

Syntheses of New Film-Forming Aromatic Poly(amide-imide)s Containing Isoindoloquinazolinedione Unit in the Backbone: Poly(biphenylphthalicdianhydride-oxydianiline-4,4'-diamino-3'-carbamoyl-benzanilide) (Poly(BPDA-ODA-DACB))

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Abstract: New film forming aromatic poly(amide-imide)s containing isoindoloquinazolinedione (IQ) unit in the backbone chain (polymer XIV) have been successfully synthesized by preparing prepolymers of poly(amic acid-carbonamide), followed by subsequent thermal cyclization of the prepolymers. 4,4'-Diamino-3'-carbamoylbenzanilide (DACB) V has been synthesized by reduction of 3'-carbamoyl-4'-amino-4-nitrobenzanilide IV. The prepolymers of poly(amic-acid-carbonamide) (polymers VII and VIII) which exhibit viscosities ranging from 1.4 to 1.7 dl/g have been prepared by a condensation polymerization of monomers such as BPDA, ODA, and DACB. Polymer XIV has been obtained by thermal cyclization of the polymers VII and VIII. During the thermal cyclization reaction, imide ring structure was first introduced and then transformed to the structure of IQ unit. The thermal degradation rate of the resultant polymers were influenced by the cleavage of amide bond but the final char yield was comparable to that of poly(BPDA-ODA).

Keywords: New film forming poly(amide-imide)s, Isoindoloquinazolinedione (IQ), 4,4'-Diamino-3'-carbamoylbenzanilide (DACB), Poly(biphenylphthalicdianhydride-oxydianiline-4,4'-diamino-3'-carbamoyl-benzanilide) (Poly(BPDA-ODA-DACB))

Introduction

In recent years, applications in various fields of high technology require high performance films of better mechanical and thermal properties than those of polyester. Liquid crystalline polymers, such as poly(p-phenylene terephthalamide) (PPTA) and some polyimides, have thus emerged as promising materials for the formation of high performance films[1-3]. However, these polymers have some drawbacks in processability. Indeed, one of the problems involved in making PPTA films is that the corresponding polymers of high molecular weight are difficult to dissolve in organic solvents and, as a consequence, a strong inorganic acid, such as concentrated sulfuric acid, must be used as the solvent. In order to overcome these problems, chemical modification of PPTA molecules has been attempted by copolymerization of a unit containing halogen groups[1,4-8] or other types of substituents on the aromatic nucleus of a linearly para-oriented aromatic polyamide[2,9-11]. From the modified soluble polymer could be obtained a transparent and homogeneous film which has, however, somewhat poor thermal properties due to the comonomers or substituents introduced. It has thus been suggested for the production of a film with both good processability and high thermal resistance that the aromatic polyamide should be modified by introducing the cyclic side substituents containing polar groups[3,12]. However, Hitachi Co. has recently commercialized a new

polyimide which has much improved thermal and chemical resistance by the introduction of isoindoloquinazolinedione (IQ) units in the polyimide structure[13,14]. Kurihara has also reported a thermally stable poly(IQ) resulting from the reaction of aromatic diamidodiamines, such as 5,5'-bis-(2-aminobenzamide) and 5,5'-methylene-bis(2-aminobenzamide), with pyromellitic dianhydride in N-methyl-2-pyrrolidone (NMP) solution[15,16].

The facts mentioned above tempted us to synthesize a new aromatic poly(amide-imide) by introducing IQ unit directly into the polyamide backbone chain rather than as a side substituent. So, this paper reports the successful results of the syntheses of new aromatic poly(amide-imide)s with which we can expect to cast a film of high chemical and thermal resistance.

Experimental

Chemicals

Dimethylacetamide (DMAc) was shaken over barium oxide for 2 days, followed by high vacuum distillation. 2-Chloro-5-nitrobenzoic acid was used after recrystallization from ethanol. Benzoyl chloride was distilled under reduced pressure. Lithium chloride (LiCl) was dried at 200°C in high vacuum. Terephthaloyl chloride, biphenylphthalic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) were used after sublimation. Pyromellitic dianhydride (PMDA) was used after recrystallization in acetic anhydride and subsequent sublimation. N-methyl-2-pyrrolidone (NMP) was stirred with benzene, then

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vacuum distilled. Pyridine was dried by refluxing with sodium, followed by fractional distillation.

Synthesis of 5-nitroisatoic Anhydride (I)

Into 250 ml of fuming HNO_3 ($d=1.5$) cooled to $0\sim 5^\circ\text{C}$ was added 100 g of isatoic anhydride in proportions of 10 g. During addition, reaction products precipitated over 1.5 hrs. After complete addition, the reaction mixture was stirred vigorously with a mechanical stirrer for 2 hrs at $0\sim 5^\circ\text{C}$. The precipitate was filtered, washed with distilled water, and weighed to yield 118 g (yield 92.5%). Compound **I** was purified by recrystallization from a mixture of ethanol and acetone (II) (m.p. 283.5°C).

Synthesis of 5-aminoisatoic Anhydride (II)

1 g of Pd/C (10%) and 20 g of compound **I** was added to 250 ml of ethanol, and then **II** was reacted at $60\sim 70^\circ\text{C}$ for 4 hrs in an autoclave under a pressure of 20 kg/cm^2 with purging of hydrogen gas. The product was dissolved in DMAc to filter the catalyst off and then vacuum-dried at 50°C to obtain 16.1 g of product (yield 94.0%) (m.p. 233.5°C).

Synthesis of 4-(p-nitrobenzamido)-1,2-isatoic Anhydride (III)

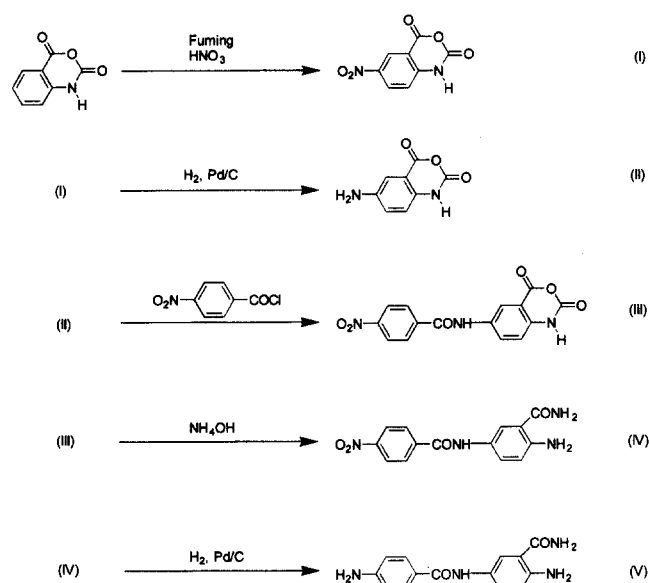
5 ml of pyridine was added under a nitrogen atmosphere to 300 ml of DMAc kept at $5\sim 10^\circ\text{C}$. Then, 19.3 g (0.108 mol) of compound **II** was dissolved with stirring. When 20.1 g (0.108 mol) of 4-nitrobenzoyl chloride was added all at once with vigorous stirring, the yellow precipitate formed promptly a paste. After the completion of the reaction for 6~7 hrs with stirring, **III** was poured into water to obtain a precipitate which was filtered, washed, and vacuum dried to obtain 31 g of product (yield 82.7%) (m.p. 330.6°C).

Synthesis of 3'-carbamoyl-4'-amino-4-nitrobenzanilide (IV)

200 ml of 28% aqueous ammonium hydroxide solution saturated with ammonium acetate was cooled to $5\sim 10^\circ\text{C}$, and then 18.8 g (0.0574 mol) of compound **III** was added to the solution with mechanical stirring for 1 day. After neutralization of the reaction solution with concentrated HCl, the precipitate was filtered, washed, and dried to yield 16.3 g of **IV** (yield 95%) (m.p. 230.7°C).

Synthesis of 4,4'-diamino-3'-carbamoylbenzanilide (DACB) (V)

20 g (0.0666 mol) of compound **IV** and 1 g of Pd/C (10%) was added to 250 ml of ethanol, and then reduced at $60\sim 70^\circ\text{C}$ for 4 hrs in an autoclave under a pressure of 20 kg/cm^2 with hydrogen gas. After filtration, the reaction product was dissolved in DMAc to filter off the catalyst. From the evaporation of DMAc, 13.2 g of crude product (yield 73.3%) was obtained. After this product was poured into distilled water to obtain a precipitate, the addition of HCl to make



Scheme 1. Reaction scheme for the synthesis of DACB.

$\text{pH}=12$ made the precipitate dissolve to yield a clear solution. This solution was then filtered and treated with activated carbon in order to decolorize it. Further addition of HCl to the filtered solution produced a HCl salt as a precipitate. This was filtered, dissolved again in water, and neutralized with Na_2CO_3 solution until a new precipitate formed. After washing enough to make the precipitate neutral, the precipitate was filtered and vacuum dried (m.p. 190.6°C).

The overall reaction is summarized in synthetic scheme 1.

Preparation of Aromatic Poly(amide-imide)s Containing IQ Unit in the Chain Backbone

Poly(BPDA-ODA) (VI)

1.822 g (9.10 mmol) of ODA was dissolved in 30 ml of NMP containing 0.15 ml of pyridine in a stream of nitrogen at room temperature. With vigorous stirring, 2.678 g (9.10 mmol) of powdered BPDA was added all at once at room temperature to make the solution viscous after 1 hr.

Poly(BPDA-ODA(75)/DACB(25)) (VII)

1.320 g (6.59 mmol) of ODA and 0.594 g (2.20 mmol) of DACB was dissolved in 30 ml of DMAc containing 1.5 ml of pyridine in a stream of nitrogen at room temperature. With vigorous stirring, 2.586 g (8.79 mmol) of biphenylphthalic anhydride was added at once at room temperature. The solution became viscous after 3 hrs.

Poly(BPDA-ODA(50)/DACB(50)) (VIII)

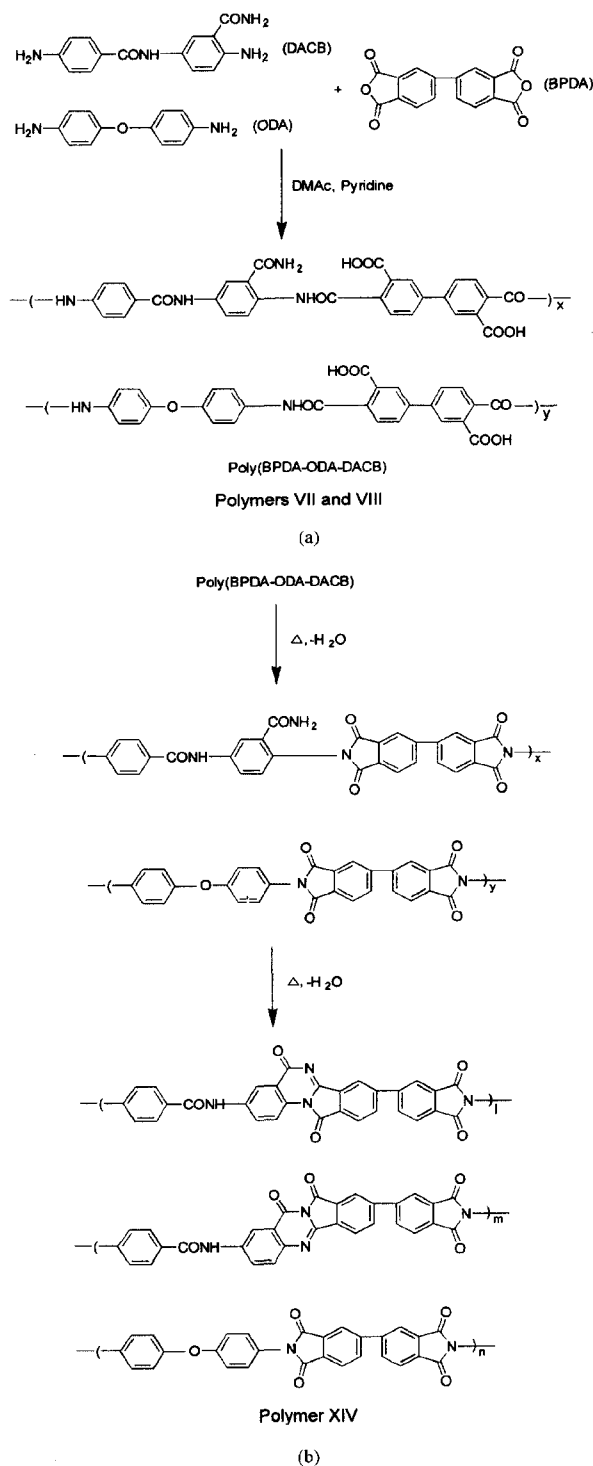
0.589 g (2.94 mmol) of ODA and 0.795 g (2.94 mmol) of DACB was dissolved in 30 ml of NMP containing 0.15 ml of pyridine in a stream of nitrogen at room temperature. With vigorous stirring, 1.731 g (5.88 mmol) of BPDA was added all at once at room temperature. The solution then became

viscous after about 3 hrs.

Preparation of Model Compounds

Synthesis of Isoindoloquinazolidione (IX)

N-phthaloyl-2-amino-benzamide was heat treated at



Scheme 2. Synthetic route of poly(amide-imide-IQ).

250°C for 1.5 hrs in the presence or absence of LiCl and the product was then recrystallized in acetone/hexanone and acetone, respectively (m.p. 220~221°C). Elemental analysis: theoretical; C 72.58% H 3.25% N 11.28%, found; C 72.44% H 3.26% N 11.23%. IR(KBr); 1779, 708 cm^{-1} (imide carbonyl), 1640 cm^{-1} (isoindoloquinazolidione imine stretching), 1364, 1352 cm^{-1} (isoindoloquinazolidione C-N).

Synthesis of Imide-isoindoloquinazolidione (X)

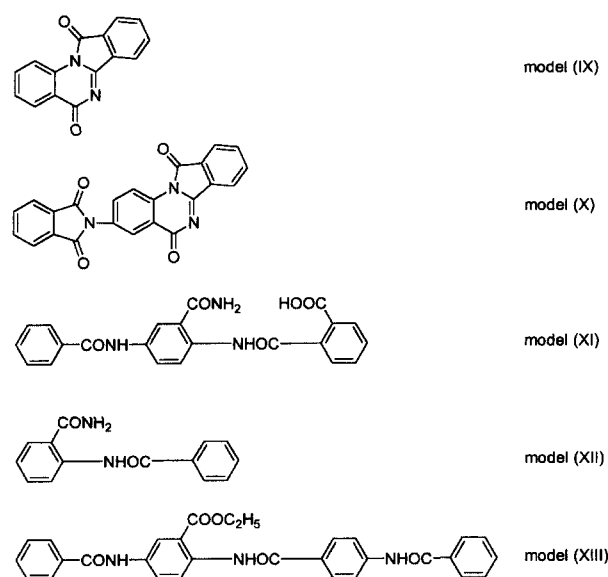
0.5 g (3.3 mmole) of 2,5-diaminobenzamide dissolved in NMP of 10 ml was reacted under nitrogen purging with 0.98 g (6.6 mmole) of phthalic anhydride at room temperature for 1.5 hrs and the solution was then refluxed for 3 hrs. The obtained precipitate was subjected to the order of filtering, washing with, drying, and recrystallization in NMP. Elemental analysis: theoretical; C 70.23% H 2.82% N 10.68%, found; C 70.31% H 2.82% N 10.74%. IR(KBr); 1786, 720 cm^{-1} (imide carbonyl), 1383 cm^{-1} (imide C-N), 1637 cm^{-1} (isoindoloquinazolidione imine stretching), 1360 cm^{-1} (indoloquinazoline =C-N-).

Other model compounds such as 4'-(2-carboxybenzamido)-3'-carbamoylbenzanilide (XI), N-benzoyl-2-aminobenzamide (XII), and 4,4'-dibenzamido-2'-ethoxycarbonylbenzanilide (XIII) were also synthesized following the methods described elsewhere[17].

Scheme 3 summarizes the structures of the abovementioned model compounds.

Thermal Cyclization

Both of prepolymer, poly(amic-acid-carbonamide), and the model compounds were put into a test tube, and cyclized



Scheme 3. Chemical structures of the model compounds used in this study.

by heating at specified temperatures under a nitrogen atmosphere to obtain aromatic poly(amide-imide)s (polymer XIV) containing IQ units in the chain backbone.

Characterization

A Perkin Elmer FTIR spectrometer 1760X was used to examine whether or not DACB was successfully synthesized and to monitor the process of thermal cyclization of new aromatic poly(amide-imide)s.

NMR spectra of synthesized monomers and resultant polymers have been recorded at room temperature on a Bruker FT-NMR (200 MHz) spectrometer in DMSO- d_6 or $CDCl_3$ with tetramethylsilane (TMS) as an internal standard.

The inherent viscosities of prepolymers, i.e. poly(amic-acid-carbonamide) and poly(amide-imide), have been measured with an Ubbelohde viscometer at 30°C in 97% H_2SO_4 and DMAc at the concentration of 0.5 g/100 ml, respectively.

Results and Discussion

Figures 1 and 2 illustrate the spectra of the synthesized monomer, DACB, obtained from NMR and FTIR spectroscopy, respectively. It can be seen clearly from Figure 1 that, in

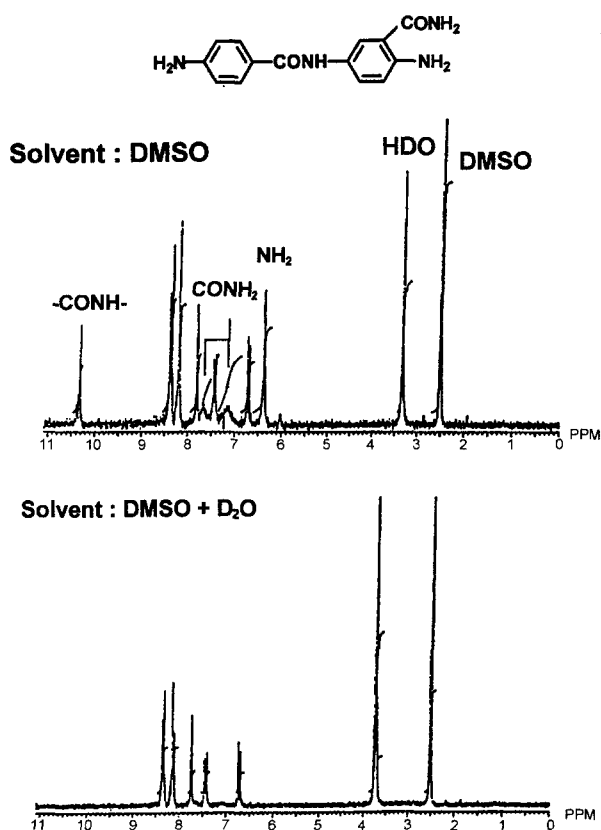


Figure 1. NMR spectra of DACB.

DMSO- d_6 solution, chemical shifts of protons in DACB appear at 6.4 and 6.7 ppm for NH_2 , 10.4 ppm for CONH groups, and 7.1 and 7.7 ppm for $CONH_2$, whereas proton resonances by amine and amide groups disappear in DMSO- D_2O . An FTIR spectrum shows characteristic absorption bands indicating the presence of amide and amine groups at 3,100 to 3,500 cm^{-1} (see Figure 2). From the spectral analysis, it can be concluded that the monomer, DACB, has been successfully synthesized.

Table 1 lists the inherent viscosities of the obtained poly(amic-acid-carbonamide)s. The viscosities range from 1.4 to 1.7 dl/g, which suggests that tough films may be cast from the obtained prepolymers. Indeed, a tough and transparent film can be cast directly from the solution of poly(amic-acid-carbonamide). When a thin film attached to an aluminum frame was heat treated at a specified temperature, the structure change was monitored with FTIR spectroscopy.

Figure 3 shows the spectral change of poly(BPDA-ODA) with heat treatment temperature. It is clearly shown that imidization starts at 150°C as confirmed from the appearance of cyclic imide carbonyl absorption bands at 1,720 cm^{-1} and 1,779 cm^{-1} , and a C-N stretching absorption band of imide ring at 1,378 cm^{-1} ; the peak intensities become strong with increasing the heat-treatment temperature.

On the other hand, Figure 4 which shows the FTIR spectral changes of poly(BPDA-ODA-DACB) with heat treatment, indicates a slight shift of cyclic imide carbonyl

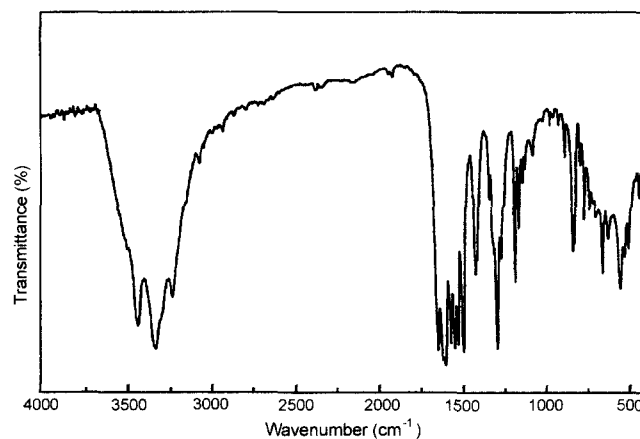


Figure 2. FTIR spectrum of DACB.

Table 1. Inherent viscosity of poly(amic-acid-carbonamide)

Polymer	Inherent viscosity (dl/g)
Poly(BPDA-ODA)	1.4 ^{a)}
Poly(BPDA-ODA(75)-DACB(25))	1.7 ^{b)}
Poly(BPDA-ODA(50)-DACB(50))	1.4 ^{a)}
Poly(BPDA-DACB)	1.4 ^{b)}

^{a)}Measured at 30°C in NMP and with 0.5% concentration.

^{b)}Measured at 30°C in DMAc and with 0.5% concentration.

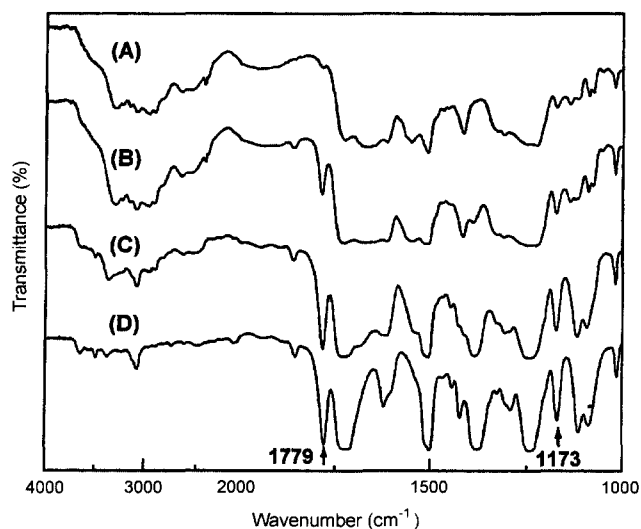


Figure 3. FTIR spectra of poly(BPDA-ODA); (A) control, (B) 150°C×1 hr, (C) 200°C×1 hr, and (D) 270°C×1 hr.

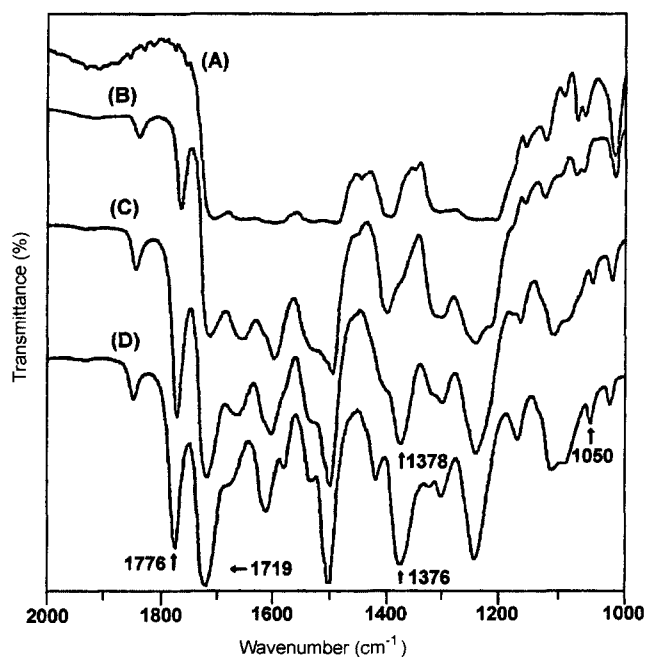


Figure 4. FTIR spectra of poly(BPDA-ODA-DACB); (A) control, (B) 150°C×1 hr, (C) 200°C×1 hr, and (D) 270°C×1 hr.

absorption bands to 1,719 cm^{-1} and 1,776 cm^{-1} , and the C-N stretching band to 1,376 cm^{-1} . The shift of the C-N band towards lower wave numbers suggests the superposition of a C-N band from an imide ring and from the formation of an IQ ring in the polymer backbone chain. In fact, depending on the heat treatment temperature, the backbone structure of polymer is expected to be of various forms of ring structures such as imide, quinazolone and benzoxazinone. It may thus be appropriate at this juncture to examine in detail the

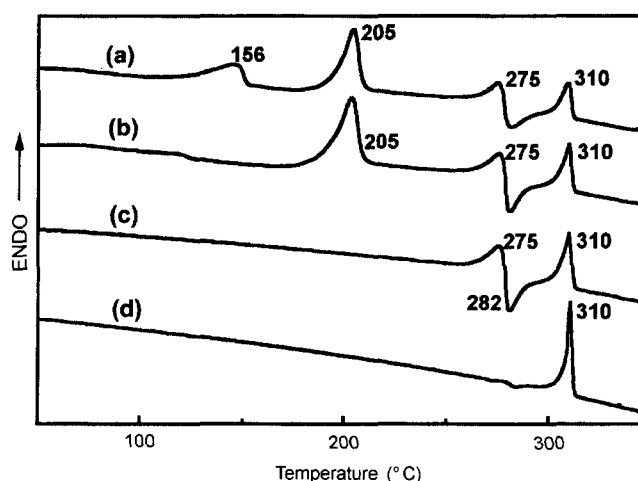
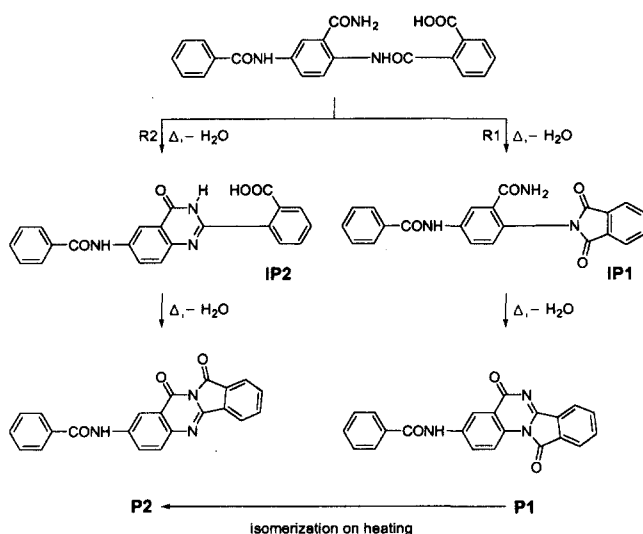


Figure 5. Variation of DSC thermogram of the model compound XI with heat treatment. (a) untreated, (b) 170°C×1 hr, (c) 250°C×1 hr, and (d) 290°C×1 hr.

formation of IQ ring unit in the chain backbone using some model compounds. As mentioned earlier, in the case of the model compound IX, isoindoloquinazolinone, the absorption band of cyclic imide carbonyl was at 1779 cm^{-1} and C-N band of isoindoloquinazolinone at 1352, 1364 cm^{-1} . For the model compound X, imide-isoindoloquinazolinone, the absorption bands of imide carbonyl and imide C-N appeared at 1786 cm^{-1} and 1383 cm^{-1} , respectively. In addition, C-N peak of isoindoloquinazolinone appeared at 1360 cm^{-1} which is considerably lower than that of imide C-N. This observation suggests that, on the heat treatment of precursor polymers VII and VIII, the absorption bands of imide and isoindoloquinazolinone may appear at the range of 1345~1380 cm^{-1} , but the absorption of the latter be slightly at lower wavenumber than that of the former. Indeed, when the precursor polymers was heat treated at a specified temperature, the characteristic absorption bands of imide start to appear at 1776, 1719 cm^{-1} (symmetric stretching vibration of carbonyl) and 1379 cm^{-1} (stretching C-N vibration) (see Figure 4). With increasing temperature of heat treatment, the intensities of these peaks become stronger and the peak position of C-N band shifts to lower wavenumber, 1376 cm^{-1} . This is a clear indication of the formation of IQ as well as a further imidization, and is in good agreement with the result observed from the model compounds. The discrepancy in the peak positions of IQ between the model compound and the polymer may be attributed to the influence of biphenylene unit in the backbone structure.

From the above discussion, it can be concluded that the imide unit is first introduced by heat treatment at 150°C and after then IQ unit is formed on the heat treatment above 200°C. This structural formation process can also be confirmed with DSC thermograms of the model compound XI (see



Scheme 4. Ring structure formation by heat treatment of the model compound XI.

Figure 5). The endothermic peaks at 146, 205, and 275°C can be attributed to the melting points of the compound XI, intermediate product (IP1) containing imide unit formed by the reaction between amide and carboxyl groups, and another intermediate product (P1) containing IQ unit, respectively. The only exothermic peak at 282°C is supposed to arise from the isomerization of IQ to a more stable form P2, and the peak at 310°C is thus the melting point of the compound P2. Depending on the reaction route, the compound P2 can also be formed from the other intermediate compound IP2 as shown in Scheme 4. The possibilities for this reaction route and the formation of benzoxazinone ring have been reported from the study of synthesizing 2-phenyl-4-(3H)-quinazolinone from the model compound XII and 2-(4-benzamidophenyl)-6-benzamido-3,1-benzoxazinone-4-one from the model compound XIII, respectively[17]. Figure 5 reveals that with the heat treatment temperature develops the structure gradually from IP1 or IP2, P1 and finally to P2, and this is in good agreement with the results of FTIR spectroscopy mentioned earlier. So, based on these results, the overall structural changes of poly(BPDA-ODA-DACB) by heat treatment can be presented as in Scheme 2.

It was found from thermogravimetric analysis (data not shown) of poly(BPDA-ODA-DACB) and poly(BPDA-ODA) that the precursor polymer shows the first weight loss due to cyclization from 150 to 250°C and the second one at 580°C due to degradation. The decomposition onset temperatures of the heat treated poly(BPDA-ODA) and poly(BPDA-ODA-DACB) at 270°C for 3 hrs are 584°C and 566°C, respectively. This implies that the imide unit itself does not increase the onset temperature since the thermal degradation is governed by thermal cleavage of amide bond.

Conclusions

New film forming aromatic poly(amide-imide)s containing IQ unit in the backbone chain have been successfully synthesized by preparing prepolymers of poly(amic-acid-carbonamide)s, followed by the subsequent thermal cyclization of the prepolymers. The prepolymers which exhibit viscosities ranging from 1.4 to 1.7 dl/g, have been prepared by a condensation polymerization of monomers such as BPDA, ODA, and DACB. It has been expected that a tough aromatic polyamide film of high chemical and thermal resistance can be cast since the prepolymer is soluble in DMAc and NMP. It is imperative to synthesize beforehand the monomer, DACB, in order to enhance solubility of the prepolymer and to introduce subsequently the IQ unit in the chain backbone of aromatic polyamides by thermal cyclization. During the thermal cyclization reaction, imide ring structure was first introduced and then transformed to the structure of IQ unit. The thermal degradation rate of the resultant polymers were influenced by the cleavage of amide bond but the final char yield was comparable to that of poly(BPDA-ODA).

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