

A New Synthetic Route to Poly(benzimidazole) and the Related Model Reactions to Imidazoline and Benzimidazole

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Mono-, or di-substituted chlorodicyanovinyl benzene compound was reacted with an excess amount of ethylenediamine to give corresponding imidazoline product with high reaction yield. This reaction occurs by stable imidazoline ring-forming process through nucleophilic attack of terminal amine on the enamionitrile adduct, the reaction intermediate, toward electropositive enamine carbon, which is accompanied by the release of neutral malononitrile moiety. The similar reaction with 1,2-phenylenediamine produced stable enamionitrile-amine adduct at lower temperature which could be cyclized intramolecularly to thermally stable benzimidazole at elevated temperature in solution or in solid state. From the difunctional compound of both reactants, poly(enamionitrile-amine) could be prepared as a new soluble precursor polymer for well-known polybenzimidazole (PBI). The thermal cyclization reaction accompanying the release of malononitrile molecules was studied using thermal analysis and infrared spectroscopy.

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 prepared and reacted with amines to form enamionitrile 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 difunctional 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.³⁻⁶ 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 by-product) at elevated temperature to give excellent thermal stability to these materials.

Recently, we have found an interesting chemistry in which the (chloro dicyanovinyl)benzene react with excess amount of ethylenediamine to give 2-phenyl-2-imidazoline at room temperature. It seems that the reaction proceed to form enamionitrile adduct first, which subsequently give stable imidazoline ring by kicking out malononitrile moiety through nucleophilic attack of terminal amine toward electropositive enamine carbon.

It was of interest to try model reaction with 1,2-phenylenediamine, from which enamionitrile-amine adduct resulted and the adduct could be transformed to benzimidazole by similar ring forming process.

In this paper, we present several model reactions which give imidazoline or benzimidazole ring structures as discussed above. A difunctional monomer, 1,4-bis(chloro-dicyanovinyl)benzene, was reacted with 3,3'-diaminobenzidine to pro-

vide poly(enamionitrile-amine) as a new precursor polymer for a typical polybenzimidazole (PBI). The cyclization curing reaction was studied using FT-IR and thermal analysis (DSC & TGA).

Experimentals

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 Ethylene diamine (99+%), and 3,3'-diamino-benzidine (99%) was purchased from Aldrich Chemical Co. and used without purification. 1,2-Phenylene diamine (Aldrich, 98%) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purified by sublimation. Other chemicals and solvents were purified by conventional methods.

IR spectra were obtained on a Unicam 1000 FT-IR Spectrometer. NMR spectra were taken on a Bruker AMX-400 Spectrometer. Thermal analysis (DSC and TGA) was carried out on a Perkin-Elmer 7 Series thermal analysis system. Melting point was measured by DSC calibrated by standard Zinc and Indium sample.

Reaction to 2-phenyl-4,5-dihydro-imidazole (2-phenyl imidazoline). Ethylenediamine (2.28 g, 37.9 mmol) and 20 mL of THF 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 (0.36 g, 1.91 mmol) solution in 5 mL of THF dropwise and the stirring was continued for 10 h. The resulting clear violet-colored solution was rotary evaporated to remove solvent and excess ethylenediamine. The resulting dark solid product was placed in sublimator and a white crystalline product was collected under vacuum (76% yield). Mp 101 °C (DSC, Lit. 101 °C).

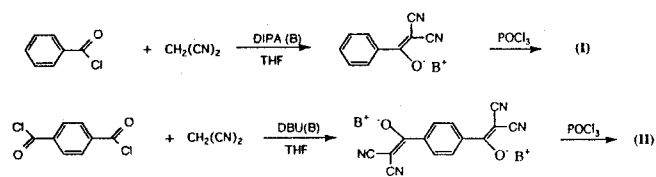
Reaction to 2,2'-phenylene-bis(4,5-dihydroimidazole). 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (1.00 g) and 15 mL of ethylenediamine were charged in a 50 mL, 3-neck flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer and the stirring was continued for 10 h. As the reaction proceed, white product was precipitated out of solution. The solid product was simply filtered after

reaction and dried to give 0.52 g of expected bis-imidazoline product (72% yield). Mp 314 °C (DSC, Lit. 318 °C).

Reaction to 2-phenyl-4,5-benzimidazole via 1-(2-amino phenyl)imino-2,2-dicyanovinyl benzene. (A) 1-Chloro-2,2-dicyanovinylbenzene (1.02 g, 5.40 mmol) and 1,2-phenylene diamine (0.584 g, 5.4 mmol) were placed in a 100 mL, 3-neck flask fitted with a nitrogen inlet, a magnetic stirrer, and a condenser, and then dissolved in 40 mL of THF. To above solution was added equivalent amount of DABCO in THF dropwise. After stirring for about 12 h, the reaction mixture was precipitated into water to give light brown powder which was filtered and dried to obtain the desired 1:1 adduct, enaminonitrile amine, with almost quantitative crude yield. The product was purified by recrystallization from ethanol. Melting around 180 °C was followed by exotherm (DSC). IR (KBr): 3476, 3378 (–NH₂), 3209 (NH), 2215 (CN), 1560, 1415, 740 cm^{–1}. ¹H NMR (DMSO-d₆): δ 10.1 (NH), 6–8 (arom.H), 5.2 (NH₂). ¹³C NMR (DMSO-d₆): δ 168.2 (vinyl C–N), 144.8, 133.7, 131.7, 129.3, 128.4, 127.9, 121.4, 118.3, 115.7, 115.4, 113.9, 50.3 (C–CN). Anal. Calcd for C₁₆H₁₂N₄: C, 73.8; H, 4.65; N, 21.52. Found: C, 74.1; H, 4.55; N, 21.15. (B) The adduct obtained in (A) was dissolved in NMP and stirred at 130–140 °C for 5 h. The resulting dark brown solution was precipitated into large amount of water, and then filtered to obtain light brown powder which was recrystallized from acetone to give the desired 2-phenyl benzimidazole with good yield (85%). Also the same cyclization reaction in the solid state was monitored by DSC and TGA. Mp 295 °C (DSC onset, Lit. 296–7 °C). IR and NMR were matched well with those of known 2-phenyl-4,5-benzimidazole.

Reaction to 2,2'-phenylene-bis-4,5-benzimidazole via 1,4-bis[1-(2-aminophenyl)imino-2,2-dicyanovinyl] benzene. (A) 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (1.00 g, 3.34 mmol) and 1,2-phenylene diamine (0.7245 g, 6.70 mmol) were placed in a 100 mL, 3-neck flask fitted with a nitrogen inlet, a magnetic stirrer, and a condenser, and then dissolved in 40 mL of NMP. To above solution was added equivalent amount of DABCO in NMP dropwise. After stirring for about 12 h, the reaction mixture was precipitated into water to give light brown powder which was filtered and dried to obtain the desired 1:2 adduct, bis(enaminonitrile-amine), with high yield (89%). The product was purified by recrystallization from acetone. IR (KBr): 3441, 3363 (–NH₂), 3261 (NH), 2215 (CN), 1553, 755 cm^{–1}. ¹H NMR (DMSO-d₆): δ 10.3 (NH), 6.5–8.0 (arom.H), 5.3 (NH₂). ¹³C NMR (DMSO-d₆): δ 167.2 (vinyl C–N), 145.0, 136.3, 129.4, 128.0, 121.2, 118.0, 115.6, 115.4, 113.7, 50.6 (C–CN). (B) The adduct obtained in (A) was dissolved in NMP and stirred at 150–160 °C for 5 h. The resulting dark brown solution was precipitated into large amount of water, and then filtered to obtain light brown powder which was recrystallized from acetone with good yield (65%). Also the cyclization reaction was monitored by DSC and TGA. IR and NMR spectra were matched well with those of known 2,2'-phenylene-bis(4,5-benzimidazole).

Polymerization Reaction between 1,4-bis(1-chloro-2,2-dicyanovinyl) benzene with 3,3'-diaminobenzidine. 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'-Diaminobenzidine (0.7245 g,



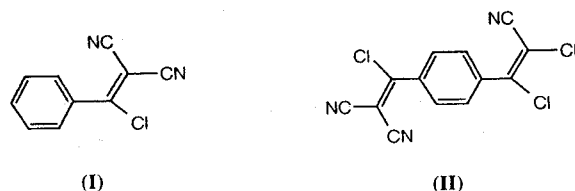
DIPA : Diisopropylamine
DBU : 1,8-Diazabicyclo[5.4.0]undec-7-ene

Scheme 1.

3.38 mmol), and DABCO (0.75 g, 6.70 mmol) were weighed into the flask and dissolved in 30 mL NMP. To above solution 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (1.0013 g, 3.35 mmol) was added and stirred for about 12 h, while warming up the temperature to 80 °C. After reaction, the brown reaction mixture was poured into large amount of water. The light brown precipitate was filtered and washed several times with water and methanol, and dried *in vacuo* at 120 °C for 24 h to give 1.03 g (99% yield) of polymer with an inherent viscosity of 0.35 dL/g at 25 °C in DMF. IR(KBr): 3366 (–NH₂), 3222 (NH), 2213 (CN), 1656, 1517, 1302, 852, 810 cm^{–1}. ¹H NMR (DMSO-d₆): δ 10.3 (NH), 6.5–8.4 (arom.H), 5.3 (br, NH₂).

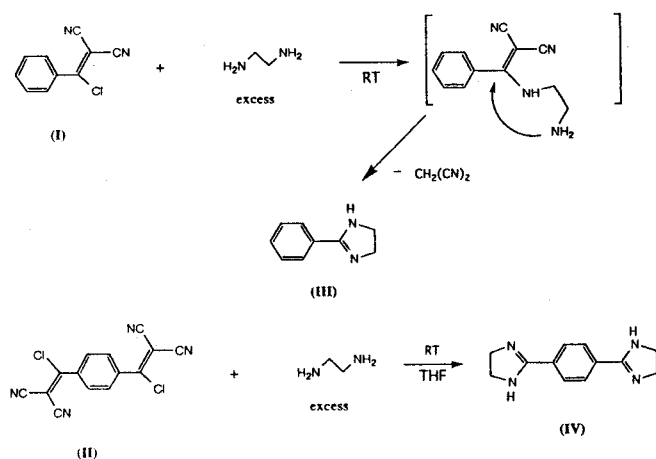
Results and Discussion

1-Chloro-2,2-dicyanovinyl benzene (I) is a chemical analog of benzoyl chloride in the sense that dicyanomethylidene group are analogous with carbonyl oxygen in their strong inductive effect and resonance effects, and also many useful well-known reactions have been shown to have close parallels between compounds with these two units. Reactions of compound (I) with a nucleophiles, for example aromatic or aliphatic amines, are rapid and lead to enaminonitrile adducts in good yields *via* nucleophilic vinylic substitution pathways.



Compound (I) and the difunctional compound (II), 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene, were prepared in two step from corresponding acid chloride using modified procedure reported previously (Scheme 1).³ Model reactions of these compounds with typical strong nucleophiles such as amines or phenoxide were studied by Moore and Gong *et al.* during the past several years. Several difunctional monomers were synthesized and used to make various novel polymers which contain dicyanovinyl moiety in the polymer backbone. These polymers possess very good solubility in common organic solvents and exhibit excellent thermal stability which is attributed to the suggested inter and/or intra chain reaction *via* thermally reactive cyanovinyl groups at high temperature (>300 °C).⁷

Recently we have found an interesting chemistry in which compound (I) react with excess amount of ethylenediamine to give 2-phenyl-2-imidazoline (III) at room temperature. It seems that the reaction proceed to form intermediate enami-

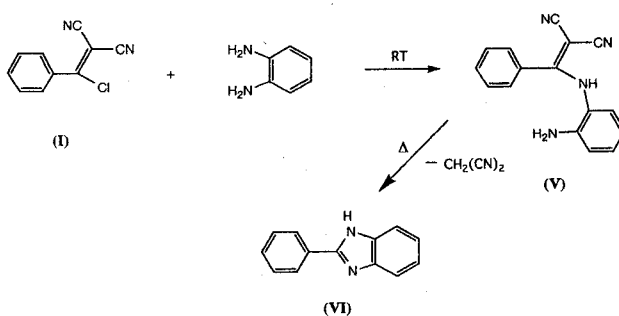


Scheme 2.

nonitrile adduct in excess amount of ethylenediamine, which subsequently give stable imidazoline ring by kicking out malononitrile moiety through nucleophilic attack of terminal amine toward electropositive enamine carbon as shown in reaction Scheme 2. Similar result was expected from the reaction of compound (II) with excess ethylenediamine and the bis-imidazoline product (IV) were easily separated from the reaction and identified to be the expected product. These model reaction was conducted at room temperature which suggested very low activation energy involved in this reaction. This reaction was thought to be driven by the formation of stable 5-membered imidazoline ring which is accompanied by the release of malononitrile moiety.

It was of interest to try model reaction with 1,2-phenylenediamine, from which enaminonitrile-amine adduct would result and the adduct could be transformed to stable benzimidazole structure by similar ring forming process. The reaction of compound (I) with 1,2-phenylenediamine gave stable enaminonitrile-amine (V) at low temperature, which is compared to the previous reaction with ethylenediamine. Because of the weakly basic (also nucleophilic) nature of the aromatic amine at ortho position to enamine linkage compared to aliphatic amine, a stable enaminonitrile-amine adduct, in this case, was obtained with quantitative yield at room temperature. Elemental analysis, IR and NMR were obtained to elucidate the structure of product (V). This product, however, was expected to undergo cyclization reaction to provide stable 2-phenyl benzimidazole (VI) by heating to some elevated temperature (see Scheme 3). The cyclization reaction was conducted in NMP solution by simply stirring at 130–140 °C. The precipitated product into water was filtered and recrystallized from acetone to give yellow crystalline product with high reaction yield. The melting point measured by DSC and spectroscopic data confirmed the structure of the known compound.

The cyclization reaction was monitored by DSC and TGA. Figure 1 shows the DSC thermogram of compound (V). As observed in the first scan of sample, the compound showed melting at around 175 °C which was followed by immediate sharp exotherm suggesting intramolecular cyclization reaction. The second scan did not show any appreciable transition to 250 °C and further heating showed rather broad endothermic peak centered at 290 °C, attributed to the melting



Scheme 3.

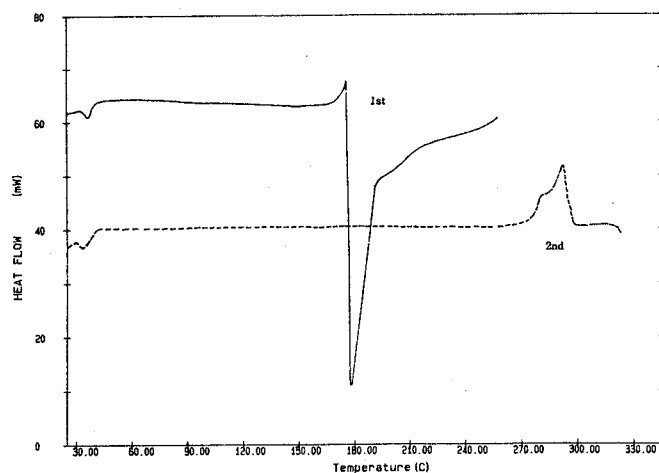


Figure 1. DSC thermograms of compound (V).

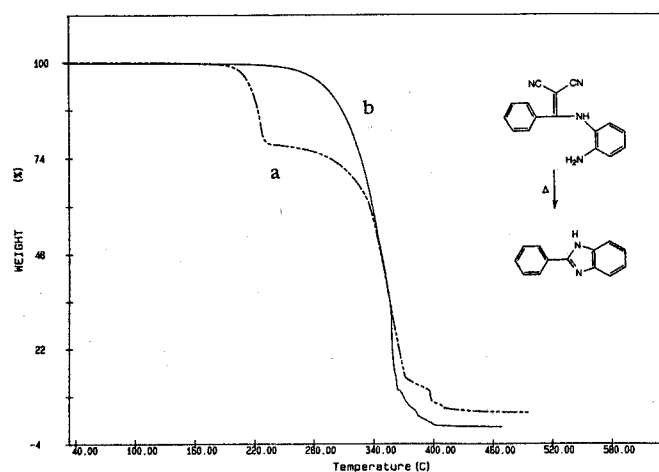


Figure 2. TGA thermograms of compound (V).

of cyclized imidazole product. It is noticed that the cyclization reaction can occur in solution at lower temperature as described earlier, but, in solid state the reaction is only facilitated at the temperature above melting of the compound where the molecule can possess enough energy for the molecular rearrangement. TGA thermogram also clearly support the cyclization which involves the release of malononitrile from the reaction. The malononitrile, which was sublimed out during the cyclization process, could be recovered and identified easily. Curve a in Figure 2 shows two stage weight loss

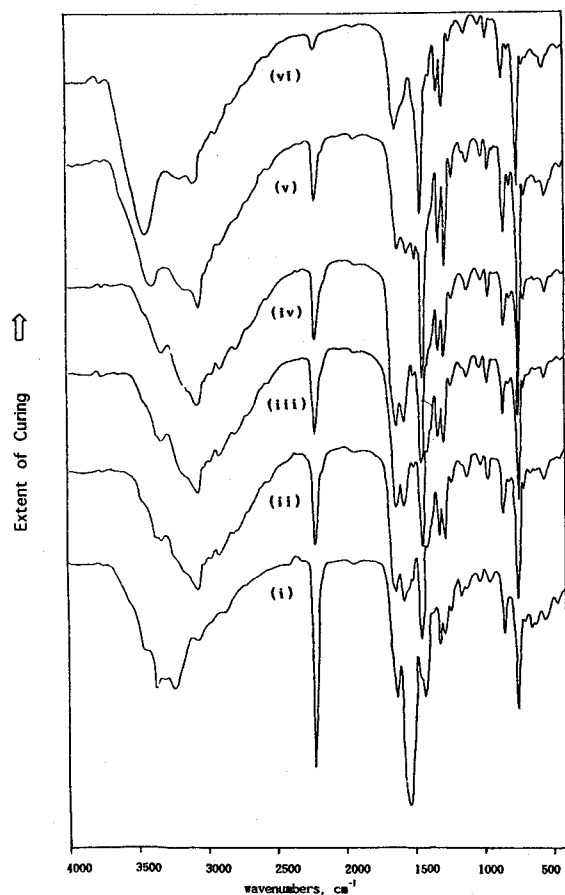


Figure 3. IR spectral change of compound (VII) as the extent of cyclization reaction proceeds; (i) untreated (ii) 160 °C, 15 min (iii) 160 °C, 30 min (iv) 180 °C, 10 min (v) 200 °C, 10 min (vi) sample after TGA run to 300 °C (10 °C/min).

pattern. The first drop of about 24 wt%, starting at around 180 °C, are matching well with theoretical 25.4 wt% loss, which is corresponded to the weight fraction of malononitrile removed from the compound (V). Curve b shows thermogram of 2-phenyl benzimidazole prepared in solution.

The same model reaction was conducted between the difunctional compound (II) and 1,2-phenylenediamine. The resulting bis(enaminonitrile amine) product (VII) was separated with good yield. DSC thermogram of compound (VII) showed strong exothermic peak at 150-200 °C corresponding to the cyclization reaction described above. Also TGA thermogram exhibited two-stage weight loss curve with the first onset temperature of 175 °C. Both DSC and TGA results explain well the intramolecular cyclization reaction involving the release of malononitrile.

Figure 3 represent the IR spectral change as cyclization reaction proceeds using KBr pellet sample of compound (VII). The pellet sample was heated in the oven from 160 °C to 200 °C with some time interval and finally heated to 300 °C. The cyano(CN) stretching band at 2200 cm^{-1} and cyano-vinyl (C=C) band at 1530 cm^{-1} decrease, and the band at 1625 and 1441 cm^{-1} characteristic of imidazole group becomes clear as the reaction proceed.

As we have discussed above, chloro dicyanovinyl benzene

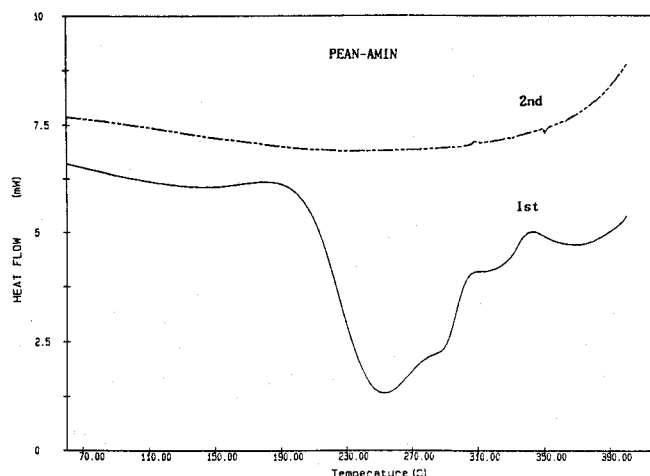
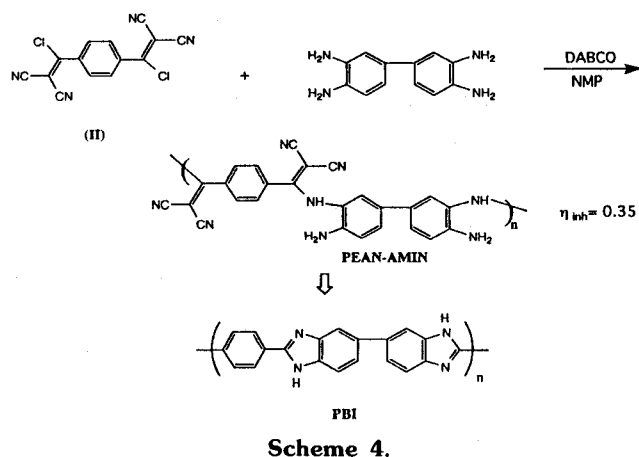
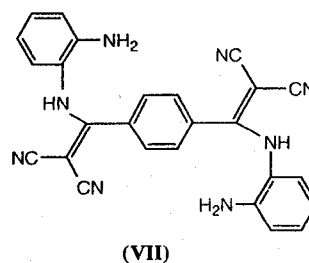


Figure 4. DSC thermograms of poly(enaminonitrile-amine) (VIII).



compound react with ortho-phenylenediamine to give stable enaminonitrile amine adduct which can be transformed to thermally stable benzimidazole product. If we use bifunctional compound of both reactants, we can produce polymer as a new precursor for the poly(benzimidazole), a class of most thermally stable, rigid polymer known. We tried polymerization of monomer compound (II) with a commercial 3,3'-diaminobenzidine as a typical example. Even the molecular weight of polymer was not high, estimated from its solution viscosity, the polymer was characterized and its thermal properties are examined. As shown in the Scheme 4, poly(enaminonitrile-amine) (PEAN-AMIN, VIII) was obtained from the polymerization reaction with quantitative yield. This precursor polymer was soluble in several polar solvents including NMP, DMF, and DMSO.

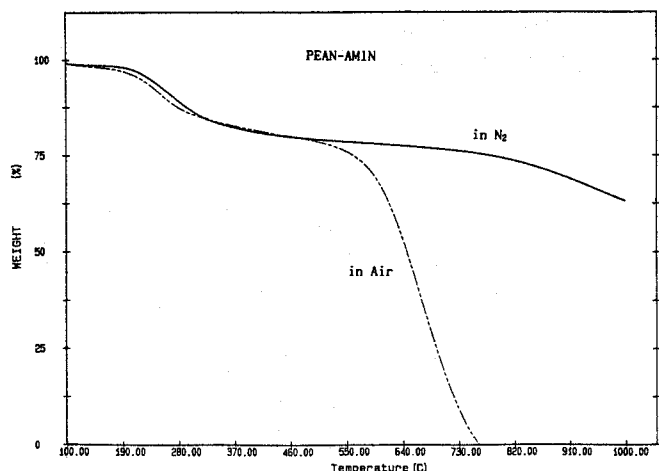


Figure 5. TGA thermograms of poly(enaminonitrile-amine) (VIII).

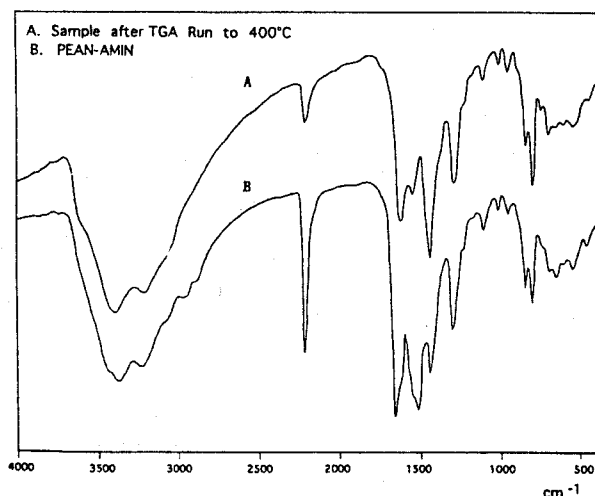


Figure 6. IR spectra of poly(enaminonitrile-amine) before and after curing reaction.

The expected thermal cyclization was examined by DSC and TGA. DSC thermograms of PEAN-AMIN showed broad exothermic transition with maxima around 250 °C, indicating cyclization 'curing' reaction to imidazole. When the sample

was cooled and rescanned, no exotherm was observed (Figure 4). TGA thermograms of PEAN-AMIN were obtained both in air and in nitrogen atmosphere (Figure 5). Both showed about 20% weight loss at temperature range between 200 and 300 °C. In air the second stage weight loss occurred around 550 °C (onset), instead in nitrogen the material seemed quite stable to higher temperature above 700 °C and indicated very high char content about 80% at 1000 °C, based on the weight of cyclized form at 500 °C. IR spectra of PEAN-AMIN and the sample after heating to 400 °C under TGA were shown in Figure 6. The intensity of the nitrile band at 2210 cm^{-1} and the cyanovinyl band at about 1530 cm^{-1} decreased dramatically, also the band at 1625 and 1441 cm^{-1} characteristic of imidazole group becomes clear after cyclization 'curing' reaction. Curve A is almost identical with that of commercial PBI known except small residual nitrile band at 2210 cm^{-1} . As we might expect, the cyclization reaction could not be completed in the solid state.

In conclusion, we demonstrated that mono-, or di-substituted chlorodicyanovinyl benzene compound react with excess amount of ethylenediamine gave imidazoline product with high reaction yield. The same reaction with 1,2-phenylenediamine produced stable enaminonitrile-amine adduct at low temperature which could be cyclized intramolecularly to thermally stable benzimidazole form at elevated temperature in solution or in solid state. From the difunctional compound of both reactants, poly(enaminonitrile-amine) could be prepared as a new soluble precursor polymer for well-known PBI. The thermal cyclization reaction accompanying the release of neutral malononitrile molecules was studied using thermal analysis and infrared spectroscopy.

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