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Synthesis and characterization of poly(amide imides) containing benzimidazole-rings

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Summary

New poly(amide imides) were prepared from benzimidazole-ring containing diamine *via* one-pot synthetic method. The diamine monomer, 6,4'-diamino-2-phenylbenzimidazole, was prepared from 4-nitrobenzoyl chloride and 4-nitro-1,2-phenylenediamine with 3 steps. It was found that the degree of imidization of the poly(amide imides) containing benzimidazole-ring can be controlled by monomer composition and solution imidization conditions. All partially imidized poly(amide imides) were soluble in polar aprotic solvent, but became insoluble in any organic solvents after thermal curing. The thermal stability of the poly(amide imides) increased as the polymers contain more benzimidazole units.

Introduction

One of the commercially available high performance polymers is poly(amide imides) (PAIs) that have amide and imide linkage in the main chain (1). As a result of the structural characteristics, PAIs have a property between aromatic polyamides and polyimides. Thermal stability of PAIs is less than that of polyimides but they are processable. Inserting a heterocyclic-ring into polymer chains generally increases thermal properties of polymers, but polymers become insoluble and infusible due to structural rigidity of the heterocyclic-rings. Therefore, introducing a flexible linking groups such as ether or kinked structure is inevitable to make rigid-rod polymers soluble and fusible (2). In this paper, we describe a synthesis and characterization of new PAIs which have rigid but kink-catenated benzimidazole-ring. Different imidization methods were employed and their effect on imidization degree and solubility of the polymers was also examined.

Experimental

Materials

Trimellitic anhydride acid chloride (TMAC) and 1,4-diazabicyclo [2,2,2]octane (DABCO) were sublimed at 65°C and 50°C, respectively. 4,4'-Diaminodiphenyl ether (ODA; Aldrich 99+%, sublimed) was used as received. N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methylpyrrolidinone (NMP) were stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure. Other commercially available

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reagent grade chemicals were obtained from Aldrich, Acros, and Junsei chemical company, and used without further purification.

General Measurement

^{1}H NMR and ^{13}C NMR spectra of synthesized compounds were recorded on Brucker Fourier Transform AC 200 or AM 300 spectrometers. Chemical shifts were reported in unit, parts per million (ppm) relative to the center line of the quintet at 2.49ppm for methyl sulfoxide-d_6. Splitting patterns designated as s (singlet), d (doublet), dd (doublets of doublet), m (multiplet), and br (broadened). FTIR spectra of the monomers and the polymers were obtained with Bomem Michelson series FTIR spectrphotometer using KBr pellet or film. Viscosities of polymer solutions were measured by a Canon-Ubbelohde type viscometer at 30°C. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system. DSC measurements were made using a closed cell at a heating rate of 10°C/min in N_2 atmosphere. TGA measurements were made at heating rate of 10°C/min in N_2 or air.

Monomer Synthesis

2'-amino-4,5'-dinitrobezanilide (1)

A solution of 4-nitro-1,2-phenylenediamine (15.1g, 98.6mmol) in 10.0g triethylamine, 100mL DMAc, and 100mL toluene was stirred at ambient temperature while a solution of 4-nitrobenzoyl chloride (18.3g, 98.6mmol) in 100mL toluene was added slowly. After stirring for 12hrs at room temperature, the product was mixed with 500mL distilled water and filtered. The precipitate was washed with hot water repeatedly and dried *in vacuo*. (27.3g, 91.6% yield): m.p. 247-248°C (lit.(3) 247-250°C). IR (KBr, cm^{-1}): 3434, 3332 (NH_2); 1652 (C=O); 1600, 1490 (aromatic); 1527, 1310 (NO_2). ^{1}H NMR (DMSO-d_6, ppm): 10.14 (s, 1H, -C(=O)NH-); 8.37-8.23 (dd, 4H); 8.13 (d,1H), 7.91(dd, 1H), 6.80 (d, 1H); 6.72 (s, 2H, -NH_2).

6,4'-dinitro-2-phenylbenzimidazole (2)

1 (23.0g, 76.1mmol) was grounded to a powder and added slowly to 300g of warm polyphosphoric acid with stirring mechanically. The mixture was slowly heated to 190°C, held at that temperature for 1hrs and allowed to cool to 100°C. The black solution was poured into 1L distilled water and stirred for 24hrs. The precipitate was filtered off, washed with hot water, and recrystallized from DMAc to give gray product. (19.7g, 91.1% yield): m.p. 356-357°C (lit.(3) 357-358°C). IR (KBr, cm^{-1}): 3339 (NH of benzimidazole); 1620, 1472 (C=N); 1590, 1500 (aromatic); 1518, 1329 (NO_2). ^{1}H NMR (DMSO-d_6, ppm): 13.70 (br, 1H, -NH- of benzimidazole); 8.40-8.30 (dd, 4H); 8.34 (d,1H), 8.11(dd, 1H), 7.77 (d, 1H).

6,4'-diamino-2-phenylbenzimidazole (3)

A slurry of **2** (8.50g, 30.0mmol), $SnCl_2$ (40g, 210mmol), and 100mL 95% EtOH was stirred while 70mL concentrated HCl was added slowly. After all the HCl was added, the mixture was refluxed for 12hrs. Excess EtOH was evaporated, and then the solution was poured into 300mL distilled water, and basified with 10% NaOH solution. The precipitate was filtered off, washed with hot water and cold MeOH, and recrystallized from DMF/H_2O (v/v=1:3) to give brown product. (4.95g, 73.6% yield): m.p. 217-220°C (lit.(3) 220°C with decomposition). IR (KBr, cm^{-1}): 3392, 3302 (NH_2): 1623, 1475 (C=N): 1609, 1445 (aromatic). ^{1}H NMR (DMSO-d_6, ppm, 300MHz): 11.90 (br, 1H); 7.80, 7.77, 6.67, 6.64 (q, 4H); 7.20 (d,1H), 6.65(dd, 1H), 6.50 (d, 1H); 5.51 (s, 2H), 4.83 (br, 2H).

Polymer Synthesis

Synthesis of poly(amide imdes) by one-pot method (**4a**, **5a**, **6a**, **7a**, and **8a**)

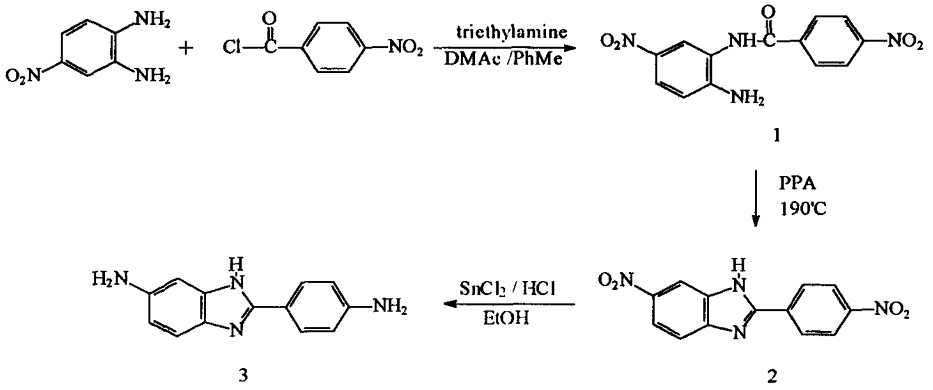
All PAIs were prepared according to the following one-pot procedure. A suitable 3-neck round-bottomed flask was charged with equimolar amount of TMAC and diamine monomer (the mixture of **3** and ODA). The polymer concentration was controlled to approximately 10 wt% in NMP. The mixture was stirred mechanically under N_2 at 80°C for 2hrs. During this period, The solution became yellow to brown. After DABCO was added to the solution, temperature was slowly raised up to 190°C and excess xylene as an azeotroping reagent was azeotroped. The mixture was stirred at 190°C for 8hrs, and poured into excess water to precipitate yellow or brown flake. The precipitate was filtered, washed with hot water, methanol, acetone, and dried *in vacuo* at 140°C for 24hrs. (quantitative yields for all cases). The films were obtained by casting of 5 wt% DMF solutions. These solutions were cast on glass plates and heated *in vacuo* at 100°C for 12hrs.

Thermal curing of the poly(amide imides) (**4b**, **5b**, **6b**, **7b**, and **8b**)

The poly(amide imides) powder obtained from the above procedure were cured by heating to 340°C for 2hrs and then additional 1hr at 340°C under a flow of N_2.

Results and discussion

Benzimidazole-ring containing diamine monomer, 6,4'-diamino-2-phenylbenzimidazole (**BIA**, **3**) was prepared according to the reported procedure as shown in Scheme 1 (3). 4-Nitro-1,2-phenylenediamine reacted with an equimolar amount of 4-nitrobenzoyl chloride at room temperature in the presence of triethylamine as an acid acceptor to yield 2'-amino-4,5'-dinitrobezanilide (**1**). This step was found to give only one product, because the nitro group predominantly deactivates the amino group at para position. Amide linkage was formed by the amino group of meta position to the nitro group in 4-nitro-1,2-phenylenediamine in the reaction condition employed. The benzanilide **1** was cyclo-dehydrated to the benzimidazole derivative **2** by gradual heating to 190°C of a solution of **1** in polyphosphoric acid. Dinitro compound **2** was hydrogenated with stannous chloride and HCl to give corresponding diamine monomer **3**. The overall yield of this three-step process was over 60%.



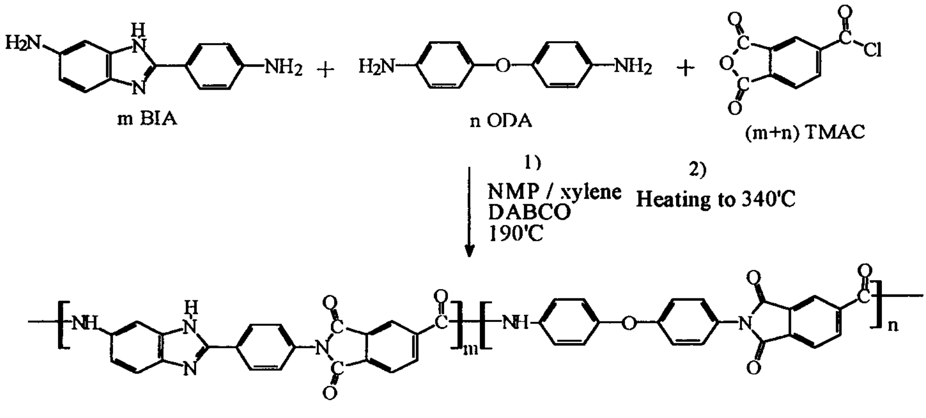
Scheme 1.

Table 1. Viscosities and imidization temperature of the PAIs.

Compds. Number	PAI	BIA contents (m) (%)	ODA contents (n) (%)	[η] [a] (dL/g)	Temperature of exothermic peaks (°C)
4	**PAI1**	100	0	0.47	326, 346
5	**PAI2**	75	25	0.56	327, 339
6	**PAI3**	50	50	0.57	325, 339
7	**PAI4**	25	75	0.69	311
8	**PAI5**	0	100	0.97	288

[a] Intrinsic viscosity in DMF (0.5 g/dL) at 30°C.

The poly(amide imides) were synthesized from **3** with 4,4'-diaminodiphenyl ether (ODA) and trimellitic anhydride acid chloride (TMAC). (Scheme 2.) Precipitation was not occurred during polymerization in all cases. Polymers obtained as yellow or brown fibrous precipitates (**4a**, **5a**, **6a**, **7a**, and **8a**) were thermally cured by successive heating to 340°C under a flow of N_2 to imidize the polymers completely (**4b**, **5b**, **6b**, **7b**, and **8b**). In the case of homopolymerization of **BIA** with **TMAC**, the PAIs were obtained with three different ways to examine the effect of reaction conditions on degree of imidization. First, the polymerization method previously described was used, but with different reaction time, 14hrs at 190°C. The powdery product, **4c**, obtained by precipitation of the reaction mixture in water was thermally cured by successive heating to 340°C under a flow of N_2 to obtain completely imidized polymer, **4d**. Second, to obtain wholly imidized poly(amide imide) in solution state, the same polymerization method was used except using *p*-toluenesulfonic acid as a catalyst for imidization (**4e**). Generally, imidization is catalyzed by strong acids (4), and the use of a strong acid catalyst can promote an imidization resulting in wholly imidized PAI in solution state. However, in this case, the precipitation was formed during imidization. Third, to compare solution-imidized polymers with thermal-imidized polymers, the film of the poly(amide amic acid) (PAAC) was prepared, and cyclodehydrated by successive heating of the films up to 340°C under stream of N_2 (**4f**).



Scheme 2.

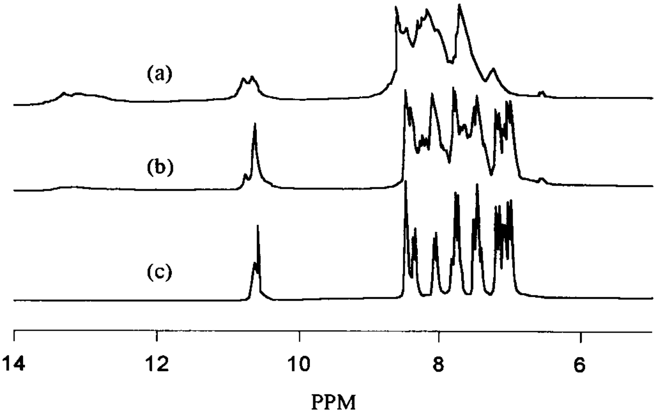


Figure 1. ^{1}H NMR spectra of PAIs; (a) **4c**, (b) **6a**, (c) **8a**.

The formation of PAIs was confirmed by FTIR spectroscopy. The FTIR spectra of the all polymers show the characteristic absorption bands of amide bonds at 3350-3200, 1650, and 1160 cm^{-1} (N-H stretching, C=O stretching of amide, C-N stretching of amide, respectively) as well as the characteristic absorption bands of imide bonds at 1775, 1710, 1360, and 720 cm^{-1} (C=O assymetric and symmetric stretching of imide, C-N stretching of imide, C=O bending of imide, respectively). The intensity of absorption bands of 1470 (C=N stretching of benzimidazole) and 1225 cm^{-1} (C-O-C stretching) are varied in proportion to contents of **BIA** and **ODA**. ^{1}H NMR spectra of the synthesized polymers are shown in Figure 1.

The intrinsic viscosities of the polymers prepared by one-pot synthetic method were between 0.47 to 0.97 dL/g (Table 1.). However, **4e** have very low intrinsic viscosity (0.29 dL/g) due to premature precipitation of the polymers during polymerization. The polymers (**4c**, **5a**, **6a**, **7a**, and **8a**) gave flexible films on casting except **4a**, **4e**, and **4f** that have relatively low degrees of polymerization. The films of **4a**, **4e**, and **4f** were brittle.

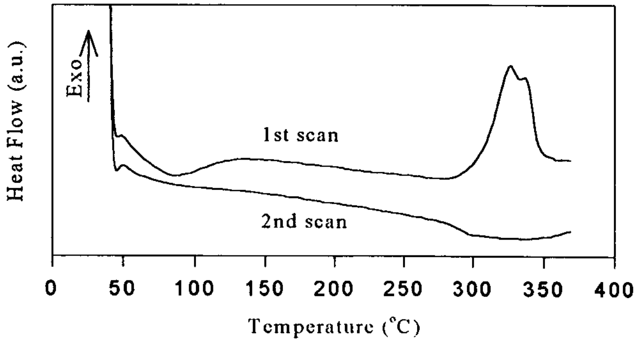


Figure 2. The DSC scans of poly(amide imide) **3a**.

It was found that the polymers synthesized from one-pot synthesis were not fully imidized from DSC analysis except **4e** which was imidized with an acid catalyst. The polymers show the exothermic peak at 288-348°C in the first scan, but this peak was disappeared in the second scan (Figure 2.). The exothermic peak temperature increased as the **BIA** contents of the polymers increased probably because of increased chain rigidity that requires higher imidization temperature. The degree of imidization of the polymers prepared by one-pot synthetic method was examined with FTIR in detail by comparing the intensity of absorption band at 1370 cm^{-1} (5). The internal aromatic absorption bands was used as reference to normalize the intensity of imide-ring. The 1500 cm^{-1} band were used as a reference in all case except **4**. In the case of **4**, 1472 cm^{-1} band (C=N stretching of benzimidazole) were used as a reference instead of 1500 cm^{-1} because phenyl-ring region (1500cm^{-1}) was not clearly resolved. The degree of imidization of polymers prepared by one-pot synthetic method were 74.1, 76.5, 80.3, 84.4, and 97.7% for **4a**, **5a**, **6a**, **7a**, and **8a**, respectively. It was reported that benzimidazole-ring has a catalytic activity on the imidization reaction (6). Therefore higher degree of imidization was expected for the polymer with more benzimidazole units under the same reaction conditions. However, the degree of imidization of the PAIs prepared in this study was mainly affected by the chain rigidity rather than by the catalytic activity of benzimidazole-ring. The more flexible **ODA** units incorporated in the polymer, the higher degree of imidization occurred with same reaction time. The **4e** treated with *p*-toluenesulfoninc acid as an acid catalyst showed complete imidization by FTIR measurement. The degree of imidization of **4a** and **4c** that were prepared by same one-pot synthetic method but with different imidization time (8hrs and 14hrs at 190°C) were 74.1, and 93.1%, respectively. The above results indicate that the degree of imidization of the soluble PAIs containing benzimidazole can be controlled by monomer composition and solution imidization conditions. The T_g of the polymers are 346, 318, 291, 284, and 279°C for **4d**, **5b**, **6b**, **7b**, and **8b**, respectively (Figure 3). 5% weight loss temperatures of the polymers are 510, 489, 493, 484, and 486°C in N_2 for **4d**, **5b**, **6b**, **7b**, and **8b**, respectively (Figure 4.). The results shows the trends that the thermal stability and rigidity of the polymers increased as the polymers contain more **BIA** units.

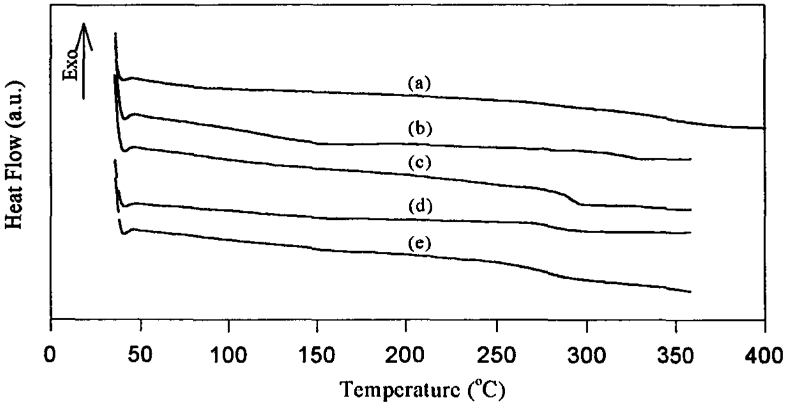


Figure 3. DSC Curves of the PAIs; (a) **4d**, (b) **5b**, (c) **6b**, (d) **7b**, (e) **8b**.

Table 2. Solubility of PAIs in various solvents. [a]

PAI	DMAc	DMF	NMP	DMSO	*m*-cresol	CL [b]	acetone	H_2SO_4
4a	+	++	+	++	++	-	-	++
4c	-	+	+	+	+	-	-	++
4e	+	+	+	++	+	-	-	++
4f	-	-	-	-	-	-	-	+
5a	+	++	++	++	++	-	-	++
6a	++	++	++	++	++	-	-	++
7a	++	++	++	++	++	-	-	++
8a	++	++	++	++	++	-	-	++

[a] (++) Soluble at room temperature; (+) partially soluble at room temperature but wholly soluble at elevated temperature; (-) insoluble.
[b] chlorobenzene.

The solubility of the poly(amide imides) are tested in various solvents, and the results were summarized in Table 2. All PAIs prepared by one-pot synthetic method were soluble in polar aprotic solvents such as NMP, DMF, DMAc, and DMSO, and phenolic solvents such as *m*-cresol. These polymers exhibited better solubility in proportion to the **ODA** contents due to reduced chain rigidity with incorporation of more flexible **ODA** units than **BIA** units. But polymers after curing were not soluble in any organic solvents except in strong acids such as concentrated H_2SO_4.

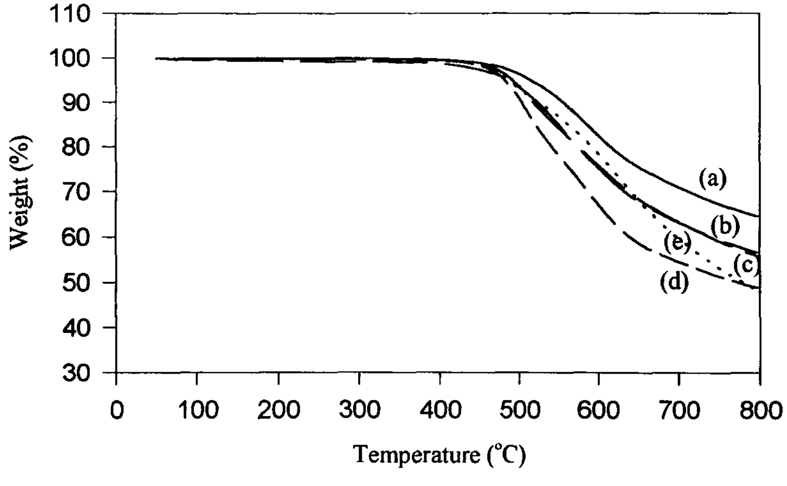


Figure 4. TGA curves of the PAIs; (a) **4d**, (b) **5b**, (c) **6b**, (d) **7b**, (e) **8b**.

Conclusions

Soluble poly(amide imides) with benzimidazole-ring were prepared through solution polymerization and imidization. The soluble polymers were partially imidized and the degree of imidization was effected by monomer composition and imidization conditions such as reaction time and presence of acid catalyst. In the same reaction condition, the imidization was mainly influenced by the rigidity of the polymer chains rather than by catalytic activity of benzimidazole-rings on imidization. The polymer became insoluble after thermal curing. The thermal stability of the polymers increases as the more benzimidazole-ring is involved in main chains.

References

1. Abajo J (1992) In: Kircheldorf HR (Ed) Handbook of Polymer Synthesis, Marcel Dekker New York pp961-964
2. Critchley JP, Knight GJ, Wright WW (1983) Heat Resistant Polymers, Plenum Press New York
3. Prost LW (1974) Canadian Patent 950,146
4. Novikova SW, Shablygin MV, Sorokin VE, Oprits ZG (1979) Khim. Volokna 3: 21
5. Pryde CA (1989) J Polym Sci Chem 27: 711
6. Nelson A, Guerra G, Williams DJ, Karasz FE, MacKnight W (1988) J Appl Polym Sci 36: 243