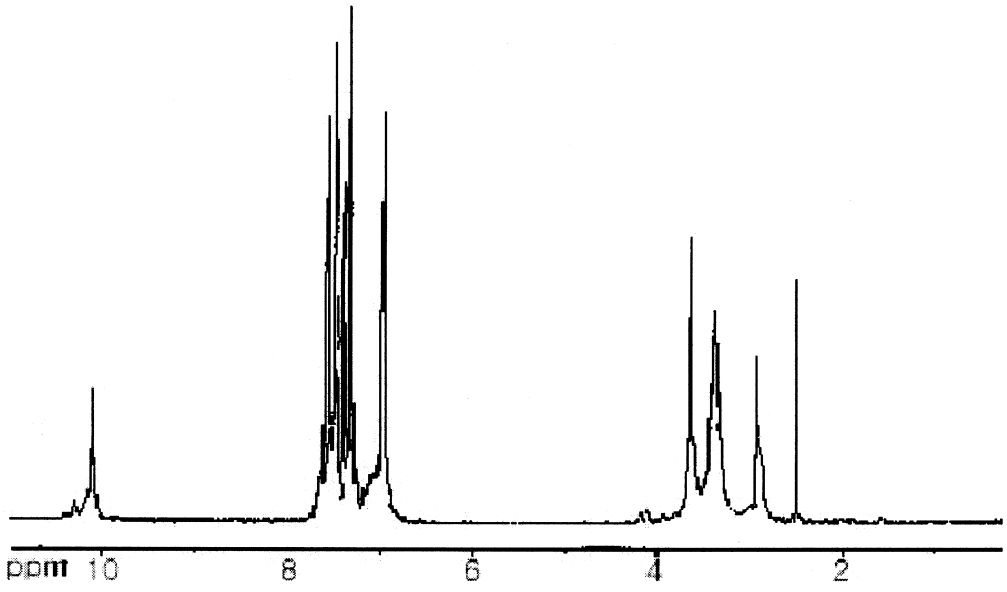


Figure 3. The ^{1}H MNR spectra of polyamide III-c.

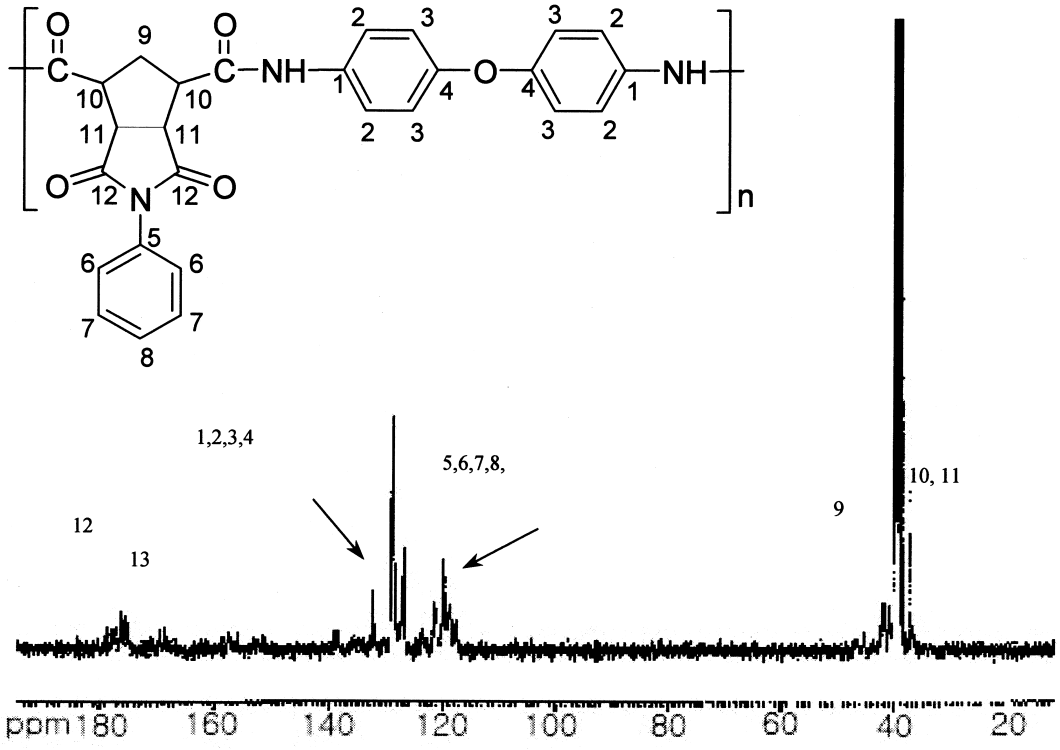


Figure 4. The ^{13}C MNR spectra of polyamide III-c.

polycondensation reaction of aromatic diacids with the diamines [29]. They suggested that the optimum condition of the reaction has LiCl concentration of 4 wt%, pyridine content in the mixture with NMP of 40 vol%, temperature of 100°C, the monomer concentration of 0.6 mol/l and the molar ratio of monomer/triphenyl phosphite of 1:1 at 100°C for 3 hours. Yamazaki's reaction made it possible for the direct synthesis of polyamide from aromatic diamines and various aliphatic diacids.

Polymer Properties

An X-ray diffraction confirmed that the polymers were semi-crystalline because of a small portion of crystalline peaks in the X-ray diffraction diagrams as shown in Figure 5. In spite of small crystalline regions, in every case, amorphous patterns are due to a lower packing of the unsymmetrical polymer backbones.

All polymers were soluble in various aprotic polar solvents such as DMAc, DMF, NMP, m-cresol, THF, and pyridine. The good solubility of these polyamides may be elucidated by loose packing of the macromolecules because of pendent

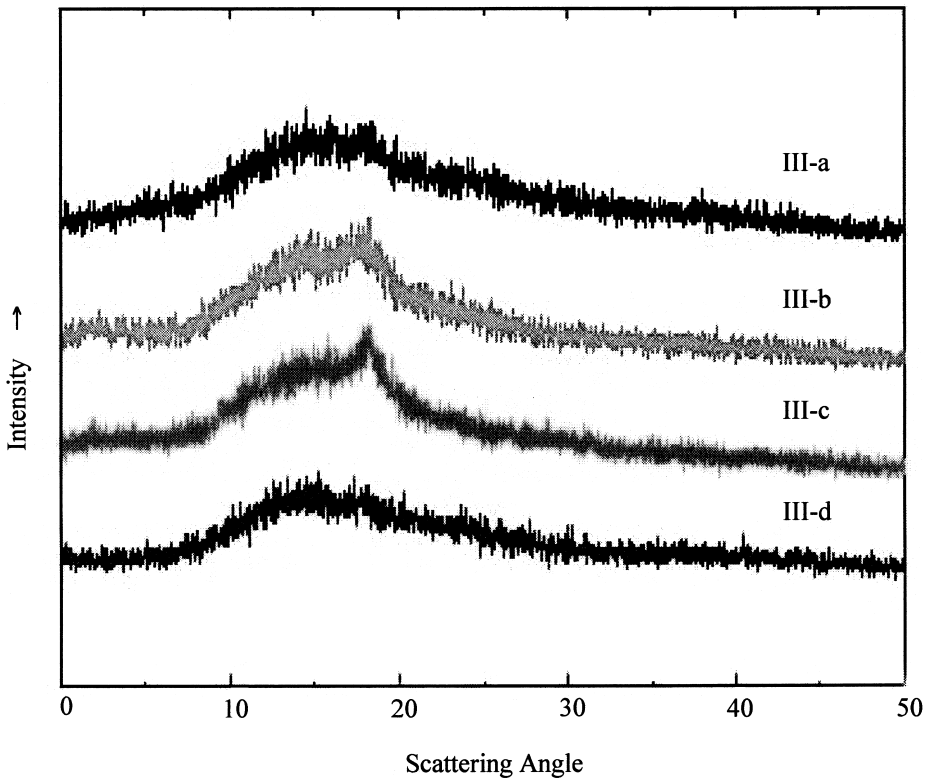


Figure 5. X-ray diffraction diagrams of polyamides.

phenyl rings and low crystallinity. As shown in Table 1, inherent viscosities of these resulting polyamides were in the range of 0.47–1.05 dL/g.

Since the influence of residual water or solvent and the history of thermal annealing are sometimes observed in the first heating run of DSC, the first heating of the samples was eliminated at 300°C; in addition, other thermal properties were evaluated according to the DSC charts of the second heating. the T_g's of the polymers observed in DSC thermograms (Figure 7) were in the range of 192–197°C. The melting endothermic peaks of polyamides on DSC thermograms (Figure 7) appeared at around 302–313°C, interpreted as a melting process accompanied by decomposition. Calculations of the Tg/Tm ratio in degrees Kelvin gave values of 0.80–0.81 for these polyamides in Table 1. It is interesting to note that the T_g/T_m ratios for these polymers are similar in spite of the use of various diamines.

The thermal resistance was investigated by TGA. Samples of polymers were subjected to a heating program under N_2 in order to elucidate how the chemical structure influenced the value of initial decomposition temperature. The results have been listed in Table 1. The decompositions of polyamide were observed around 310–323°C. The nature of the diamine moiety did not greatly influence the thermal resistance as was expected. The TGA curves represented in Figure 6 show, at first, that the weight loss step can be attributed to the initial loss of side groups.

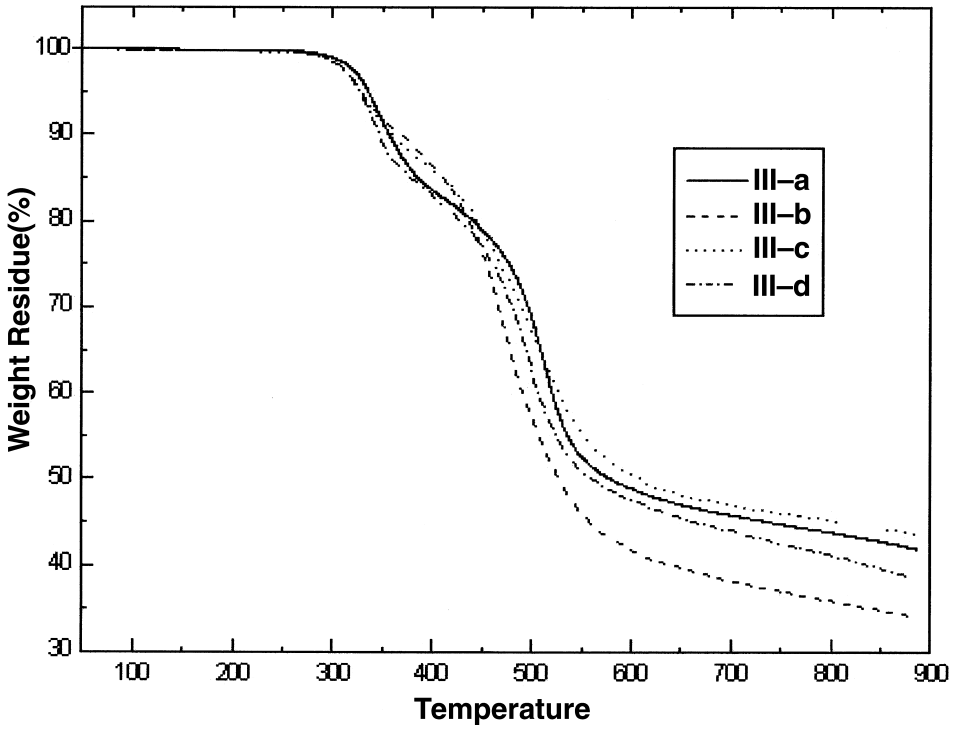


Figure 6. TGA thermograms of polyamides.

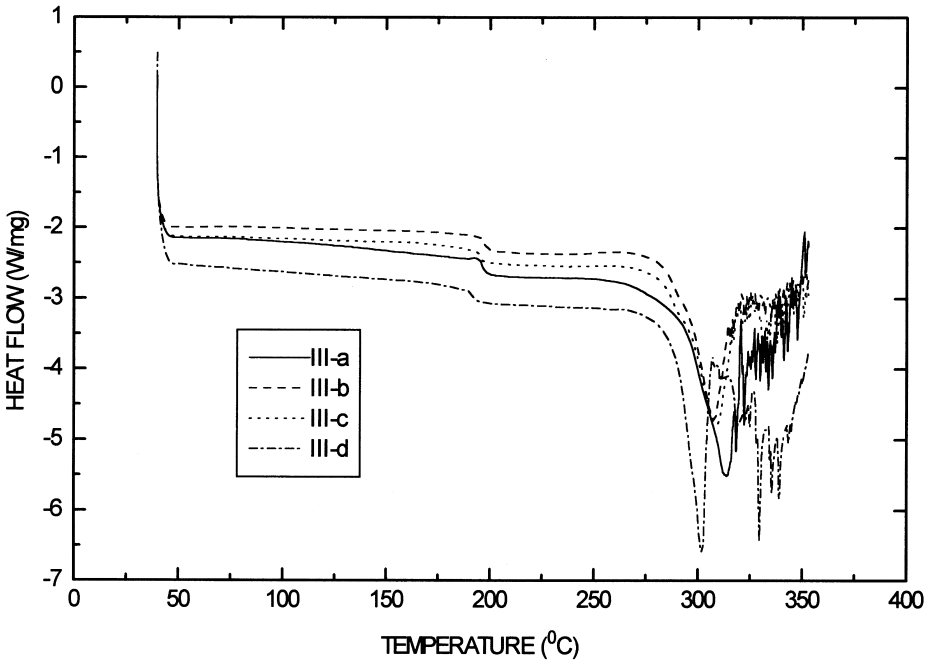


Figure 7. DSC thermograms of polyamides.

Arnold described the loss of pendent aromatic groups during the thermal analysis (TGA) of heat resistant polybenzotriazoles [30]. Transparent and tough films of these polymers could be obtained by casting from their DMAc solutions in a vacuum oven at 120°C overnight.

Mechanical properties of the films were measured by Instron®. The tensile strength, elongation at break, and tensile modulus of the polymer III-a film of were 18 kg/mm^2, 27 %, and 728 kg/mm^2. Those of the polymer III-b film were 22 kg/mm^2, 75%, and 722 kg/mm^2. Polymer films of the containing pendent groups are not as tough and flexible because of its loose chain packing. The polymer III-b film containing ether linkages exhibited higher elongation about 75%, which implies good flexibility of the film. Polymer III-c and III-d films were so breakable they could not be measured.

CONCLUSION

The N-phenyl-2,3-imide cyclopentane-1,4-dicarboxylic acid (PCPA) was designed and synthesized as a new polycondensation monomer. A new class of cycloaliphatic-aromatic polyamides, having pendent imide groups, was successfully prepared by the direct polycondensation of PCPA and various diamines by means of triphenyl phosphite and pyridine. Most of the polyamides obtained are

characterized by a high solubility in aprotic solvent. The T_g's of polymers derived from PCPA and amines were in the range of 192–197°C. The melting endothermic peaks of polyamides appeared at around 302–313°C, interpreted as a melting process accompanied by decomposition. The mechanical properties of polymer III-a and III-b films are good due to their high molecular weights.

ACKNOWLEDGMENT

The authors are grateful to the National Research Laboratory (NRL) 2000 program (Plastic Optical Fiber) by the Korea Institute of Science and Technology Evaluation and Planning (KISTEP) for their financial support. This work was supported by the Research Fund of Hanyang University (Project No. HYU-98-014).

REFERENCES

1. Yaw-Terng; Wen-Liang, Wang. Macromolecules **1995**, *28*, 5554.
2. Jeong, H.J.; Kakimoto, M.A.; Imai, Y.J. Polym. Sci., Polym. Chem. Ed. **1992**, *29*, 1051.
3. Cimecioglu, A.L.; Weiss, R.A.J. Polym. Sci.: Polym. Chem. **1992**, *30*, 1051.
4. Yang, C.P.; Lin, J.H.J. Polym. Sci. Polym. Chem. Ed. **1994**, *32*, 423.
5. Yang, C.P.; Chen, W.T. Macromol. Chem. **1993**, *194*, 1595.
6. Jeong, H.J.; Oishi, Y., Kakimoto M.A.; Imai, Y. J. Polym. Sci. Polym. Chem. Ed. **1990**, *28*, 3293.
7. Korshak, V.V.; Rusanov, A.L.; Tugishi, D.S.; Cherkasova, G.M. Macromolecules **1972**, *5,* 807.
8. Akutsu, F.; Kataoka, T.; Naruchi, K.; Miura, M.; Nagakubo, K. Polymer **1987**, *28*, 1787.
9. Imai, Y.; Malder, N.N.; Kakimoto, M. J. Polym. Sci. Polym. Chem. Ed. **1985**, *23*, 797.
10. Jadhav, J.Y.; Preston, J.;, Kakimoto, M. J. Polym. Sci. Polym. Chem. Ed. **1989**, *23*, 1175.
11. Delaviz, Y.; Gungor, A.; MacGrath, J.E.; Gibson, H. Polymer. **1993**, *34*, 210.
12. Takayangi, M.; Katoyse, T. J. Polym. Sci. Polym. Chem. Ed. **1981**, *19*, 1133.
13. Yaw-Terng; Wen-Liang, Wang. Macromolecules. **1995**, *28*, 5554.
14. Sumio I.; Masao Y. Macromolecules. **1993**, *26*, 3493.
15. Srivasan R.; Prasad A. Polym. Prepr. **1991**, *32* (1), 174.
16. Morgan P., *Condensation Polymers by Interfacial and Solution Method*, Wiley: New York, 1965.
17. Morgan P.W.; Kwole S.L. Macromolecules. **1975**, *8*, 104.
18. Yamazaki N.; Higashi F.; Kawabata J. J. Polym. Sci. Polym. Chem. Ed. **1974**, *12*, 2143.
19. Yamazaki N.; Higashi F. Adv. Polym. Sci. **1981**. *38*, 1.
20. Higashi F.; Ogata S.I.; Aoki Y. J. Polym. Sci. Polym. Chem. Ed. **1982**, *20*, 2081.
21. Higashi F.; Goto M.; Kakinoki H. J. Polym. Sci. Polym. Chem. Ed. **1986**, *24*, 701.
22. Suh, Dong Hack; Chung, Eun Young. Angew. Makromol. Chem. **1998**, *254*, 33.

23. Suh, Dong Hack; Park, Sang Hyun. Korean Pat. No. 215093, 1999.
24. Suh, Dong Hack; Park, Sang Hyun;, Lee, Jae Wook. Korean Pat. No. 245229, 1999.
25. Suh, Dong Hack; Park, Sang Hyun; Lee, Jae Wook.Korean Pat. No. 221030, 1999.
26. Sumio I.; Masao Y.; Shinji T.; Toshihiko M.; Toshikazu K. Macromolecules **1993**, *26*, 3490.
27. Suh, Dong Hack; Park, Sang Hyun. US Pat. No. 591942, 1999.
28. Choi, Joong-Kwon; Chang, Young-Kil; Hong, Sung Yeap. Tetrahedron Letter. **1988**, *16*, 1967.
29. Yamazaki, N.; Higashi, F. J. Polym. Sci. Polym Chem. Ed. **1975**, *18*, 1373.
30. Arnold, F. E. In *The Materials Science and Engineering of Rigid Polymers*, Adams, W.W.; Eby, R.K.; Mclemore, D.E.. Eds., Materials Research Society, Pittsburgh, PA, 1989; 117.

Received August 28, 2000
Revision received November 14, 2000