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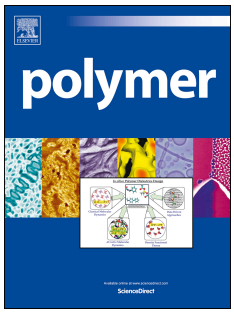

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Dhanya Augustine, Dona Mathew, C.P. Reghunadhan Nair

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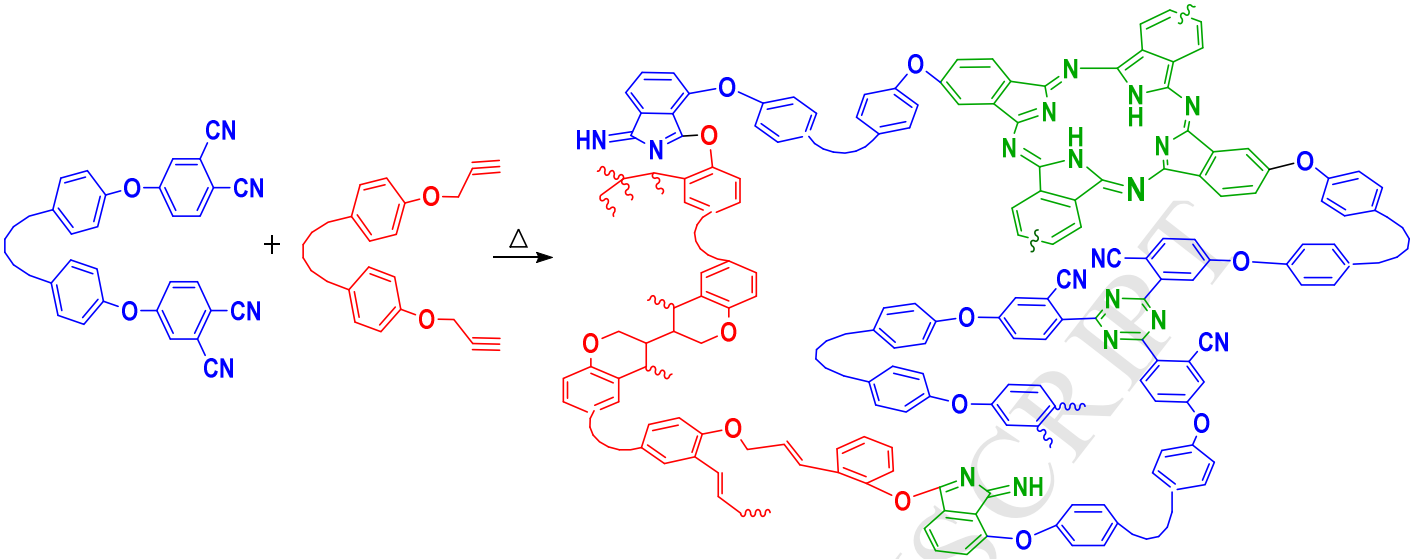


Mechanistic and kinetic aspects of the curing of phthalonitrile monomers in the presence of propargyl groups

Dhanya Augustine, Dona Mathew, C.P.Reghunadhan Nair*

Polymers and Special Chemicals Group
Vikram Sarabhai Space Centre, Trivandrum - 695022, Kerala, India.
*Corresponding author. Tel: +91 471 2565689; fax: +91 471 2564023

E-mail address: cprnair@gmail.com (C.P. Reghunadhan Nair).

ABSTRACT

The influence of propargyl groups on the thermal polymerization of phthalonitrile groups has been examined through reaction of a blend of a bisphthalonitrile *viz*. 2,2-bis(4-phthalonitrile oxy phenyl)propane and a bispropargyl ether *viz*. 2,2-bis(4-properyloxy phenyl)propane (BPhPR). The possibilities for co-reaction of the propargyl and phthalonitrile moieties and/or the catalytic nature of the cure reaction prevailing in their blends were indicated by two overlapping exotherms with maxima around 280 °C and 310 °C in the differential scanning calorimetry and dynamic rheological experiments. This has been attributed to the nitrile curing by chromene units formed by thermal rearrangement of propargyl groups. FT-IR and fluorescence emission spectroscopic investigations on model compounds confirmed that nitrile polymerization was favoured by the chromene and hydroxyl groups formed by Claisen rearrangement. Activation energy of the reaction step involving chromene mediated phthalonitrile crosslinking was found to be 89 kJ/mol which was close to the value of phenol catalyzed phthalonitrile curing.

Keywords: Phthalocyanine, triazine, chromene

1. Introduction

Phthalonitrile polymers offer many attractive features including outstanding thermo-oxidative stability, excellent mechanical properties, low water absorptivity and superior flame resistance [1-7]. However, some inherent limitations such as poor processability, brittleness and need for high curing temperature for long duration are to be overcome to effectively utilize the potential of phthalonitrile systems in engineering applications [8-12]. Many reports have revealed that the complete curing of the nitrile groups is practically impossible even after heating for long duration at elevated temperatures (300-350 °C) [13,14]. Introducing flexible chains such as ether linkages in the backbone could enhance the processability and alleviate the problem of brittleness to a certain extent [15-18]. The cure temperature can be brought down using external curing agents as well as by designing backbones with in-built, self-promoted curing moieties [19-26]. Another widely accepted approach is the incorporation of addition curable groups into the phthalonitrile polymer backbone which help the fine tuning of cure characteristics and properties of the resin [27]. The present study focuses on the feasibility of co-reaction between nitrile groups and propargyl groups leading to intercrosslinked heterocyclic networks via *in situ* generated functional groups. It investigates the mechanism of reaction, its kinetic parameters and features of the resultant heterocyclic network structures. The proposed cure mechanism has been validated using model compounds and extrapolated to polymeric networks. To our knowledge, this is the first report on the copolymerization of phthalonitrile and propargyl monomers. The study explores the possibility of utilizing this reaction as a cure aid for the otherwise high temperature curing phthalonitrile monomers.

2. Experimental

2.1 Materials

Bisphenol A (HPLC, Mumbai), 4 – nitro phthalonitrile (Acros Organics, New Jersey), propargyl bromide (80 % w/w solution in toluene, Alfa Aesar, Britain), *p*-cresol (Aldrich) and benzyl triethyl ammonium chloride (Spectrochem, Mumbai) were purchased from the indicated sources and used as obtained. Potassium carbonate was received from SRL Mumbai and was dried at 150 °C for 4 h prior to use. N-methyl pyrrolidone (NMP), tetrahydrofuran (THF) and acetone (AR grade) received from SRL Mumbai were used as received.

2.2 Characterization

Fourier Transform Infrared (FT-IR) spectra were recorded in the range of 4000-400 cm^{-1} using a Perkin Elmer spectrum GXA spectrophotometer using KBr pellets. Elemental analysis was performed using Perkin Elmer 2400 CHN Analyzer. Solution NMR spectra were recorded using a Bruker Avance FTNMR spectrophotometer operating at 300 MHz. Tetra methyl silane (TMS) was used as the internal standard and acetone–d_6 and $CDCl_3$ were used as the solvent. ^{13}C cross-polarization magic angle spinning (CP-MAS) experiments were carried out using a Bruker Avance 400 MHz wide cavity solid-state NMR spectrometer operating at a resonance frequency of 100.6 MHz. Chemical shifts were recorded relative to admantane as external reference. Gel permeation chromatography (GPC) using Waters Alliance 2690; employing polystyrene standards. A TA instrument DSC Q-20 was used to perform non-isothermal scans to study the cure reaction of model compounds and propargyl-phthalonitrile blends. Dynamic DSC was done at a heating rate of 10

^{o}C/min in nitrogen atmosphere from 30 °C to 400 °C. Thermogravimetric analysis (TG) of the cured blends was performed with TA instruments SDT Q-600 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere with a purge rate of 10 mL/min. Rheological characterization was done using a Discovery HR-3 Hybrid Rheometer in the parallel-plate assembly (20 mm diameter). The curing reaction of blend was studied in oscillatory mode at a low strain value (1 %), at a frequency of 1 Hz. The build-up of storage modulus was monitored over the temperature range of 200 °C to 400 °C at a scanning rate of 3 ^{o}C/min. The gap between the plates was maintained at 1 mm. Pyrolysis GC-MS analysis of the cured blends of model compounds, CMPPN-PR were carried out at 300 °C by SGE Pyrojector (continuous mode) Pyrolyser, in conjunction with a GC/MS system consisting of Thermo Electron Trace Ultra GC, coupled to a Thermo Electron PolarisQ (Quadrople ion trap) mass spectrometer. The fluorescence spectra were recorded on Perkin Elmer LS-55 Luminescence spectrometer by exciting the samples at their absorption maximum (lab max).

2.3 Synthesis of 4-(4-methyl phenoxy)phthalonitrile (MPPN) and Bisphenol A bisphthalonitrile (BPhPN)

The model compound MPPN and the bisphthalonitrile monomer BPhPN were synthesized by similar procedure. In a typical reaction, to the mixture containing bisphenol A (10 g, 0.044 mol) and anhydrous K_2CO_3 (30 g) in N-methyl pyrrolidone, 4-nitro phthalonitrile (18 g, 0.1 mol) dissolved in 25 mL NMP was added drop-wise and stirred continuously for 12 h at 70 °C under nitrogen atmosphere. After the reaction, the mixture was filtered and the filtrate was precipitated into 90:10 water-methanol mixture. The precipitate was filtered and washed with methanol for several times and recrystallized from methanol-THF mixture. The product was characterized by FT-IR, ^{13}C and ^{1}H NMR, elemental analysis and melting point.

Selected data of BPhPN:^{1}H NMR (300 MHz, Acetone-d_6, δ ppm): 8 (d, J = 8.7, Ar-H), 7.6 (d, J = 2.5, Ar-H), 7.4 (s, Ar-H), 7.4 (d, J = 8,Ar-H), 7.1 (d, J = 8.7, Ar-H), 1.7 (s, *gem*CH_3)

^{13}C NMR (300 MHz, Acetone-d_6, δ ppm): 152.98, 148.98, 136.83, 129.8, 129.78,129.75, 122.89, 122.69, 120.90, 118.20 (aromatic),116.36, 115.95 (CN), 109.58 (aromatic), 43.24 (**C**$(CH_3)_2$), 31.17 (CH_3)

FT-IR (KBr, cm^{-1}): 3074 (CH_3), 2230 (CN), 1588, 1485, 1419, 1310 (aromatic), 1279 (C-O)

MPPN - Yield: 86 %, m.p.: 90 °C, Anal.Calcd: C, 76.92 %; H, 4.27 %; N, 11.96 %. Found : C, 76.9 %; H, 4.14 %; N, 11.91 %.

BPhPN - Yield: 70 %, m.p.: 195 °C, Anal.Calcd: C, 77.5 %; H, 4.16 %; N, 11.66 %. Found : C, 77.43 %; H, 4.19 %; N, 11.62 %.

2.4 Synthesis of 3-(4-methyl phenoxy) propyne (MPPR) and Bispropargyl ether of bisphenol A (BPhPR)

The propargyl functional model compound MPPR and the bispropargyl monomer, BPhPR were synthesized by adopting the same procedure. In a typical reaction, to the mixture containing bisphenol A (10 g, 0.044 mol), anhydrous K_2CO_3 (30 g) and benzyl triethyl ammonium chloride (BTC) (0.5 g) dispersed in 100 mL acetone, propargyl bromide (15 g, 0.13 mol) was added drop-wise with mechanical stirring for 8 h at 60 °C under nitrogen atmosphere. The mixture was filtered and the filtrate was precipitated in cold distilled water. The yellowish orange product was recrystallized from methanol and was characterized by FT-IR, ^{13}C and ^{1}H NMR and melting point. To obtain MPPR, the filtrate was flash evaporated.

Selected data of BPhPR: ^{1}H NMR (300 MHz, Acetone-d_6, δ ppm): 7.16 (d, J = 8.7, Ar-H), 6.9 (d, J = 8.7, Ar-H), 4.7 (s, -OCH_2-), 3 (s, ≡CH), 1.6 (s, CH_3).

^{13}C NMR (300 MHz, Acetone-d_6, δ ppm): 156.1, 144.1,128, 114.6 (aromatic), 79.5 (C≡C), 76.5 (≡CH), 55.8 (-OCH_2-), 41.8 (**C**$(CH_3)_2$), 30.8 (CH_3)

FT-IR (KBr, cm^{-1}): 3289 (≡CH), 2967 (CH_3), 2121 (C≡C), 1607, 1508, 1419, 1364 (aromatic), 1029 (C-O)

MPPR - Yield: 88 %, resinous state.

BPhPR - Yield: 78 %, m.p.: 80 °C.

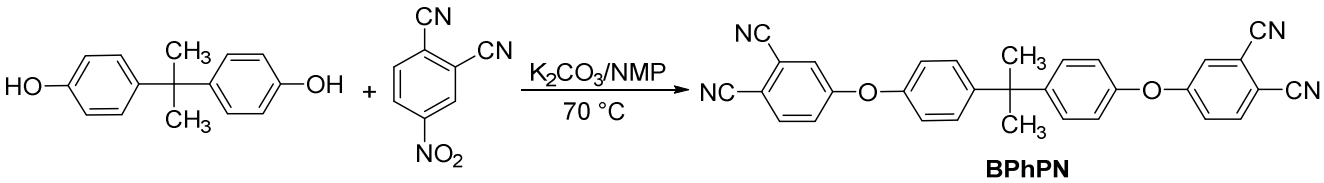
2.5 Preparation of the phthalonitrile-propargyl ether blends

Bisphthalonitrile-bispropargyl ether blends (BPhPN-PR) were prepared by mixing BPhPR and BPhPN in different molar ratios (1:1, 1:1.5, 1:3 and 1:5.7 respectively of BPhPR and BPhPN) in minimum quantity of solvent (THF). The solvent was then removed by drying in vacuum at 50 ^{o}C. In the text, these blend compositions are abbreviated as 1BPhPN-PR, 1.5BPhPN-PR, 3BPhPN-PR and 5.7BPhPN-PR. Curing of these blends were carried out under inert atmosphere according to the cure schedule represented in Fig. 1. The cured blends of BPhPN and BPhPR (330 °C, 5 h) are abbreviated as CBPhPN-PR(330). Same procedure was adopted for formulation of blend composition of model compounds viz, MPPN and MPPR by mixing them in the 1:1 molar ratio. The model compounds were cured at 230 °C for 4 h and designated as CMPPN-PR(230).

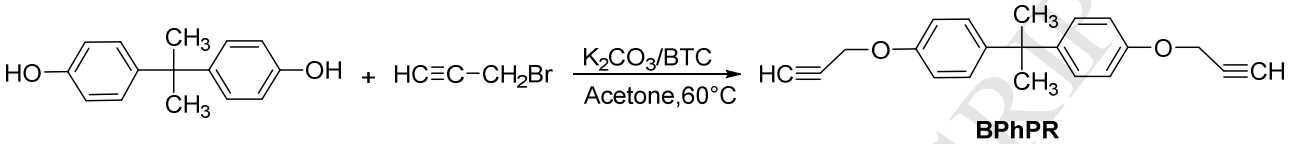
3. Results and discussion

3.1. Synthesis and Characterization of BPhPN and BPhPR

Phthalonitrile and propargyl ether derivatives of *p*-cresol (MPPN and MPPR) and bisphenol A (BPhPN and BPhPR) were synthesized by the nucleophilic substitution of NO_2 group of 4-nitro phthalonitrile and bromide group of propargyl bromide by the alkaline salts of cresol/bisphenol respectively. Synthetic routes of BPhPN and BPhPR are depicted in Schemes 1 and 2.



Scheme 1. Synthesis of bisphthalonitrile ether of bisphenol A (BPhPN)



Scheme 2. Synthesis of bispropargyl ether of bisphenol A (BPhPR)

The monomers and model compounds were characterized in terms of their melting point, elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectra (Supporting information, S1). The melting points of BPhPN and BPhPR were 195 °C and 80 °C respectively, in close agreement with the reported literature [4,28]. BPhPN and MPPN showed characteristic IR absorption owing to nitrile groups at 2230 cm^{-1}. BPhPR and MPPR showed characteristic peaks of ≡C–H around 3290 cm^{-1}, together with a weak absorption band around 2120 cm^{-1}due to C≡C stretching vibrations. In both the cases, the -OH peak was absent which ensured the complete conversion of –OH groups in the reactants to the respective derivatives. There is little possibility for residual potassium phenolate moieties as these are reacted with excess of nitro phthalonitrile for longer duration.

The ^{13}C spectral data also matched well with the structures of monomers with chemical shifts of 115 ppm and 75-80 ppm corresponding to nitrile and acetylene groups in the respective model compounds and bisphenol-based monomers. Characteristic signal due to ≡C–H was observed at 3 ppm in the ^{1}H NMR spectrum of MPPR and BPhPR.

In order to understand the mechanism of curing, composition and structure of the cured products, different proportions of MPPN and MPPR and also BPhPN and BPhPR were blended as discussed

earlier. A systematic study on mechanism of cure reaction between propargyl and nitrile groups and characterization of the resultant products have not been reported so far. This paper is an attempt in this direction to understand the possible reactions occurring in the blends. Different techniques invoking FT-IR, NMR and fluorescent emission spectroscopies and DSC technique have used for this purpose.

3.2. Cure studies

3.2.2. Spectral studies of cured systems

From the FT-IR spectra of BPhPN and CBPhPN (Fig.2), it is clear that a marginal decrease in nitirle peak (2230 cm^{-1}) intensity occurred with a concomitant increase in intensities of the absorptions corresponding to triazine (1560 and 1360 cm^{-1}), isoindoline (3400 and 1660 cm^{-1}) and phthalocyanine (1010 cm^{-1}) networks. These heteroaromatic structures are formed via homopolymerization of nitrile groups [29,30]. However, their degree of polymerization is very low and we have tried to study the impact of propargyl groups on the nitrile cure process using model compounds and monomers.

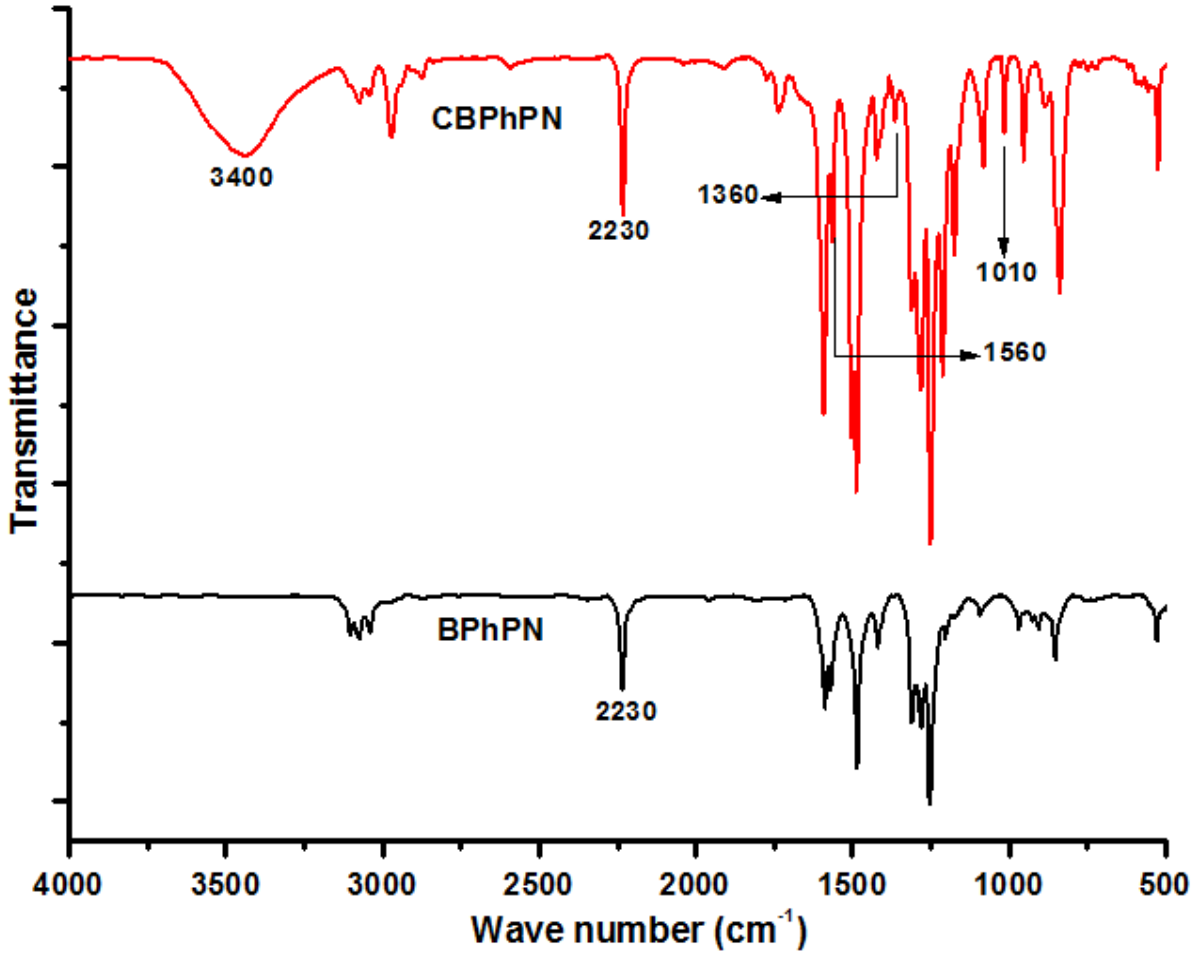


Fig 2. FT-IR spectra of BPhPN monomer and its cured form CBPhPN

Since MPPR was found to vaporize at lower temperature (DSC curve is given as Supplementary information S2), the blend of model compounds was heated in a vacuum sealed glass vessel**.** In all cases, FT-IR spectra of cured blends of model compounds CMPPN-PR(230) (Fig.3) and monomers CBPhPN-PR(330) (Fig 4) showed complete disappearance of acetylenic bond as indicated by the absence of ≡C–H (3290 cm^{-1}) and C≡C (2120 cm^{-1}) characteristic absorptions. A concomitant diminution in intensity of nitrile peak at 2230 cm^{-1} compared to their corresponding uncured blends was also noted. From Fig 5, it is clear that irrespective of the blend composition, the acetylenic

linkages in the BPhPR has completely entered into the cured network whereas a portion of the–CN functionalities still remain unreacted in the network. Further investigations show that while the FT-IR spectra of the blends of model compounds and monomers (immediately after mixing) used in the present study showed no peak at 3400 cm^{-1}. On the other hand, the corresponding cured systems exhibited a broad peak centered around 3400 cm^{-1} with considerable decrease in the nitrile peak intensity (Fig. 3 and 4). These spectral changes can be considered as indication of co-reaction between propargyl and phthalonitrile groups. This observation is substantiated by the appearance of characteristic absorptions of chromene-nitrile reaction products such as triazine (1560 and 1360 cm^{-1}), isoindoline (3300 and 1660 cm^{-1}) and phthalocyanine (1010 cm^{-1}) structures [3,31]. It can be assumed that in the high temperature conditions (200-280 °C) employed for blends, chromene groups can catalyze the polymerization of nitrile groups

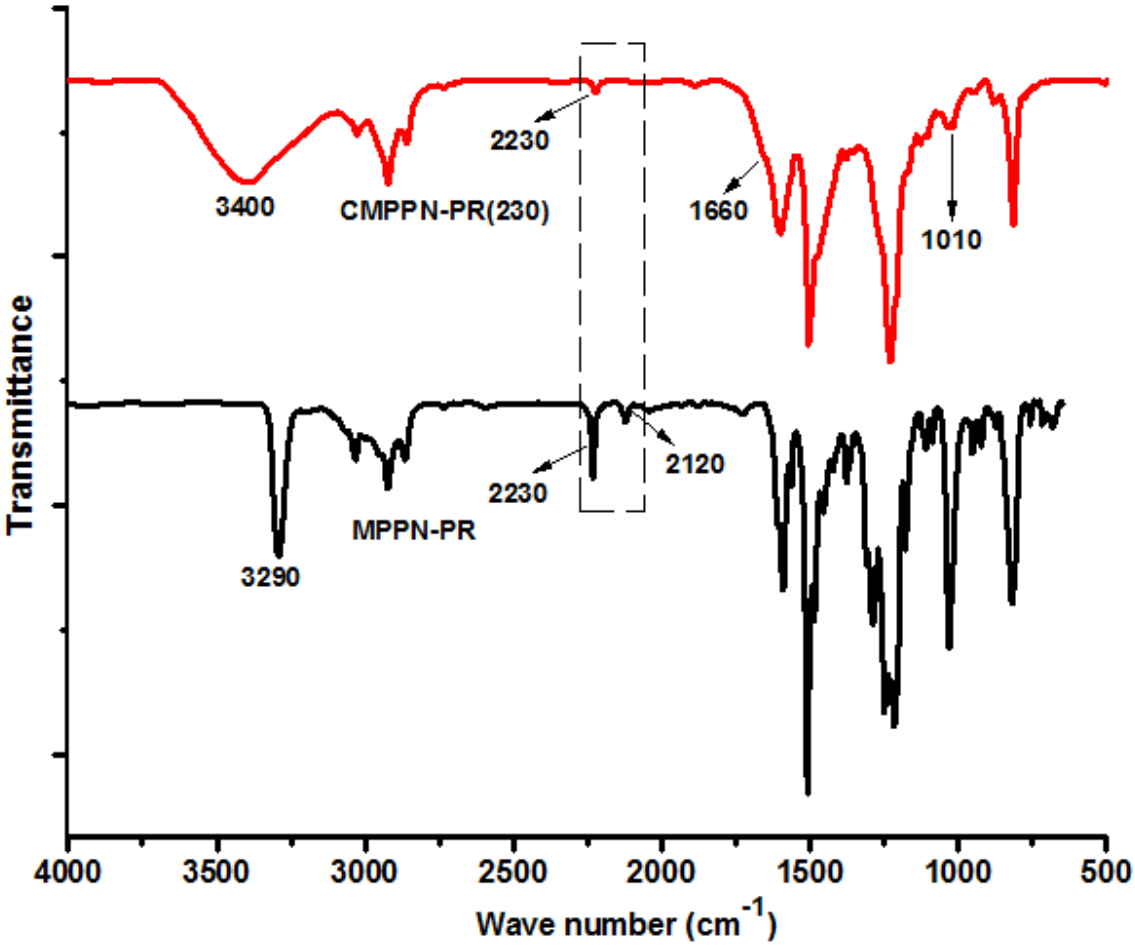


Fig. 3. FT-IR spectra of blends of model compounds MPPN-PR and its cured form

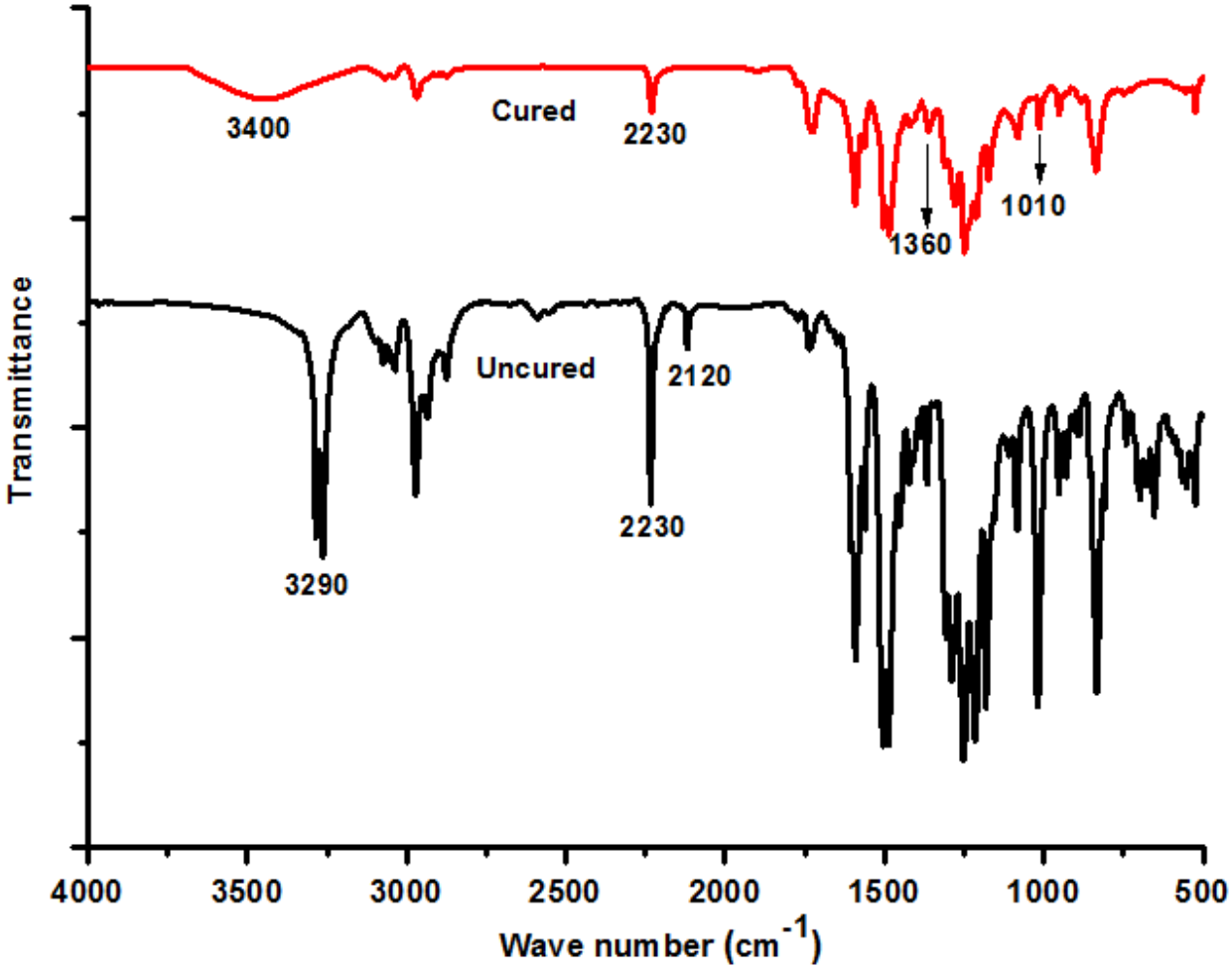


Fig. 4. FT-IR spectra of 1.5BPhPN-PR and its cured form C1.5 BPhPN-PR (330 °C, 5 h)

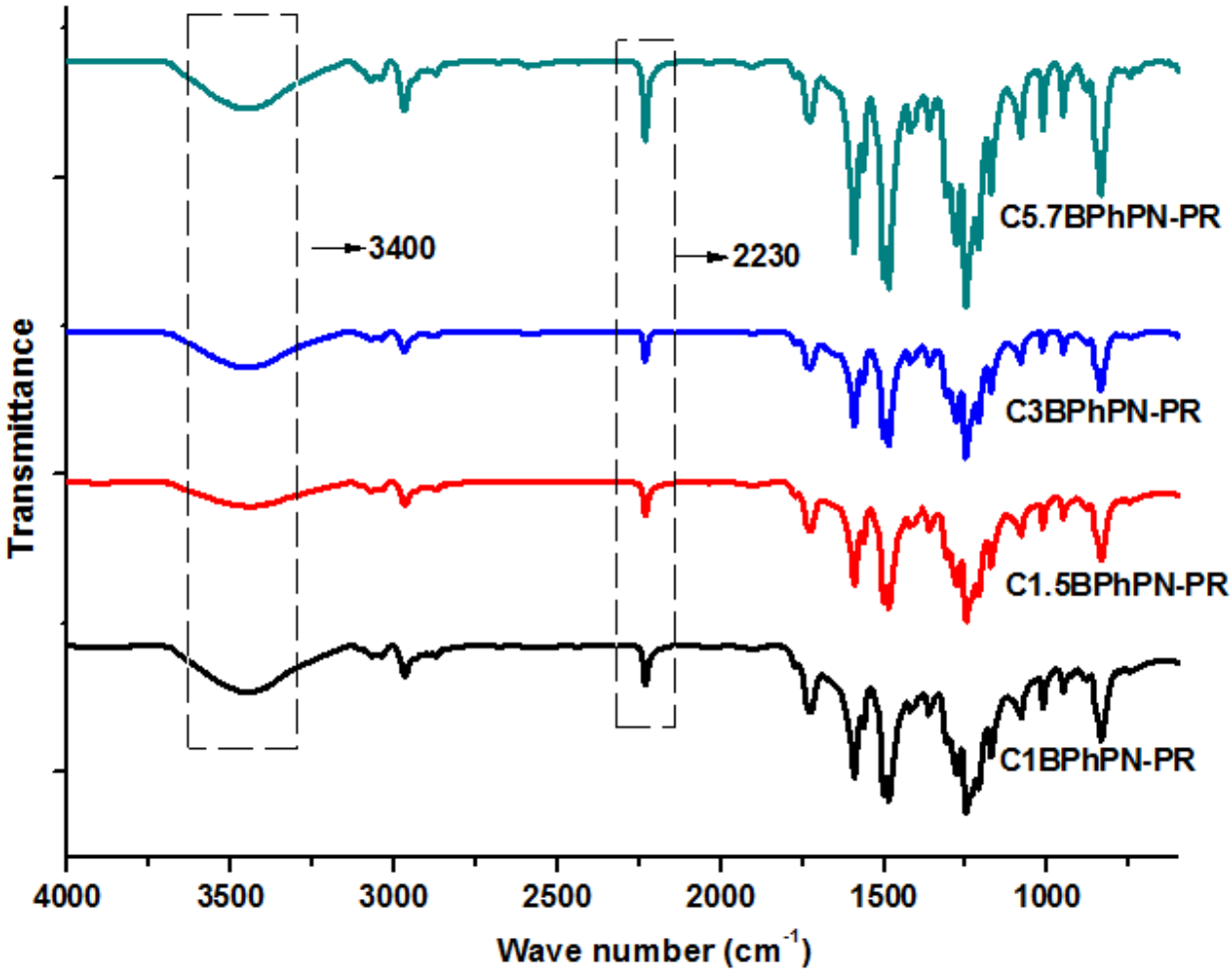
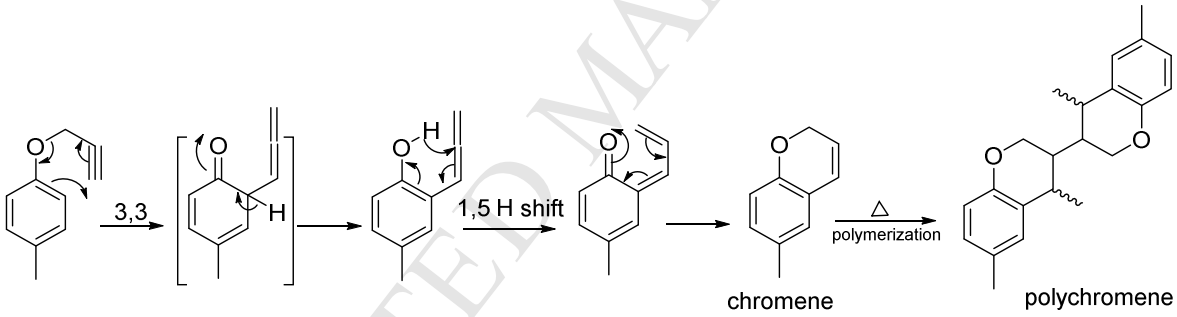


Fig. 5 FT-IR spectra of cured BPhPN-PR blends (330 °C, 5 h)

The two possibilities arising from these reactions are (1) homopolymerization of propargyl group and nitrile groups independently and (2) copolymerization of propargyl group with the nitrile functions. Thermal cyclization of propargyl ethers to chromenes and its homopolymerization are well documented in literature [28,32,33]. Possibility for independent uncatalyzed homopolymerization of nitrile groups is ruled out as no evidence was seen in NMR (^{1}H and ^{13}C) and FTIR for any reaction even after heating MPPN at 230 °C for 4 h (Supplementary information S3). In addition, a cure exotherm was not seen in the DSC profiles of MPPN or BPhPN on heating up to

400 °C. Now, the most probable reaction occurring in the blend is co-reaction between the propargyl homopolymer and nitrile groups.

In the case of MPPR, there were notable changes in the spectral data on curing, giving a clear picture of their polymerization routes. Previous studies on curing of propargyl monomers have unequivocally established their mechanism of polymerization and structures of the cured networks. Simulation studies on reaction mechanism of monopropargyl compounds by Grenier-Loustalot and Sanglar detail their crosslinking patterns and the intermediates involved in the cure process with the support of ample evidences [34]. Sigmatropic rearrangement (Claisen rearrangement) of propargyl ethers followed by cyclization produce chromene structures. On heating, they undergo homopolymerization to polychromenes. These reactions are represented in in Scheme 3



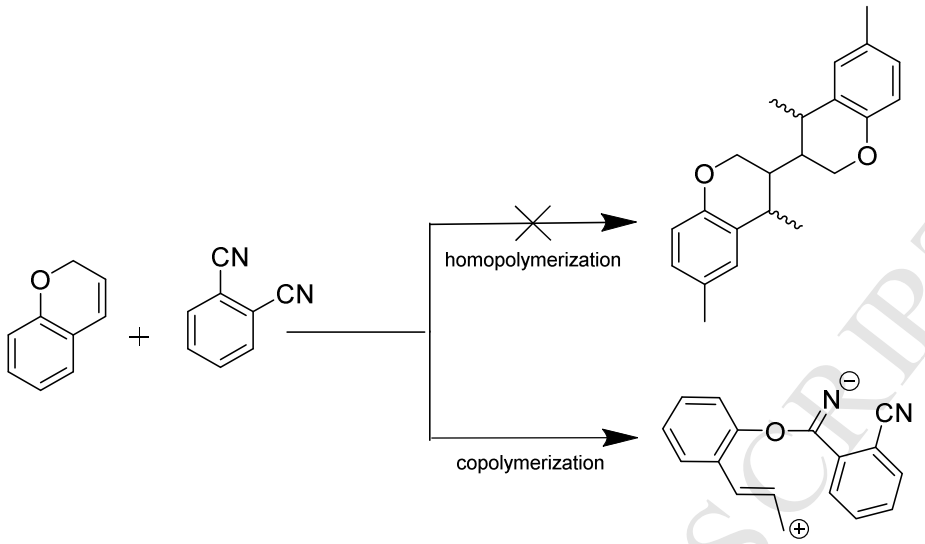
Scheme 3. Polymerization mechanism of propargyl ether functions

The FT-IR spectrum of MPPR heated at 230 °C for 4 h showed that the peaks at ≡C–H (3290 cm^{-1}) and C≡C (2120 cm^{-1}) disappeared and a weak absorption at 880 cm^{-1}, characteristic of aromatic C-H deformation of a chromene unit appeared. Bands between 1100 cm^{-1} and 1200 cm^{-1} denote the C-O vibration of a cyclic ether. FT-IR spectrum also clearly showed a broad spectrum of –OH groups at around 3400 cm^{-1} arising from intermediate formed by the reactions of propargyl functions at elevated temperatures (Fig 6 & Scheme 3) which propagate nitrile polymerization. In ^{1}H NMR

spectrum of cured MPPR, the signal at 4.5 ppm denoted the methylene group and the doublet resonating at 6.5 ppm represented the ethylene hydrogen of chromene units. ^{13}C NMR spectrum of cured MPPR showed characteristic absorption of OCH_2 in the chromene ring around 65 ppm. Ethylene carbons of chromene unit resonated in the same region as that of aromatic carbons (115-130 ppm) and the fused ring carbons appeared at 150-153 ppm (Supplementary information, S4).

Intermediates in the principal reaction, particularly the enol state and final chromene units, and phenolic fractions from secondary reactions can accelerate nitrile cure reaction. Some of the characteristic signals of co-reacted products were identifiable in the ^{1}H and ^{13}C NMR analyses of cured blends of model compounds (Supplementary information, S5).

Solid state ^{13}C CP/MAS spectra of cured blend C1BPhPN-PR and their respective monomers are shown in Fig.7. BPhPR monomer exhibited additional peaks in solid state ^{13}C NMR compared to the solution state NMR which are likely due to the arrangement of molecule in the unit cell. The unit cell is likely to contain two molecules and the arrangement leads to inequivalence of the carbons compared to the solution state. BPhPN also shows inequivalence for the resonances but degree of inequivalence is not evident as in the case of propargyl derivative. Comparison of solid state ^{13}C CP/MAS spectra of cured blend C1BPhPN-PR and their respective monomers showed that the propargyl groups have completely entered into the co-cured network by the disappearance of chemical shift characteristic of C≡CH in 75-80 ppm range. The nitrile signal at 115 ppm was unresolvable due to overlap of peaks. The signal at 105 ppm of BPhPN disappeared on curing with propargyl groups, which is indicative of the co-reaction. Further, the absence of characteristic absorption of $–OCH_2$ at 55 ppm in the cured network showed that the product formed from propargyl cyclization are more likely to induce the –CN curing rather than chromene undergoing homopolymerization as shown in Scheme 4.



Scheme 4. Probable mechanism and induced polymerization of phthalonitrile functions

GC-MS chromatograph of pyrolysed product CMPPN-PR(230) gave chromene peaks at m/z = 145 and high molecular ion peaks corresponding to co-reaction products (Supplementary information S6).

In the cured model compounds with stoichiometric ratio of 2:1 (nitrile:propargyl) functions, about 80 % nitrile conversion was estimated when normalized to ether linkage. However, during the reaction of monomers (bisphthalonitrile-propargyl ether blends), only 35 % nitrile conversion was attained, probably due to the prevalence of steric factors compared to the simple model compounds.

3.2.3. DSC and rheological studies of blends

In order to investigate the possibilities for homo-/copolymerization of the monomers, thermal transitions of the monomers and their blends were examined by DSC and the resultant thermograms are depicted in Figures 8a and 8b.

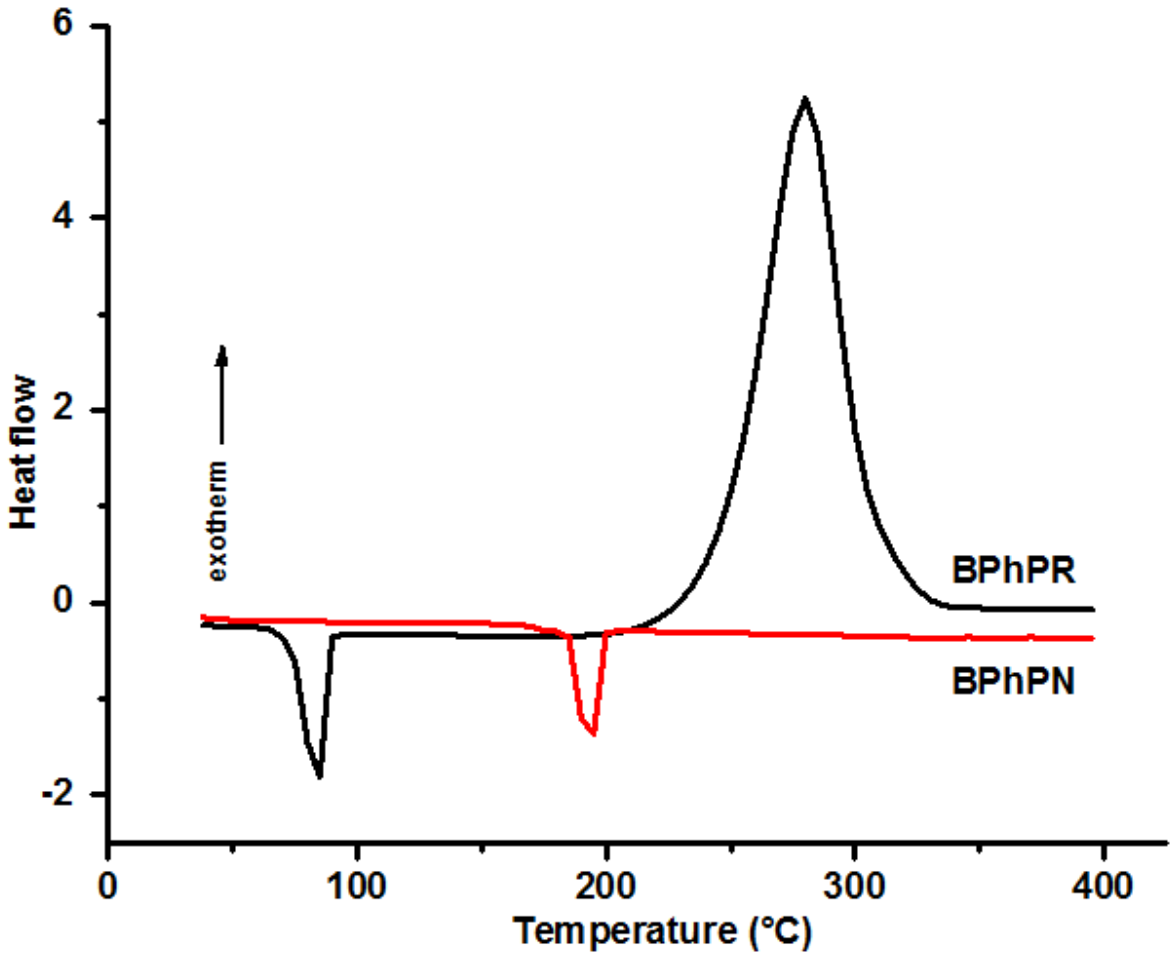


Fig.8a. DSC profile of bisphthalonitrile and bispropargyl monomers

Thermogram of BPhPR exhibits two transitions, corresponding to its melting at 80 °C and an exotherm starting at 198 °C with a peak of 280 °C ascribed to its self-polymerization through propargyl moieties. BPhPN shows only a melting transition at 195 °C and no cure exotherm was observed up to 400 °C. However, this monomer formed a green coloured crosslinked polymer on heating at 330 °C for 5 h under nitrogen atmosphere which was insoluble in organic solvents [35]. This green color being typical of phthalocyanine, it implied formation of this structure through slow nitrile polymerization. As the kinetic is slow, and the conversion insignificant, it goes without

getting detected in DSC (heating rate: 10 °C/min). However, under favourable conditions such as sudden heating at elevated temperatures (say, 330 °C), there is every possibility for the polymerization reaction of phthalonitrile groups with sufficient heat release as to be detected in DSC.

On the contrary, thermograms of the blends showed two well resolved endothermic transitions corresponding to the melting of the two monomers (BPhPR and BPhPN) and an overlapping exotherm with two maxima peaked around 280 °C and 310 °C. The first exotherm is in the same temperature range as that of BPhPR and may be attributed to the Claisen rearrangement and self-curing of propargyl groups in the blend, yielding chromene networks. The overlapping high temperature exotherm with peak temperature at around 310 °C was not present originally in either of the thermograms of the monomers. This can thus be attributed to polymerization of nitrile groups triggered by the chromene units. A close examination of the DSC curve revealed a discontinuity at around 290 °C (enlarged portion in Fig 8b) which can be assigned to the nitrile polymerization facilitated by hydroxyl functions generated in the polymerization step/secondary reactions of propargyl ethers (Scheme 5). Phenolic moieties accelerating nitrile crosslinking has been already reported [31].

These observations were supported by rheological analysis of the blends (Fig. 10). It is to be understood that the co-reaction is sluggish when compared to the homopolymerization of BPhPR. This was confirmed from the FT-IR studies which show majority of the –CN groups remaining unreacted in the network of BPhPN-PR blend. Bispropargyl-bisphthalonitrile blends (BPhPN-PR) with lesser phthalonitrile content showed cure initiation at a lower temperature compared to phthalonitrile dominant blend compositions as evident from data in Table 1. In addition, when the molar ratio of phthalonitrile monomer (with respect to propargyl ether) was increased from 1 to 5.7,

the ultimate cure temperature shifted from 341 °C to 394 °C, drawing more nitrile functions into the cured networks. A considerable decline in heat of reaction occurred with the increase in phthalonitrile content of blends. Thus, the enthalpy for the nitrile cure in 1BPhPN-PR is 235 kJ/mol and that for 5.7BPhPN-PR is 79 kJ/mol only.

Comparison of ΔH_{exp} and ΔH_{theo} (Fig.9) calculated from the enthalpies of homopolymerization and composition of the blends show that on blending and curing, the heat of polymerization is more than that expected from the respective heat of polymerization of the individual components. This shows the possibility of co-reaction between the two monomers or catalytic nature of the cure reaction.

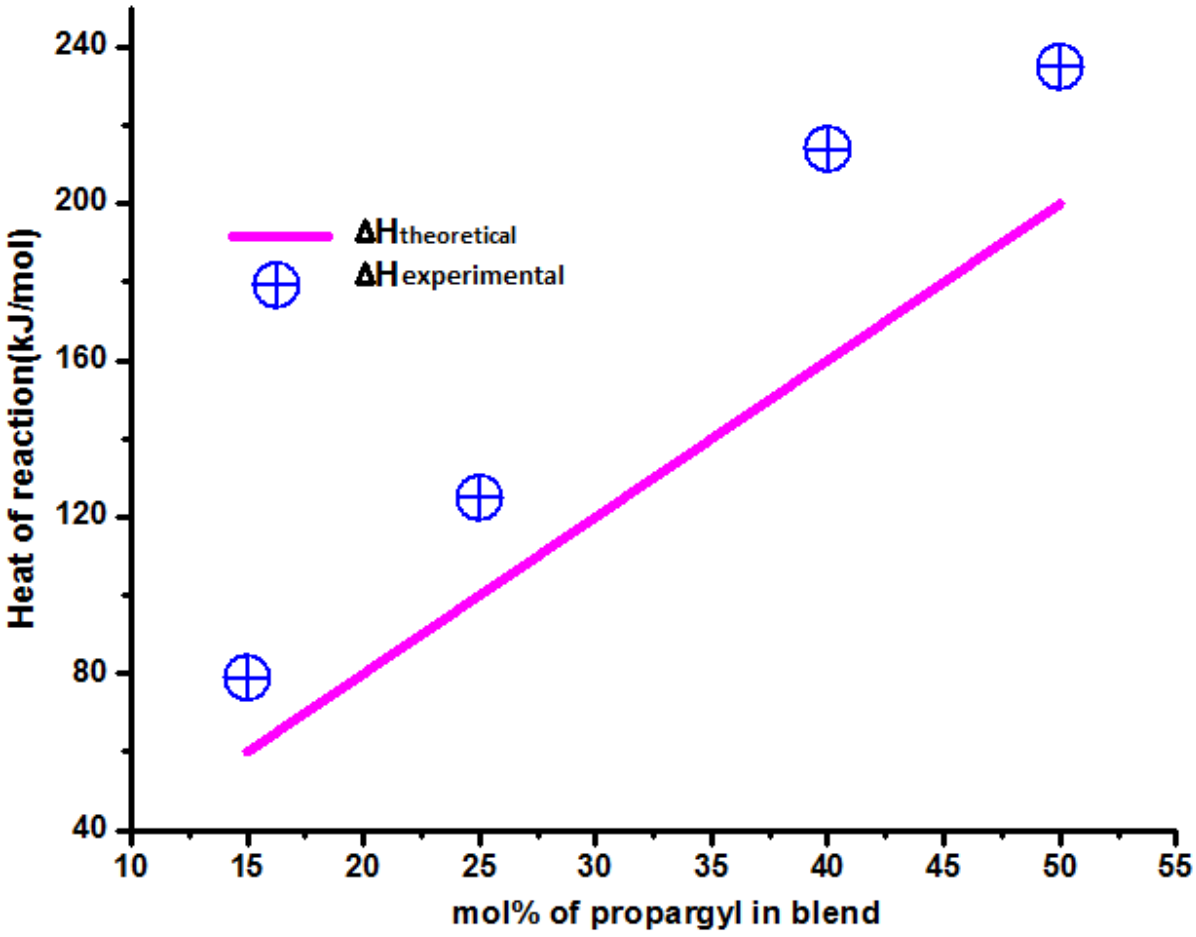
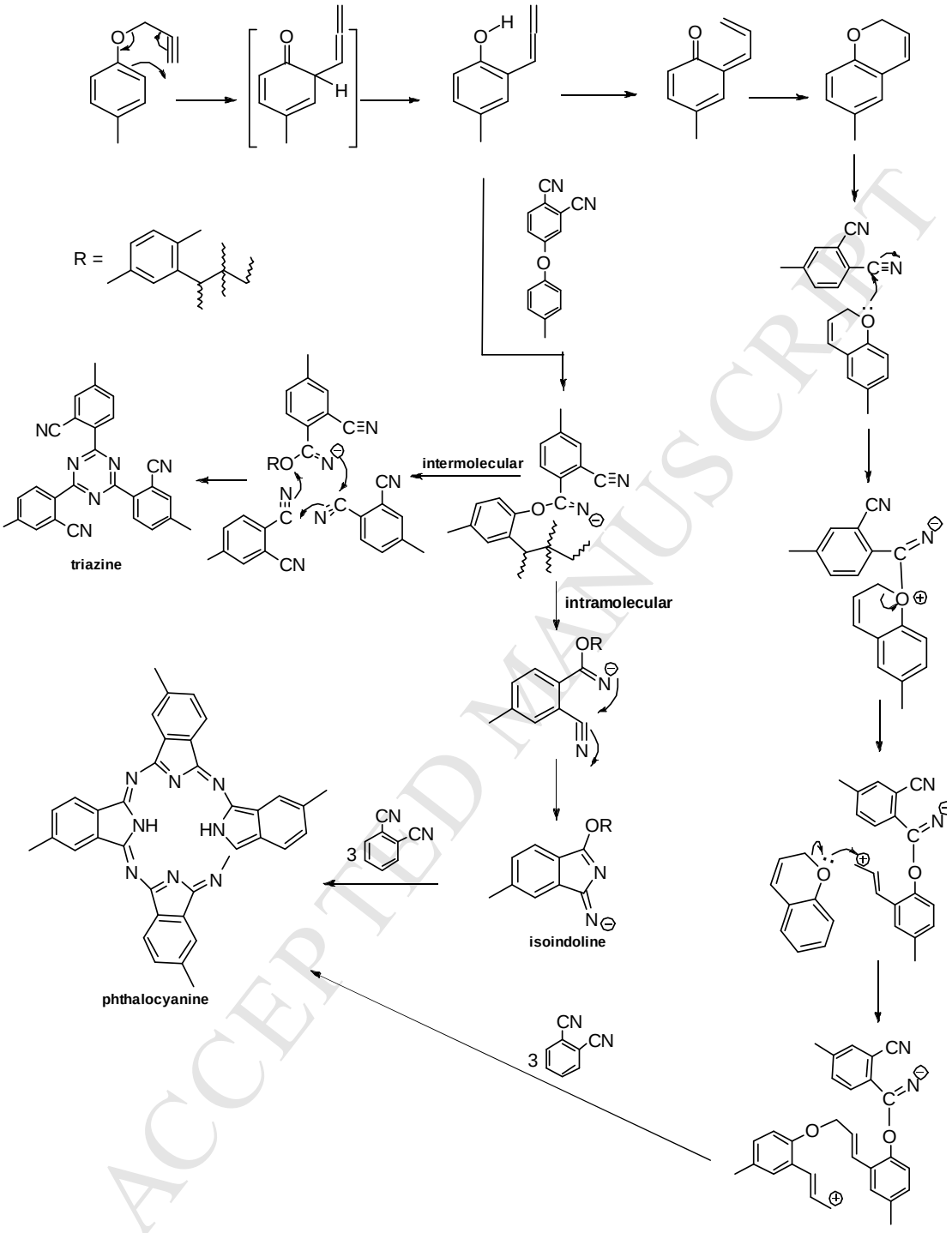


Fig. 9. Variation of enthalpy of cure reaction with propargyl content in BPhPN-PR blends

Dynamic rheological experiment was performed typically for 3BPhPN-PR blend from 200 °C to 400 °C (Fig.10). The rheogram shows that storage modulus build-up initiates at 270 °C and reaches a plateau at around 340 °C. As seen in DSC themogram, there were some discontinuities in the steady increase of storage modulus probably due to the overlapping of different stages in cure process. The first derivative of the storage modulus curve (dG′/dT) clearly indicated three prominent transitions corresponding to propargyl polymerization (280 °C) and nitrile crosslinking mediated by –OH groups (297 °C) and chromene units (310 °C) . Based on cure optimization by DSC and rheological studies, the blends were cured at 330 °C for 5 h for further analysis of the cured network.

The probable overall co-cure reaction mechanism can be depicted as in Scheme 5.



Scheme 5. Phthalonitrile cure reaction pathways in the presence of propargyl functions

3.2.4. GPC and Fluorescence emission spectra of cured model compounds

In order to confirm the molecular weight build up due to co-reaction, GPC technique was used. In the Gel permeation chromatogram using low molecular weight column shown in Fig.11, retention times corresponding to the model compounds MPPN and MPPR are at 16 min and 18 min respectively. It is evident that, on heating MPPR (230 °C for 4 h), higher molecular weight products are formed by polymerization of chromenes which resulted from cyclization of propargyl groups. For MPPN, the cure conditions employed do not favour the structural modifications as evident from their spectral analyses (Supporting information S3). There was no differences in the ^{1}H and ^{13}C NMR spectra of MPPN and CMPPN(230). In the case of co-reacted model compounds, CMPPN-PR under same conditions, the product is eluting at still lower retention time. This molecular weight build-up can be due to the co-reaction between the propargyl and nitrile functions under the reaction condition employed. Polymerized product of MPPR showed number average M_n ~ 446 and that of copolymerized product was 846. From the GPC graphs, it is clear that no unreacted model compounds remain in the co-reacted products. However, since the columns are calibrated against polystyrene standards, absolute molecular weight of the products could not be computed.

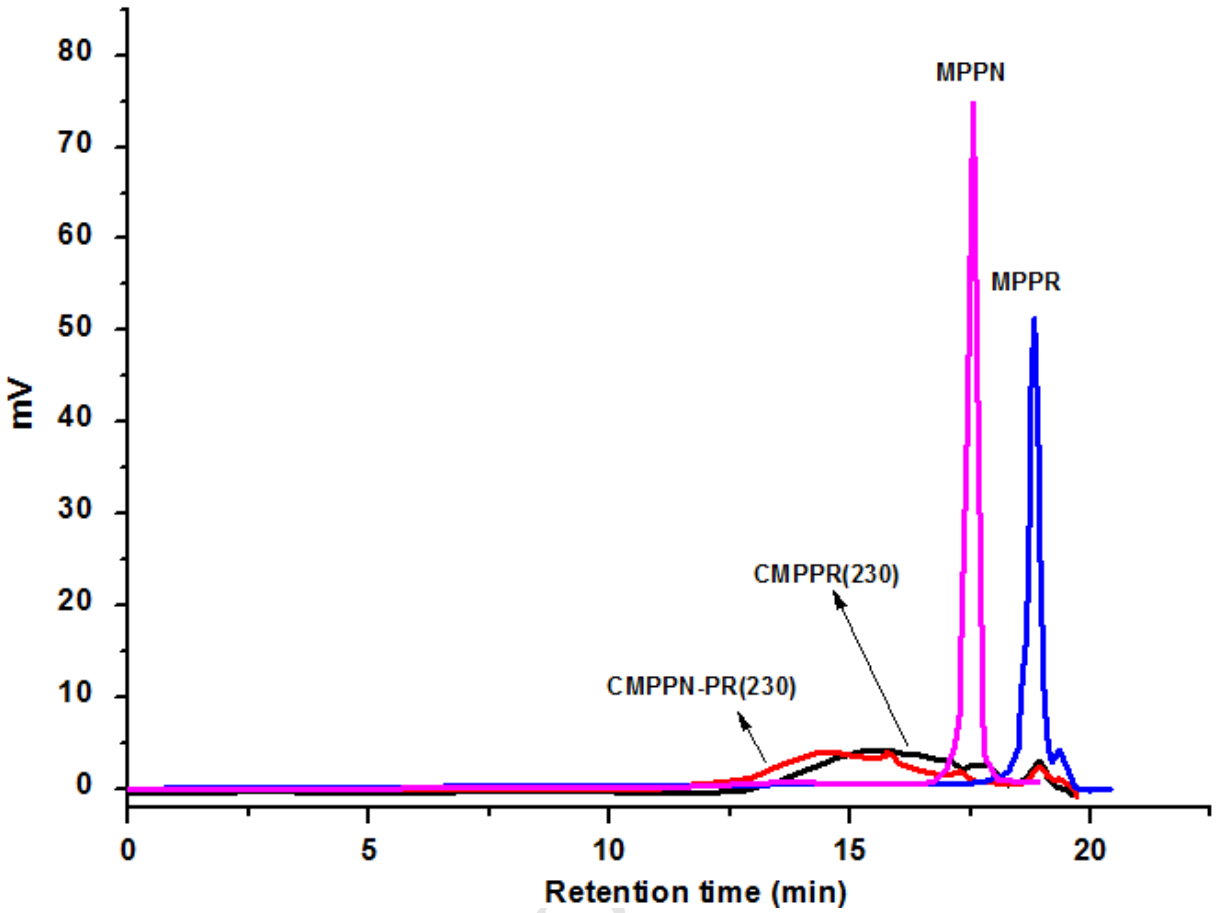


Fig.11. GPC chromatogram of model compounds and their cured forms

With an intention to monitor the formation of any fluorochromic structures such as phthalocyanines, fluorescence emission of cured model compounds was evaluated. Fig 12 depicts the fluorescence emission spectra of CMPPR, CMPPN(230) and CMPPN-PR(230) at 650 nm excitation. In CMPPN-PR(230), the formation of extended conjugated structures with fluorochromic nature such as phthalocyanine was obvious from its fluorescence emission band in the 670-720 nm region. However, under the same cure condition (230 °C) such an emission band was absent for MPPN, CMPPN and CMPPR. The cure conditions employed are not conducive for uncatalyzed polymerization of nitrile groups (Supporting information S3). These observations establish that the propargyl groups can acts as a possible cure aid for nitriles and their probable reaction pathways are

shown in Scheme 5. A complete insight of the cured network structures in propargyl-phthalonitrile blends require further investigations in this direction.

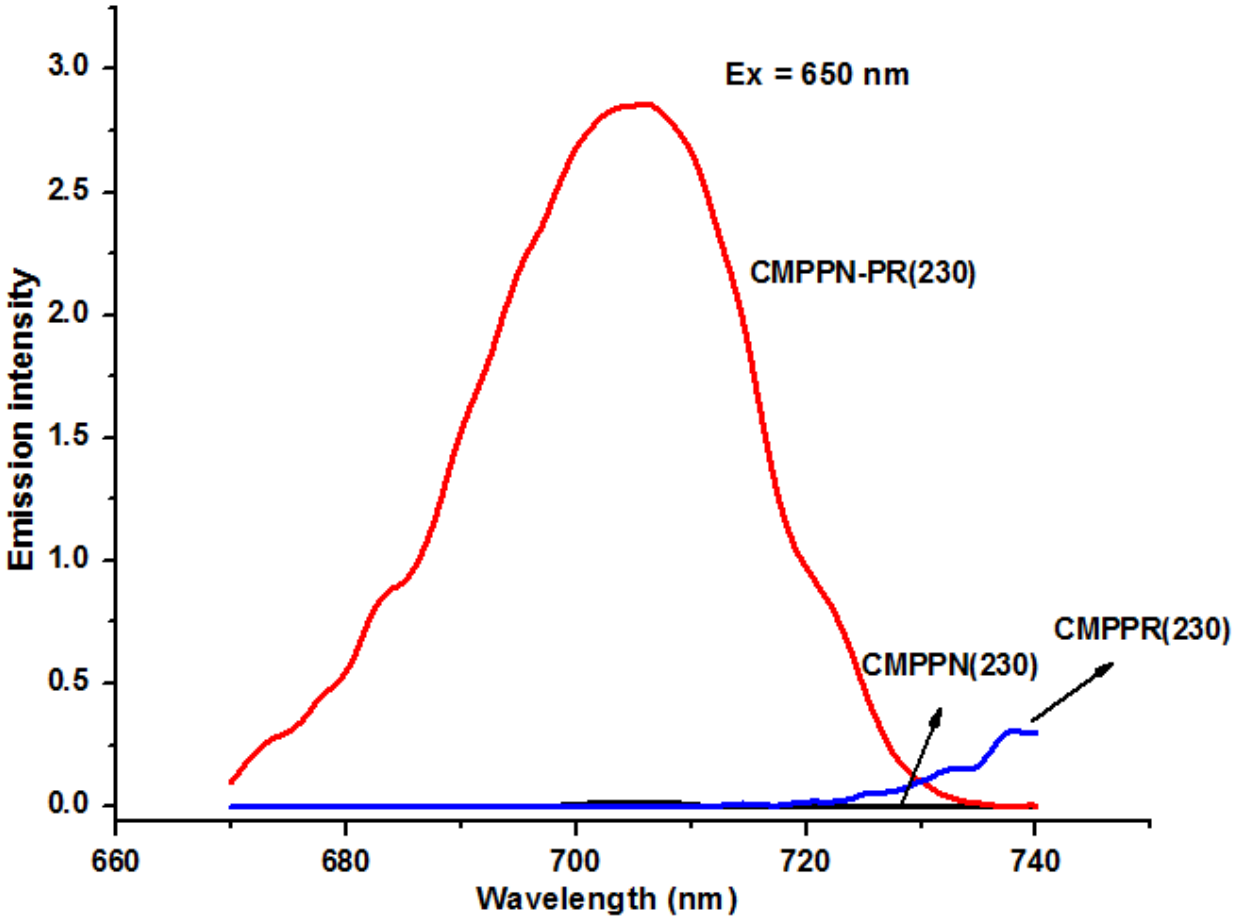


Fig .12 Fluorescence emission spectra of cured model compound and their blend

3.3 Kinetic parameters

The present study also investigated the influence of kinetic factors in favouring the co-cure reaction of phthalonitrile functionalities with propargyl groups, based on the kinetic parameters derived. For this, the blend composition 1BPhPN-PR was subjected to non-isothermal DSC studies using multiple-heating rate methods proposed by Ozawa and Kissinger (2 °C/min, 4 °C/min, 7 °C/min, 10

°C/min and 15 °C/min). The advantage of these methods is that, they do not demand any advance knowledge of reaction mechanism for calculations [36-39].

Kissinger and Ozawa methods relate activation energy, E_a with the heating rate ϕ and iso-conversion temperature T_p as shown in equation (1) and (2) respectively. The reaction rate is presumed to be maximum at the peak temperature (T_p).

$$\frac{2.303d\left[\log\left(\frac{\phi}{T_p^2}\right)\right]}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R} \quad (1)$$

$$\frac{2.15d[\log(\phi)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (2)$$

Collision factor 'A' was found in both the cases using the equation (3)

$$A = \frac{\phi E e^{E/RT_p}}{RT_p^2} \quad (3)$$

The peak of exotherms got shifted to higher temperature with the increase in heating rate. Thus, on changing the heating rate from 2 °C/min to 15 °C /min, the first exotherm peak being shifted from 255 °C to 288 °C and the overlapping second exotherm peak shifted from 271 °C to 324 °C.

The merged exotherms indicate that the co-cure reaction of the propargyl and nitrile functionalities comprises of multi-stages, each proceeding by different mechanisms. To determine the kinetic aspects of the whole cure process, the kinetic parameters of the major two steps were determined separately after deconvoluting the peaks manually and plotting their corresponding Ozawa and Kissinger plots. Ozawa plots of each step of cure reaction are shown in Fig. 13.

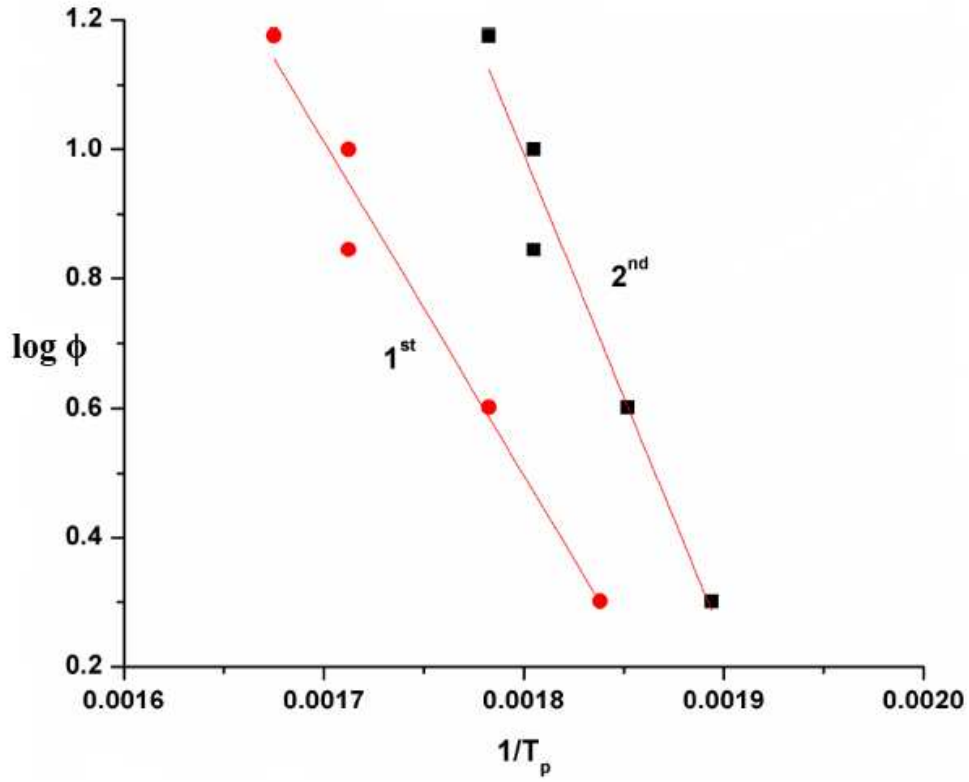


Fig. 13. Ozawa plots for the 1st and 2nd step of co-cure reaction

The calculated values of kinetic parameters from Kissinger and Ozawa kinetic models were almost similar. The derived kinetic parameters (E_a and A) are tabulated (Table 2).

As per Ozawa method, activation energy and frequency factor of BPhPR are 156 kJ/mol and 6 x 10^{12} s^{-1} respectively and the rate constant of their reaction at 280 °C was found to be 10^{-2} s^{-1}. In the case of propargyl-phthalonitrile blends, the first curing step showed higher activation energy (136 kJ/mol) compared to the second (89 kJ/mol). On the basis of our cure studies, the first step may be attributed to a dominant self-curing of propargyl groups and a probable co-curing with phthalonitrile functionalities to a minor extent. The second step is considered mainly due to crosslinking of remaining phthalonitrile groups in the blend by co-reaction with propargyl groups or due to self-

curing of nitrile groups promoted by reaction products of 1st step. Energy of activation required for the second step was very close to the phenol catalysed polymerization (90 kJ/mol) in phenol-phthalonitrile oligomers as per the Coats Redfern method. This again substantiates the indirect involvement of phenolic groups derived from the secondary reactions of propargyl groups in the phthalonitrile cure reactions.

The cure kinetic scenario of polymers is significantly different from that of simple reaction systems. Thus, the kinetic parameters derived from the kinetic models will be valid for the early stages of cure, prior to diffusion control where the reactants retain their liquid consistency. In the later stages of polymerization, the whole reaction system get converted to a highly crosslinked network, restricting the mobility to a great extent. Now, the system becomes just similar to a solid state reaction where the kinetic parameters have only empirical significance and can be used to forecast the isothermal cure profiles at a particular temperature.

The order (n) of each step involved in cure reaction was found from the Coats-Redfern treatment using the relationship (Equation 4) [40].

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left\{\left(\frac{AR}{\phi E}\right)\left(1-\frac{2RT}{E}\right)\right\} - \frac{E}{RT} \qquad (4)$$

where $g(\alpha) = \left\{\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right\}$ for $n \neq 1$

and when n = 1, $g(\alpha) = -\ln(1-\alpha)$

The plots of $\ln[g(\alpha)/T^2]$ against reciprocal of absolute temperature for different assumed values of 'n' ranging from 1-3 were executed. The best linear fit was determined based on the correlation

coefficient. Best linear fitting was observed for the n values 1.5 and 2 for the first and second step of cure reactions respectively.

3.4. Thermal stability of the cured networks

All compositions of the cured BPhPN-PR blends were thermally stable upto 400 °C with peak decomposition temperature around 450 °C. The thermal stability of the cured blends can be attributed to the combined contribution of homopolymerization and copolymerization products in the cured networks.

Contrary to expectations, TG of co-cured blends of monomers (Fig 14) showed a proportionate decrease in char residue with the increase in phthalonitrile content. This indirectly implied that, beyond 35 %, incorporation of nitrile groups (quanitatively estimated by FT-IR) into the co-cured networks became practically difficult due to steric factors and require higher activation energy for achieving complete conversion. Thus, when the homopolymer of BPhPR showed 58 % weight retention at 900 °C, BPhPN showed only 8 % weight retention. The high char yield of BPhPR is due to the formation of cured polymer network via chromene intermediate during self-curing of propargyl functionalities whereas cured BPhPN exhibited low char yield due to its partially cured state.

4. Conclusions

A multi-stage curing reaction was exhibited by the propargyl mediated nitrile cure reactions. Polymerization of nitrile groups is triggered by the chromene moeities/hydroxyl intermediates derived from the rearrangement of propargyl groups. The resultant co-cured network containing both phthalocyanine and chromene derived groups contained also triazine and isoindoline structures.

Formation of extended conjugated structures with fluorochromic nature such as phthalocyanine was substantiated by fluorescence emission spectroscopic analysis. Kinetic parameters showed that energy of activation required for the propargyl-phthalonitrile co-curing was very much close to the estimated value of phenol catalyzed phthalonitrile curing. Thermal stability of the blends was adversely affected by propargyl content in the co-cured network.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at Supporting Information.pdf

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Table 1. Thermal properties of bispropargyl and bisphthalonitrile monomers and blends

Monomer/Blends	**Composition** **Phthalonitrile : Propargyl**	**T_i (°C)**	**T_{p1} (°C)**	**T_{p2}** **(°C)**	**T_f** **(°C)**	**ΔH_{exp}** **(kJ/mol)**	**ΔH_{theo}** **(kJ/mol)**
BPhPR	0:1	195	279	-	336	400	
1BPhPN-PR	1:1	214	281	310	341	235	200
1.5BPhPN-PR	1.5:1	218	281	310	345	214	160
3BPhPN-PR	3:1	221	282	310	392	125	100
5.7BPhPN-PR	5.7:1	230	282	310	394	79	60
BPhPN	1:0	-	-	-	-	0	

T_i - Intial temp, T_{p1} - 1st peak temp, T_{p2} -2nd peak temp, T_f - Final temp,
ΔH_{exp} - experimental enthalpy of cure, ΔH_{theo}- theoretical enthalpy of cure

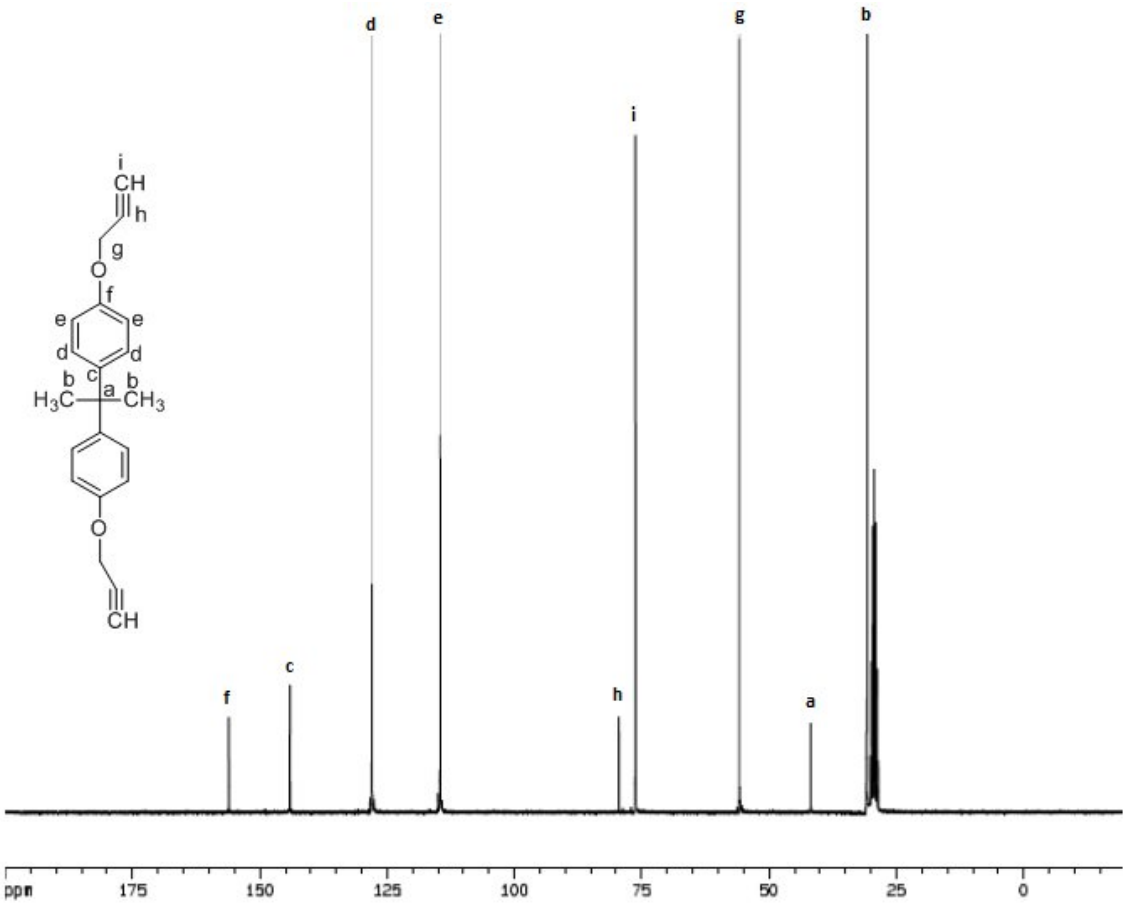
Table 2. Kinetic parameters from kinetic models

Ozawa						Kissinger			
1st step			2nd step			1st step		2nd step	
E_a (kJ/mol)	A(s^{-1})	k at 280 °C	E_a (kJ/mol)	A(s^{-1})	k at 310 °C	E_a (kJ/mol)	A(s^{-1})	E_a (kJ/mol)	A(s^{-1})
136	5.1×10^{10}	8×10^{-3}	92	9×10^{5}	5×10^{-3}	136	5.9×10^{10}	89	4.71×10^{5}

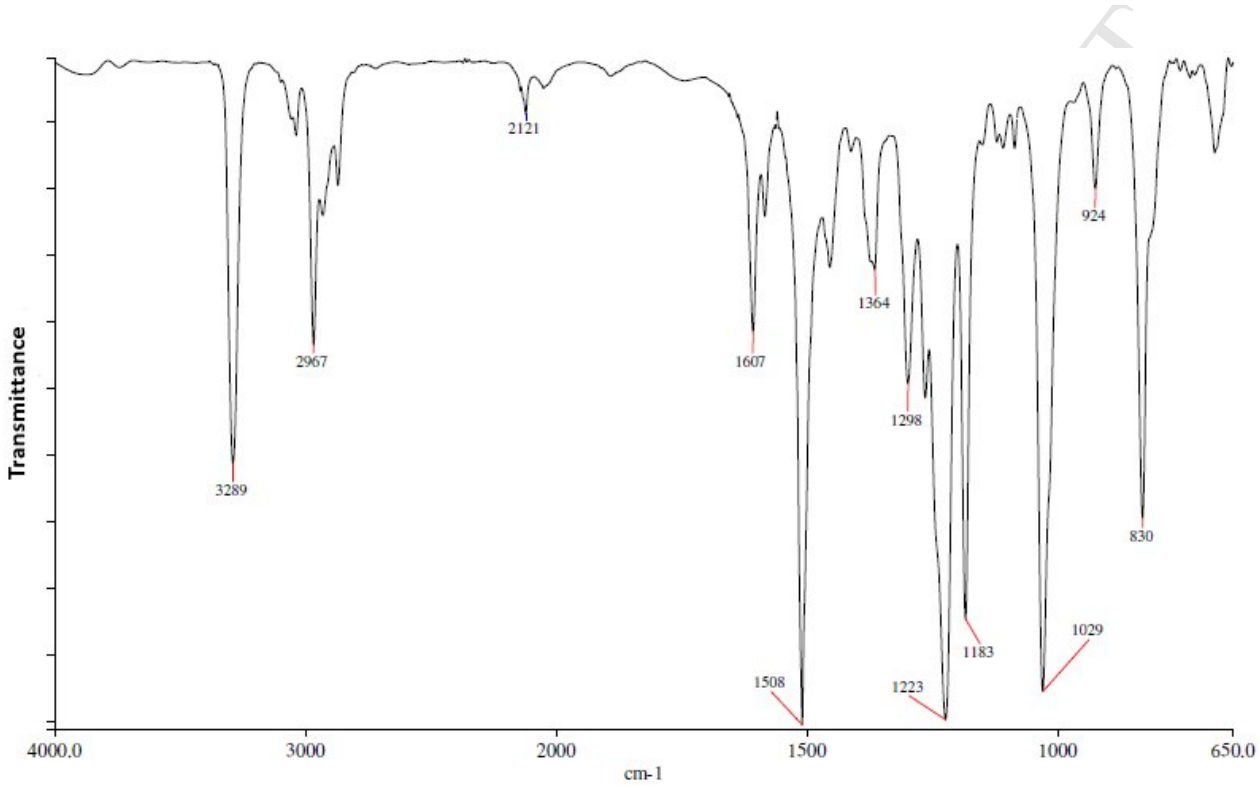
- First time report on the copolymerization of phthalonitrile and propargyl monomers
- Mechanism of chromene mediated nitrile polymerization is established
- Formation of a co-cured network comprised of phthalocyanine, triazine, and chromene structures are identified.
- A mean for co-curing of phthalonitrile system at a relatively lower temperature evolved.

S1. Spectral characterizations of monomers and model compounds

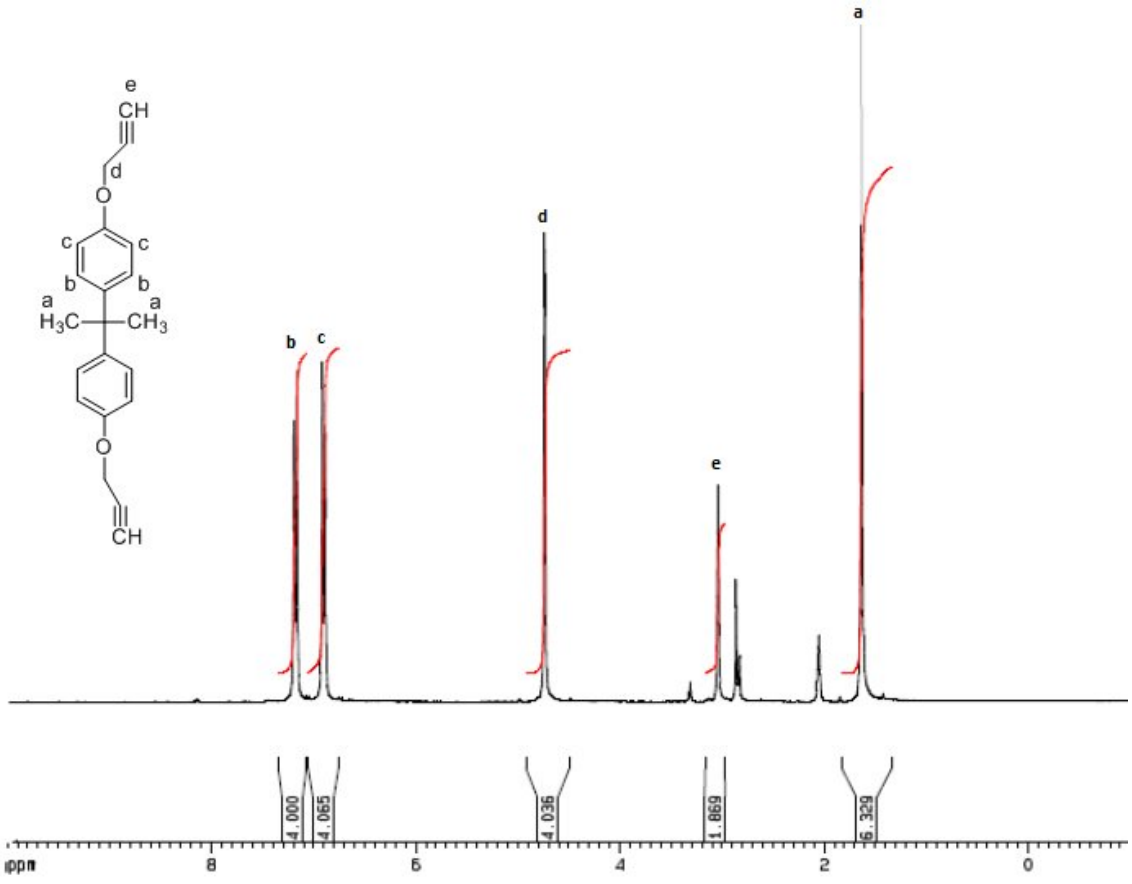
(a) ^{13}C NMR spectrum of BPhPR monomer (solvent : acetone *d6*)



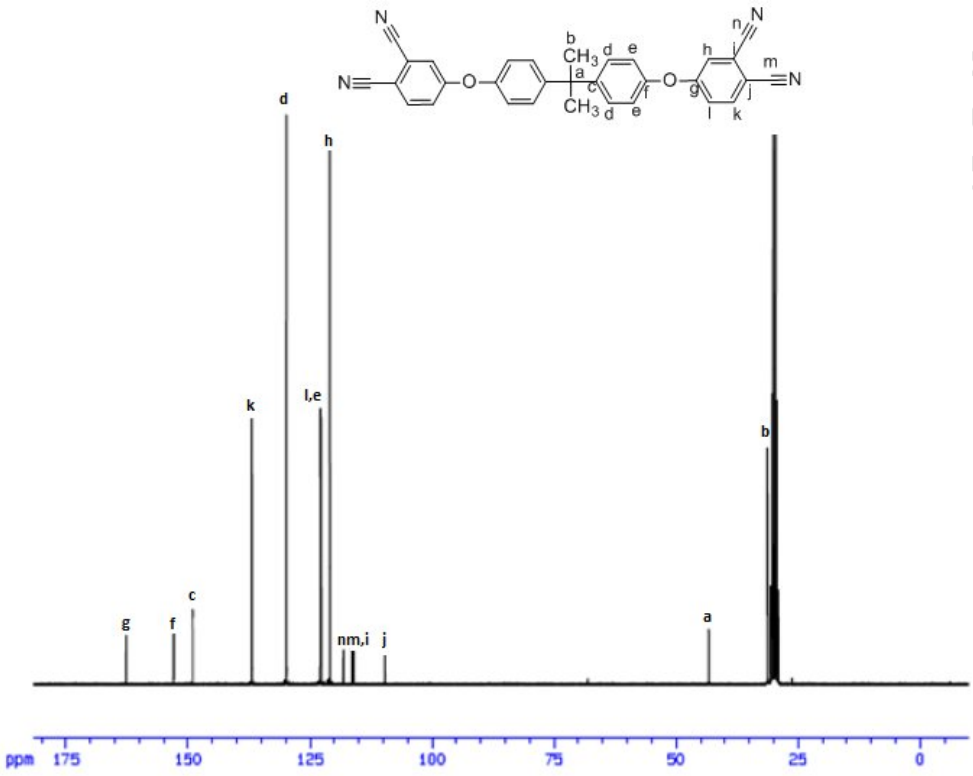
(b) FT-IR spectrum of BPhPR monomer



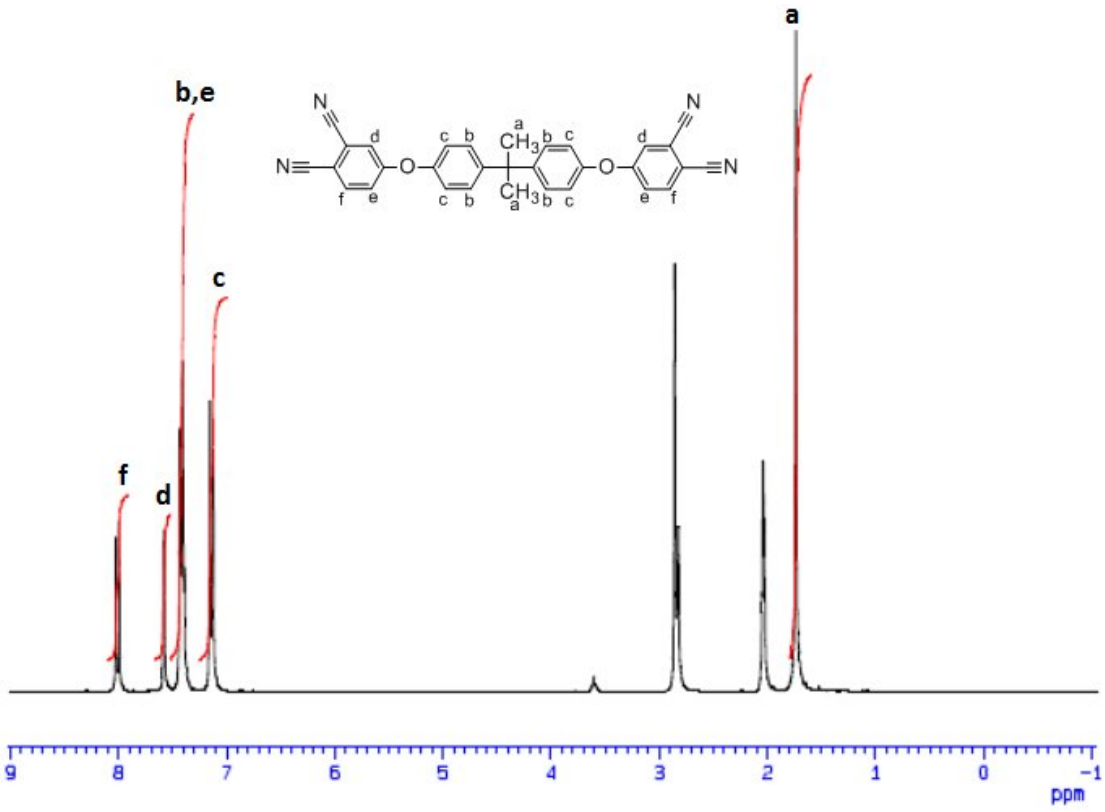
(c) ^{1}H NMR spectrum of BPhPR monomer (solvent : acetone *d6*)



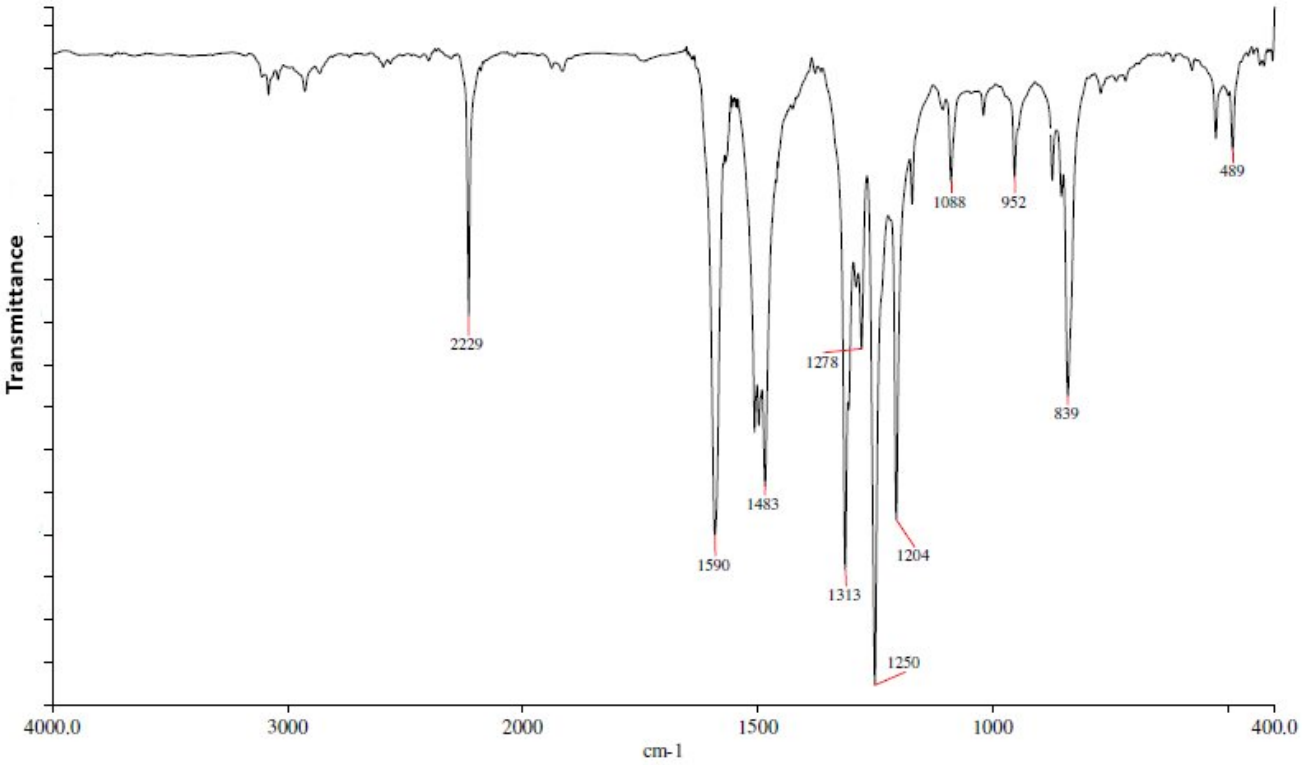
(d) ^{13}C NMR spectrum of BPhPN monomer (solvent : acetone *d6*)



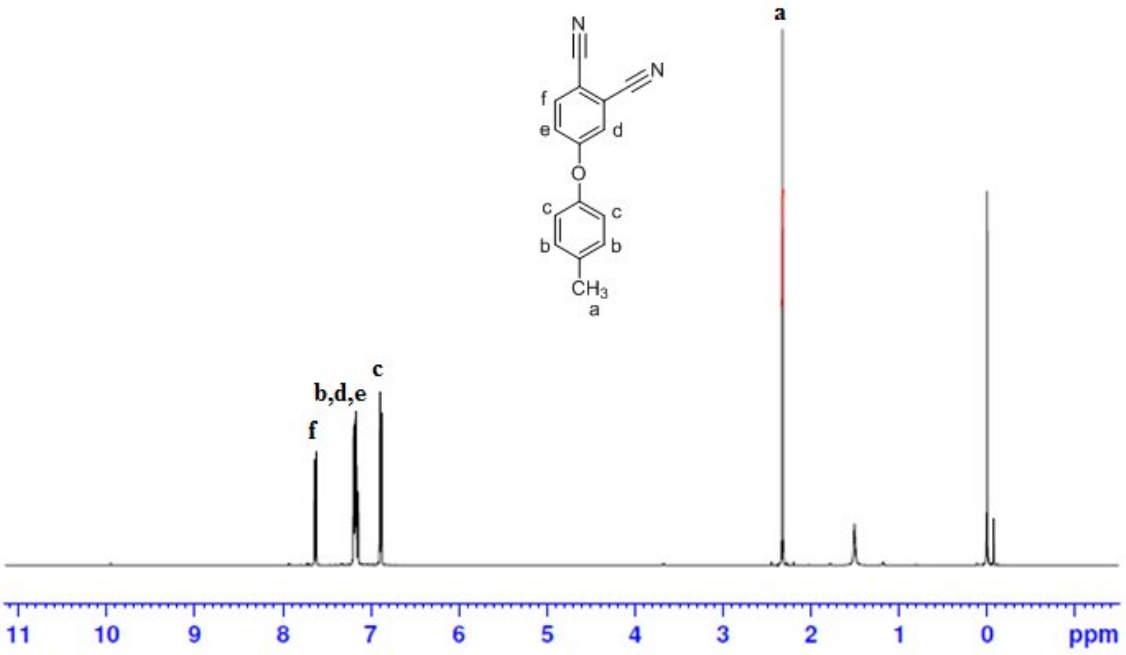
(e) ^{1}H NMR spectrum of BPhPN monomer (solvent : acetone *d6*)



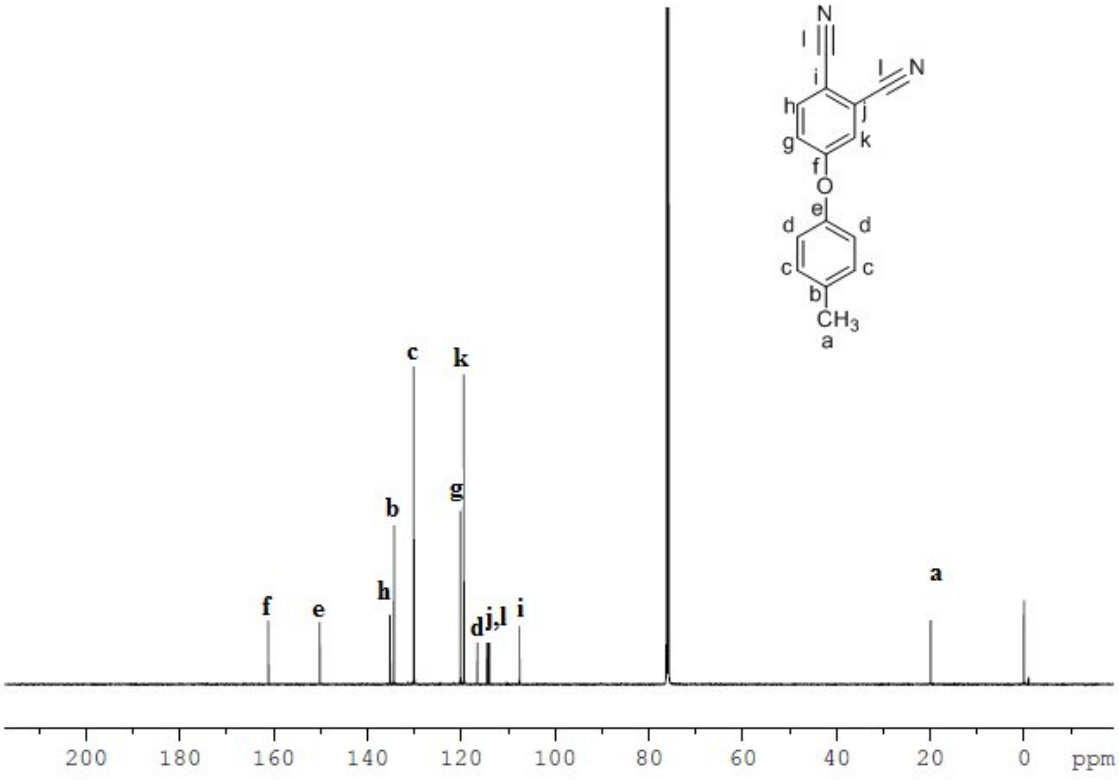
(f) FT-IR spectrum of MPPN monomer



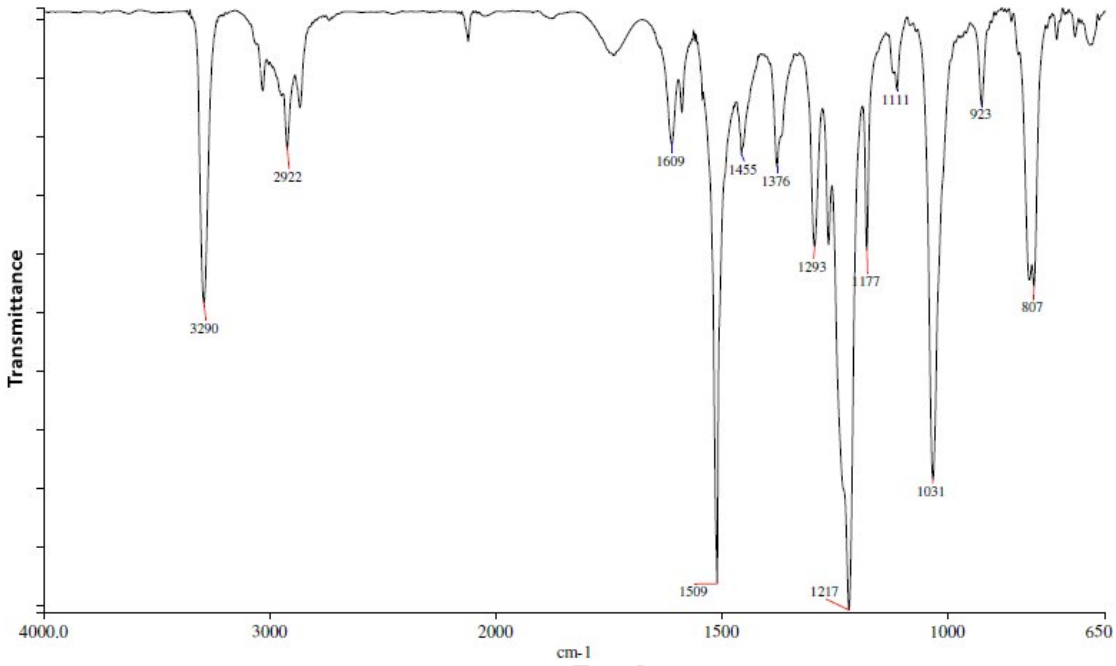
(g) ^{1}H NMR spectrum of MPPN (solvent : $CDCl_3$)



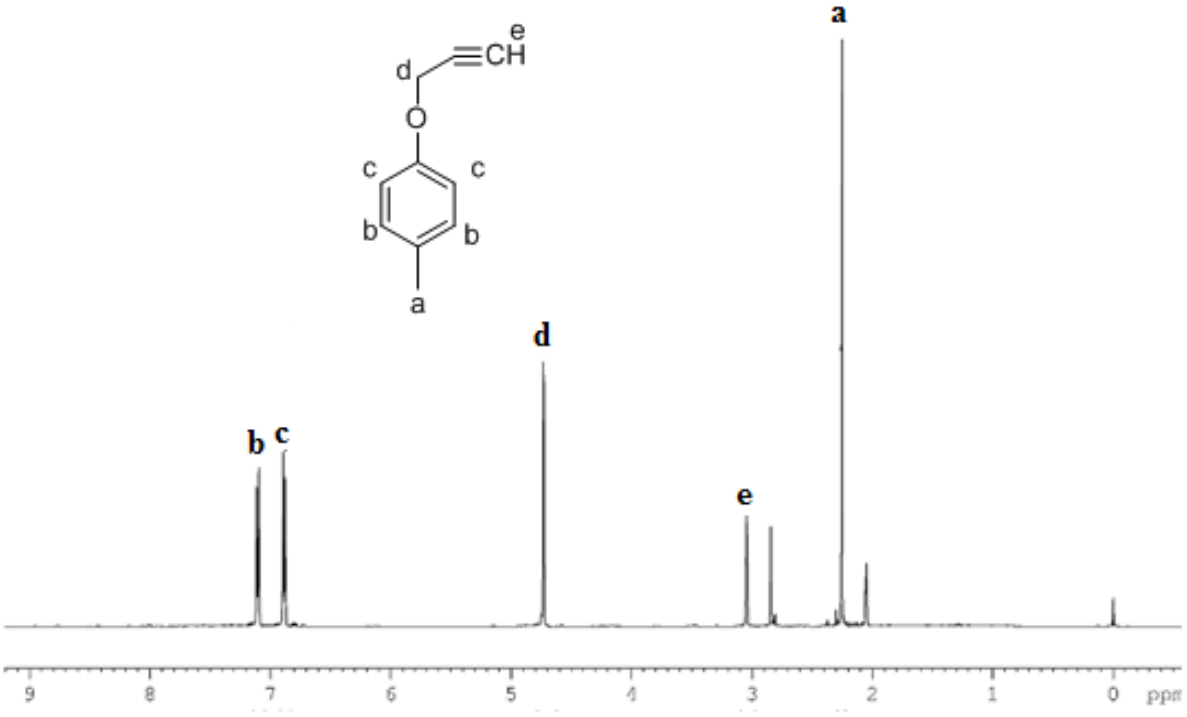
(h) ^{13}C NMR spectrum of MPPN (solvent : $CDCl_3$)



(i) FT-IR spectrum of MPPR

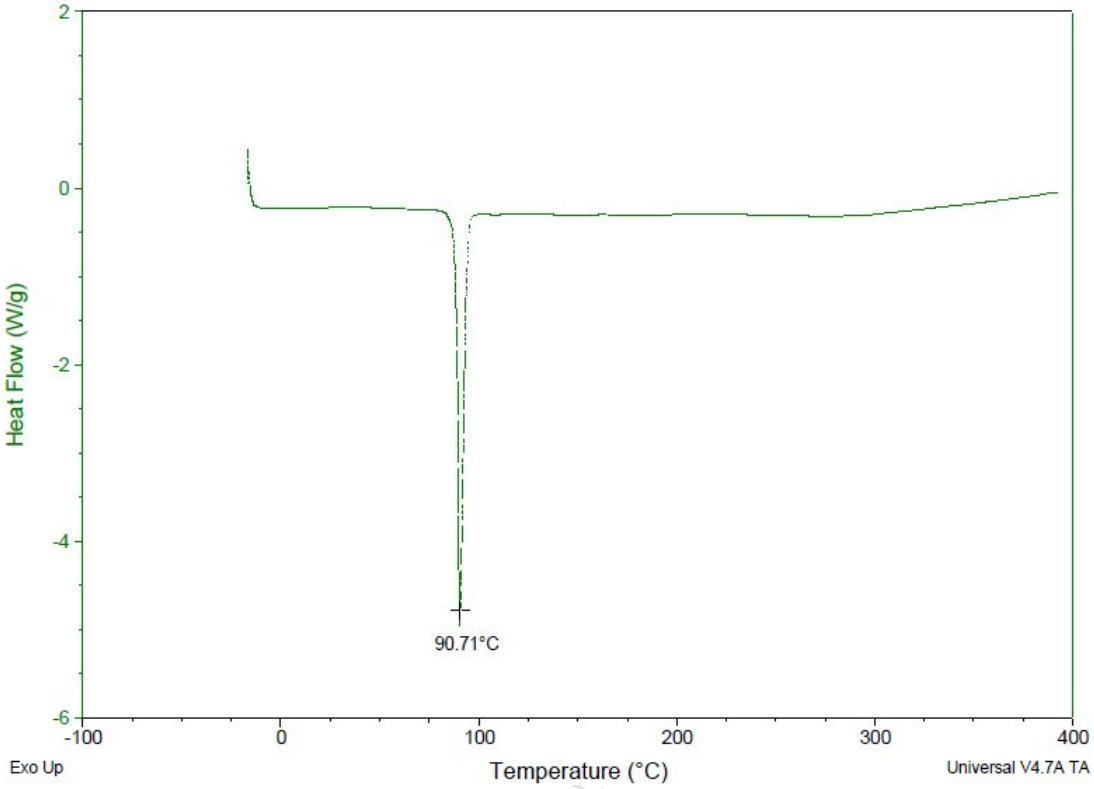


(j) ^{1}H NMR spectrum of MPPR (solvent : acetone *d6*)

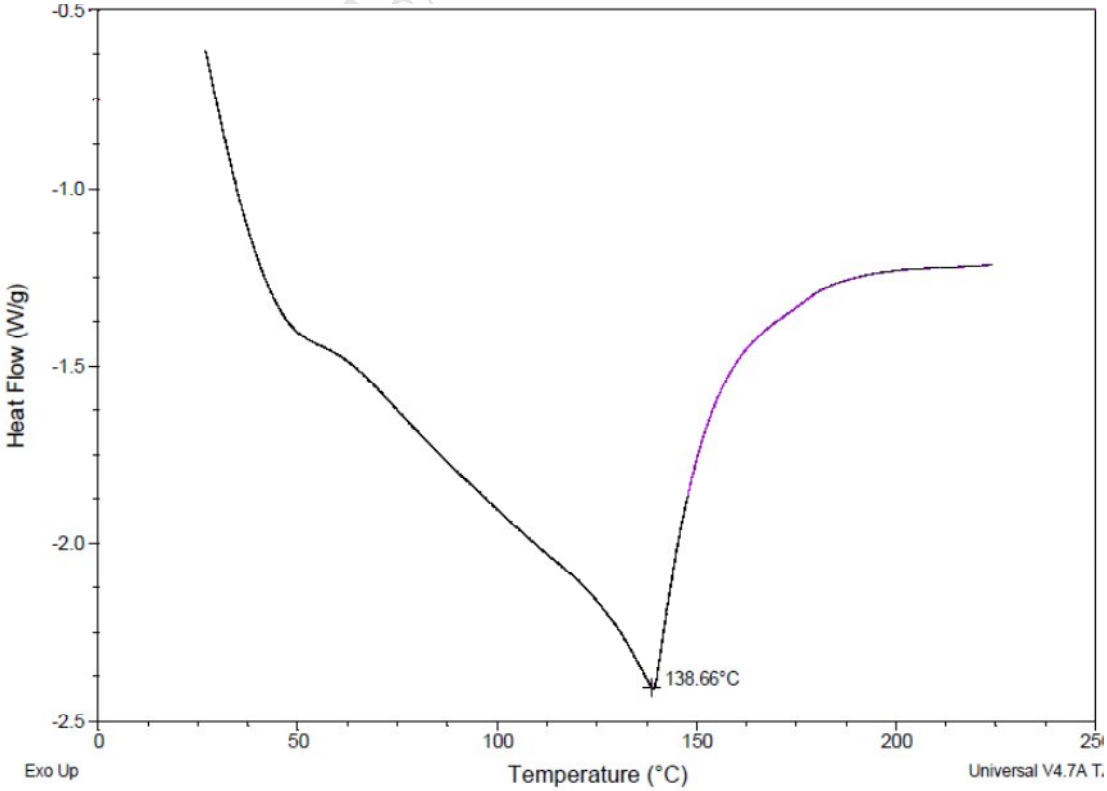


S2. DSC graphs of model compounds

(a) DSC graph of MPPN

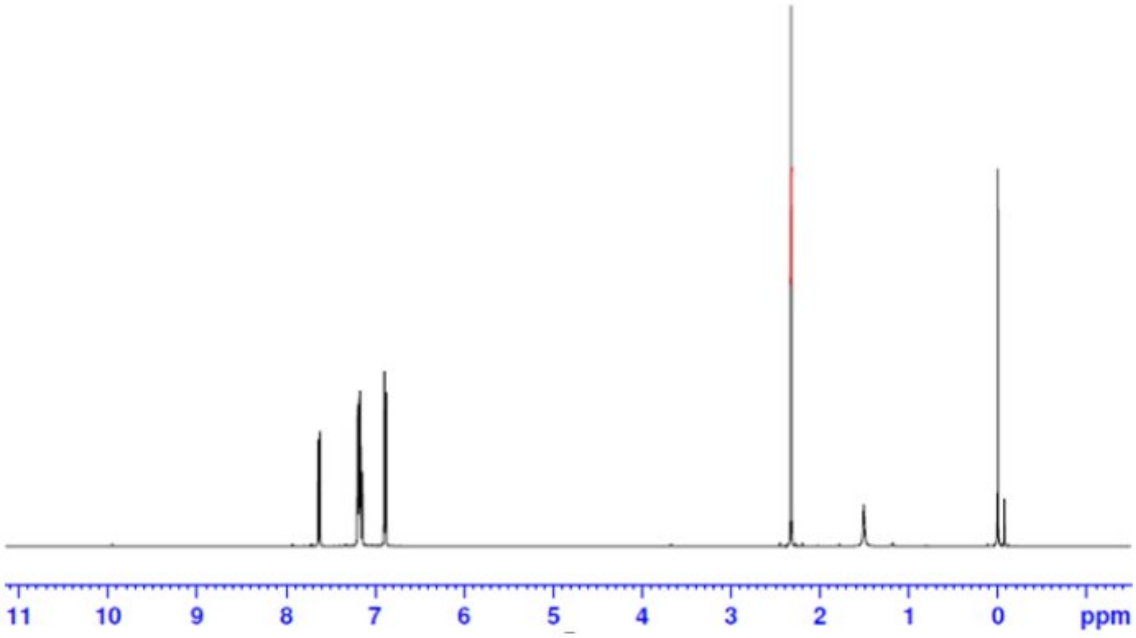


(b) DSC graph of MPPR

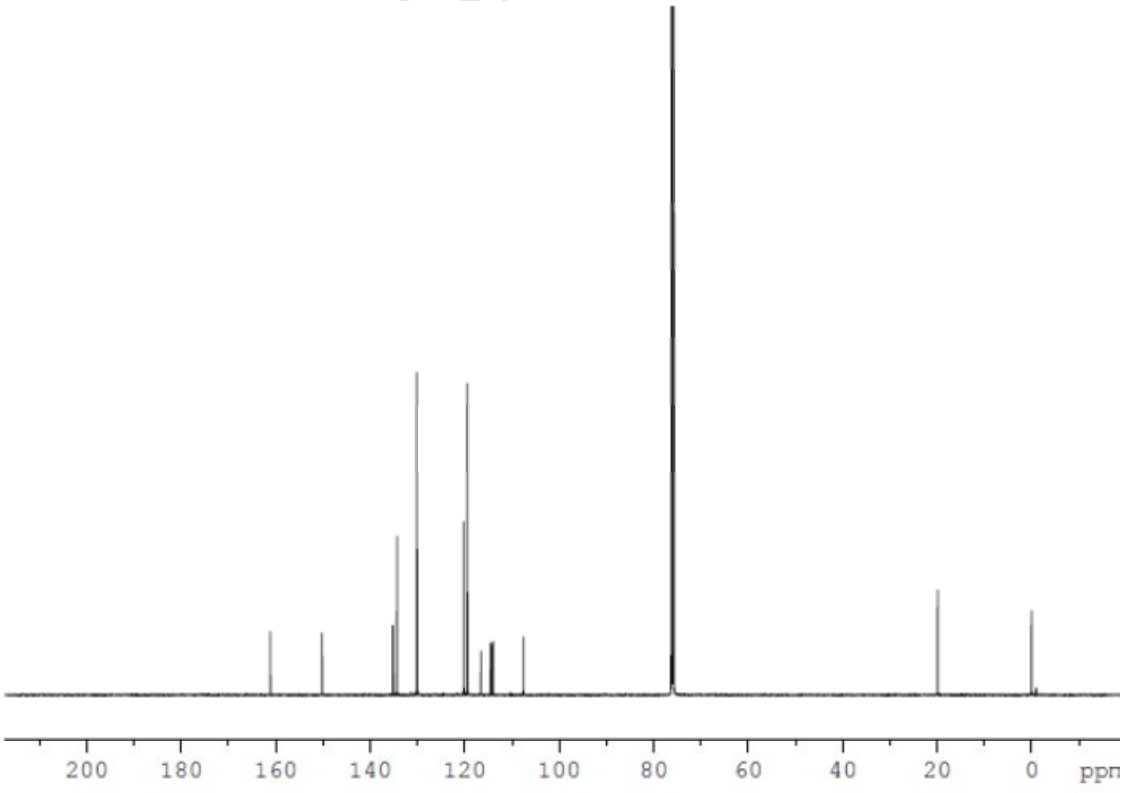


S3. Spectra of model compound MPPN after heating at 230°C for 4 h

(a) ^{1}H NMR spectrum of cured MPPN, CMPPN(230) (solvent : $CDCl_3$)

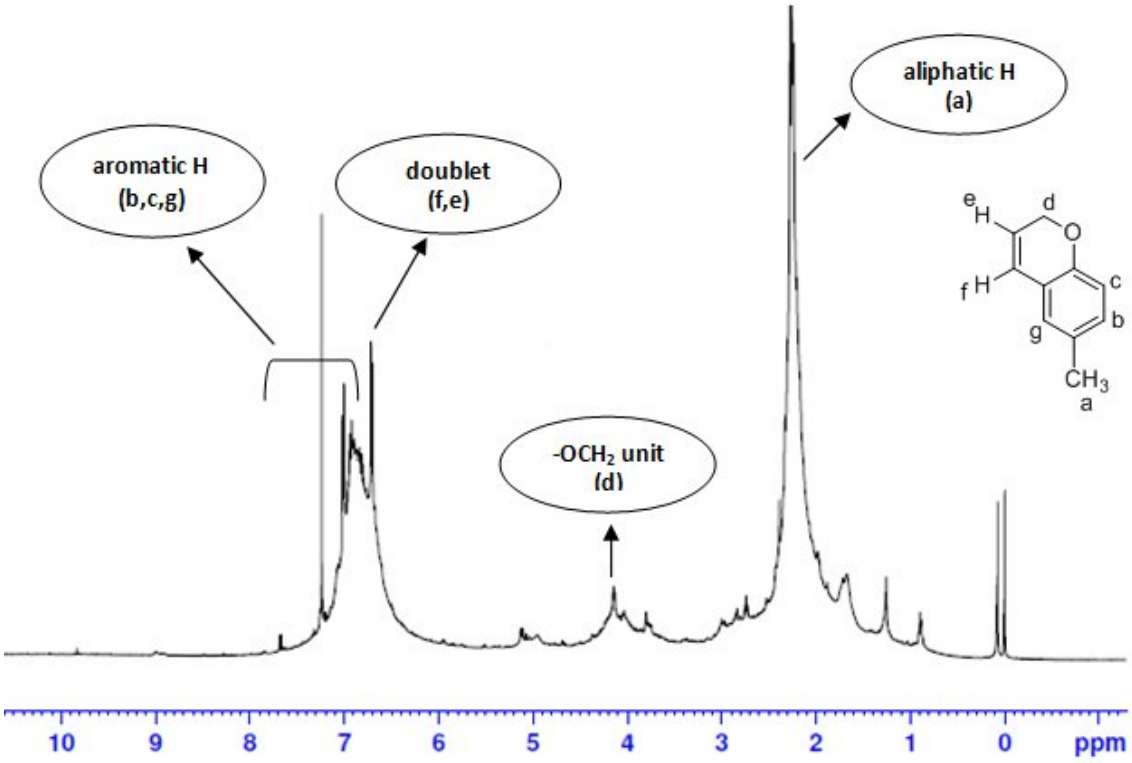


(b) ^{13}C NMR spectrum of cured MPPN, CMPPN(230) (solvent : $CDCl_3$)

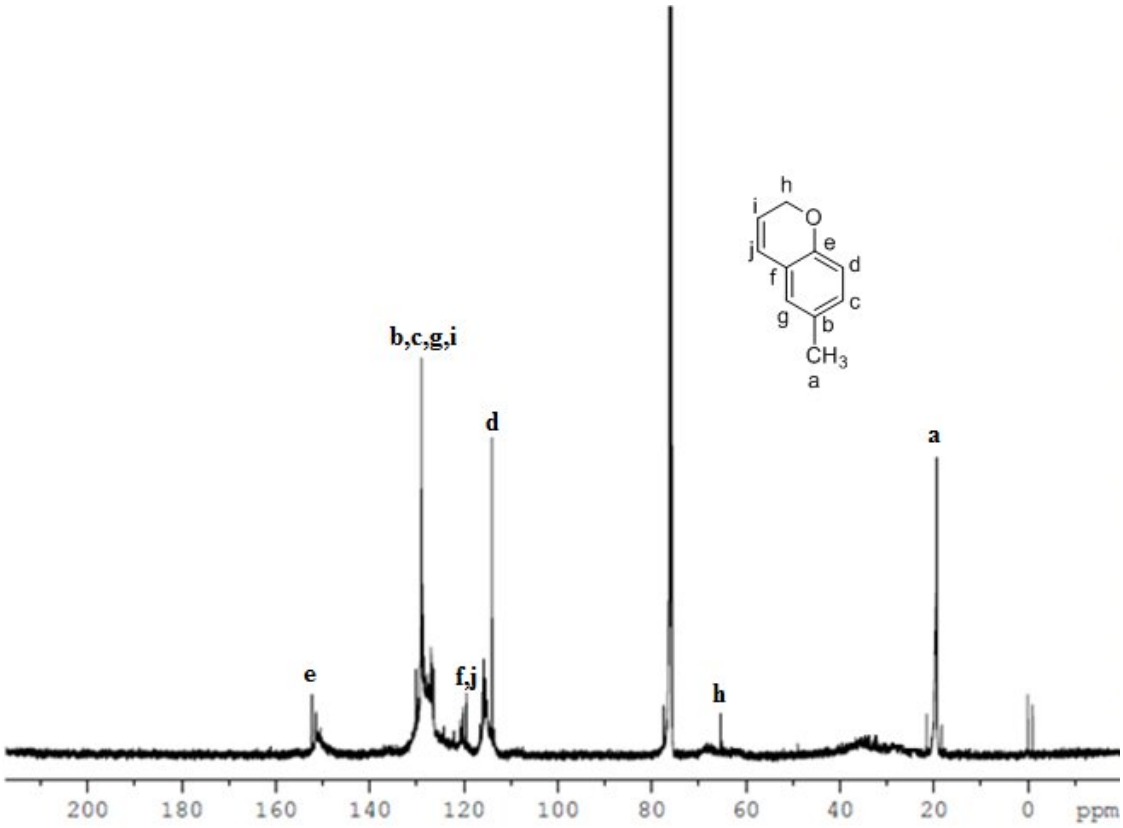


S4. Spectral investigations on cured MPPR

In ^{1}H NMR spectrum of cured MPPR, the absorption at 4.5 ppm denotes the methylene group of chromene units. Aromatic peaks were observed in the range of 6-7.2 ppm. Signals at 2.39 ppm are indicative of $–CH_3$ groups and doublet resonating at 6.5 ppm represents the ethylene hydrogen of chromene unit. ^{13}C NMR spectrum of cured MPPR showed characteristic absorption of OCH_2 in the chromene ring around 65 ppm. Ethylene carbons resonate in the same region as that of aromatic carbons (115-130 ppm) and the fused ring carbons appear at 150-153 ppm.



^{1}H NMR spectrum of cured MPPR (solvent : $CDCl_3$)

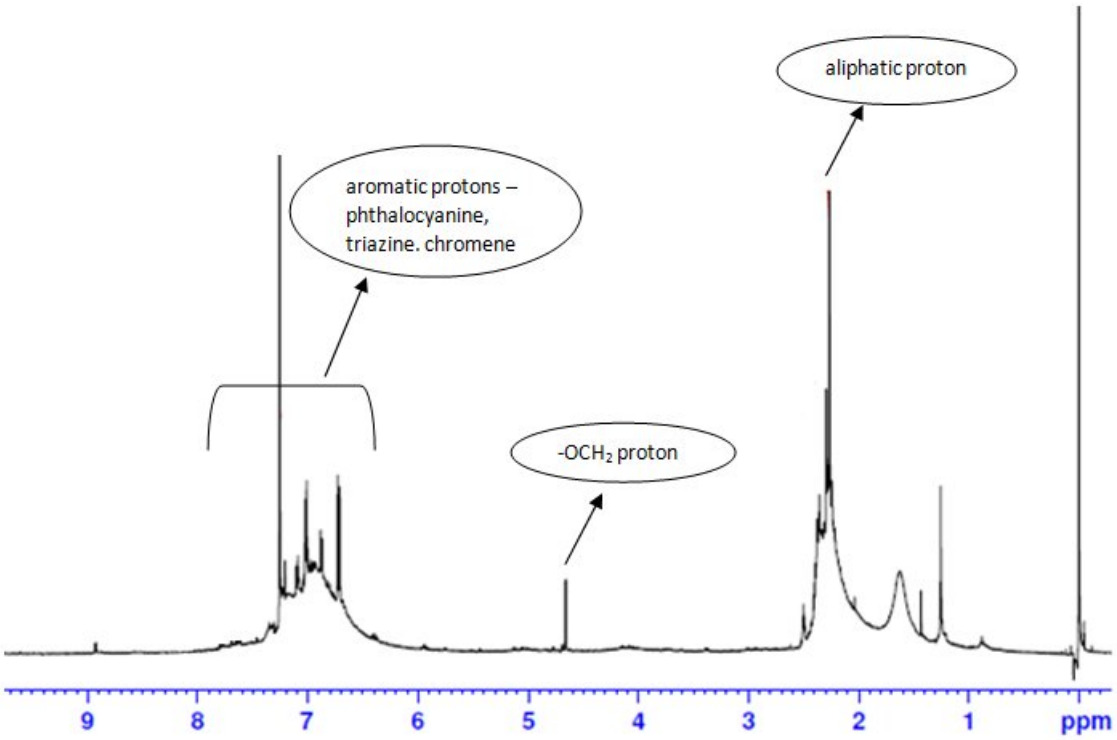


^{13}C NMR spectrum of cured MPPR (solvent : $CDCl_3$)

S5. Spectral data of cured blends of model compounds

NMR analyses of cured blends of model compounds

The aromatic proton peaks of phthalocyanine and triazine structures appear in the region 7.2-7.5 ppm. Absorption due to methylene group of chromene units are visible at 4.5 ppm. Aromatic peaks overlapped and appear as a broad peak in the range of 6-7.5 ppm. Signal at 2.39 ppm is indicative of $-CH_3$ groups. Some of the ^{13}C NMR absorptions identified for the cured blend are shown in the table.



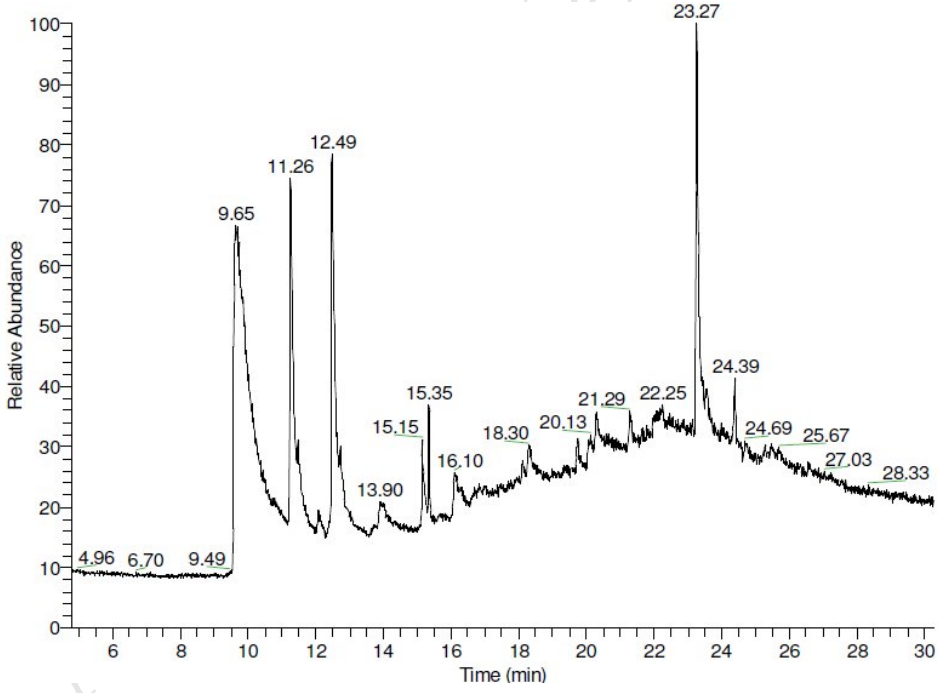
^1H NMR spectrum of cured blends (CMPPN-MPPR) (solvent : $CDCl_3$)

Table 1. ^{13}C NMR chemical shifts of cured blends

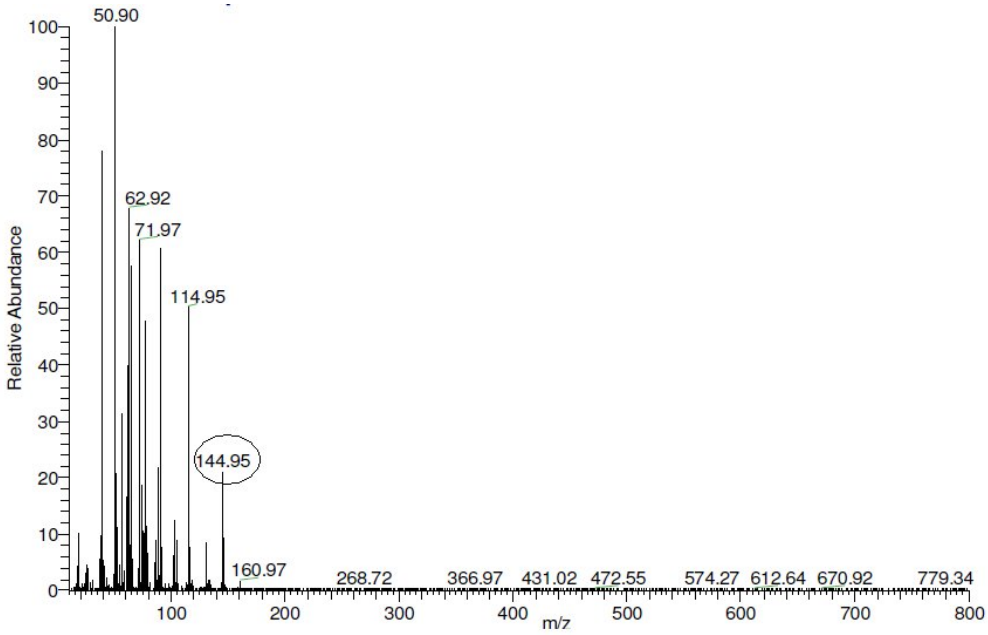
Linkages	ppm
Ar-C	151
Ar-C of phthalocyanine rings	128-135
-CN ring	115
$-OCH_2$	56
$-CH_2$	29.7
CH_3	20

S6. Pyrolysis GC-MS analysis of cured blend of model compounds

Pyrolysis GC-MS analysis of the cured blends of model compounds, CMPPN-PR were carried out at 300 °C by SGE Pyrojector (continuous mode) Pyrolyser, in conjunction with a GC/MS system consisting of Thermo Electron Trace Ultra GC, coupled to a Thermo Electron PolarisQ (Quadrople ion trap) mass spectrometer. Chromatogram of the pyrolysed products is shown in revised manucript. A typical mass spectrum of pyrolysed products indicated the presence of high molecular mass ion in the range of 400-800 with very low intensity peaks. However, the peak corresponding to chromene units was clearly detectable at m/z of 145 in the pyrolytic decomposition patterns of model compounds. The high molecular mass ions can be most probably assigned to phthalocyanine and triazine networks formed by reactions with propargyl polymerization intermediates.



Pyrogram of CMPPN-MPPR at 300 °C



Typical mass spectrum of the pyrolysed sample