Hydroxy-Substituted Polyenaminonitrile as a Soluble Precursor for Rigid-Rod Polybenzoxazole

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(1-Chloro-2,2-dicyanovinyl)benzene or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene was reacted with 2-aminophenol to give the model compound, hydroxy enaminonitrile, which was found to undergo thermal cyclization reaction to form the corresponding benzoxazole. This intramolecular cyclization reaction is expected to occur through nucleophilic attack to electropositive enamine carbon by ortho-hydroxy group on the phenyl ring, which is accompanied by the release of neutral malononitrile through rearrangement. From each bifunctional monomer, *o*-hydroxy substituted polyenaminonitrile was prepared and characterized as a new precursor polymer for well-known aromatic polybenzoxazole. Also the unusual macrocyclic dimer formation from the 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane polymerization reaction system was discussed. The thermal cyclization reactions and the properties of polymers were investigated using FT-IR and thermal analysis (DSC & TGA).

Keywords : Polyenaminonitrile, Thermal cyclization, Soluble precursor, Condensation polymer, Polybenzoxazole.

Introduction

A useful analogy between dicyanomethylidene, $=C(CN)_2$, and the carbonyl oxygen was pointed out early by Wallenfells.[1] The two units have similar inductive and resonance effects, and many well-known reactions with carbonyl groups have been shown to have close parallels with the dicyanovinyl groups. For example, (chlorodicyanovinyl)benzene, as an analog of the corresponding acid chloride, has been reacted with amines to form enaminonitrile linkage via a vinylic nucleophilic substitution reaction.[2]

Moore *et al*.[3-5] has been studying synthetic routes for the introduction of dicyanomethylidene groups in place of carbonyl oxygen as a means of modifying reactivity as well as properties of such materials. A bifunctional monomer, for example, *p*-bis(1-chloro-2,2-dicyanovinyl)benzene, was synthesized and used for polymerization with various diamines or diols to give high mol. wt. polymers containing the dicyanomethylidene group in the polymer backbone.[3-7] Introduction of this rather bulky and polarizable group make the polymer more soluble in common solvents, also provide site for the thermal curing (*without volatile byproduct*) at elevated temperature to give excellent thermal stability to these materials. This curing reaction occurs at the temperature around 300 °C depending on the structure.

Because of their high performance properties, *e.g*., high glass transition temperature, high melting points, and generally high termooxidative stability, wholly aromatic polyheterocyclics, such as polybenzimidazoles, polybenzoxazoles, and polyimides, have long been of interest as heat-resistant fibers and as matrix materials for fiber-reinforced composites. These polyheterocyclics are infusible, and only soluble in concentrated sulfuric acid. A common approach has been to synthesize a more flexible and soluble precursor polymer which upon subsequent treatment ('curing') cyclizes intramolecularly to produce the final thermally stable, rigid rod polymer. Polyimides are a familiar and successfully applied example of this approach.

During our efforts to expand the synthetic strategy related to enaminonitrile chemistry, we have found that hydroxy-substituted polyenaminonitrile could be used as a novel, soluble precursor for rigid-rod polybenzazoles.

The present paper deals with model reaction and polymerization by using 1,4-bis(chloro-dicyanovinyl)benzene with (bis)ortho-aminophenol compound, to obtain hydroxy-substituted model compounds and polyenaminonitrile as a soluble precursor for polybenzoxazole. Their characterization and thermal cyclization were discussed.

Experimental Section

Chemicals and Measurements. 1-Chloro-2,2-dicyanovinylbenzene (I) and 1,4-bis(1-chloro-2,2-dicyanovinyl) benzene (II) were prepared by the modified methods previously reported.[3] 3,3'-Diamino-4,4'-dihydroxybiphenyl (99%) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (98%) were purchased from TCI Co. (Japan) and used without purification. 2-Aminophenol (Aldrich, 99%) was purified by recrystallization and sublimation. Other chemicals and solvents were purified by conventional methods.

The IR spectra were obtained on a Unicam 1000 FT-IR Spectrometer. The NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer. Thermal analysis (DSC and TGA) was carried out on a Perkin-Elmer 7 Series thermal analysis system. The molecular weight data were obtained by gel permeation chromatography (GPC, Waters)

using tetrahydrofuran as the eluent at a flow rate of 1 mL/min. Polystyrene standards were used to calibrate the molecular weight.

Model Reaction. Model Compound (III) was prepared by the procedure below; 2-aminophenol (0.723 g, 6.625 mmol) and 20 mL of DMAc were charged in a 50 mL, 3-neck flask equipped with a nitrogen inlet, outlet and a condenser. To above stirred solution was added 1-chloro-2,2-dicyanovinylbenzene (0.5 g, 2.651 mmol) solution in 10 mL of DMAc, and the mixture was stirred at room temperature for 10 h. The resulting orange solution was precipitated into water to obtain light yellow powder, which was filtered, washed with water repeatedly, and then dried in vacuum (yield 89%). Model compound (V) was also prepared from 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and two molar excess of 2-aminophenol by using the same procedure (yield 78%).

Model Compound (III): Melting around 171 °C was followed by exotherm (DSC). IR (KBr): 3379 (OH), 3202 (NH), 2916, 2219 (CN), 1594, 1558, 1493, 1402, 697 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.3 (1H, OH), 10.1 (1H, NH), 6.57.5 (9H, arom. H). ^{13}C NMR (DMSO-d_6): δ 168.8, 153.7, 134.2, 132.9, 130.2, 129.6, 129.2, 125.4, 120.1, 119.0, 117.2, 115.5, 52.4.

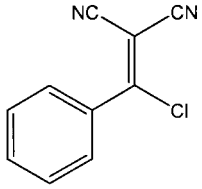
Model Compound (V): Endothermic melting around 312 °C seemed to be overlapped with the immediate cyclization exothermic transition, and another sharp melting transition appeared at 356 °C due to the bisoxazole compound formed by intramolecular cyclization (DSC). IR (KBr): 3312 (OH), 3227 (NH), 2909, 2217 (CN), 1543, 1480, 1432, 1362, 1295, 750, 691 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.5 (2H, OH), 10.1 (2H, NH), 6.87.8 (12H, arom. H), ^{13}C NMR (DMSO-d_6): δ 167.7, 153.8, 136.6, 130.5, 129.0, 124.8, 120.1, 118.7, 117.2, 115.2, 52.4.

Polymerization Reaction between 1,4-Bis(1-chloro-2,2-dicyanovinyl) Benzene (II) with 3,3'-Diamino-4,4'-dihydroxybiphenyl. A 100 mL three-necked flask was equipped with a gas inlet, a reflux condenser and a magnetic stirrer. The glassware was flame-dried under nitrogen to remove surface moisture, and then cooled. 3,3'-diamino-4,4'-dihydroxybiphenyl (1.118 g, 5.17 mmol) was weighed into the flask and dissolved in 30 mL DMAc. To above solution 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (1.5 g, 5.01 mmol) was added and stirred for about 20 h at the temperature of 70 °C. The brown reaction mixture was poured into a large amount of water. The light brown precipitate was filtered, washed several times with water and ether, and dried *in vacuo* at 80 °C for 24 h to give 2.20 g (98% yield) of the polymer with an inherent viscosity of 0.58 dL/g at 25 °C in DMAc. IR (KBr): 3450-3248 (OH and NH, br), 2928, 2219 (CN), 1613, 1554, 1491, 1451, 1280, 762, 699 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.5 (OH), 10.3 (NH), 6.9-8.0 (arom. H).

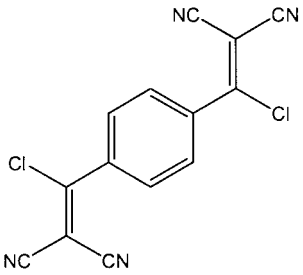
Polymerization Reaction between II with 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane. The polymerization reaction between monomer (II) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane was also tried using the same procedure above, and the resulting product (yield 98%) was characterized. Unusually, the product possessed very low inherent viscosity (0.05 g/dL, in DMAc). The GPC analysis showed binodal distribution, composed of broad and multiple peaks resulting from a series of low mol. wt. linear polymers along with very intense and sharp one from the potential macrocyclic single compound. The single compound could be separated easily by fractional crystallization from the methanol solution and the structure was analyzed and confirmed to be the macrocyclic dimer as the analytical data shown below; IR (KBr): 3362, 2956, 2220 (CN), 1678, 1626, 1589, 1554, 1522, 1455, 1314, 1259, 1204 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.7 (OH), 10.5 (NH), 7.26 (1H, d, arom. proton para to NH), 7.20 (2H, arom. protons of center benzene ring), 7.01 (1H, arom. proton ortho to OH), 5.68 (1H, arom. proton ortho to NH). ^{13}C NMR (DMSO-d_6): δ 170.0, 155.1, 134.0, 130.7, 130.1, 129.3, 127.3, 123.3, 117.6, 117.2, 115.7, 53.2. Mass (MALDI TOF-MS): 615.45 (M+23).

Results and Discussion

Compound (I) and the bifunctional monomer (II), 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene, were prepared in two step from the corresponding acid chloride using the procedure reported previously.[3,9]



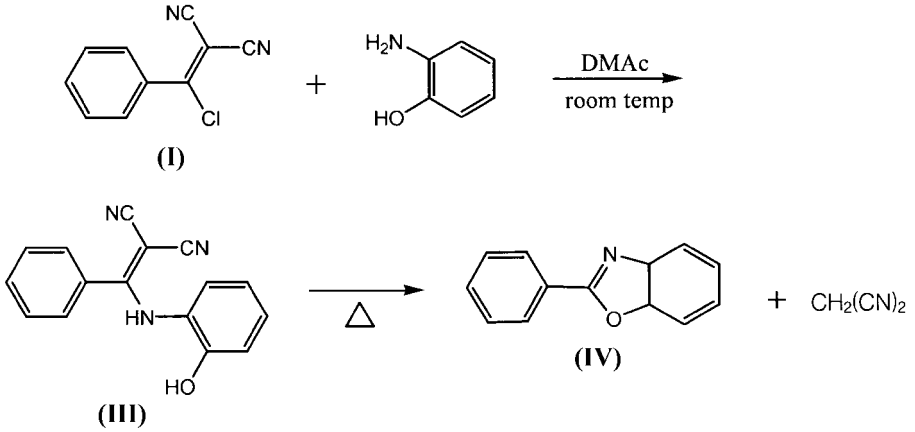
(I)



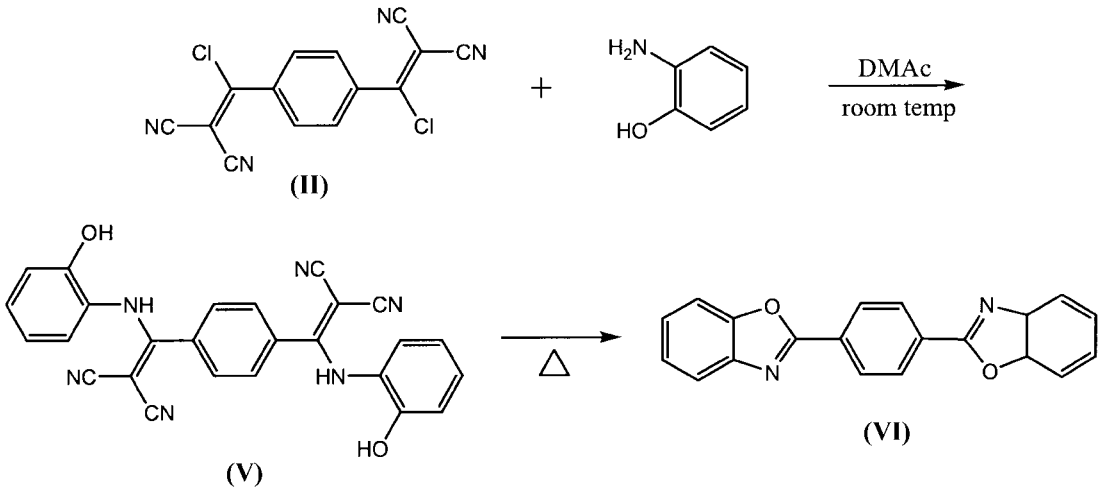
(II)

From the reaction of compound (I) with 2-aminophenol, a stable *o*-hydroxy enaminonitrile compound (III) was separated in a good yield at room temperature. FT-IR and NMR were obtained to elucidate the structure of the product (III). This product, then, is expected to undergo thermal cyclization reaction to give stable 2-phenyl benzoxazole (IV) (see Scheme 1).

The cyclization reaction was monitored by DSC and TGA. Figure 1 shows the DSC thermogram of compound (III). As observed in the first scan of sample, the compound showed melting at around 170 °C which was followed by immediate exotherm (appeared with rather small peak, probably caused by the overlapping with prior melting transition) suggesting intramolecular cyclization reaction. The second scan did show rather broad endothermic peak at 90-100 °C, attributed to the melting of 2-phenylbenzoxazole, the cyclized product (lit. 102-104 °C). It is presumed that the cyclization reaction can occur in solution at a relatively low temperature range, but, in solid state the reaction is only facilitated at the temperature above melting of the pristine compound where the molecule can possess enough energy for the molecular



Scheme 1



Scheme 2

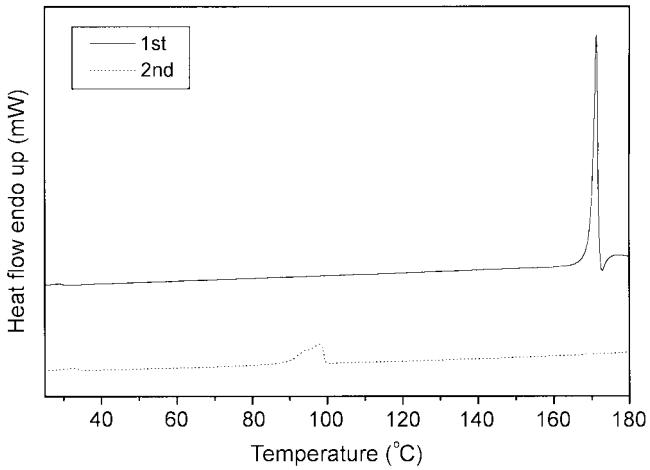


Figure 1. DSC thermograms of compound (III), heating rate 10 °C/min.

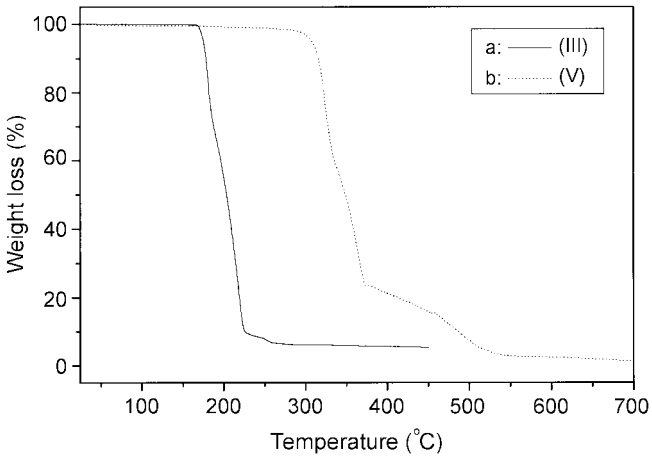


Figure 2. TGA thermograms of compound (III, V), heating rate 10 °C/min.

rearrangement. TGA thermogram also clearly support the cyclization which involves the release of malononitrile from the reaction. From curve (**a**) in Figure 2, two stage weight loss pattern is discernible. The first drop of about 25 wt%, starting at around 170 °C, are matching theoretical 25.3 wt% loss, which is corresponded to the weight fraction of malononitrile removed from the compound (III). Curve (**b**) shows similar thermogram of model compound (V) with

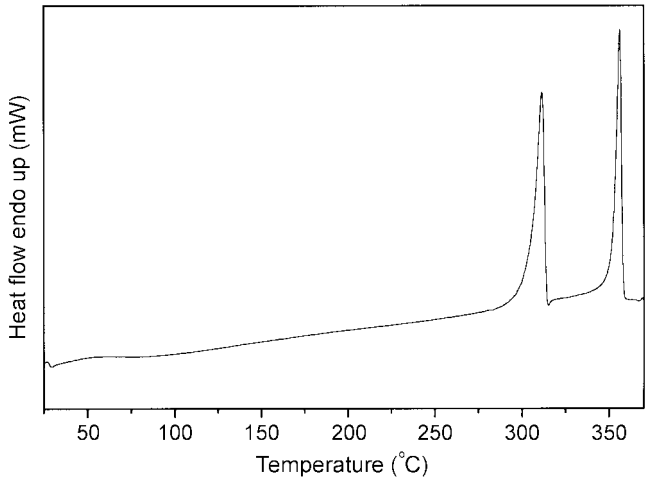


Figure 3. DSC thermograms of compound (V), heating rate 10 °C/ min.

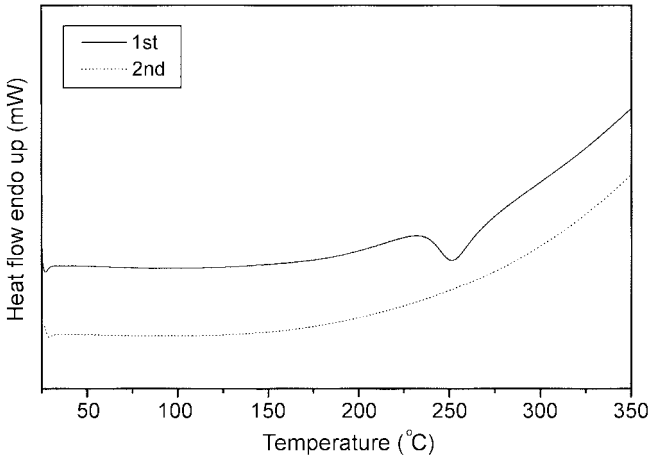


Figure 4. DSC thermograms of *o*-hydroxy polyenaminonitrile (VII).

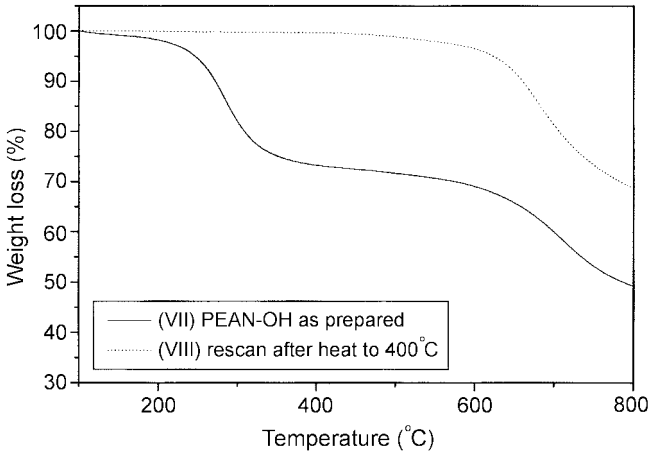


Figure 5. TGA thermograms of *o*-hydroxy polyenaminonitrile (VII); (a) before and (b) after curing reaction.

higher thermal stability.

The similar model reaction between the bifunctional compound (II) and 2-aminophenol resulted in forming bis(*o*-hydroxy enaminonitrile) (V) in a good yield (see Scheme 2). DSC thermogram of compound (V) in Figure 3 showed endothermic melting peak at 312 °C, which is followed by cyclization exotherm as described above. Further heating showed another strong endothermic peak at 356 °C, assignable to the melting transition (lit. 358 °C) of the cyclized bisoxazole product. When the sample was heated to 325 °C and rescanned after cooling, only single melting transition at 356 °C reappeared. Both DSC and TGA results explain well the same intramolecular cyclization reaction involving the release of malononitrile.

Complementally to the solid-state cyclization reactions above described, the same reactions were attempted in solution. Both model compounds (III and V) was dissolved in DMAc and heated at 150 °C for 5 h. The products were isolated by precipitation into water and subsequent drying in high yields. The purified products by sublimation were characterized to identify the exact structures of the known (bis)benzoxazole compounds (IV and VI) by IR, ^{1}H NMR and their melting temperatures.

The IR spectral changes also explain the proposed cyclization reaction of model compound (III). The IR spectrum of the pellet sample heated to 175 °C was compared with the original sample. The nitrile (CN) stretching band at 2215 cm^{-1} and vinyl (C=C) band at 1560 cm^{-1} of the original sample disappeared almost completely, and the band at 1415 cm^{-1} and many peaks at finger print region between 1300-700 cm^{-1} matched well the characteristic bands of the structure of 2-phenylbenzoxazole. The IR measurements on the model compound (V) exhibited the similar results.

Above model studies clearly demonstrate that *o*-hydroxy enaminonitrile product can be transformed thermally into stable benzoxazole product efficiently. If we use both bifunctional compounds as monomers for condensation polymerization, we can produce polymer as a precursor for the polybenzoxazole, known as a class of most thermally stable, rigid-rod polymer. We attempted the polymerization of monomer (II) with a commercial 3,3'-diamino-4,4'-dihydroxy biphenyl as the reaction is shown in Scheme 3. From the polymerization reaction the *o*-hydroxy poly(enaminonitrile) (PEAN, VII) was obtained in an almost quantitative yield. The polymer possessed moderate to high molecular weight as indicated by the solution viscosity value (inherent viscosity of 0.58 dL/g at 25 °C in DMAc) and could be cast into film from its solution. This precursor polymer possessed good solubility in typical polar aprotic solvents such as DMF, DMSO, and NMP, and also in acetone and THF. The good solubility in various organic solvents can be ascribed to the very polar structure of polymer backbone with cyano-vinyl amine and hydroxy groups and their strong dipolar and hydrogen bonding interactions.

The expected thermal cyclization of polymer(VII) was examined by DSC and TGA. DSC thermograms of PEAN showed no noticeable endothermic transition, suggesting the amorphous nature, but showed a broad exothermic transition in the temperature range of 235-280 °C, suggesting the

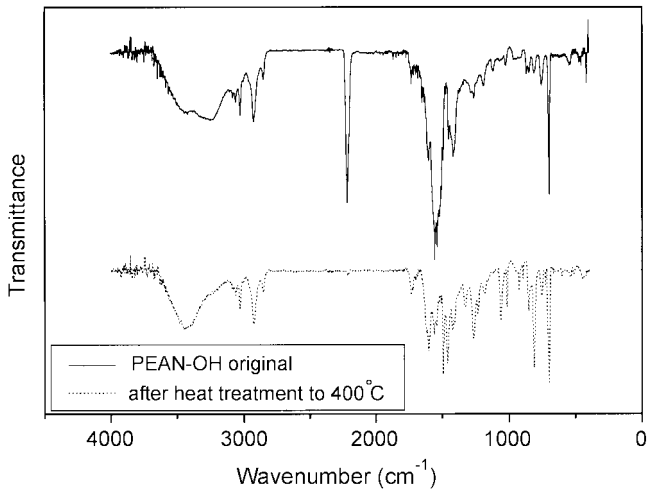


Figure 6. IR spectra of *o*-hydroxy polyenaminonitrile (VII); (a) before and (b) after curing reaction.

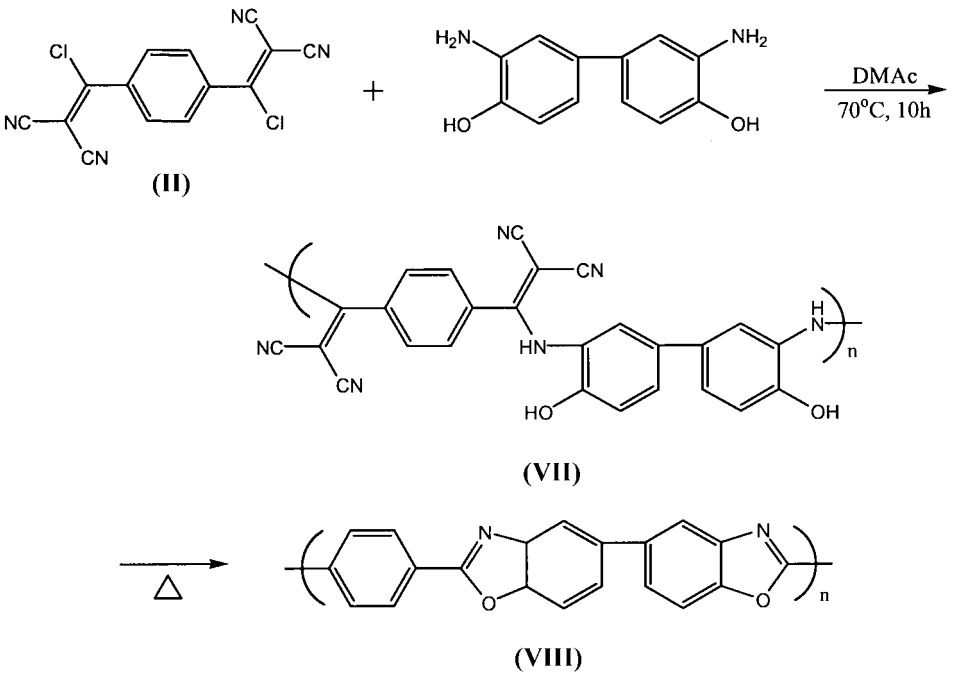
cyclization 'curing' reaction to polybenzoxazole. When the sample was cooled and rescanned, no exotherm was observed (Figure 4). TGA thermograms of PEAN were obtained in nitrogen atmosphere (Figure 5). It showed about 29.1% weight loss at the temperature range between 210 and 340 °C, matching well the theoretical fraction (29.8 wt%) of malononitrile to be removed from the cyclization process. After thermal conversion to the polybenzoxazole (VIII), the material seemed stable to high temperature above 600 °C and indicated very high char content about 70% at 800 °C. IR spectral change of the polymer after heating to 400 °C were shown in Figure 6 and compared with the original sample. The NH absorption band at 3200-3300 cm^{-1}, nitrile band at 2215 cm^{-1}, and the cyanovinyl band at about 1560 cm^{-1} decreased dramatically, also the change into characteristic bands of polybenzoxazole structure after heat treatment is obvious.

Contrary to above high polymer formation, it was found that the reaction between monomer (II) with 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane did not yield high polymer. As described in the experimental section, the product contained macrocyclic compound as the major component (presumably *ca*. 60-70 wt%)

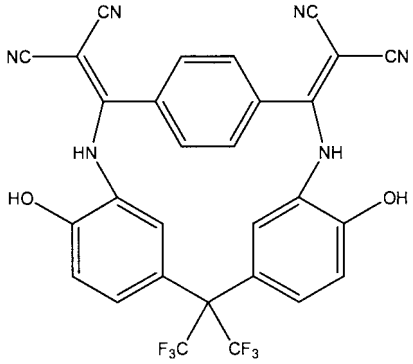
The pure crystal could be separated easily from the methanol solution and the structure was analyzed by IR and NMR. Also MALDI-TOF MS showed the molecular ion in the form of M-Na^+ as 592.46 to identify the structure as the cyclic dimer (see structure below). It seems that the formation of cyclic dimer in this system is due to the existence of a preferred conformation of the initial 1 : 1 adduct which favors cyclization to form a stable cyclic molecules, while competing with polymerization to give linear-chain polymer.

DSC thermogram showed endothermic transition centered at 265 °C and the followed exothermic transition between 270-300 °C, which suggested the melting and the occurrence of some type of reaction involving cyclization and/or other intermolecular process, respectively. Because of the rigid conformation of the cyclic compound, the heterocyclization to benzoxazole structure will be limited to proceed only in part. TGA showed about 10% weight loss at the temperature range between 250 and 300 °C, and 40 wt% of original weight remained at 800 °C in nitrogen.

In conclusion, we demonstrated that mono-, or di-substituted (chloro dicyanovinyl)benzene compound reacted with 2-aminophenol to prepare the molar equivalent model product with a high yield, and the resulting *o*-hydroxy enaminonitrile products underwent thermal cyclization to provide the



Scheme 3



corresponding benzoxazole compounds at elevated temperature efficiently. From the bifunctional compounds of both reactants, *o*-hydroxy polyenaminonitrile could be prepared as a new soluble precursor polymer for well-known polybenzoxazole. The thermal cyclization reaction was elucidated by thermal analysis and infrared spectroscopy. Interesting cyclic dimer formation from the 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane reaction system was also observed and the macrocyclic compound was characterized.

References

1. Wallenfels, K.; Friedrich, K.; Rieser, J.; Ertel, W.; Thieme, H. K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 261.
2. Rappoport, Z. *Acc. Chem. Res*. **1981**, *14*, 7.
3. Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084.
4. Moore, J. A.; Mehta, P. G. *Macromolecules* **1993**, *26*, 916.
5. Kim, J.-H.; Moore, J. A. *Macromolecules* **1993**, *26*, 2679.
6. Moon, H.-S.; Kim, S.-T; Gong, M. S. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 591.
7. Moore, J. A.; Kaur, S. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1994**, *35*(1), 385.
8. Shin, G. I.; Lee, J. I.; Kim, J.-H. *Bull. Korean Chem. Soc.* **1996**, *17*(1), 29.
9. Kim, J.-H.; Moore, J. A. *Korea Polymer J.* **1993**, *1*(2), 116.