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EFFECT OF MOLECULAR WEIGHT ON THERMAL BEHAVIOR AND PROCESSABILITY OF OLIGOMERIC PHTHALONITRILE RESINS

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ABSTRACT

A series of phthalonitrile end-capped oligomers having controlled molecular weights were prepared by the reaction between aromatic diols, dichloro compounds and 4(4'-aminophenoxy) phthalonitrile. The average molecular weight of the oligomers can be controlled by varying the stoichiometric ratio of diols and dichloro compounds used. The structure of the prepared compounds was characterized by FT-IR and NMR spectral techniques. The average molecular weights (Mn & Mw) and polydispersity index (PDI) values of the oligomers were determined by Gel permeation chromatographic (GPC) analysis. Differential scanning calorimetric (DSC) analysis was used to follow the cure behavior of the oligomeric phthalonitrile with 4,4'-oxydianiline (ODA) curing agent mixtures. The oligomeric phthalonitriles were converted into cross-linked network structure by three step curing process at elevated temperatures. As the average molecular weight of the oligoimides increases, an enhancement of thermal stability was observed. Such oligomeric system is expected to be quite useful for the advanced composite applications that need high temperature capabilities.

Keywords: phthalonitrile oligomer, controlled molecular weight, GPC analysis, thermal properties.

1. INTRODUCTION

Currently there is a great demand for a new class of high performance composite materials which bridge the gap between organic, metal and ceramic based materials. The requirements for this new class of composite material are that it must have good processability, show good mechanical performance characteristics and long term, high service temperature capabilities [1-2]. A major advantage of phthalonitrile resins compared with other plastics is their ability to withstand temperature in excess of 200˚C for extended periods without permanent damage to the coatings, plastics or composites made [3]. Polymerization takes place through the terminal cyano group by an addition mechanism to afford cross-linked networks. These materials exhibit good thermal and oxidative stability [4-5].

The chemical and physical properties of the polymers primarily depend on the bridging groups. The aromatic moieties provide the high mechanical strength, modules. Although these polymers have flexible moieties in the linking group, the toughness of the polymers is not high because of the shortness on the bridging group [6]. Phthalonitrile monomers with short bridging chains are difficult to polymerize. The processability of the prepolymers plays a vital role in the preparation of high temperature advanced composites with enhanced mechanical properties [7].

Phthalonitrile polymers usually contain highly stable structural units such as aromatic and heterocyclic rings. Unfortunately, polymers composed solely of these high temperature structural moieties tend to brittle and intractable. Thus, the attention has been directed towards the introduction of flexible linkages into the chain together with the high temperature units [8-10]. In order to overcome the above disadvantages, a new oligomeric phthalonitrile resins as potential matrices for composite formulations has been developed. Several oligomeric phthalonitriles of varying average molecular weight in which the two terminal phthalonitrile units are interconnected by moieties with aromatic ether and sulfone linkages have been synthesized.

2. EXPERIMENTAL

2.1 Materials

4-nitrophthalonitrile was synthesized according to the procedure given in a previous study [5]. *N,N*-dimethylformamide (DMF) and toluene were purchased from SRL, India. These solvents were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. Phthalimide, hydroquinone, 1,5-dihydroxy naphthalene, 4,4’-dichlorodiphenyl sulfone, 4,4’-dichloro benzophenone and potassium hydroxide were used as received from E-Merck, India.

2.2 Measurements

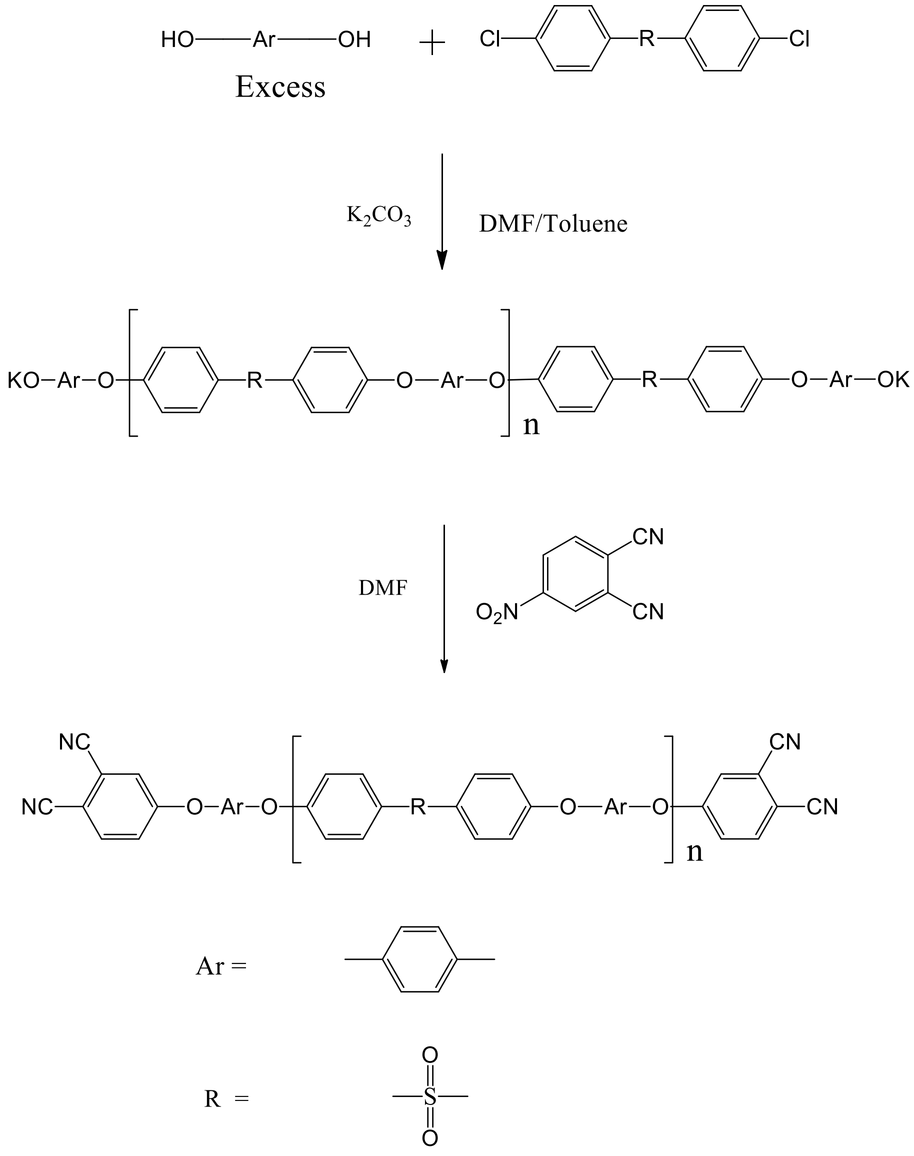
Fourier Transform Infra Red (FT-IR) spectra were recorded on a Perkin-Elmer RX-1 spectrometer using a KBr disk at a scanning range from 4000 to 400 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Joel Ex-400 spectrometer (400MHz) using DMSO-d$_6$ as solvents and the chemical shifts were calibrated by using 1% TMS as a reference. Elemental analysis was carried out with a Perkin-Elmer model 2400. The viscosity measurements were performed on a TA Instruments AR-2000 Rheometer, with an environmental testing chamber for temperature control. 40 mm diameter parallel plates were used in the test chamber of the rheometer. The melt viscosity of the phthalonitrile prepolymers were monitored in air at 270°C as a function of time. The viscosity measurement was used to determine the optimum level of curing additive concentration and processing temperature. DSC analysis was performed on a Q$_{10}$ series TA instruments Differential scanning calorimeter using 3 mg of the sample crimped in aluminium pans at a heating rate of 10°C/min and a flow rate of 40 ml/min. Thermo gravimetric data were obtained on a Q$_{100}$ series TA instruments in flowing Nitrogen/air at a heating rate of 20°C/min.

2.3 Synthesis of oligomeric phthalonitriles

To a 250 mL, three-necked flask equipped with a thermometer and Dean-Stark trap with a condenser, and a nitrogen inlet was charged 4.4g of (0.04 mol) hydroquinone, 5.8g (0.02mol) of 4, 4'-dichlorodiphenyl sulfone and 50 ml of dimethylformamide. While stirring to dissolve the two reactants, the solution was purged with dry nitrogen for 30 minutes and the Dean-Stark trap was filled with toluene. 8.28g (0.6mol) of andydrous potassium carbonate was then added. The temperature of the reaction mixture was increased to 100˚C and held at this temperature for 1 hour. The mixture was then refluxed at 135-145˚C under nitrogen atmosphere for 12 hour or until no more water was observed being collected in the Dean-Stark trap. FT-IR spectroscopy was used to confirm and monitor the formation of the desired oligomeric product. After the toluene was removed by distillation, the reaction mixture was cooled to room temperature, and 6.92g (0.04mol) of 4-nitrophthalonitrile was added in one portion. The resulting mixture was stirred at 80˚C for 6 hour. The mixture was allowed to cool to the ambient temperature and poured into a 5% aqueous KOH solution. A solid product was collected by suction filtration, washed with water, and dried to afford 9.8g. All the other oligomers were prepared by varying the stoichiometric ration of reactants.

FT-IR (A1) (KBr pellet, cm^{-1}): 2233 (C≡N), 1778 (asymmetry C=O str), 1728 (symmetry C=O str), 1365 (C-N str), 721 (imide ring deformation, out of plane), 1256 (C-O), 1110 (C-O); ^{1}H NMR

(300MHz, DMSO-d_6) δ (ppm): 7.39-7.54 (m), 7.55-7.68 (m), 7.70-7.95 (m), 6.72-6.90 (m), 7.10-7.38 (m), 8.10-8.32 (m)



Scheme 1. Synthesis of phthalonitrile oligomer

2.4. Synthesis of prepolymers

The synthesized oligomeric phthalonitriles were washed with 5% sodiumhydroxide solution to remove insoluble impurities, dried in a vacuum oven at 80˚C for about 10 hours. A reaction kettle added 25 g of phthalonitrile monomer (A1) and heated at 245-255˚C in air atmosphere for about 5 minutes. Then added 4.0wt % of curing agent 4, 4’-diaminodiphenyl sulfone (DDS) in one portion and stirred well for another 5-10 minutes. After homogeneity occurs, the product was quenched to room temperature. A dark color amorphous solid prepolymer product was obtained. It has the solubility in common organic solvents such as methylene chloride, chloroform, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and 1-methyl- 2-pyrrolidinone (NMP).

2.5 Polymerization of perpolymers

All prepared oligomeric prepolymers were converted into crosslinked networks by three step thermal curing process based on the results obtained from DSC cure analysis. 10 g of each of the prepolymers were weighed in a reaction kettle and polymerized in air atmosphere. The samples were cured at 250°C for 5 hours, 260°C for 5 hours and 280°C for 8 hours. Finally, the samples were post-cured at 300°C for about 10 hours.

3. RESULTS AND DISCUSSION

3.1 Syntheses of phthalonitrile oligomers

A series of oligomeric phthalonitriles (A1-A3), in which the average molecular weights were varied by reacting different mole ratios of (excess) of dialkali salt of aromatic dihydroxy compounds with dichloro compounds followed by endcapping with 4-nitrophthalonitrile were synthesized. The synthesis was performed by mixing the reactants together in one reaction vessel. The reaction was carried out by in situ one-pot, two-step method. The average chain length of the oligomeric linkage between the terminal phthalonitrile units depends on the molar ratio of the reactants used.

In the first step, the diphenols were converted into alkali phenolate by the reaction with potassium carbonate in polar aprotic solvent, *N*,*N*-dimethylformamide. Toluene was added for removing water by azeotropic distillation. The reaction was performed in nitrogen atmosphere. In the second step, dichloro compound was added to the diphenolate (excess) in a specific mole ratio. The reaction mixture was refluxed at about 155-165˚C for about 13 hrs. The water formed as by-product was removed by azeotropic distillation. When the reaction is complete (no more water gets collected), toluene was removed from the reaction mixture by distillation and the reaction mixture was cooled to room temperature.

The last step consists of adding 4-nitrophthalonitrile to the dipotassium salt of bisphenol, resulting in the formation of ether linkages connecting oligomeric phthalonitriles. The phthalonitrile end-capped product was obtained by the displacement of the nitro group by the phenolate in the presence of potassium carbonate. The reaction mixture was then poured into 5% potassium hydroxide solution and the phthalonitrile endcapped oligomer was separated by vacuum filtration. The oligomeric phthalonitriles with different molecular weights were prepared by varying the mole ratio (1.5-2.5) of reactants. The synthetic scheme provides a versatile method for obtaining a wide array of phthalonitrile oligomers of varying average molecular weight. By increasing the distance between the terminal phthalonitrile moieties and by incorporating flexibility into the interconnecting unit by means of the ether linkages, the toughness of the corresponding polymers should be enhanced. In addition, the cross-linking density of the polymers can be readily controlled as a function of the molar ratios of the reactants used in the synthesis. All the oligomer samples were obtained in good yield and were found to have low melting points comparably with phthalonitrile monomers [11-12].

3.2 FT-IR Analysis

The representative infrared spectrum of the oligomer (A1) shown in Figure 1. The absorptions around 2230-2233 cm^{-1} correspond to the stretching vibration of terminal nitrile (C≡N) group. The absorption band around 1039-104 cm^{-1} is due to the sulphoxide linkages. The asymmetric and symmetric stretching vibration of C-O-C were observed around 1241-1252 and 1080-1092 cm^{-1} respectively and absence of band around 3300-3500 cm^{-1} due to OH group confirms the completion of reaction. In addition, decrease of intensity of the nitrile absorption was observed for all the oligomers relative to the other characteristic absorptions. This may be attributed to the enhancement of molecular weight, which leads to the increase of interconnecting chain length [13-14].

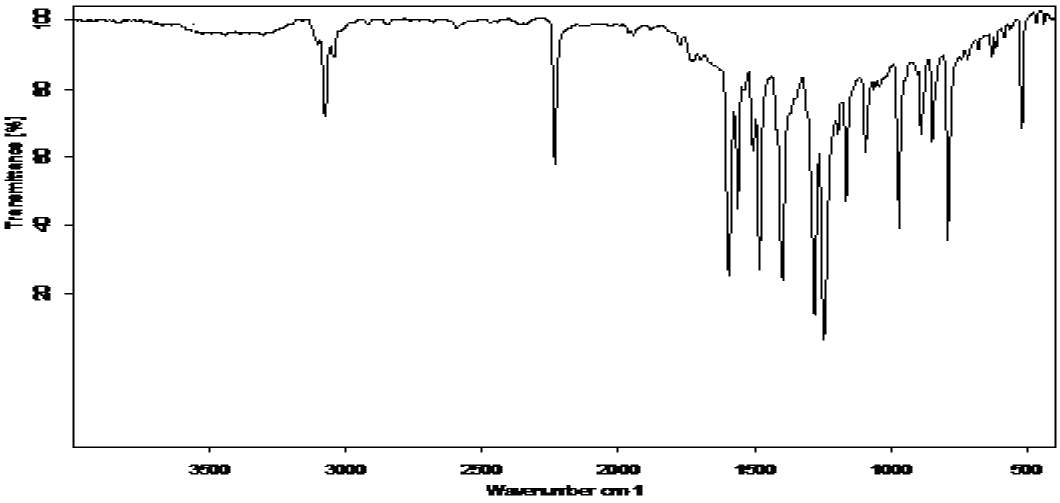


Figure 1. FT-IR spectrum of oligomeric phthalonitrile (AI)

3.3 ^{1}H NMR spectral analysis of oligomers

^{1}H NMR spectroscopy was used to confirm the structure of the oligomeric phthalonitriles. The representative ^{1}H NMR spectra of the oligomers are shown in Figure 2. All the proton signals were observed in the aromatic region in the range of 6.72-8.32 ppm [1]. This result shows that the formation of oligomeric phthalonitriles. All the proton signals are broad and multiplets, which confirms the presence of dimer and oligomeric species in the synthesized product [5].

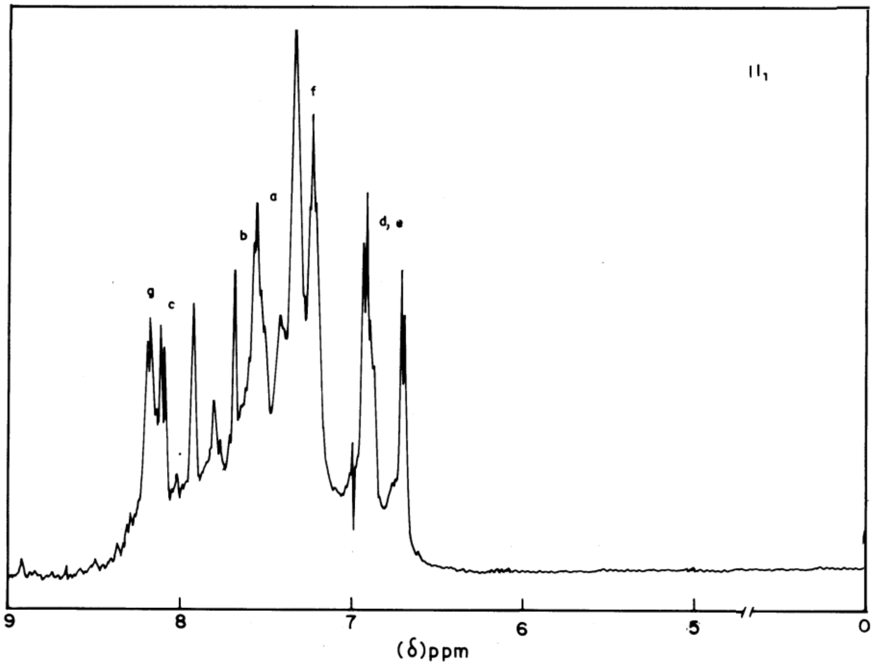
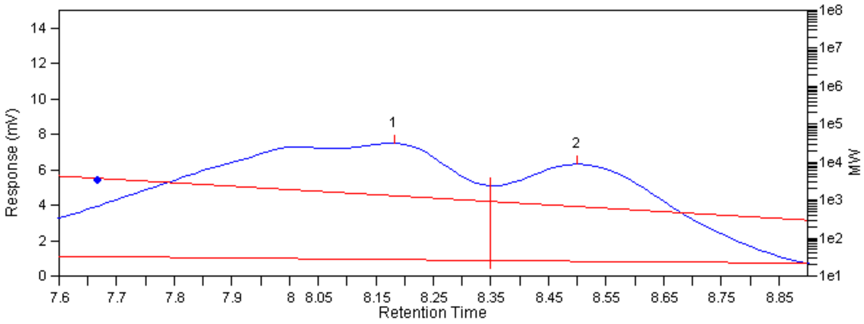


Figure 2. ^{1}H NMR spectrum of oligomeric phthalonitrile (AI)

3.4 Molecular weight Distribution (GPC analysis)

The average molecular weights and molecular weight distributions of the phthalonitrile oligomers were determined by GPC analysis in THF as solvent. It was observed that the average molecular weights are enhanced with increases of mole ratio of the individual reactants.



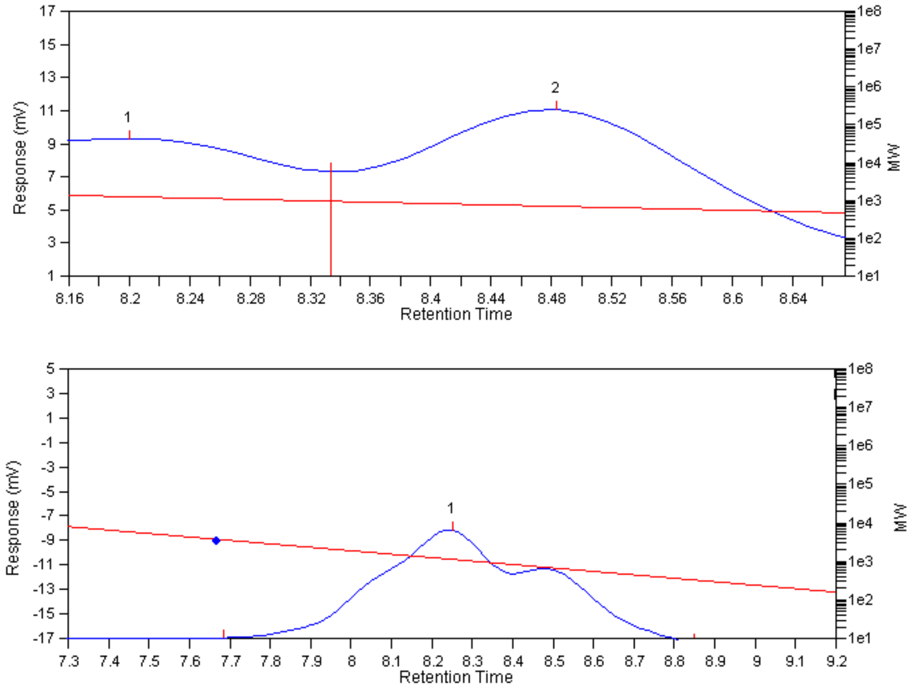


Figure 3. GPC molecular weight distribution of oligomers A1, A2 and A3

Code	Dichloro/ dihydroxy ratio (mol)	Molecular weight (g mol^{-1})			Repeating units (~n)
		Mn	Mw	Mp	
A1	1: 1.5	1775	2230	1298	3.5
A2	1: 2.0	1541	1877	1171	3
A3	1: 2.5	1041	1219	1232	2

Table.1 GPC average molecular weight analysis results

3.5 Cure behavior (DSC studies)

The cure behavior of oligomeric phthalonitriles was studied by differential scanning calorimetric technique and the results are given in Table 2. The DSC thermograms of oligomers (A1-A3) with 5 wt% of ODA (curing agent) are shown in Figure 3. The DSC thermograms exhibit a melting transition around 172-196˚C. The cure exotherm was initiated (T_i) around 242-265˚C, the maximum cure (T_{max}) was observed around 268-279˚C and the cure reaction was completed (T_{end}) around 288-306˚C. The DSC cure studies reveal that the oligomeric phthalonitriles were cured at fairly lower temperatures upto n=~4 relative to the phthalonitrile monomers. In addition, the oligomers were cured in comparatively short periods. The reason may be due to the incorporation of multiple ether groups which leads to flexibility and thus the chain mobility enhanced. Moreover, these oligomeric phthalonitriles show large processing window (~80-90˚C) which can be easily processed as composite components with enhanced toughness [15-16].

3.6 Polymerization

The neat curing of phthalonitrile resins has been shown to proceed very slowly even during extended periods of time at elevated temperatures. The phthalonitrile monomers thus converted into amorphous prepolymers at a curing rate dependant upon both the amount of curing additive and the curing temperatures. The samples were cured at 245 ˚C for 5 hrs, 280 ˚C for 5 hrs, 300 ˚C for 5 hrs and post-cured at 340 ˚C for 5 hrs, respectively.

3.7 Thermal properties

The thermal stability of the oligomeric cured resins were evaluated by TGA analysis at a heating rate of 20˚C/min in nitrogen atmosphere. The temperature at 5, 10% weight loss and residual weight retention at 800˚C are summarized in Table 2. The representative TGA thermogram of the oligomeric phthalonitrile resins are shown in Figure 4. The polymers did not show any considerable weight loss upto 450˚C. The temperature at 5 and 10% weight loss are in the range of 456-469 and 471-512˚C respectively. The results shows that thermal stability increases with enhancement of molecular weight (n= ~4). The stability can be attributed to the fact that, upon curing, the cyano groups of the phthalonitrile react to form triazine ring structures. The formation of heterocyclic ring structures promotes high thermal stability, as well as good mechanical properties [17-18].

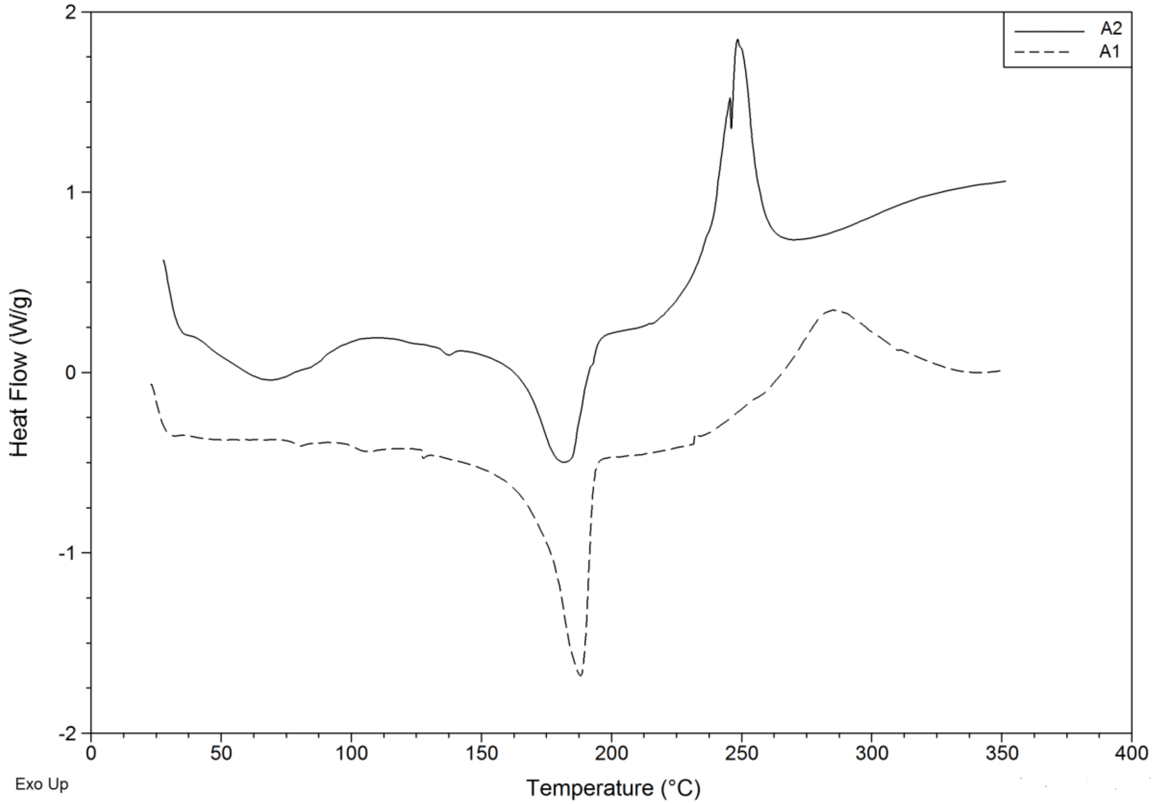


Figure. 3 DSC cure profile of oligomeric prepolymer A1 and A2

Oligomer code	**DSC cure temp (˚C)**			**TGA**		
	Initial (T_i)	Maximum (T_{max})	End (T_{end})	$T_{5\%}$ (˚C)	$T_{10\%}$ (˚C)	Char yield (%)
A1	247	268	288	456	471	58.3
A2	251	274	293	462	488	55.1
A3	254	274	299	467	504	56.2

Table.2 DSC and TGA analysis results

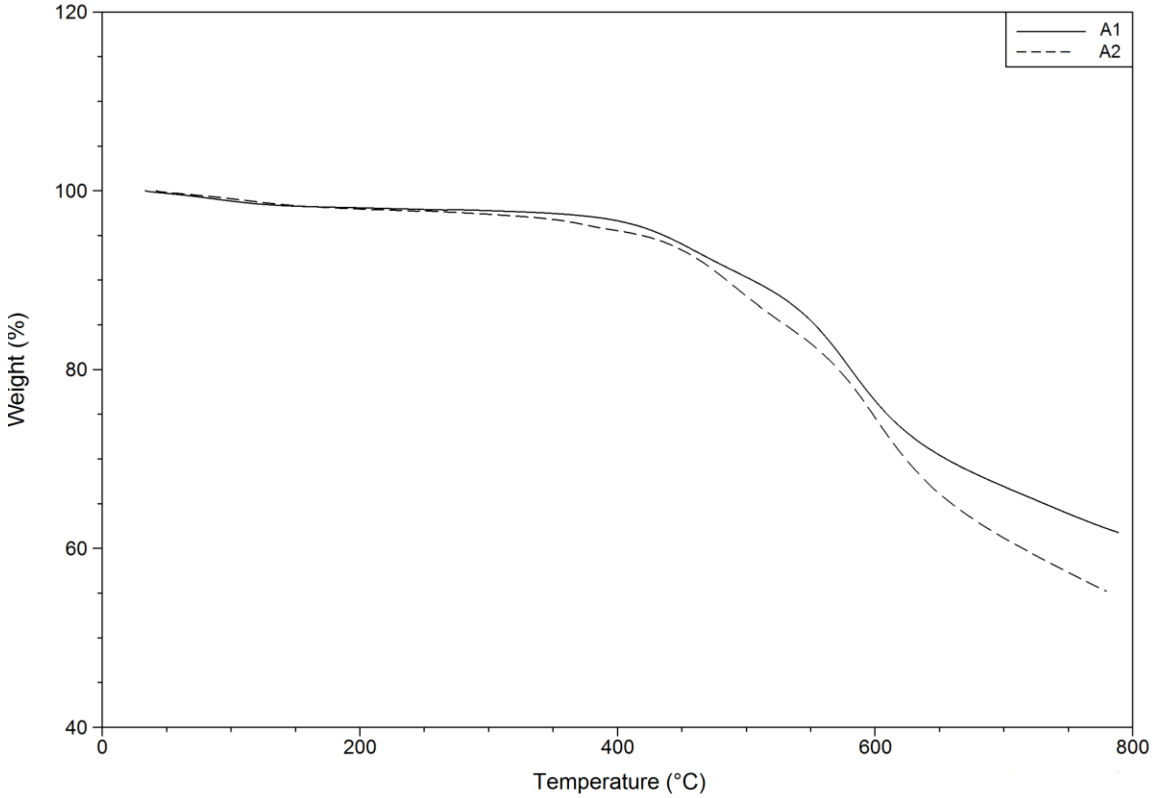


Figure. 3 TGA analysis of oligomeric cured resin A1 and A2

4. CONCLUSIONS

Oligomeric phthalonitriles bearing multiple aromatic ether linkages with various average molecular weights were prepared from the reaction of diols, hydroquinone, 1,5-dihydroxy naphthalene and dihalides 4,4'-dichlorodiphenyl sulfone, 4,4'-dichloro benzophenone, and 4-nitrophthalonitrile. The average molecular weights of the oligomeric phthalonitriles were determined by GPC analysis in DMF as eluent. The number average molecular weight (Mn) and weight average molecular weight (M_w) are in the range of 2042-4103 and 2480-4973 respectively. The prepared oligomers were comparatively low melting and easily processable as thermosetting composite materials. In addition, these materials are expected to be enhanced flexibility and other mechanical properties.

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