# Synthesis and Properties of Polyarylene ether Nitrile Copolymers

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## Summary

Polyether nitrile and its copolymers were synthesized by nucleophilic substitution reaction of 2,6-dichlorobenzonitrile with resorcinol and with varying mole proportions of resorcinol and hydroquinone. The polymers were characterized by different physico-chemical techniques. Thermogravimetric studies showed that all the polymers were stable up to 400°C with a char yield of above 48% at 900°C in $N_2$ atmosphere. The glass transition temperature was found to increase with increase in concentration of hydroquinone units in the polymer; however no trend was observed in their crystalline melt temperatures. Copolymer composition was determined using FT-IR technique. Crystallinity of the polymers was also studied using wide angle X-ray diffraction.

## INTRODUCTION

In the recent past, a number of engineering polymers have been developed for use as matrices in advanced composites for structural applications in aerospace industry.. Among these, polyether ether ketone [1] (PEEK, ICI, Wilmington, Del) and polyarylene ether nitrile [2] (PEN, Idemitsu) have been identified as excellent matrix resins for carbon reinforcement. Owing to their crystalline/semi crystalline nature, they exhibit high tensile strength and melting point that qualify composites for use at elevated temperatures and in aggressive chemical environments encountered in aerospace, industrial and automotive applications. In addition, the pendant nitrile group on aromatic ring in PEN appears to promote adhesion of the polymer to many substrates [3,4], possibly through polar interaction with other functional groups; and it also serves as a potential site for polymer cross-linking [5,6] However, high crystalline property and insolubility in common organic solvents often restrict the use of these polymers for wide range applications.

Various attempts have been made by several researchers and in our laboratory to improve the solubility of PEN type polymers by incorporation of bisphenol monomers containing imido or dicyanoarylene groups [7], sulfide groups [8], sulfone groups

[9,10], alkyl pendant groups [11] and amide or amide imide groups [12]. The resultant polymers were found to be soluble in dipolar aprotic solvents.

However, it appears that polyether nitriles containing isomeric monomers have not been reported in detail in the open literature. In this paper, we report the synthesis and structure-property relationship of the copolymers derived from 2,6'-dichloro benzonitrile (DCBN) with hydroquinone (HQ) and resorcinol (RE).

## EXPERIMENTAL

### Materials

High purity 2,6-dichlorobenzonitrile [Fluka], hydroquinone [SRL, India], resorcinol [SRL], were used as received. Anhydrous $K_2CO_3$ [BDH] was dried in vacuum at $100^\circ C$ before use. N-methyl pyrrolidone [SRL] was distilled under vacuum over phosphorous-pentoxide and stored over 4A molecular sieves.

### Polymer Synthesis

The poly ether nitrile copolymers were prepared by nucleophilic substitution reaction of 2,6-dichlorobenzonitrile (DCBN) with hydroquinone (HQ) and resorcinol (RE) using anhydrous $K_2CO_3$ in NMP medium with 25% solid content and at $196^\circ C$ under $N_2$ atmosphere, as per the procedure described earlier [13]. The product was repeatedly refluxed with water, subjected to soxhlet extraction with acetone, filtered and dried under vacuum at $100^\circ C$ for 15 hours. Typical Structure of PEN and copolymer formed is shown in Figure-i.
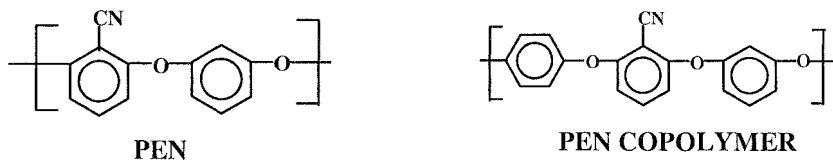


PEN                                          PEN COPOLYMER

**Figure 1**

## Characterization

Elemental analysis was performed with Perkin Elmer model 2400 CHN analyser. Inherent viscosities were determined at $60^\circ C$ for 0.2% polymer solution in p-chlorophenol using an Ubbelhode suspended level viscometer. Glass transition temperature ($T_g$) and melting temperature were measured using a Mettler thermal analyser model 3000 coupled to a DSC 20, at a heating rate of $10 K min^{-1}$.

The FT-IR spectra of the polymers in KBr pellets (2%) were recorded using a Nicolet FT-IR (510P) spectrophotometer. Wide angle X-ray scattering data were obtained on pellets of the polymer using a Seimens D5005 X-ray diffractometer with Cu-K$\alpha$ radiation at 40KV and 20mA. The diffractograms were recorded at room temperature over the $2\theta$ range of 10-40 $\theta$. Thermogravimetric analysis of the polymers was carried out under $N_2$ using a Dupont thermal analyser system 2000 in combination with a Dupont 951 thermogravimetric analyzer at a heating rate of $20^\circ K min^{-1}$. Solubilities were determined at 1% (W/W) concentration.

## RESULTS AND DISCUSSION

Polyarylene ether nitrile copolymers were synthesized by aromatic nucleophilic displacement of chlorine from an activated substrate (DCBN) by RE/HQ. Feed ratios and some properties of the polymers are given in Table 1. Inherent viscosity values reveal that N-methyl pyrrolidone (NMP) as reaction medium yields high molecular weight polymers. All polymers are insoluble in common organic solvents including dipolar aprotic solvents like DMSO, DMF, NMP, DMAc, pyridine and THF at room temperature. However, polymer-III is found to dissolve in DMF, DMSO, NMP and pyridine under hot condition. Polymer-II and IV were found to dissolve in NMP on heating.

*Characterization*

The elemental analysis, that is, C, H and N contents of polymers I-V (Table1) are in close agreement with theoretical values confirming the proposed structure.

Table 1: Conditions and properties of polymers

| Polymer | Feed Ratio | | | Elemental Analysis, % | | | Inherent [a] Viscosity (dL/g) | $T_m$ °C |
|---|---|---|---|---|---|---|---|---|
| | RE | DCBN | HQ | C | H | N | | |
| I | 0.5 | 0.5 | -- | 75 (74.6) | 2.4 (3.3) | 6.6 (6.6) | 0.49 | 336 |
| II | 0.375 | 0.5 | 0.125 | 73.5 (74.6) | 3.1 (3.4) | 6.52 (6.6) | 0.76 | 266 |
| III | 0.25 | 0.5 | 0.25 | 73.2 (74.6) | 2.9 (3.3) | 6.45 (6.6) | 0.49 | 200 |
| IV | 0.125 | 0.5 | 0.375 | 73.8 (74.6) | 3.22 (3.3) | 6.55 (6.6) | 1.11 | 307 |
| V | -- | 0.5 | 0.5 | 73.4 (74.6) | 3.2 (3.3) | 6.6 (6.6) | 0.79 | 366 |

a= Inherent viscosity in p-chlorophenol for 0.2% polymer solution at 60°C

FT-IR technique was used for polymer characterization and for semi-quantitative information of copolymer composition. The FT-IR spectra of all polymers show characteristic bands at around 2230cm$^{-1}$ due to symmetrical stretching of nitrile groups (S,ν C≡N). In polymer-I (Figure ii) the reaction between DCBN and RE is indicated by the disappearance of —OH and C—Cl stretching vibrations at 3419cm$^{-1}$ and 784 cm$^{-1}$ respectively. The band at 1128cm$^{-1}$ is due to φ—O skeletal vibrations (oxygen attached on either side of the ring). The 1030 cm$^{-1}$ band is assigned to ether linkage, ortho to C≡N. The formation of the product can be confirmed by the shift in the ring vibrations from 1490cm$^{-1}$ to 1456cm$^{-1}$ in polymer-I, indicating a change in the

substitution pattern. The peak at 1601cm$^{-1}$ is assigned to C=C stretching of benzene ring where oxygen is ortho to CN. In polymer-V, the band at 1450cm$^{-1}$is due to the ring vibrations. The peak at 1030 cm$^{-1}$ is attributed to the ether linkages ortho to —CN and the peaks in the region between 1240 to 1190cm$^{-1}$ are due to skeletal vibrations of phenoxy group. There is a shift observed in the case of 1,4 band by approximately 20cm$^{-1}$ to the higher wave number compared to HQ i.e. from  827 to 846 and 758 to 775. This is due to the influence of adjacent ring.

The formation of the copolymers is confirmed by the additional bands corresponding to HQ & RE as well as the disappearance of OH and φ—Cl bands. The 1128cm$^{-1}$ band corresponds to the RE part of the polymer and the bands at 1242 and 1190 cm$^{-1}$ originate from HQ. The band corresponding to HQ shifts from 827 to 848 cm$^{-1}$ because cyanobenzene is flanked by ortho substituted HQ & RE. Oxygen in the 2-positon influences the IR absorption of the unsaturation in benzene and shifts it to 1601cm$^{-1}$
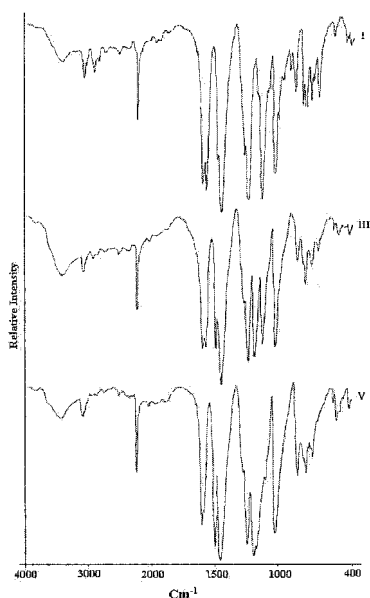


**Figure 2.** FT-IR spectra of polymers I, III, V

The peaks at 1190 (polymer-V) and 1128cm$^{-1}$ (polymer-I) are assigned to vφ—O skeletal vibrations of HQ & RE respectively. The difference in frequency is due to the substitution pattern. These peaks are used to obtain reactivity ratio of the reaction between DCBN—RE and DCBN—HQ. The ratio of integral intensities vφ—O (RE)/vCN(DCBN) for polymer-I and v φ— O(HQ)/ vCN(DCBN) for polymer-V are nearly the same, suggesting the same reactivity of  DCBN with RE and HQ .

The infrared spectrum of RE–DCBN–HQ system shows the presence of two characteristic peaks, 1190cm$^{-1}$[vφ—O(HQ)] and 1128cm$^{-1}$ [vφ—O(RE)]. This indicates that both RE and HQ are incorporated in the copolymer chain. An attempt

was made to obtain semi-quantitative information on the relative amounts of RE and HQ in the co-polymers using integral intensities of the peaks $\nu CN$, $\nu \phi$—O (HQ) and $\nu \phi$—O (RE).

The intensities $\nu \phi$—O(RE) and $\nu \phi$—O(HQ) are ratioed with respect to $\nu CN$(DCBN) and then normalized to 1 so as to get the approximate information of the components present in the copolymers with different feed ratios. The values show that the larger component among co-monomers does not react fully (Table 2).

Table 2: Feed ratio and intensity ratio of co monomers in copolymers

| Polymer | Feed Ratio | | Intensity in copolymers | |
|---------|------|------|------|------|
| | HQ | RE | HQ | RE |
| III | 0.5 | 0.5 | 0.46 | 0.49 |
| II | 0.25 | 0.75 | 0.24 | 0.64 |
| IV | 0.75 | 0.25 | 0.55 | 0.23 |

*Thermal Transitions*

The $T_g$s of the copolymers were determined by DSC and the results are given in Table 3. Samples were heated to 330°C (polymer-I), 350°C(polymer-V), 300°C(polymer-IV), 250°C(polymer-II) and 200°C(polymer-III) at a rate of 10Kmin$^{-1}$ in N$_2$, quenched to –50°C and reheated to obtain $T_g$. The Tg values of the copolymers increase with increase in concentration of HQ in the polymer, which can be attributed to the greater asymmetry of the polymer chain due to the incorporation of hydroquinone groups. Though the melt crystallization temperature of polymer-V is higher than that of polymer-I, no trend was observed in the copolymers, which may be due to the addition of HQ and RE units into the polymeric backbone in a random fashion. This trend was further confirmed from the X-ray diffraction data (Table 3, Figure iii). The copolymers possess less crystalinity in comparison to the individual homopolymers, may be due to the random distribution of HQ and RE units in copolymers, leading to distorted version of the symmetry and alignment. It is interesting to note that Polyether nitriles derived from isomeric monomers (HQ/RE) retained crystalline property unlike polyether ether ketones derived from isomeric monomers (HQ/RE) where the resorcinol based PEEK homopolymer and copolymers were found to be amorphous [13].

*Thermogravimetric Analysis*

Thermal degradation behaviour of polymers I-V was studied by thermogravimetry (TG) in a N$_2$ atmosphere at a heating rate of 20Kmin$^{-1}$. All polymers are stable up to 415°C ( IDT=415 to 490°C) and gave a char residue of 42-55% at 900°C (Table 3).

The relative thermal stability of the copolymers can be assessed by their integral procedural decomposition temperature (IPDT) proposed by Doyle [14]. IPDT values indicate that there is no appreciable change in the overall thermal stability of the polymers.

Table 3: Thermal properties and degree of crystallinity of the polymers

| Polymer | IDT (°C) | Char Residue, % [a] | IPDT | $T_g$ | Degree of crysytallinity, % [b] |
|---------|----------|---------------------|------|-------|----------------------------------|
| I | 480 | 50 | 686 | 145 | 30 |
| II | 415 | 53 | 682 | 153 | 16 |
| III | 430 | 52 | 678 | 158 | 3 |
| IV | 470 | 42 | 674 | 169 | 11 |
| V | 490 | 48 | 679 | 175 | 28 |

a= Char residue at 900°C under $N_2$
b= By Hermans and Weidinger method
IDT= Initial degradation temperature
IPDT= Integral procedural decomposition temperature
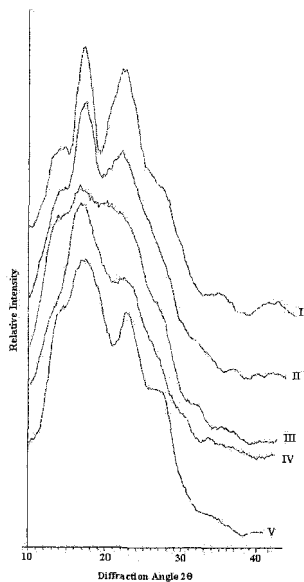


**Figure 3.** X-Ray analysis of polymers I-V

The overall activation energy ($E_a$) for decomposition was calculated using Coats and Redfern equation [15], assuming the order of reaction to be 1.

$$\ln\,[-\ln\,(1-\alpha)/T^2] = \ln\,[(AR/\,\Phi E)\,(1\text{-}2\,RT/E)]\text{-}\,E/RT$$

where $\alpha$ is the fraction decomposed at temperature T, $\phi$ is the heating rate, R is the gas constant and A is the Arrhenius factor. E was calculated from the plot of $\ln[-\ln(1-\alpha)/T^2]$ versus 1/T. The results obtained are given in Table 4.

Table 4: Kinetic parameters of polymers I- V

| Polymer | T ($^{\circ}$C) | $\propto$- Range | $\Delta$E (KJ/mol) | Corelation coefficient |
|---|---|---|---|---|
| I | 410 - 510 | 0.0039 - 0.6724 | 186 | 0.9936 |
|  | 520 - 770 | 0.6983 - 0.9611 | 8.4 | 0.9880 |
| II | 410 - 480 | 0.0206 - 0.5827 | 236 | 0.9920 |
|  | 490 - 690 | 0.6109 - 0.8628 | 6.2 | 0.9790 |
| III | 410 - 480 | 0.0222 - 0.4040 | 198 | 0.9946 |
|  | 530 - 690 | 0.5008 - 0.7586 | 15.7 | 0.9838 |
| IV | 410 - 530 | 0.0016 - 0.5807 | 193 | 0.9994 |
|  | 570 - 730 | 0.7120 - 0.9177 | 13.3 | 0.9930 |
| V | 410 - 550 | 0.0013 - 0.5966 | 201 | 0.9951 |
|  | 560 - 780 | 0.6827 - 0.9841 | 17.4 | 0.9798 |

The Coats–Redfern plot indicates two-stage decomposition. The first stage of decomposition corresponds to a weight loss of 20-30% of the active material decomposed. The activation energy for polymer-V, which contains only hydroquinone units, is 201 KJ/mol and that for polymer–I, which contains only resorcinol units is 186KJ/mol. However, the copolymers do not follow any trend.

The E values for the second stage of decomposition ($\Delta$E= 6-17 KJ/mol) suggest that it is a physical process which could be the volatilization of the product formed during the first stage of decomposition.

## CONCLUSION

The important conclusions that can be drawn from the present study are as following:
1.  High molecular weight poly ether nitrile copolymers can be synthesized by nucleophilic displacement reaction of DCBN with HQ and RE in NMP medium using $K_2CO_3$ as catalyst.

2. The infrared spectrum of RE–DCBN–HQ system shows the presence of two characteristic peaks at $1190cm^{-1}$[$\nu\phi$—O(HQ)] and $1128cm^{-1}$ [$\nu\phi$—O(RE)]. This indicates that both RE and HQ are incorporated in the copolymer chain.

3. The $T_g$ values of the copolymers increase with increase in concentration of HQ in the polymer.

4. The copolymers possess less crystallinity than individual homopolymers due to the random distribution of HQ & RE units in the copolymers, leading to distorted version of the symmetry and alignment.

5. Kinetic analysis shows a two stage thermal decomposition process, with the second stage having very low activation energy, indicative of physical process.

6. Polyether nitriles obtained from isomeric monomers (HQ/RE) retained crystalline property .

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