

Novel Novolac-Phthalonitrile and Siloxane-Phthalonitrile Resins cured with low melting Novolac Oligomers for Flame Retardant Structural Thermosets

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composite matrix

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ABSTRACT

The chemical modification of low molecular weight novolac oligomers and siloxane/silane-containing monomers has led to novel phthalonitrile derivatives with low glass transition temperatures, ranging from -25 to 75 °C. Multi-functional, low molecular weight phenol-formaldehyde novolac resins were blended with these novel phthalonitrile derivatives to achieve low viscosity resin blends. Moderate temperatures and rapid curing cycles were employed (200 °C, 1 h and 225 °C, 4h) to produce networks with high glass transition temperatures (> 250 °C). A decrease in the sharp band at 2230 cm^{-1} , attributed to the nitrile functionality of the phthalonitrile resin, was monitored in FTIR studies and indicated the progress of the reactions. Ninety percent conversion was achieved within ~ 30 min.

Thermal analysis of siloxane-phthalonitrile/novolac networks cured for 1h at 200 °C and 4h at 225 °C did not exhibit glass transition temperatures below 250 °C. In dynamic TGA studies, 5% weight loss temperatures up to 418 °C were observed, and the materials exhibited 50 to 56 % char at 800 °C in nitrogen. Networks prepared from a resin blend containing 50 weight% of a phthalonitrile derivative of a 260 g mol^{-1} novolac oligomer, 50 weight% of the 260 g mol^{-1} novolac oligomer, and 1.5 mol % triphenylphosphine (based on novolac) (NOV/NOV/TPP) cured at 200 °C for 1h, did not exhibit a T_g below 250 °C via DSC. These networks exhibited a 5% weight loss temperature of 350 °C, and 70 % char at 800 °C in TGA studies under nitrogen.

This degree of char formation makes these materials appealing for use in carbon-carbon composites. Post-curing these networks at 200 °C for 1h, and then at 225°C for 4h, resulted in high thermo-oxidative stability, with a 5% weight loss observed at 447 °C and 50 % char at 800 °C.

Blending tetramethyldisiloxane phthalonitrile monomers with 260 g mol⁻¹ novolac oligomers afforded prepolymer resins with low melt viscosities, 560 mPa s at 80 °C. Such viscosities may allow these resins to be processed via vacuum assisted resin transfer molding (VARTM) at low temperatures and heated at elevated temperatures to produce flame resistant three-dimensional networks.

To my loving grandmother whose strength, leadership, and will I have admired all the days of my life —thank you for all you have done for me.

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CHAPTER 1: INTRODUCTION

The expansive use of advanced composites is evident by an increase in the production of carbon-fiber composites, at a growth rate of ~30% per year.¹ Light weight, high strength to weight ratios, corrosion resistance, and non-magnetic characteristics are among many properties which make these materials ideal for use in civil, aerospace,² and marine³ engineering. Several research efforts have been devoted to the investigation of tough, high temperature polymers for composite matrix materials.^{4,5} Typically, efforts toward this goal have involved incorporating increased aromatic character to achieve high thermal and thermo-oxidative stability and improved mechanical properties.⁶ Although high aromatic character has been shown to enhance thermal stability and mechanical properties to an extent, polymers may become brittle, thereby diminishing their mechanical strength and limiting this approach.

Epoxy networks are considered high strength materials and are commonly employed in structural applications. By crosslinking phenol-formaldehyde novolac resins with epoxies, void-free phenolic networks may be prepared. Researchers in our laboratories have investigated epoxy resins cured with novolac oligomers with high phenolic compositions, up to 80 wt % .⁷ Bisphenol A based epoxy resins cured with novolac oligomers in a 5:1 phenol/epoxy molar ratio exhibited a T_g of 110°C and the cured networks exhibited high toughness, $K_{Ic} = 1.02 \text{ MPa m}^{1/2}$.⁸

¹ Hollaway, L.; Head, P. *Advanced Polymer Composites and Polymers in the civil infrastructure*. Elsevier Science Ltd.: Oxford, UK, 2001.

² Yokota, R. High Performance Polymers and Advanced Composites for Space Application. In *Aerospace Materials*. Cantor, B, Assender, H, Grant, P, Eds. Institute of Physics Publishing: Bristol, UK, 2001. 47-58.

³ Smith, C. *Design of Marine Structures in Composite Materials*. Elsevier Science Publishers Ltd.: London, 1990.

⁴ Critchley, J.; Knight, G.; Wright, W. *Heat-Resistant Polymers*. Plenum Press: New York, 1983.

⁵ Cassidy, P. *Thermally Stable Polymers*. Marcel Dekker: New York, 1980.

⁶ Keller, T. *Chemistry and Materials* **1994**, *6*, 302.

⁷ Tyberg, C. S. Void-Free Flame Retardant Phenolic Networks: Properties and Processability. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2000.

⁸ Tyberg, C. S.; Bergeron, K.; Sankarapandian, M.; Shih, P.; Loos, A. C.; Dillard, D. A.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2000**, *41*, 5053-5062.

Although the flame properties of these networks were considered good, the epoxy component contributed to burning. Similar materials with good flame properties were reported for epoxy-novolac networks prepared from multi-functional epoxy resins cured with novolac derivatives containing aromatic moieties.⁹

Numerous research efforts have been directed toward achieving tough composite matrix materials with high flame resistance. Halogenation and crosslinking have been the most common routes. Halogenation has been shown to significantly improve flame properties. However, in many cases this improvement is achieved at the cost of increased toxic smoke. The use of high-temperature thermoplastics end-capped with functional groups that may be polymerized into thermosets has also proved successful in this effort. Studies in this regard have placed a heightened focus on phenylethynyl,^{10,11,12,13} maleimide,^{14,15,16,17} and acetylene^{18,19,20} functional polymers. Curing reactions of these groups require elevated temperatures and long curing cycles. Highly flame resistant phthalonitrile resins have been studied as potential composite matrix materials.^{21,22,23,24} Keller et al.²⁵ have reported studies of

⁹ Iji, M.; Kiuchi, Y. *Polym. Adv. Technol.* **2001**, *12*, 393-406.

¹⁰ Meyer, G.; Glass, T.; Grubbs, H.; McGrath, J. *Polymer Preprints* **1994**, *35*, 549.

¹¹ Mecham, S. Synthesis and Characterization of Phenylethynyl Terminated Poly(arylene ether sulfone)s as Thermosetting Structural Adhesives and Composite Matrices. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 1997.

¹² Hergenrother, P.; Bryant, R.; Jensen, B.; Havens, S. *J Polym Sci Pt A: Polym Chem* **1994**, *32*, 3061.

¹³ Hergenrother, P.; Connell, J.; Smith, J. *Polymer* **2000**, *41*, 5073.

¹⁴ Mikroyannidis, J. *Journal of Macromolecular Science-Pure and Applied Chemistry* **1992**, *A29*, 127.

¹⁵ Moy, T.; Konas, M.; McGrath, J.; Fields, E. *J Polymer Science: Part A: Polymer Chemistry* **1994**, *32*, 2377.

¹⁶ Maes, C.; Devaux, J.; Legras, R.; Parsons, I. *Journal of Polymer Science: Part A: Polymer Chemistry* **1995**, *33*.

¹⁷ Yuan, Q.; Huang, F.; Jiao, Y. *Journal of Applied Polymer Science* **1996**, *62*, 459.

¹⁸ Sundar, R. A. *Journal of polymer Science: Part C: Polymer Letters* **1997**, *35*, 2387-2394.

¹⁹ Homrighausen, C. L.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **2002**, *40*, 1334-1341.

²⁰ Homrighausen, C. L.; Keller, T. *Polymer* **2002**, *43*, 2619-2623.

²¹ Keller, T.; Price, T. *Polymer Communications* **1984**, *25*, 42.

²² Keller, T. *Journal of polymer Science: Part C: Polymer Letters* **1986**, *24*, 211.

²³ Keller, T. *CHEMTECH* **1988**, *18*, 635.

²⁴ Keller, T. *Polymer* **1993**, *34*, 952.

²⁵ Sastri, S.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1999**, *37*, 2105.

biphenoxyphthalonitrile (BPh) monomers cured with low concentrations (1 to 3 mole %) of aromatic diamines. Thermal analysis of these networks post-cured at 375°C revealed T_g s in excess of 450°C and high thermal and thermo-oxidative stability with 70-85% char remaining at 1000°C. The thermal and thermo-oxidative resistance of these networks was attributed to a high level of aromatic character and the formation of heterocyclic crosslinks within the network structure. Although the networks prepared from biphenoxyphthalonitrile monomers possessed high thermo-oxidative stability, the elevated curing temperatures and extended cure cycles required to achieve such properties were not cost effective for large-scale commercial composite fabrication.

In our laboratories, high molecular weight (740 g mol⁻¹) phenol-formaldehyde novolac resins were cured with low weight fractions (15 - 20 wt %) of BPh monomer to produce void-free, highly flame resistant, tough networks with T_g s in excess of 180°C.²⁶ These materials exhibited excellent thermal and thermo-oxidative stability in TGA analyses in both air and nitrogen. Five percent weight loss temperatures, $T_{5\%}$, above 500°C were observed and 60 – 80 % char remained after heating to 800°C. BPh/novolac networks combined the flame resistance promoted by the heterocyclic network structure with good mechanical properties. Although the BPh/novolac networks displayed excellent thermal stability and good mechanical properties, the processability of the resin mixture from the melt proved difficult. The biphenoxyphthalonitrile monomer has a melting point of 234°C, while the novolac oligomer has a T_g of 85°C. It was necessary to heat the resin mixture to 140°C to achieve sufficient fiber wetting during composite melt processing, and the curing “window” at this temperature was narrow.

²⁶ Sumner, M.; Sankarapandian, M.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 5069-5076.

The focus of the research presented herein involves curing multi-functional, low molecular weight phenol-formaldehyde novolac resins with novel phthalonitrile derivatives to achieve low viscosity resin blends. These resins can be polymerized to produce flame resistant networks with high T_g s. The chemical modification of novolac oligomers and siloxane/silane monomers has led to novel phthalonitrile derivatives with low glass transition temperatures, between -25 and 75°C. The highly aromatic nature of these materials affords tough and thermally stable networks. The phthalonitrile resins were cured with low molecular weight novolac oligomers (256 and 348 g mol⁻¹) at moderate temperatures (200°C for 1 h and 225°C for 4h) to produce networks with glass transition temperatures > 250°C. The curing reactions were monitored by FTIR, and a decrease in the sharp band at 2230 cm⁻¹, attributed to the nitrile functionality of the phthalonitrile resin, was observed and served as an indication of the progress of the reaction. Substantial crosslinking was achieved within ~ 30-50 min, as indicated by ≥ 90% conversion of the nitrile.

Thermogravimetric analysis of these networks revealed high thermal and thermo-oxidative stability. Blending the low T_g phthalonitrile resins with low T_g novolac curing agents affords prepolymer resins of low melt viscosity, which suggests that fabrication via cost effective commercial processes, such as vacuum assisted resin transfer molding (VARTM), may be feasible.

CHAPTER 2: LITERATURE REVIEW

2.1 *Phenolic Resin Chemistry*

2.1.1 Introduction

Bakelite, first prepared by Leo Baekeland in 1907, is a phenolic resin produced from the reaction of formaldehyde with phenol.²⁷ Although Baeyer discovered phenol-formaldehyde resins as early as 1872, their commercial significance was not apparent until Baekeland developed an economical method using heat and pressure to convert the resins to hard, chemically resistant moldable parts. Phenol-formaldehyde resins are of great industrial interest because they have excellent insulating and mechanical properties and are lightweight compared to wood or metal. Since first commercialized in 1909, Bakelite has been employed in numerous applications including, woodworking, electrical laminates, adhesives, coatings, and other high-temperature applications.

In the phenol/formaldehyde reaction, two prepolymer types may be achieved depending on the reaction conditions (e.g., pH) and molar ratio of phenol to formaldehyde (P/F). Novolacs are derived from an excess of phenol, P/F 1:0.75-0.80, under neutral to acidic conditions, while reactions under basic conditions using an excess of formaldehyde, P/F 1:1.0-3.0, result in resoles.²⁸

²⁷ Baekeland, L. US Patent 942,699, July 13, 1907.

²⁸ Lin-Gibson, S.; Riffle, J. S. Chemistry and Properties of Phenolic Resins and Networks. In *Synthetic Methods in Step-Growth Polymers*. Rogers, M E, Long, T E, Eds. John Wiley & Sons, Inc., 2003. 365.

2.2 Resole Chemistry and Networks

Resoles are highly branched multi-functional hydroxymethylphenols (HMP) (**Figure 2.1**) formed from a base catalyzed electrophilic aromatic substitution reaction of phenol and formaldehyde. There are two pathways by which resole prepolymers may be formed (**Figure 2.2**). The first occurs under neutral to weakly acidic conditions and at temperatures less than 130 °C, dihydroxydibenzylether structures are predominant. The second occurs under alkaline conditions and at temperatures between 130 and 150 °C, where dihydroxydiphenylmethane is a major product. Resole prepolymers can be converted to crosslinked phenolic networks with heating under neutral conditions between 130 and 200 °C or in presence of an acid catalyst such as hydrochloric acid, phosphoric acid, *para*-toluenesulfonic acid, or phenolsulfonic acid under ambient conditions.²⁹ Resole resins have been successfully cured in the presence of sodium carbonate.³⁰ All resole networks contain a significant amount of voids due to volatiles, i.e., water and formaldehyde, released during the curing reactions, irrespective of the curing conditions.^{31,32} Voids may significantly decrease the structural integrity of the network.

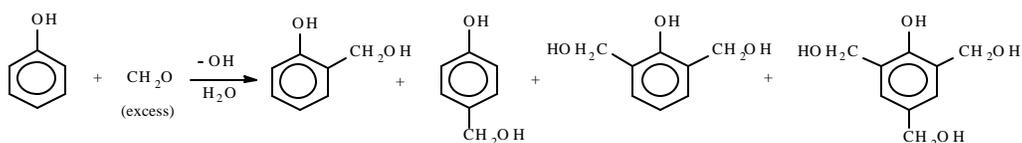


Figure 2.1: Reaction of phenol with formaldehyde under basic conditions.³³

²⁹ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

³⁰ Park, B. D.; Riedl, B. *J Appl Polym Sci* **2000**, 77, 1284-1293.

³¹ Lin-Gibson, S.; Riffle, J. S. Chemistry and Properties of Phenolic Resins and Networks. In *Synthetic Methods in Step-Growth Polymers*. Rogers, M E, Long, T E, Eds. John Wiley & Sons, Inc., 2003. 365.

³² Mark; Bakales; Overberger; Menges. Phenolic Resins. In *Encyclopedia of Polymer Science and Engineering*. John Wiley & Sons: New York, 1988. Vol. 11.

³³ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

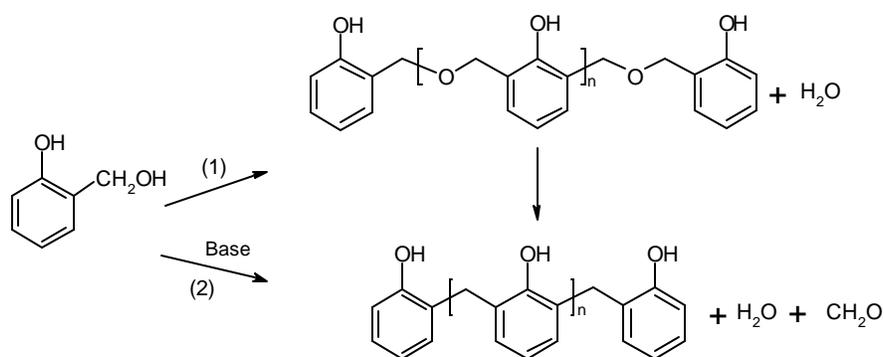


Figure 2.2: Resole prepolymer formation.³⁴

2.3 Novolac Chemistry and Networks

Novolac resins are linear or slightly branched chains of phenolic units linked by methylene groups, and their molecular weights typically range between 500 and 1000 g mol⁻¹. Under strongly acidic conditions employing acid catalysts, novolacs are produced via the electrophilic aromatic substitution of phenol with formaldehyde. Three reactive sites are available for electrophilic substitution on phenol, which gives rise to three different aromatic linkages: ortho-ortho, ortho-para, and para-para. A novolac resin of ten phenolic monomer units may give rise to 13,203 possible isomers.³⁵ This large distribution of isomers leads to amorphous materials, which prove difficult to characterize. As shown in **Figure 2.3**, the first step involves the formation of a hydroxymethylene carbonium ion from methylene glycol. In the rate-determining second step, the hydroxymethylene carbonium ion reacts with phenol to produce a methylol-substituted phenol intermediate, which is transient under acidic conditions

³⁴ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

³⁵ Megson, N. *Chem-Ztg.* **1972**, 96, 15-19.

and cannot be isolated. Therefore, benzylic carbonium ions result and react with phenol molecules to produce dihydroxydiphenylmethane.

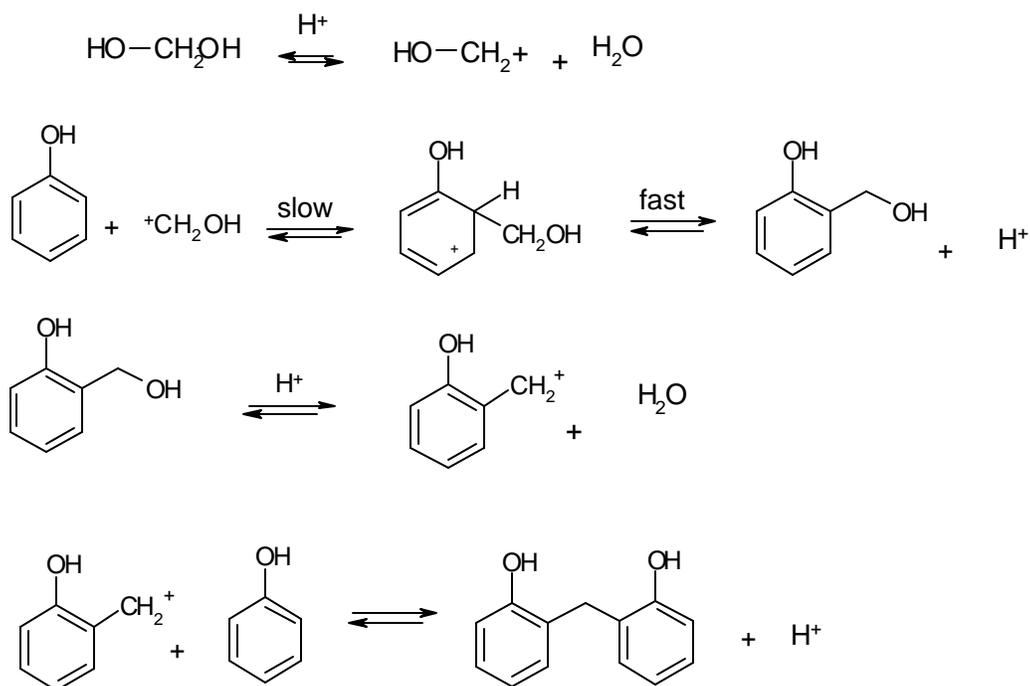


Figure 2.3: Novolac prepolymer formation.³⁶

Oxalic acid is the most commonly used catalyst, however, sulfuric acid and *p*-toluenesulfonic acid are also used. Oxalic acid is preferred because resins of low color may be prepared. In addition, oxalic acid decomposes at high temperatures (>180 °C) to CO₂, CO, and water, which facilitates the removal of the catalyst thermally. Typically, 1-6 wt % catalyst is used. Under strongly acidic conditions, methylol substitution and methylene bridge formation both occur preferably at the *para* positions. However, by controlling the reaction conditions and catalysts,

the molecular weight distribution and the substitution pattern of methylene linkages may be somewhat tailored.

High ortho-ortho' phenolic resins have been of great interest since Bender and Farnham³⁷ reported an unusually rapid cure rate of an ortho-ortho' material compared to other isomers with hexamethylenetetramine (HMTA). It was believed that the accessibility of the vacant *para* position enhanced the curing rate of these resins.

In early studies, the production of high ortho structured novolacs was achieved using a large excess of phenol at a pH between 4 and 7 and divalent metal acetates including Zn^{+2} , Ca^{+2} , Mg^{+2} , and Cd^{+2} as catalysts.³⁸ More recently, bromomagnesium salts of phenols, through quinone methide intermediates, have been employed for this purpose.³⁹ However, the major route to tailored high ortho novolac structures involves a two-step, two-pot synthetic procedure.^{40,41,42,43} In the first step, bishydroxymethyl cresol is prepared from the base-catalyzed condensation between cresol and formaldehyde at room temperature. In a second step, another cresol molecule is reacted with the bishydroxymethyl cresol formed in the first step, under acidic conditions. This procedure not only produces high-ortho linked, linear novolac resins, it may also be employed to prepare alternating and semi-alternating copolymers, which are of great

³⁶ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

³⁷ Bender, H.; Farnham, A.; Guyer, J.; Apel, F.; Gibb, T. *Ind Eng Chem* **1952**, *44*, 1619.

³⁸ Kopf, P. In *Encyclopedia of Polymer Science and Engineering*. Kroschwitz, J, Ed. John Wiley: New York, 1988. Vol. 11. 45.

³⁹ Dradi, E.; Casiraghi, G.; Sartori, G.; Casanti, G. *J Am Chem Soc* **1978**, *11*, 1295.

⁴⁰ Ueno, T. In *Microlithography Science and Technology*. Sheats, J, Smith, B, Eds. Marcel Dekker: New York, 1998. 429.

⁴¹ Zampini, A.; Turci, P.; Cernigliaro, G.; Stanford, H.; Swanson, G.; Meister, C.; Sinta, R. *Proc SPIE-Internat Soc Opt Engng* **1990**, *1262*, 501.

⁴² Bogan, L. J.; Graziano, K. *Proc SPIE-Internat Soc Opt Engng* **1990**, *1262*, 180.

⁴³ Jeffries, A.; Brzozowy, D.; Greene, N. *Proc SPIE-Internat Soc Opt Engng* **1993**, *1925*, 235.

interest in the fabrication of photoresists used in micro-lithographic processing.⁴⁴ Also, the moderate reaction conditions of the first step allow for high conversion of formaldehyde (~97%),⁴⁵ contrary to what is observed in the conventional synthesis performed at elevated temperatures (50-75%)⁴⁶.

High ortho-novolacs are unique in their inherent ‘hyperacidity’ and tendency to form complex compounds with di- and tri-valent metals and nonmetals. The linearity of the novolac structure places the hydroxyl functional groups in close proximity to one another, promoting high intra-molecular bonding. The acidity demonstrated by these materials falls between that of phenols and carboxylic acids.

Phenolic networks may be prepared from thermoplastic novolac resins cured with a formaldehyde source. Most commonly 8-15 wt % hexamethylenetetramine (HMTA) is used. A model study of the reaction of 2,4-xylenol with HMTA was performed by Zhang et al.^{47,48,49,50,51,52} to investigate the novolac/HMTA reaction mechanism. Several reaction intermediates including hydroxylbenzylamines, benzoxazines, triazines, diamines, and, in the presence of trace amounts of water, benzyl alcohols and ethers were proposed (**Figure 2.4**). The HMTA concentration was determined to be a major factor in the resulting structure of the networks formed from 2,4-xylenol/HMTA reactions. The formation of heterocyclics, as observed in the model study, enhanced mechanical strength and toughness. However, curing

⁴⁴ Baehr, G.; Westerwelle, U.; Gruetzner, G. *Proc SPIE-Internat Soc Opt Engng* **1997**, 3049, 628.

⁴⁵ Baehr, G.; Westerwelle, U.; Gruetzner, G. *Proc SPIE-Internat Soc Opt Engng* **1997**, 3049, 628.

⁴⁶ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

⁴⁷ Zhang, X.; Looney, M. G.; Solomon, D. H.; Whittaker, A. K. *Polymer* **1997**, 38, 5835-5948.

⁴⁸ Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, 39, 399-404.

⁴⁹ Zhang, X.; Solomon, D. H. *Polymer* **1998**, 39, 405-412.

⁵⁰ Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, 39, 1957-1966.

⁵¹ Zhang, X.; Solomon, D. H. *Polymer* **1998**, 39, 6153 - 6162.

⁵² Lim, A. S. C.; Solomon, D. H.; Zhang, X. *J Polym Sci Pt A: Polym Chem* **1999**, 37, 1347 - 1355.

reactions employing HMTA produce several volatile side products, including ammonia gas. The evolution of volatiles results in voids in the networks, although novolac/HMTA networks demonstrate this phenomenon to a lesser extent than resole networks.

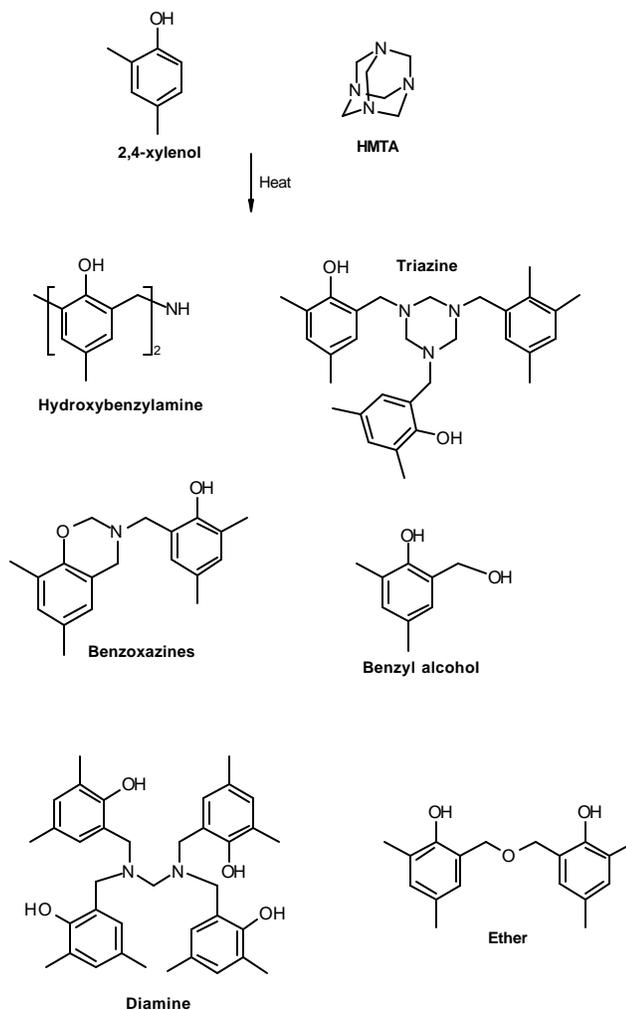


Figure 2.4: Reaction intermediates proposed from the model study of the reaction of 2,4-xyleneol and HMTA.⁵³

⁵³ Zampini, A.; Turci, P.; Cernigliaro, G.; Stanford, H.; Swanson, G.; Meister, C.; Sinta, R. *Proc SPIE-Internat Soc Opt Engng* **1990**, 1262, 501.

2.4 Characterization of Phenolic Resins

Phenolic resins and their networks have been studied using a wide variety of analytical techniques. Molecular weight and molecular weight distributions (MWD) of phenolic oligomers have been effectively determined with gel permeation chromatography (GPC),^{54,55} NMR spectroscopy,⁵⁶ vapor pressure osmometry (VPO),⁵⁷ intrinsic viscosity,⁵⁸ and matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOFMS)⁵⁹. Determining the molecular weight and molecular weight distributions of phenol-formaldehyde oligomers is an important issue in terms of quality control during production. Dargaville and co-workers showed that these factors directly affect the properties of cured networks.⁶⁰ However, accurate measurements of these properties is complicated by the presence of a wide distribution of isomers.

GPC, the most widely used tool for the quantitative measure of molecular weight and molecular weight distribution, separates compounds based on variations in hydrodynamic volume relative to monodisperse polymer standards, typically polystyrene. Yoshikawa et al.⁶¹ reported that a single calibration plot was not applicable to the GPC analysis of phenol-formaldehyde resins due to the fact that isomers elute at different times, and therefore, a single relationship between elution volume and molecular weight could not be determined. Dargaville et al. and Yoshikawa et al. researched the GPC analysis of phenol-formaldehyde resins by

⁵⁴ Yoshikawa, T.; Kimura, K.; Fujimura, S. *J Appl Polym Sci* **1971**, *15*, 2513-2520.

⁵⁵ Yamagishi, T.; Nomoto, M.; Ito, S.; Ishida, S.; Nakamoto, Y. *Polym Bull* **1994**, *32*, 501-507.

⁵⁶ Bogan, L. J. *Macromolecules* **1991**, *24*, 4807 - 4812.

⁵⁷ Kim, M.; Nieh, W.; Sellers, T. J.; Wilson, W.; Mays, J. *Ind Eng Chem Res* **1992**, *31*, 973-979.

⁵⁸ Tobiason, F.; Chandler, C.; Schwarz, F. *Macromolecules* **1972**, *5*, 321-325.

⁵⁹ Mandal, H.; Hay, A. S. *Polymer* **1997**, *38*, 6267-6271.

⁶⁰ Dargaville, T. R.; Guerzoni, F.; Looney, M. G.; Shipp, D.; Solomon, D. H.; Zhang, X. *J Polym Sci Pt A: Polym Chem* **1997**, *35*, 1399-1407.

⁶¹ Yoshikawa, T.; Kimura, K.; Fujimura, S. *J Appl Polym Sci* **1971**, *15*, 2513-2520.

constructing calibration curves from a series of low molecular weight novolac model compounds, whose chemical architecture was more similar to phenol-formaldehyde resins than the polystyrene standards typically employed. Dargaville et al.⁶² prepared model compounds and divided them among three series which included a series of compounds with a high proportion of ortho-ortho' methylene linkages (ortho series), a series in which all positions para to the phenolic hydroxyl were substituted (para series), and a statistical mixture of ortho and para substitutions (ortho, para series). Calibration curves were constructed based on the elution volume and molecular weight of each series and the elution behavior of each series was compared to that of polystyrene standards. It was revealed that para isomers eluted earlier than ortho isomers of comparable degrees of polymerization. This observation was attributed to the reduced hydrodynamic volume of ortho isomers, resulting from high intra-molecular hydrogen bonding. In their study of trimeric resins, Yoshikawa et al.⁶³ reported similar conclusions. Comparisons of the calibration curves from the model novolac series to polystyrene standards only demonstrated a slight deviation compared to the para-ortho and para series. However, large deviations were observed when considering the ortho series. The work of Dargaville and Yoshikawa clearly demonstrated that polystyrene standards were insufficient for quantitative measurements of the molecular weight and molecular weight distributions of phenol-formaldehyde resins due to high intra-molecular hydrogen bonding within novolac resins. As molecular weight increases, intra-molecular hydrogen bonding increases within novolac resins; this phenomenon results in complex elution behavior, which proves difficult to quantify using GPC. Although, GPC

⁶² Dargaville, T. R.; Guerzoni, F.; Looney, M. G.; Shipp, D.; Solomon, D. H.; Zhang, X. *J Polym Sci Pt A: Polym Chem* **1997**, *35*, 1399-1407.

⁶³ Yoshikawa, T.; Kimura, K.; Fujimura, S. *J Appl Polym Sci* **1971**, *15*, 2513-2520.

employing polystyrene standards can be a useful tool in a qualitative manner, more reliable quantitative characterization must be pursued by an alternate means.

NMR spectroscopy can be utilized for obtaining several microstructural details and is exceptionally important for determining the nature and degree of substitution patterns on different ring carbons in novolac resins.⁶⁴ The NMR absorption pattern for methylene carbons of novolac resins is sensitive to the positional isomerism.^{65,66} In their study of calibration curves for novolac resins, Dargaville et al.⁶⁷ employed ¹³C NMR spectroscopy to determine the relative compositions of ortho-ortho, ortho-para, and para-para linked methylene groups in various commercial novolac resins. This isomeric distribution was used to determine the weight fraction of ortho-ortho, ortho-para, and para-para isomers in each of the resins, and to determine a single weighted number average molecular weight, $M_{n(w)}$, for each of the commercial resins. This study was based on three calibration curves: ortho-ortho (experimental), ortho-para (simulated) and para-para (simulated). By taking the ratio of the integrations of methylene (aliphatic) protons to aromatic protons from the ¹H NMR spectra, the number average molecular weight of each commercial novolac resin was calculated.^{68,69} $M_{n(w)}$ values calculated from ¹³C NMR studies compared well to ¹H NMR data. GPC data, based on ortho-ortho (experimental), ortho-para (simulated), and para-para (simulated) calibration curves, agreed well with NMR data for phenol-formaldehyde resins below 800 g mol⁻¹.

⁶⁴ Roy, D.; Basu, P.; Raghunathan, P.; Eswaran, S. *Polym Intl* **2003**, *52*, 757-767.

⁶⁵ Dradi, E.; Casiraghi, G.; Casanti, G. *Chem Ind* **1978**, *19*, 627.

⁶⁶ Mukoyama, Y.; Tanno, T.; Yokokawa, H.; Fleming, J. *J Polym Sci* **1973**, *11*, 3193.

⁶⁷ Dargaville, T. R.; Bruyn, P. J. D.; Lim, A. S. C.; Looney, M. G.; Potter, A. C.; Solomon, D. H. *J Polym Sci Pt A* **1997**, *35*, 1389-1398.

⁶⁸ Szymanski, H.; Bluemle, A. *J Polym Sci. Part A* **1965**, *3*, 63.

⁶⁹ Dankelman, W.; de Wit, J. *Angew Makromol Chem* **1977**, *62*, 101.

Sojka et al.⁷⁰ used ¹³C NMR to study the positional isomers of bis(hydroxybenzyl)phenols and bis(hydroxyphenyl)methanes. From these studies, they assigned ¹³C NMR chemical shifts to these oligomers, grouped them into classes, and compiled the list shown in **Figure 2.5**. Microstructure elucidation has also proven successful by multidimensional ¹³C NMR spectroscopy methods including attached proton test (APT), insensitive nuclei enhanced by polarized transfer (INEPT), distortionless enhancement by polarization transfer (DEPT), and 2-D incredible nature abundance double quantum experiments (INADEQUATE).⁷¹ More recently, solid-state NMR has been used for precise determination of bond structure in cured novolacs.^{72,73,74,75} Roy et al.⁷⁶ presented a comprehensive review expressing the nature of NMR spectroscopy applications in the field of phenol-formaldehyde resins. In an effort to achieve 'tailored' high ortho, low MWD cresylic novolac-formaldehyde resins for high performance photoresists for lithographic processes, an intense study of microstructures was undertaken. The micro-lithographic process is contingent upon the differential solubility of the exposed and the unexposed parts of the photoresist, which is governed by the structure of the matrix polymer. Novolac resins with high-ortho structure have more 'free' para positions, and those positions can undergo an azo coupling reaction with the diazo compounds in the unexposed parts.^{77,78} Coupling reactions result in an increase in molecular weight, which could lead to insolubility issues in the alkaline developer. INEPT and DEPT ¹³C NMR techniques were

⁷⁰ Sojka, S. A.; Wolfe, R. A.; Guenther, G. D. *Macromolecules* **1981**, *14*, 1539-1543.

⁷¹ Roy, D.; Basu, P.; Raghunathan, P.; Eswaran, S. *Polym Intl* **2003**, *52*, 757-767.

⁷² Fyfe, C.; Rudin, A.; Tehir, W. *Macromolecules* **1980**, *13*, 1320.

⁷³ Hatfield, G.; Maciel, G. *Macromolecules* **1987**, *20*, 608.

⁷⁴ Sojka, S. A.; Wolfe, R. A.; Guenther, G. D. *Macromolecules* **1981**, *14*, 1539-1543.

⁷⁵ Bryson, R.; Hatfield, G.; Early, T.; Palmer, A.; Maciel, G. *Macromolecules* **1983**, *16*, 1669.

⁷⁶ Roy, D.; Basu, P.; Raghunathan, P.; Eswaran, S. *Polym Intl* **2003**, *52*, 757-767.

⁷⁷ Ueno, T. In *Microlithography Science and Technology*. Sheats, J, Smith, B, Eds. Marcel Dekker: New York, 1998. 429.

⁷⁸ Hanabata, M.; Uetani, Y.; Furuta, A. *J Vac Sci Technol* **1989**, *B7*, 640.

employed to quantitatively determine the percentage of 'free' para positions in the novolac resin. Correlations were made between novolac microstructure and the lithographic performance of the photoresists. Improved photoresist performance was evident with the use of novolac resins with higher contents of 'free' para positions. The 2-D INADEQUATE technique, in which one axis of the two-dimensional ^{13}C NMR spectrum displays the normal single-quantum transition frequency while the orthogonal axis displays the double-quantum ^{13}C frequency as summed and scaled chemical shifts,^{79,80} was employed to determine the exact carbon skeleton in novolac resins. NMR studies in this capacity have led to a better understanding of the photoresists, and to improvements in lithographic performance.

Solid-state ^{13}C NMR has also been utilized effectively in studying cure behavior. Using ^{13}C NMR with cross polarization (CP) and magic angle spinning (MAS) Ottenbourgs et al.⁸¹ monitored the cure behavior of high-ortho novolac resins with paraformaldehyde. This NMR technique was ideal in this application because it was noninvasive and sample preparation, i.e. solubility, was not an issue. The disappearance of paraformaldehyde, as indicated by a peak at ± 90 ppm, and the increase of a peak at 33 ppm attributed to aliphatic methylene carbons were observed over time. The cure reaction was completed in 25 minutes; however, the reaction did not reach 100% conversion due to vitrification. The F/P ratio and degree of conversion were calculated with the analysis of sequential spectra from solid state ^{13}C CP/MAS NMR. The degree of conversion was shown to be largely dependent on the curing conditions, i.e., cure time, temperature, and pressure.

⁷⁹ Bax, A.; Freeman, R.; Frenkiel, T. *J Am Chem Soc* **1981**, *103*, 2102.

⁸⁰ Silverstein, R.; Webster, F. *Spectroscopic Identification of Organic Compounds*. John Wiley: New York, 1996. 250.

⁸¹ Ottenbourgs, B.; Adriaensens, P.; Carleer, R.; Vanderzande, D.; Gelan, J. *Polymer* **1998**, *39*, 5293-5300.

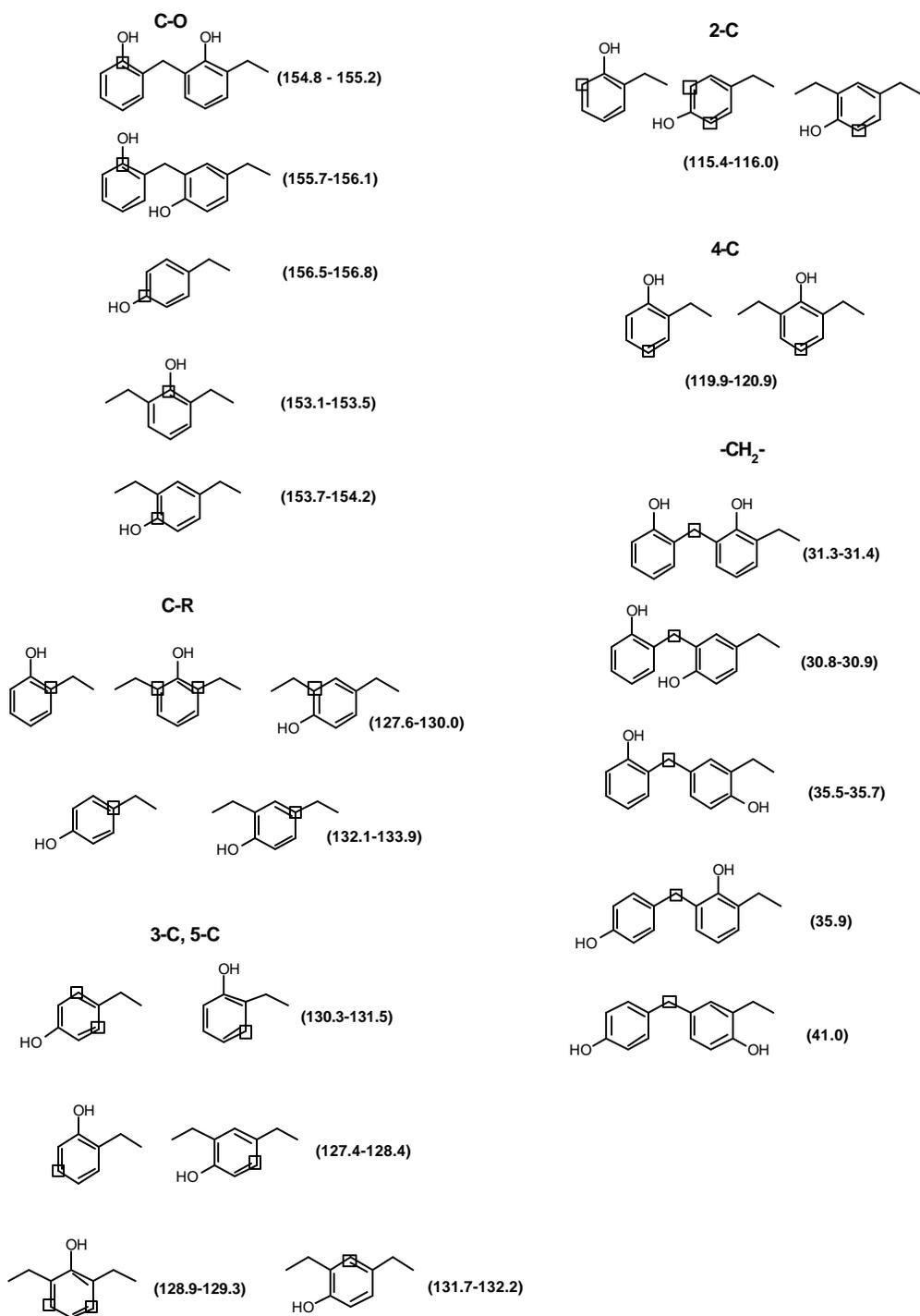


Figure 2.5: Compilation of ^{13}C NMR chemical shift regions identified in phenolic resins.⁸²

⁸² Sojka, S. A.; Wolfe, R. A.; Guenther, G. D. *Macromolecules* **1981**, *14*, 1539-1543.

Fourier transform infrared (FT-IR) and fourier transform raman spectroscopy have been used to characterize phenolic resins and their curing behavior with various curing agents. Sojka et al.⁸³ employed FT-IR to monitor the reaction between phenol and HMTA. The spectra were plagued with interferences due to broad hydroxyl stretching and line broadening during the reaction. In addition, interference of IR bands from the starting materials made it difficult to identify new stretches due to the formation of intermediates or products. Although FT-IR spectroscopy is a powerful tool for the identification of functional groups, it is limited in its capabilities in determining structural detail. FT-Raman spectroscopy, based on polarization changes during the vibrational motions was also explored for the qualitative characterization of phenol-formaldehyde resins.⁸⁴ FT-Raman spectroscopy proved advantageous over FT-IR. The interference resulting from presence of the hydroxyl functionality was not observed in Raman spectroscopy. In the analysis of phenol-formaldehyde resins, the areas of interest in Raman spectroscopy include 2800 – 4000 cm⁻¹, where phenyl C–H stretching and methylene bridges are observed, and between 400 and 1800 cm⁻¹, where bands due to elongation of aromatic bonds (C=C) and methylene were discernable. Within the 2800 – 4000 cm⁻¹ range, two strong bands are characteristic to phenol-formaldehyde resins, a band at 3060 cm⁻¹ due C–H of the phenyl ring and 2940 cm⁻¹ due to C–H of the methylene bridges. By calculating the ratio of these two band areas, estimations of the F/P ratio, and number average molecular weights were made.

Mandal and Hay have used matrix assisted-laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) to characterize *para*-substituted phenol-formaldehyde resins⁸⁵

⁸³ Sojka, S. A.; Wolfe, R. A.; Guenther, G. D. *Macromolecules* **1981**, *14*, 1539-1543.

⁸⁴ Ottenbours, B.; Adriaensens, P.; Carleer, R.; Vanderzande, D.; Gelan, J. *Polymer* **1998**, *39*, 5293-5300.

⁸⁵ Mandal, H.; Hay, A. S. *Polymer* **1997**, *38*, 6267-6271.

and polycyclic siloxane phenol-formaldehyde resins⁸⁶. Siloxanes with dimethyl and diphenyl substituents were synthesized by reacting dimethyl and diphenyl chlorosilanes with para-substituted novolac resins under high dilution conditions. In analyses of the siloxanes reacted with 4-t-butylphenol-formaldehyde oligomeric species, three siloxane rings were observed. The MALDI-TOF spectrum revealed $m/z = 477$ Da corresponding to monocyclic siloxane with silver ion and the following masses: 639 Da corresponding to trimeric monocyclic siloxane with one free phenol, 800 Da corresponding to tetrameric species with one cyclic siloxane and two free phenols, and 857 Da corresponding to bicyclic siloxane resin with one silver ion. Polycyclic species were found in much higher abundance than their counterparts with free phenolic moieties. The intensities of cyclic siloxane species revealed in MALDI-TOF correlated well with HPLC data, which further confirmed the presence of a high concentration of cyclic siloxane species.

2.5 Phenolic-Epoxy Chemistry

2.5.1 Introduction

A vast number of studies investigating reactions between phenolic resins and epoxies and their applications have been reported. Schechter and Wynstra^{87,88,89} conducted some of the earliest and most significant work in this field. Epoxy resins are of great industrial interest because they may be crosslinked with phenolic resin to yield void-free phenolic networks.^{90,91}

⁸⁶ Mandal, H.; Hay, A. S. *Journal of Polymer Science: Part A: Polymer Chemistry* **1998**, *36*, 2429-2437.

⁸⁷ Shechter, L.; Wynstra, J. *Industrial and Engineering Chemistry* **1956**, *48*, 86.

⁸⁸ Shechter, L.; Wynstra, J.; Kurkky, R. *Industrial and Engineering Chemistry* **1956**, *48*.

⁸⁹ Shechter, L.; Wynstra, J.; Kurkky, R. *Industrial and Engineering Chemistry* **1957**, *49*, 1107.

⁹⁰ Lee, H.; Neville, K. *Handbook of Epoxy Resins*. McGraw Hill: London, 1967.

⁹¹ Potter, W. G. *Epoxy Resins*. Iliffe Books: London, 1970.

Novolac oligomers may be reacted with an excess of epichlorohydrin to produce epoxidized novolacs that have high strength, excellent dielectric properties and improved oxidative resistance.⁹² Microelectronics packaging applications comprise a large sector of the commercial uses in which epoxidized phenolic networks are employed.

2.5.2 Phenolic-Epoxy Reaction Mechanism

In phenol-epoxy reactions, the reaction mechanism and the extent of side reactions are highly dependent on the reaction conditions and the catalysts employed. The reaction between the phenolic hydroxyl groups of novolac oligomers and the epoxide may be catalyzed with a wide variety of catalysts including acids, bases, triaryl or trialkyl nucleophiles of Group 5a compounds,⁹³ and quaternary ammonium complexes⁹⁴. Typically, tertiary amine or phosphine catalysts are employed, with triphenylphosphine being the most commonly used reagent. Romanchick et al.⁹⁵ proposed a mechanism for the triphenylphosphine-catalyzed phenol-epoxy reaction as shown in **Figure 2.6**. In the first step, the triphenylphosphine catalyst ring-opens the epoxide ring and produces a zwitterion. A rapid proton transfer follows this from the hydroxyl group of the phenol to the zwitterion. The third step of the mechanism shows two reaction pathways available for the phenoxide molecule. Phenoxide may react with the electrophilic carbon next to the phosphorus of the secondary alcohol, regenerating triphenylphosphine, or it

⁹² Mark; Bakales; Overberger; Menges. Phenolic Resins. In *Encyclopedia of Polymer Science and Engineering*. John Wiley & Sons: New York, 1988. Vol. 11.

⁹³ Banthia, A.; McGrath, J. *Polymer Preprints* **1979**, *20*, 629-633.

⁹⁴ Biernath, R.; Soane, D. Cure Kinetics of Epoxy Cresol Novolac Encapsulants for Microelectronics Packaging. In *Contemporary Topics in Polymer Science: Volume 7, Advances in New Materials*. Salamone, J, Riffle, J S, Eds., 1992. 103-159.

⁹⁵ Romanchick, W.; Sohn, J.; Geibel, J. Synthesis, Morphology, and Thermal Stability of Elastomer-Modified Epoxy Resin. In *ACS Symposium Series 221-Epoxy Resin Chemistry II*. Bauer, R, Ed. American Chemical Society: Washington, DC, 1982. Vol. 221. 85-118.

may react with another epoxide ring and abstract a proton from a phenol molecule, thus regenerating the nucleophilic phenoxide. In an uncatalyzed reaction, the secondary hydroxyl generated from the initial phenol-epoxy reaction can react with another epoxy to give a branched species (**Figure 2.7**). Branching is undesirable in the pursuit of high molecular weight polyhydroxyethers. The extent of the branching reaction may be limited with the use of sterically hindered catalysts such as those described above.⁹⁶

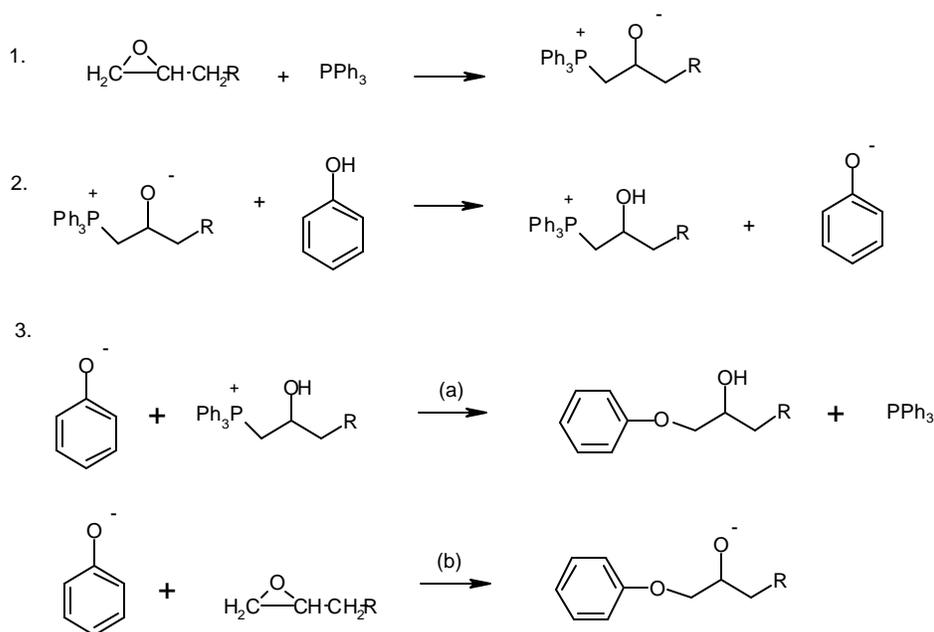


Figure 2.6: Mechanism for a triphenylphosphine-catalyzed epoxy-phenol reaction.⁹⁷

⁹⁶ Biernath, R.; Soane, D. Cure Kinetics of Epoxy Cresol Novolac Encapsulants for Microelectronics Packaging. In *Contemporary Topics in Polymer Science: Volume 7, Advances in New Materials*. Salamone, J, Riffle, J S, Eds.; 1992. 103-159.

⁹⁷ Romanchick, W.; Sohn, J.; Geibel, J. Synthesis, Morphology, and Thermal Stability of Elastomer-Modified Epoxy Resin. In *ACS Symposium Series 221-Epoxy Resin Chemistry II*. Bauer, R, Ed. American Chemical Society: Washington, DC, 1982. Vol. 221. 85-118.

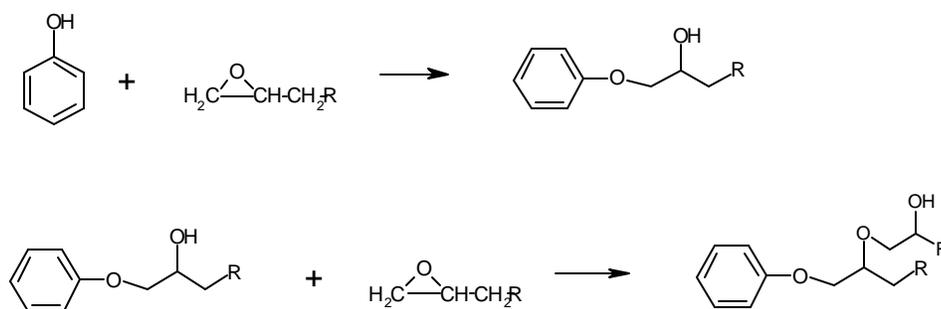


Figure 2.7: Phenol-epoxy branching reaction

Aliphatic amines are also commonly used to catalyze phenol-epoxy reactions. The melt reaction mechanism of tertiary aliphatic amine-catalyzed phenolic-epoxy reaction was proposed by Gagnebien et al. (**Figure 2.8**).⁹⁸ In the first step, trialkylamine abstracts a proton from the phenol to form an ion pair. The ion pair complexes with the epoxide ring, and the complex dissociates to form a β-hydroxyether and trialkylamine.

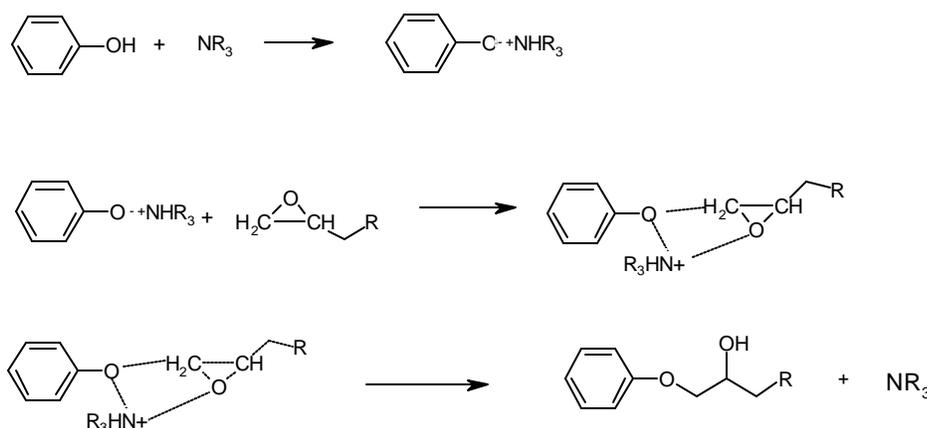


Figure 2.8: Proposed mechanism for tertiary amine-catalyzed phenol-epoxy reaction.

⁹⁸ Gagnebien, D.; Madec, P.; Marechal, E. *Eur Polym J* **1985**, *21*, 273-283.

Phenol-epoxy reactions exhibit three different side reactions: epoxy homopolymerization, a branching reaction through the secondary hydroxyl, and zwitterion catalyzed branching through the secondary hydroxyl.⁹⁹ The branching reaction is the predominant side reaction. However, the extent of branching should decrease as the ratio of epoxy to phenol decreases because the phenolate anions are more nucleophilic than the competing aliphatic hydroxyl groups.

2.5.3 Phenolic-Epoxy Networks

By crosslinking phenol-formaldehyde novolac resins with epoxies, void-free phenolic networks may be prepared. Epoxy resins can be used in this capacity to toughen phenolic networks, which tend to be brittle when cured with formaldehyde sources such as HMTA. By pairing the strength inherent to epoxy resins and the thermal stability inherent to phenolic networks, network materials may be tailored to meet the requirements of many flame resistant structural applications. Schroeder et al.¹⁰⁰ were among several pioneers to highlight the importance of correlating characteristics such as crosslink density, thermal transitions, and Young's modulus, with macroscopic properties such as stress relaxation, fracture toughness, and moisture absorption, as a means to quantitatively relate end-use requirements to molecular structure. In studies of the structure-property relationships of a series of networks from aromatic-epoxy/aliphatic epoxy resin cured with imidazole, a 43/57 w/w composition exhibited the greatest toughness, $1/M_c = 2.6 \times 10^{-3} \text{ mol g}^{-1}$. The properties of this network were intermediate between the two extremes, 100/0 aromatic epoxy/aliphatic epoxy and 0/100

⁹⁹ Tyberg, C. S. Void-Free Flame Retardant Phenolic Networks: Properties and Processability. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2000.

¹⁰⁰ Schroeder, J. A.; Madsen, P. A.; Foister, R. T. *Polymer* **1987**, *28*, 929-940.

aromatic epoxy/aliphatic epoxy. The high crosslink density exhibited in the predominantly aromatic networks demonstrated low toughness, as did the lightly crosslinked, predominantly aliphatic networks. Tyberg et al.¹⁰¹ performed similar studies in their investigation of void-free phenolic-epoxy matrix materials. In this study, phenolic novolacs were cured with epoxy resins employing a stoichiometric offset between the phenol and epoxy groups to control crosslink density, thereby tailoring the mechanical properties. Three epoxy resins with variations in structure were investigated (**Figure 2.9**). Networks with as much as 80 wt % phenolic content were targeted to maintain the high flame properties inherent to the phenolic component. A triphenylphosphine catalyst was used to promote the phenol-epoxy reaction and the networks were cured at 200 °C.

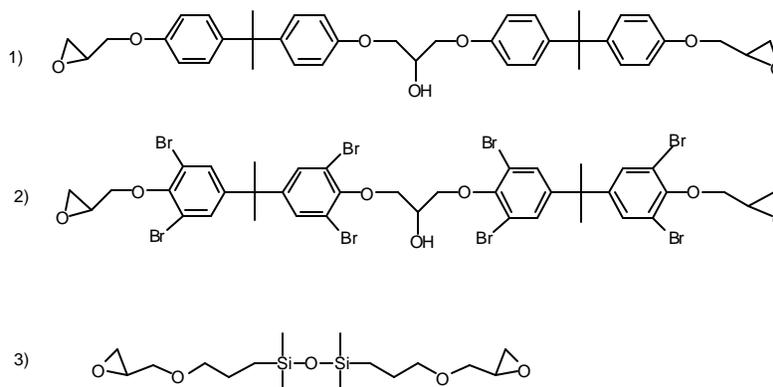


Figure 2.9: Epoxy structures: 1) bisphenol-A-based epoxy, 2) brominated bisphenol-A-based epoxy, and 3) siloxane epoxy.

¹⁰¹ Tyberg, C. S.; Bergeron, K.; Sankarapandian, M.; Shih, P.; Loos, A. C.; Dillard, D. A.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2000**, *41*, 5053-5062.

The fracture toughness of the resulting networks was studied with plane stress intensity factors, K_{Ic} . A stoichiometric ratio of 5/1 eq/eq phenol/epoxy yielded optimal mechanical properties, with a K_{Ic} of 1.02 MPa m^{1/2}. A lower phenol/epoxy ratio, 1.8/1, led to increased brittleness (K_{Ic} 0.64 M Pa m^{1/2}); however, the 7/1 phenol/epoxy ratio also resulted in decreased toughness (K_{Ic} 0.70 M Pa m^{1/2}). These results correlated well with variations in characteristics such as crosslink density. A 3/1 phenol/epoxy network (K_{Ic} 0.85 M Pa m^{1/2}) resulted in an average molecular weight between crosslinks, M_c , of 1413 g mol⁻¹, while the 1.8/1 phenol/epoxy ratio had $M_c = 644$ g mol⁻¹ and the 7/1 phenol /epoxy ratio had $M_c = 4539$ g mol⁻¹. Lower phenol/epoxy ratios produced higher crosslink densities. Tight packing was associated with highly crosslinked networks, and this enhanced the mechanical properties to an extent, after which, the networks became brittle. Although the observed trend was similar, the decrease in toughness observed with the higher phenol/epoxy ratios was attributed to an excess of phenols, which led to an increase in the number of un-reacted phenolic chains that did not contribute to the network structure or mechanical strength. Overall, all of the phenol-epoxy networks studied possessed equal or greater toughness compared to both the epoxy control, a bisphenol A epoxy cured with 4,4'-DDS (K_{Ic} 0.62 M Pa m^{1/2}), and the phenolic control, a thermally cured resole (K_{Ic} 0.16 M Pa m^{1/2}). Also, as expected, the glass transition temperatures of the networks decreased as the distances between crosslinks increased. **Table 2.1** shows the results of the compositions studied.

Flame properties of the networks were investigated using cone calorimetry in which a heat flux of 50 kW/m² and 20.95 mol % O₂ content (atmospheric oxygen) were employed. The results of these studies are compiled in **Table 2.2**. All of the networks had peak heat release rates (PHRR) lower than the epoxy control, 1230 kW/m². Considering PHRR, char yield, and smoke

toxicity collectively, the bisphenol-A based epoxy cured with 80 wt % novolac performed well exhibiting K_{Ic} of 0.70 MPa·m^{1/2}, PHRR of 260 kW/m², 33% char yield, and a CO/CO₂ ratio of 0.027. An even lower PHRR (226 kW/m²) was observed in the case of the disiloxane epoxy system (80/20 w/w phenol/epoxy). In addition, this network exhibited increased char yields and decreased smoke toxicity, however the K_{Ic} values were slightly lower (0.62 MPa·m^{1/2}).

Table 2.1: T_g and K_{Ic} values for Phenolic Novolac-Epoxy Networks.¹⁰²

Epoxy	Phenol/Epoxy	Phenol/Epoxy	T_g	K_{Ic}	M_c
	(w/w)	(mol/mol)	(°C)	(MPa m ^{1/2})	(g/ mol)
Bisphenol-A- epoxy cured with 4,4'-DDS	–	–	127	0.62	–
Phenolic Control (thermally cured resol)	–	–	–	0.16	–
	80/20	7:1	114	0.70	4539
Bisphenol-A	–	5:1	110	1.02	–
	65/35	3:1	127	0.85	1413
	50/50	2:1	151	0.64	643
Brominated Bisphenol-A	65/35	5.8:1	130	0.74	3511
	50/50	3.1:1	148	0.84	1554
Disiloxane epoxy	80/20	7.2: 1	96	0.62	4051
	65/35	3:1	87	0.77	1030

¹⁰² Tyberg, C. S. Void-Free Flame Retardant Phenolic Networks: Properties and Processability. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2000.

Table 2.2: Flame Retardance of Networks Prepared from Phenolic Novolac Crosslinked with Various Epoxies. ¹⁰³

Epoxy	Phenol/Epoxy	PHHR	Char Yield	CO/CO ²
	(w/w)	(kW / m ²)	(%)	(x 10 ⁻³)
Bisphenol-A- epoxy cured with 4,4'-DDS	–	1230	5	44
Phenolic Control (thermally cured resol)	–	116	63	–
	80/20	260	33	27
Bisphenol-A	65/35	360	29	34
	50/50	380	23	36
Brominated Bisphenol-A	65/35	165	8	189
	50/50	158	9	175
Disiloxane epoxy	80/20	226	35	15
	65/35	325	24	27

Halogenated polymers burn relatively slowly due to a gas phase mechanism wherein gaseous decomposition products inhibit the release of oxygen to the flame. However, the production of dense smoke, with high concentrations of toxic carbon monoxide, is characteristic upon burning these materials.^{104,105,106} This trend was observed in the study of the brominated bisphenol-A epoxy resin compositions via cone calorimetry. Although the brominated bisphenol-A epoxy cured with 50 wt % novolac exhibited the lowest PHRR, it also had a high smoke toxicity rating and very low char yield which limits its flame resistance.

Lin-Gibson et al.^{107,108} studied high molecular weight, 2000 g mol⁻¹, linear ortho-cresol novolac oligomers cured with either bisphenol-A diepoxide (Epon 828) or epoxidized novolac

¹⁰³ Tyberg, C. S.; Bergeron, K.; Sankarapandian, M.; Shih, P.; Loos, A. C.; Dillard, D. A.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2000**, *41*, 5053-5062.

¹⁰⁴ Koo, J.; Venumbaka, S.; Cassidy, P.; Fitch, J.; Grand, A. *J Fire and Materials* **2000**, *24*, 209-218.

¹⁰⁵ Hirschler, M. *J Fire Science* **1991**, *9*, 183-222.

¹⁰⁶ Hshieh, F.; Beeson, H. *Fire and Materials* **1997**, *21*, 41 - 49.

¹⁰⁷ Lin-Gibson, S. *Cresol Novolac/Epoxy Networks: Synthesis, Properties, and Processability*. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2001.

¹⁰⁸ Lin-Gibson, S.; Baranauskas, V.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 7389-7398.

oligomers (DEN 438) to improve the processability of novolac-epoxy networks while maintaining mechanical properties. The networks were cured in the presence of a triphenylphosphine catalyst at 200 °C for 2 hours and post-cured at 220 °C for an additional 2 hours. **Figure 2.10** illustrates the cresol novolac-epoxy cure reaction. The 60/40 w/w novolac/epoxy compositions had good toughness. The *o*-cresol novolac/ Epon 828 epoxy 60/40 w/w network had a K_{Ic} of 1.20 MPa m^{1/2}. This was an improvement over the 63/37 w/w 700 g mol⁻¹ novolac/Epon 828 epoxy (0.85 MPa m^{1/2}) previously reported.¹⁰⁹ As the novolac content was increased to 70 wt%, a maximum T_g (152-154 °C) was achieved, beyond which the T_g decreased. The mechanical properties correlated well with crosslink density. For the Epon 828 epoxy cured with 70 wt % *o*-cresol-novolac, a glass transition temperature of 154 °C and $M_c = 1510$ g mol⁻¹ were observed. The M_c proved reasonable for well-connected networks and this was also evident from the high T_g s observed. In both the Epon 828 and epoxidized novolac series, the 60/40 w/w *o*-cresol-novolac/epoxy networks had the highest fracture toughness. The networks with lower crosslink densities (80/20 w/w compositions) resulted in brittle networks.

Cone calorimetry measurements at a heat flux of 50 kW/m² were used to analyze the flame properties of the *o*-cresol-novolac/epoxy networks. PHRR of all the *o*-cresol-novolac/epoxy networks, 300 – 450 kW/m², were significantly lower than the epoxy control, 1230 kW/m². However, the PHRRs were higher than those of the phenolic novolac/Epon 828 networks, and this was attributed to the increased aliphatic character of the *o*-cresol oligomer.

¹⁰⁹ Tyberg, C. S. Void-Free Flame Retardant Phenolic Networks: Properties and Processability. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2000.

In an effort to identify the time-temperature limits of a processing window, Lin-Gibson et al. measured resin viscosities.¹¹⁰ The temperature at which the resin mixtures reached 2 Pa s was chosen as the ‘process temperature’. The 60/40 w/w *o*-cresol-novolac/Epon 828 resin mixture had a processing temperature of 120 °C, while all *o*-cresol-novolac/epoxidized novolac resin mixtures required elevated temperatures, 160 °C, to achieve comparable viscosities. Isothermal viscosity studies revealed that the 60/40 w/w cresol-novolac/ Epon 828 resin mixture had a relatively low viscosity at 120 °C stable over a two hour period. Incorporation of low molecular weight *o*-cresol novolac resin proved to reduce the melt viscosities significantly compared to the phenolic novolac resin (DEN 438). Resin mixtures of 60/40 w/w *o*-cresol novolac/ Epon 828 epoxy achieved viscosities less than 2 Pa s while the 65/35 w/w phenolic novolac/ Epon 828 epoxy composition required heating to 145 °C to achieve similar viscosities.

Iji et al.¹¹¹ investigated structure-property relationships of novolac-epoxy networks by tailoring their crosslink densities using multifunctional epoxy resins and novolac derivatives containing aromatic moieties. Flame retardance properties were determined by the limited oxygen index (LOI) method (UL94V), and cone calorimetry measurements employing a heat flux of 50 kW/m². The series of epoxy and novolac derivatives studied is shown in **Figure 2.11**. The trends observed by Iji et al. were supported in studies reported by Lin-Gibson et al.

¹¹⁰ Lin-Gibson, S.; Baranauskas, V.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 7389-7398.

¹¹¹ Iji, M.; Kiuchi, Y. *Polym. Adv. Technol.* **2001**, *12*, 393-406.

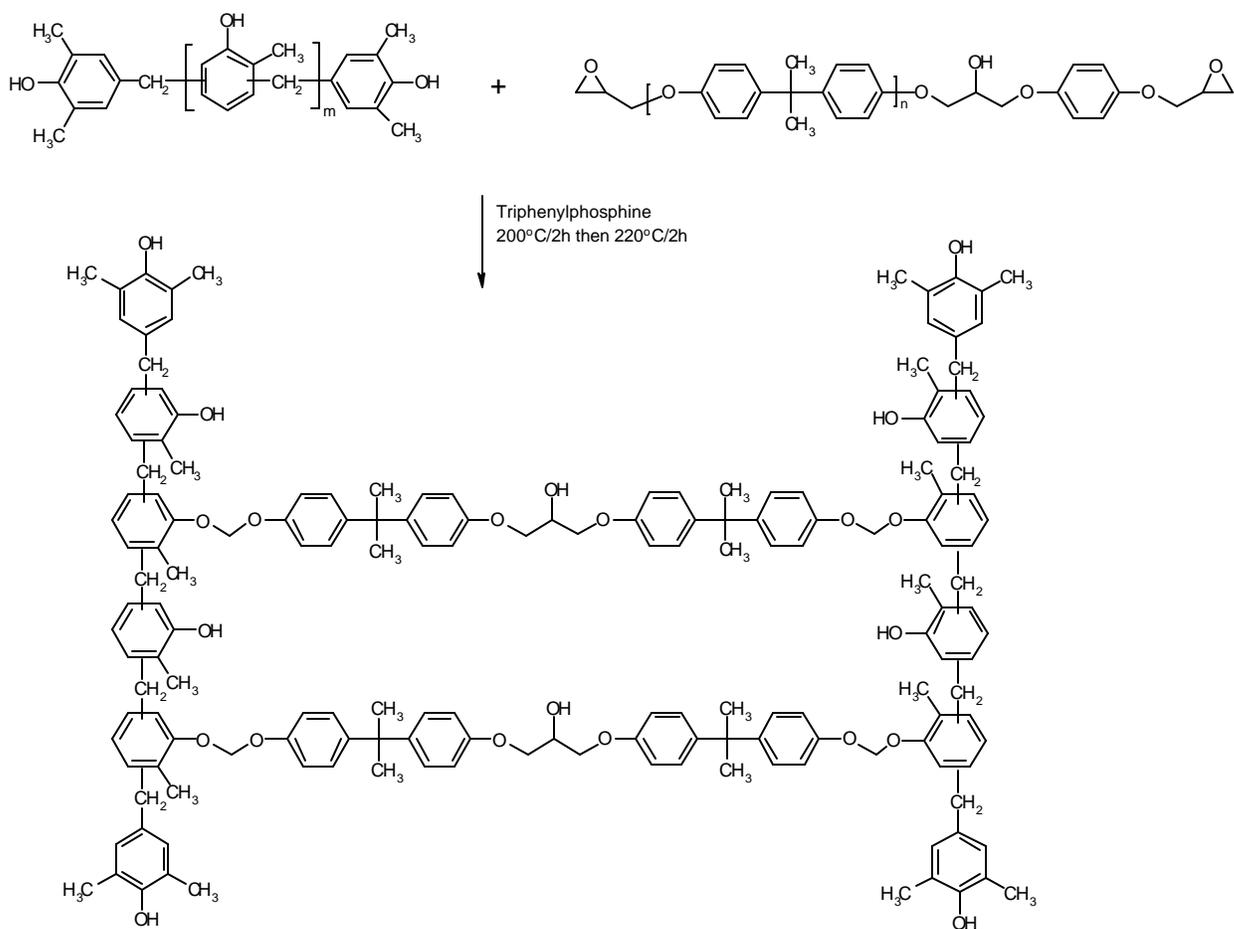


Figure 2.10: Cresol novolac –epoxy network formation.¹¹²

In general, Iji et al. demonstrated that novolac derivatives with increased aromatic character displayed higher flame retardancy than those with non-aromatic groups, with the biphenylene moiety proving the most effective. The limited oxygen index (LOI) method reports the amount of oxygen, in an oxygen/nitrogen mixture, needed to support combustion. Phenol biphenylene-type epoxy/phenol biphenylene novolac compositions exhibited the highest LOI, 73.0%. The investigation of a stoichiometric offset (excess of phenols) for each composition revealed that as

¹¹² Lin-Gibson, S.; Baranauskas, V.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 7389-7398.

the hydroxy/epoxy (H/E) ratio increased the LOI, and thus the flame resistance of the networks increased. Cone calorimetry measurements of phenol biphenylene-epoxy cured with a phenol-biphenylene novolac resin demonstrated low a PHRR (140 kW m^{-2}) and time to ignition values of ~85 sec, which are comparable to poly(dimethylsiloxane-b-etherimide) (97 sec), a high performance poly(arylene ether).^{113,114} Iji also utilized flexural strength studies at room temperature and 240 °C to analyze the toughness of the networks. Characterization data for biphenylene-type epoxy/phenol biphenylene and biphenyl-type epoxy/phenol biphenylene resins is presented in **Table 2.3**. At room temperature, the flexural strength increased with H/E ratio, and then decreased. At elevated temperatures, a maximum flexural strength of was achieved for each resin at H/E = 1, however, further increases in the H/E ratio resulted in decreased flexural strength. Furthermore, a maximum glass transition temperature was observed at H/E = 1, after which the T_g decreased. The observed trends were attributed to the incorporation of aromatic groups into the networks. The aromatic groups acted as spacers along the main chain, thereby limiting the crosslink density of the network. These materials had low elasticities at high temperatures, and low elastic moduli.¹¹⁵ An intumescent phenomena, wherein after ignition, stable foam layers are formed at the surface, was observed for these materials. In standard UL94V studies, the networks were exposed to a flame for 60 seconds, and then analyzed under a microscope. The formation of foam layers on the surface effectively retarded the heat transfer from the surface to the inside of the network. This phenomenon was attributed to low crosslink densities and low elastic moduli. Low elasticity allows the volatiles generated early on by thermal degradation from within the compound to evolve to the surface to form protective foam

¹¹³ Koo, J.; Venumbaka, S.; Cassidy, P.; Fitch, J.; Grand, A. *J Fire and Materials* **2000**, *24*, 209-218.

layers. Conversely, rigid network structures are unable to produce foam layers due to their high crosslink density. Iji et al. showed that an excess of the phenol derivatized curing agent decreases the crosslink density and reduces the amount of flammable substances generated from the epoxy resins during combustion, by facilitating the formation of foam layers and increasing pyrolysis resistance.

Great strides have been made in the study of novolac-epoxy networks. Networks may be tailored to meet specific requirements of mechanical strength and flame properties. In an effort to better understand and further improve the flame properties of phenolic networks, it is necessary to understand the phenolic degradation mechanisms and how the two relate.

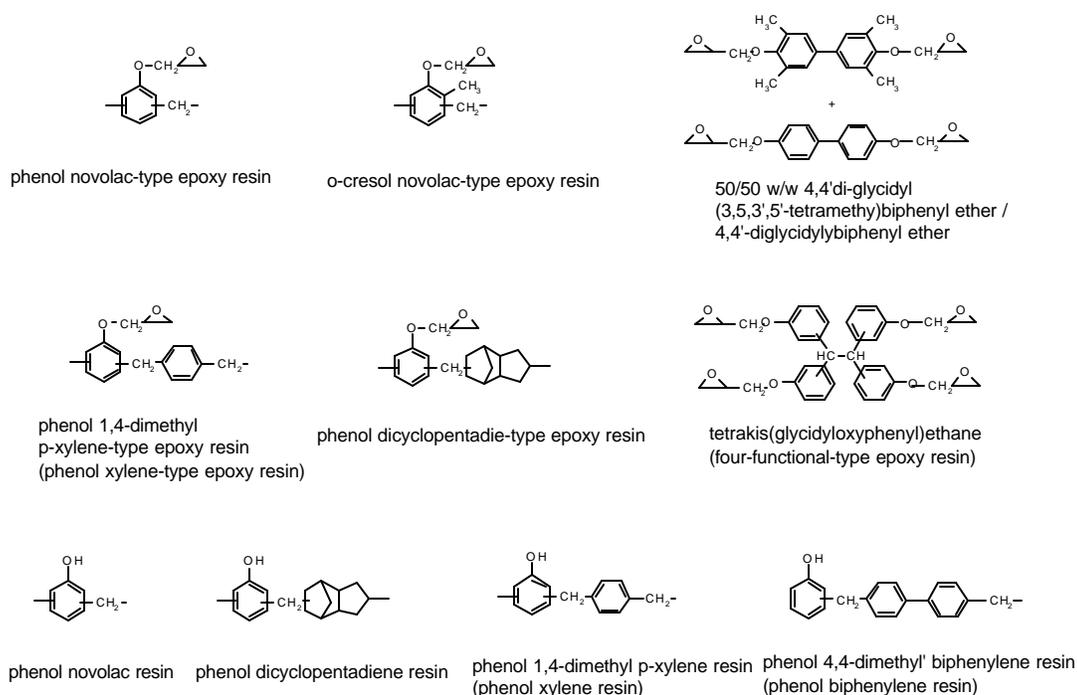


Figure 2.11: Epoxy and Novolac structures.

¹¹⁴ Riley, D.; Gungor, A.; Srinivasan, S.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M.; Ward, T.; McGrath, J. *Polymer Engineering and Science* **1997**, *37*, 1501-1511.

¹¹⁵ Iji, M.; Kiuchi, Y. *Polym. Adv. Technol.* **2001**, *12*, 393-406.

Table 2.3: Characterization Epoxy/Novolac resins of various structures and hardener to epoxy ratios. ¹¹⁶

Epoxy resin/hardener	H/E	TMA			Water absorption ratio (wt%)	Flexural strength at room temp. (kgf/mm ²)	Flexural modulus at room temp. (kgf/mm ²)	Flexural strength at 240 °C (kgf/mm ²)	Flexural modulus at 240 °C (kgf/mm ²)	Volume resistance at 150 °C (W/cm)
		T _g (°)	a ₁ (x10 ⁶)	a ₂ (x10 ⁶)						
Phenol biphenylene-type/ phenol biphenylene resin	0.5	75	2.2	5.9	0.38	10.5	1410	0.21	5.0	-
	1.0	118	2.1	5.4	0.30	13.2	1300	0.68	28.2	4.6 x 10 ¹²
	1.5	105	2.0	5.5	0.34	13.2	1350	0.37	11.3	1.4 x 10 ¹²
	2.0	95	1.8	5.1	0.44	10.4	1390	0.19	3.7	-
Biphenyl-type/phenol	0.5	96	2.2	5.3	0.46	12.1	1370	0.64	12.4	-
Biphenylene resin	1.0	120	2.1	5.4	0.37	13.8	1240	1.09	33.5	2.0 x 10 ¹²
	1.5	101	1.8	4.5	0.49	10.0	1350	0.34	6.2	5.8 x 10 ¹¹

2.6 Phenolic Degradation and Flame Retardance

2.6.1 Introduction

Phenol-formaldehyde resins are known as highly temperature resistant polymeric materials that yield high amounts of char upon pyrolysis.¹¹⁷ In civil and aerospace applications, phenolic networks are of great interest because they are moderately flame resistant, exhibit low smoke generation, and possess self-ignition temperatures above 480 °C.¹¹⁸ Such properties make phenolic networks ideal for use in the interior of airplanes, such as the DC-10. Efforts to

¹¹⁶ Iji, M.; Kiuchi, Y. *Polym. Adv. Technol.* **2001**, *12*, 393-406.

¹¹⁷ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

¹¹⁸ Sunshine, N. Chapter 4: Flame retardancy of Phenolic Resins and Urea- and Melamine-Formaldehyde Resins. In *Flame retardancy of Phenolic materials*. Kuryla, W, Papa, J, Eds. Marcel Dekker, Inc.: New York, 1973. Vol. 2.

enhance the flame resistance of phenolic resins and networks has led to much research on the factors contributing to these properties, i.e. phenolic degradation mechanisms.

2.6.2 Phenolic Degradation Mechanisms

The thermal degradation of phenol-formaldehyde resins occurs in three temperature-dependent stages: a low temperature stage (< 200°), an intermediate temperature stage (200 – 600 °C), and a high temperature stage (> 600 °C).¹¹⁹ Progressive changes in the network structure, as revealed with IR spectroscopy, are characteristic of each of the three stages. Employing thermogravimetric analysis coupled with mass spectrometry (TGA-MS), Chang and Tackett¹²⁰ identified the pyrolysates observed over all three temperature-dependent stages in an inert atmosphere (**Table 2.4**).

Several investigations of phenolic resin degradation mechanisms in inert versus oxygen-rich atmospheres have been reported. In their study of the thermo-chemical degradation of phenol-formaldehyde resins, Conley et al.^{121,122} ascertain that thermo-oxidative processes take place regardless of whether the pyrolysis reaction occurs in an oxidative or inert atmosphere. Lochte et al. suggested that at elevated temperatures the resin itself could act as an oxygen source for the oxidative process.¹²³ Furthermore, the degradation process has been reported to depend on the stability and concentration of the dihydroxyphenylmethane units.^{124,125}

¹¹⁹ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

¹²⁰ Chang, C.; Tackett, J. *Thermochimica Acta* **1991**, *192*, 181.

¹²¹ Conley, R.; Bieron, J. *Journal of Applied Polymer Science* **1963**, *7*, 103-117.

¹²² Conley, R. *Thermal Stability of Polymers*. Marcel Dekker, Inc.: New York, 1970.

¹²³ Lochte, H.; Strauss, E.; Conley, R. *Journal of Applied Polymer Science* **1965**, *9*, 2799 - 2810.

¹²⁴ Kourtides, D.; Gilwee, W.; Parker, J. *Polym Engineering and Science* **1979**, *19*, 24.

¹²⁵ Kourtides, D.; Gilwee, W.; Parker, J. *Polymer Engineering and Science* **1979**, *19*, 226.

Table 2.4: Volatiles of phenolic resins pyrolyzed over three temperature dependent degradation stages.¹²⁶

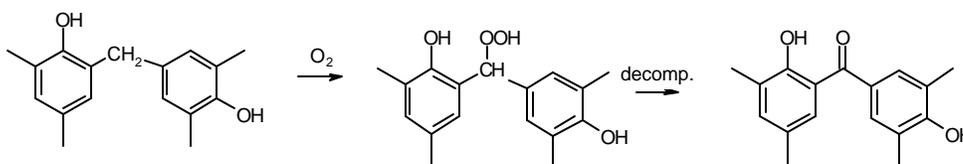
Peak Temperature (°C)	Gas	Estimated Weight Loss (%)
120	Water	.8
145	Phenol	.3
210	Water	4.4
	Phenol	1.8
	Methanol	1.2
	Carbon dioxide	.4
270	Ammonia	2.7
370	Unidentified	.3
420	Water	5.0
	Carbon dioxide	.7
580	Water	5.7
	Carbon dioxide	1.3
650	Methane	3.8
	Benzene	3.4
	Toluene	2.7
	Xylene	1.3
	Trimethylbenzene	.2
720	Phenol	4.1
	Cresol	2.6
	Dimethylphenol	1.1
	Trimethylphenol	.1
	Carbon Monoxide	6.1

At temperatures below 200 °C, phenolic networks are relatively stable in inert atmospheres. However, small amounts, 1-2 weight %, of gaseous products are liberated in some cases. This weight loss has been attributed to the evolution of gaseous components entrapped during curing reactions. These components include water, formaldehyde and phenol. More significant network changes have been observed at low temperatures in oxygen-rich atmospheres. Conley et al. studied the degradation behavior of phenolic resins in oxygen, nitrogen and in vacuo at low (100 – 200 °C) temperatures.

¹²⁶ Chang, C.; Tackett, J. *Thermochimica Acta* **1991**, *192*, 181.

In IR studies, no spectral changes were observed for phenolic resins pyrolyzed at 200 °C for 50 hours in nitrogen or in vacuo, suggesting that degradation did not occur. However, in oxygen-rich atmospheres oxygenated products were observed, and the initial degradation stage was dependent on the presence of oxygen. The spectra of pyrolyzed resol and novolac samples were similar, and therefore, it was hypothesized that similar degradation mechanisms occurred under these conditions.¹²⁷ As a result of these studies, Conley et al. proposed a mechanism for the low temperature oxidative degradation of phenolic resins (**Figure 2.12**). Oxidative degradation was shown to be the predominant degradation pathway at temperatures below 200 °C.

Primary Oxidation



Secondary Oxidation

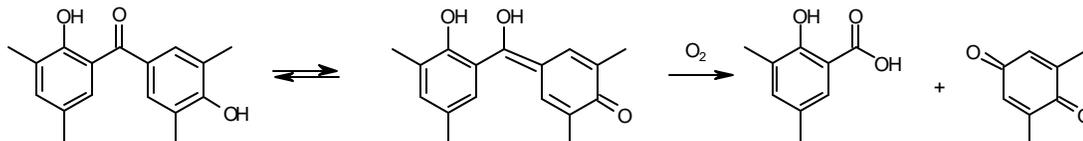


Figure 2.12: Low temperature oxidative degradation of phenolics.¹²⁸

In the second stage (200 - 600 °C), the most significant structural changes are observed in the networks. TGA studies revealed maximum weight losses in this temperature range. Gaseous components such as water, carbon dioxide, methane, phenols, cresols, and xylenols are also released during this stage. As higher molecular weight products volatilize, the density of the

¹²⁷ Conley, R.; Bieron, J. *Journal of Applied Polymer Science* **1963**, 7, 103-117.

phenolic resin/network decreases as the internal porosity increases. However, shrinkage was relatively low. In addition to oxidative degradation, thermal chain scission, including that of the bridging methylene and methylol groups between the phenol units, is characteristic in this temperature range. As a result, a high concentration of carbonyls and ketones was observed with IR spectroscopy. Jackson and Conley also investigated the oxidative degradation of phenolics at temperatures > 200 °C using infrared spectroscopy, vapor phase chromatography, thermogravimetric analysis, and X-ray analysis.¹²⁹ Water and paraformaldehyde were detected as the major volatile products. These volatiles were attributed to the loss of methylol groups through high-temperature post curing reactions or thermal scission at pyrolysis temperatures up to 400 °C (**Figure 2.13**).

Morterra and Low^{130,131} reported results in support of Jackson and Conley. From their studies, Jackson and Conley proposed three degradation routes to account for all of the products produced during high temperature oxidative degradation (**Figure 2.14**). The first route describes oxidative degradation in general and accounts for the production of carbon monoxide and carbon dioxide. The second route accounts for the formation of methane, phenol, cresol, and other methyl substituted species by radical bond rupture during thermal pyrolysis. The third route detailed the formation of benzene, toluene, benzaldehyde, and methane as a result of the loss of the hydroxyl from the phenolic species of the first two degradation routes. These mechanisms support oxidative degradation as the predominant mechanism for the degradation of phenolic resins.

¹²⁸ Conley, R.; Bieron, J. *Journal of Applied Polymer Science* **1963**, *7*, 103-117.

¹²⁹ Jackson, W.; Conley, R. *Journal of Applied Polymer Science* **1964**, *8*, 2163 - 2193.

¹³⁰ Morterra, C.; Low, M. *Carbon* **1985**, *23*, 525-530.

¹³¹ Morterra, C.; Low, M. *Langmuir* **1985**, *1*, 320-326.

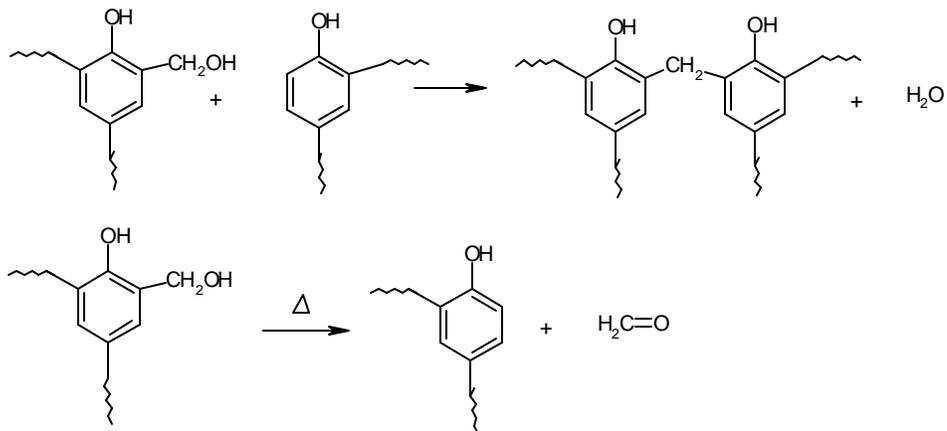


Figure 2.13: High temperature reactions that may result in loss of methylol groups.¹³²

At temperatures above 600 °C, carbon dioxide, methane, water, benzene, toluene, phenol, cresols, and xylenols are liberated. Other low volatility compounds including naphthalene, methylnaphthalenes, biphenyl, dibenzofuran, fluorine, phenanthrene, and anthracene were detected with pyrolysis gas chromatography and mass spectrometry. These volatiles may result from the condensation of hydroxyl groups of adjacent ortho-ortho linked phenolic rings.¹³³ As a result, the network structure collapsed to form low molecular weight aromatic compounds, which was evident from high shrinkage and carbonized char observed. Also, a decrease in permeability is observed due to increased density.

¹³² Jackson, W.; Conley, R. *Journal of Applied Polymer Science* **1964**, 8, 2163 - 2193.

¹³³ Hetper, J.; Sobera, M. *Journal of Chromatography A* **1999**, 833, 277-281.

Madorsky¹³⁵ studied resol networks pyrolyzed at elevated temperatures, 800 °C and 1200 °C. High concentrations of carbon monoxide and methane were detected in analyses of the volatiles released during pyrolysis. Analysis of the resulting char revealed high carbon content, 99.2%, and crosslinked phenolic fragments with an average of three to four benzene rings per chain. Taking these results into consideration, Madorsky proposed a mechanism for the degradation of resols at elevated temperatures. The mechanism involved breakdown of the benzene ring, which could lead to the formation of free radicals capable of stripping residual hydrogen and oxygen, which lead to the carbonized char.

Morterra and Low supported carbonization as the predominant mechanism above 500 °C due to the disappearance of all oxygenated products, observed in a stage two pyrolysis, by IR spectroscopy.¹³⁶ Jackson and Conley¹³⁷ also proposed degradation mechanisms to explain the formation of char using IR and GC (**Figure 2.15**). IR analyses revealed hydroxyl and carbonyl groups at 700 °C. In addition, char formation was discovered to proceed through quinone intermediates. In GC studies, carbon monoxide evolved simultaneously with the formation of graphite-like char at elevated temperatures. The production of structural char results in low flame spread rates, and thus good flame resistance.

Although some discrepancy regarding the mechanisms involved in phenolic degradation may exist, two aspects of the degradation process have been made apparent. It was consistent that the bridging methylene groups were the weakest units of phenolic networks and that thermal scission of these groups was a major contributor in the degradation process. In addition, the

¹³⁵ Madorsky, S. Thermal Degradation of Organic Polymers, Chapter XVI. In *Phenolic Resin*. Interscience Publishers: New York, 1964. 288-292.

¹³⁶ Morterra, C.; Low, M. *Carbon* **1985**, *23*, 525-530.

¹³⁷ Jackson, W.; Conley, R. *Journal of Applied Polymer Science* **1964**, *8*, 2163 - 2193.

formation of carbonized char resulted from the pyrolysis of phenolic networks at elevated temperatures, which function to decrease flame spread and promote thermo-oxidative stability.

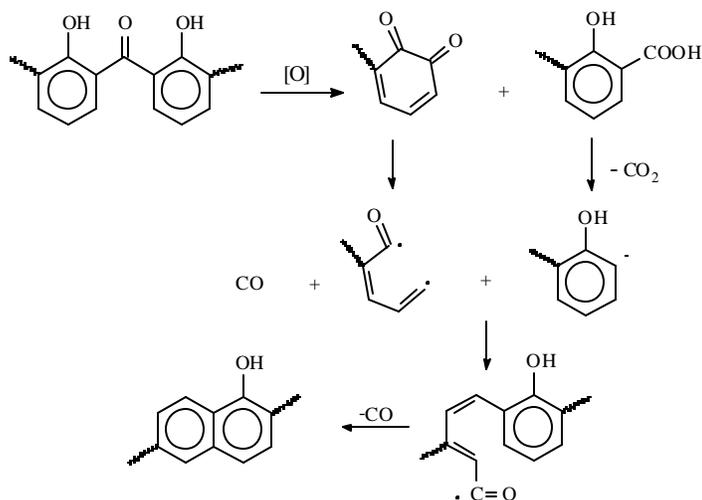


Figure 2.15: Mechanisms of char formation in phenolic resins.¹³⁸

2.6.3 Flame Retardance

The flame retardance of phenolics is directly related to their structure and degradation mechanisms. As outlined in the previous section, studies of phenolic degradation revealed that the methylene bridges and phenolic hydroxyl groups are highly susceptible under thermal and thermo-oxidative conditions. However, the production of carbonized char, formed in the degradation of phenolic resins, decrease the rate of flame spread.

¹³⁸ Sunshine, N. Chapter 4: Flame retardancy of Phenolic Resins and Urea- and Melamine-Formaldehyde Resins. In *Flame retardancy of Phenolic materials*. Kuryla, W, Papa, J, Eds. Marcel Dekker, Inc.: New York, 1973. Vol. 2.

The thermal resistance of phenolic resins can be improved by crosslinking phenols with heteroatoms or by chemically modifying the phenolic hydroxyl group to form a more stable functionality. In addition, self-extinguishing phenolic resins may be prepared by incorporating ~ 6 wt % elemental phosphorus or a combination of ~2 % nitrogen and 2 % phosphorous.¹³⁹ Addition of boron has also resulted in non-flammable phenolic compounds.¹⁴⁰

Overall, halogenation and crosslinking represent the two most commonly employed means of improving the flame resistance of phenolic networks. Although the incorporation of halogens in phenolic resin structures increases flame retardance of resols greatly and novolacs to a lesser extent, in many cases such modification results in an increase in toxic smoke emission.¹⁴¹

In 1974, van Krevelan reported a linear relationship between the char residue and the limiting oxygen index of polymers based on the **Equation 2.1**.¹⁴² van Krevelan later used this relationship to investigate correlations between the residues from pyrolysis and the composition of the polymer. van Krevelan studied the limiting oxygen indices (LOI) as a function of structure for aliphatic, substituted and unsubstituted aromatic compounds pyrolyzed at 850 °C. Experimental data suggested that during pyrolysis all the functional groups making up a polymer behave regularly, each contributing to the resulting residue in its own characteristic way.¹⁴³ Therefore, “the char-forming tendency of a polymer is an additive property which may be calculated from group contributions”.¹⁴⁴ In the van Krevelan study, the calculated char residues correlated quite well with experimental values, demonstrating a mean deviation of ±3.5% for the

¹³⁹ Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance*. Springer-Verlag Berlin Heidelberg, 1985.

¹⁴⁰ Hoechst. DE OS 24 36 358, 1974.

¹⁴¹ Sunshine, N. Chapter 4: Flame retardancy of Phenolic Resins and Urea- and Melamine-Formaldehyde Resins. In *Flame retardancy of Phenolic materials*. Kuryla, W, Papa, J, Eds. Marcel Dekker, Inc.: New York, 1973. Vol. 2.

¹⁴² van Krevelen, D. *Chimia* **1974**, *28*, 504.

¹⁴³ van Krevelen, D. *Polymer* **1975**, *16*, 615 - 620.

100 polymers investigated. This study proved important in unveiling the fact that by tailoring the structure of the phenolic network, highly flame resistant materials may be achieved through increased char formation.

$$OI \times 100 = 17.5 + 0.4CR$$

Equation 2.1: van Krevelen correlation between the oxygen index (OI) and the char residue (CR) at 850 °C polymers.¹⁴⁵

2.7 Phthalonitrile Monomers and Networks

2.7.1 Introduction

In an effort to identify matrix materials for advanced polymeric composites for use as structural components in aerospace and marine applications, high temperature polymers with high thermo-oxidative stability and good toughness have been heavily investigated. Generally, these properties are characteristic of polymers with high aromatic character or polymers with heterocyclic rings in their backbones. Such systems allow for good mechanical properties and thermo-oxidative stability simultaneously. In addition, the composites industry requires matrix materials that may be easily processed via commercial composite fabrication processes, i.e., pultrusion and resin transfer molding (RTM).

One approach to achieving high-temperature, tough, processable materials has been to end-cap traditional, high-performance thermoplastic polymers with functional groups that can be crosslinked at elevated temperatures to produce thermoset materials with high glass transition temperatures. Emphasis has been placed on materials that cure at elevated temperatures, which

¹⁴⁴ van Krevelen, D. *Polymer* **1975**, *16*, 615 - 620.

allots extended processing time windows between the processing and curing temperatures. Phenylethynyl groups have received much attention in this regard because they require high curing temperatures (> 350 °C) and produce networks of high thermal stability.^{146,147,148,149,150,151,152,153} However, the high cost associated with the starting materials and catalysts has limited the use of these resins. In other studies, maleimides, bismaleimides, nadimides and derivatives thereof have been employed in a similar fashion to obtain crosslinkable resins with improved heat and fire resistance.^{154,155,156,157,158,159,160,161} Although each of these methods led to enhanced thermo-oxidative resistance and mechanical properties as intended, long cure cycles and high curing temperatures coupled with brittleness has limited their use. Other approaches have included the use of acetylene functional polymers.^{162,163,164,165,166} Under moderate conditions, acetylene functional polymers can be polymerized to yield networks with high moisture and solvent resistance, as well as excellent thermo-oxidative stability.

¹⁴⁵ van Krevelen, D. *Polymer* **1975**, *16*, 615 - 620.

¹⁴⁶ Bryant, R.; Jensen, B.; Hergenrother, P. *Polymer Preprints* **1993**, *34*, 566.

¹⁴⁷ Connell, J.; Smith, J.; Hergenrother, P. *High Performance Polymers* **1997**, *9*, 250.

¹⁴⁸ Connell, J.; Smith, J.; Hergenrother, P. *High Performance Polymers* **1998**, *10*, 273.

¹⁴⁹ Hergenrother, P.; Connell, J.; Smith, J. *Polymer* **2000**, *41*, 5073.

¹⁵⁰ Ooi, I.; Hergenrother, P.; Harris, F. *Polymer* **2000**, *41*, 5095.

¹⁵¹ Mecham, S. Synthesis and Characterization of Phenylethynyl Terminated Poly(arylene ether sulfone)s as Thermosetting Structural Adhesives and Composite Matrices. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 1997.

¹⁵² Meyer, G.; Glass, T.; Grubbs, H.; McGrath, J. *Polymer Preprints* **1994**, *35*, 549.

¹⁵³ Holland, T.; Glass, T.; McGrath, J. *Polymer* **2000**, *41*, 4965.

¹⁵⁴ Mikroyannidis, J. *Journal of Macromolecular Science-Pure and Applied Chemistry* **1992**, *A29*, 127.

¹⁵⁵ Yuan, Q.; Huang, F.; Jiao, Y. *Journal of Applied Polymer Science* **1996**, *62*, 459.

¹⁵⁶ Stenzenberger, H. *British Polymer Journal* **1998**, *20*, 383.

¹⁵⁷ Moy, T.; Konas, M.; McGrath, J.; Fields, E. *J Polymer Science: Part A: Polymer Chemistry* **1994**, *32*, 2377.

¹⁵⁸ Maes, C.; Devaux, J.; Legras, R.; Parsons, I. *Journal of Polymer Science: Part A: Polymer Chemistry* **1995**, *33*.

¹⁵⁹ Lin, K.; Lin, J.; Cheng, C. *Polymer* **1996**, *37*, 4729.

¹⁶⁰ King, J.; Chaudhari, M.; Zahir, S. *SAMPE Symposium* **1984**, *29*, 394.

¹⁶¹ Chaudhari, M.; Galvin, T.; King, J. *SAMPE Journal* **1985**, *21*, 17.

¹⁶² Takekoshi, T.; Terry, J. *Polymer* **1994**, *35*, 4874.

¹⁶³ Sastri, S.; Armistead, J.; Keller, T. *Polymer* **1995**, *36*, 1449.

¹⁶⁴ Sundar, R. A. *Journal of polymer Science: Part C: Polymer Letters* **1997**, *35*, 2387-2394.

¹⁶⁵ Homrighausen, C. L.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **2002**, *40*, 1334-1341.

¹⁶⁶ Homrighausen, C. L.; Keller, T. *Polymer* **2002**, *43*, 2619-2623.

In structural applications of advanced polymer composites, a high demand still exists for a network material that cures below 250 °C to produce high T_g materials with good thermo-oxidative stability and toughness. Ideally this material could be fabricated using commercial compression molding processes.

Phthalonitrile-based polymers are a class of high temperature polymers with a wide range of potential applications including adhesives¹⁶⁷ and electrical conductors.^{168,169,170,171} In addition, bisphthalonitrile monomers have been established as candidates for matrix materials in advanced composites.¹⁷² This has been driven by the fact that, upon curing, the cyano groups of the phthalonitrile react to form triazine and other heterocyclic ring structures.^{173,174} The formation of heterocyclic crosslinked structures promotes high thermo-oxidative stability, as well as good mechanical properties.^{175,176,177}

2.7.2 Networks of Amine-cured Phthalonitrile Monomers

A variety of phthalonitrile monomers with aromatic ether,^{178,179,180,181,182} thioether,¹⁸³ imide,^{184,185} and sulfone¹⁸⁶ linkages between terminal phthalonitrile units have been

¹⁶⁷ Keller, T. *Polymer* **1993**, *34*, 952.

¹⁶⁸ Keller, T. *CHEMTECH* **1988**, *18*, 635.

¹⁶⁹ Keller, T. *Journal of polymer Science: Part C: Polymer Letters* **1986**, *24*, 211.

¹⁷⁰ Keller, T. *SAMPE Symposium* **1986**, *31*, 528.

¹⁷¹ Giuliani, J.; Keller, T. *Sensors Mater.* **1989**, *1*, 2247.

¹⁷² Keller, T.; Moonay, D. *SAMPE Symposium* **1989**, *34*, 941.

¹⁷³ Sastri, S.; Armistead, J.; Keller, T.; Sorathia, U. *SAMPE Symposium* **1997**, *42*, 1032.

¹⁷⁴ Keller, T. *Chemistry and Materials* **1994**, *6*, 302.

¹⁷⁵ Achar, B.; Fohlen, G.; Parker, J. *Journal of Polymer Science: Part A: Polymer Chemistry* **1986**, *24*, 1997.

¹⁷⁶ Keller, T.; Moonay, D. *SAMPE Symposium* **1989**, *34*, 941.

¹⁷⁷ Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1988**, *26*, 3199.

¹⁷⁸ Keller, T. *CHEMTECH* **1988**, *18*, 635.

¹⁷⁹ Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1988**, *26*, 3199.

¹⁸⁰ Keller, T. *Journal of polymer Science: Part C: Polymer Letters* **1986**, *24*, 211.

¹⁸¹ Keller, T. *Polymer Communications* **1987**, *28*, 337.

¹⁸² Keller, T. *Chemistry and Materials* **1994**, *6*, 302.

¹⁸³ Keller, T.; Gratz, R. *Polymer Communications* **1987**, *28*, 334.

¹⁸⁴ Keller, T. *Polymer Communications* **1991**, *32*, 1993.

synthesized.¹⁸⁷ Using 1-3 weight % of curing agents, phthalonitrile monomers may be polymerized into high temperature networks.

Sastri and Keller¹⁸⁸ studied the curing behavior and properties of phthalonitrile monomers derived from 4,4'-bis(3,4-dicyanophenoxy)biphenyl, 2,2'-bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane and 2,2-bis[4-(3,4-dicyanophenoxy)phenyl]propane cured with 1,3-bis(3-aminophenoxy)benzene (m-APB) (**Figure 2.16**). The phthalonitrile monomers were polymerized in a two-step procedure, in which an amorphous B-stage prepolymer resin with a T_g between 75 and 90 °C was prepared. Further heating of the B-stage prepolymer at elevated temperatures (250-325 °C) produced an infusible, insoluble thermoset. DSC revealed exotherms, attributed to the onset of curing, at 250-252 °C for the BPh and 6FPh monomers, however, the cure reaction of BAPh monomer required higher temperatures, 270 °C. It was suggested that the 6FPh monomer was more susceptible to nucleophilic attack by the diamine, due to the electron-withdrawing -C(CF₃)₂ linkage.

Rheometric studies were conducted in an effort to predict processability of the resin mixtures. Changes in viscosity during the cure reaction were noted. The results revealed that the rate of change in viscosity was dependent upon the concentration of the curing agent. In addition, the viscosity studies supported the reaction kinetics revealed in DSC analysis. The viscosity of the BAPh monomer increased more slowly relative to the BPh and 6FPh monomers. The rate of increase in viscosity mirrors the cure kinetics for the series. The 6FPh monomer has

¹⁸⁵ Keller, T. *Polymer* **1993**, *34*, 952.

¹⁸⁶ Keller, T.; Price, T. *Polymer Communications* **1984**, *25*, 42.

¹⁸⁷ Keller, T. *Chemistry and Materials* **1994**, *6*, 302.

¹⁸⁸ Sastri, S.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1999**, *37*, 2105.

an electron-withdrawing $-C(CF_3)_2$ linking group, which increases its susceptibility to nucleophilic attack and it reacts more rapidly than the BAPh with a electron-donating $-C(CH_2)_2$

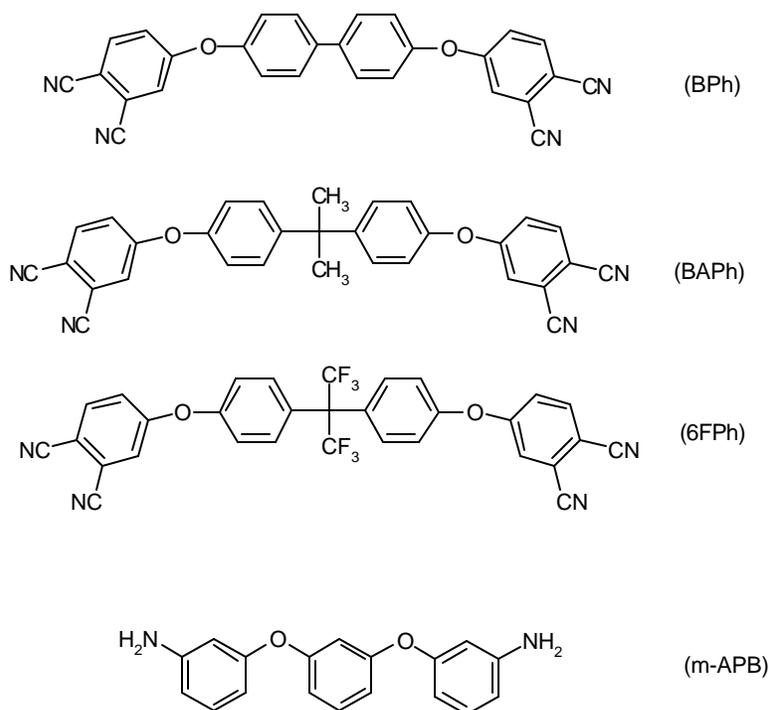


Figure 2.16: Structures of the phthalonitrile monomers and curing agent.¹⁸⁹

linking group. A small degree of progress in the curing reaction leads to significant increases in viscosity. All three monomers exhibited low viscosity, 150 cps, at 260 °C stable over an hour. The isothermal rheology studies suggested that these resins possess a processing window of approximately one hour. DMA analysis was employed to measure the glass transition temperatures of the BPh networks post-cured at three temperatures, 325, 350 and 375 °C. The material post cured at 325 °C exhibited a T_g around 230 °C, which increased to 360 °C for the 350 °C post-cured material, and no distinct T_g was observed for materials post-cured at 375 °C.

TGA studies in an inert atmosphere showed that all three networks were stable up to 450 °C, with 50-60% char remaining at 1000 °C. Flame properties including char yield at 650 °C, peak heat release rates (50 kW/m² heat flux), and total heat release at 900 °C were investigated using microscale calorimetric measurements. The BPh monomer demonstrated the highest char yield (87%), peak heat release rate (PHHR) (29.7 J g⁻¹ K⁻¹) and total heat release (4.8 KJ g⁻¹). The 6FPh resin had the lowest PHHR (7.2 J g⁻¹ K⁻¹) and total heat release (1.5 KJ g⁻¹) values.

Additionally, peak strength values obtained from the flexural strength measurements of the 6FPh, BPh, and BAPh networks cured for 8h at 325 °C were 94, 84, and 130 MPa, respectively. A slight decrease was observed in the flexural strength of networks cured for 16 h at 350 °C and 16 h at 375 °C. This decrease was attributed to increased brittleness within the networks.

Phthalonitrile resins and networks are reasonably tough materials with exceptional thermo-oxidative stability. However, extensive curing times and temperatures are necessary to achieve these properties. Furthermore, the processability of these resins is limited as the crystallinity of the phthalonitrile monomers increases. Research efforts are needed to improve the processability of phthalonitrile resins, as well as to significantly decrease the temperature and time necessary to achieve networks with high properties.

2.7.3 Phthalonitrile-functional Polybenzoxazines

Phthalonitrile-functional polybenzoxazines have been reported with significantly lower phthalonitrile curing temperatures.¹⁹⁰ Benzoxazines are key intermediates in the HMTA-novolac

¹⁸⁹ Sastri, S.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1999**, *37*, 2105.

¹⁹⁰ Ning, X.; Ishida, H. *J Polym Sci. Chem Ed* **1994**, *32*, 1121.

cure reaction.^{191,192} Crosslinking benzoxazine monomers at elevated temperatures yields void-free networks with high T_g s, excellent heat resistance, good flame retardance, and low smoke generation. In a study¹⁹³ of the phthalonitrile-functional polybenzoxazines (**Figure 2.17**), maximum post-curing temperatures of 240- 250 °C were found to be sufficient for achieving networks with high glass transition temperatures, 275-300 °C. These T_g s are comparable to those of the phthalonitrile networks cured with diamines at much higher temperatures reported by Sastri and Keller.¹⁹⁴ In thermal analyses, Compound III exhibited a 5% weight loss temperature between 450 and 550 °C and 80% char at 800 °C. Similar results were revealed in thermo-oxidative analyses: a 5% weight loss was observed at 500°C and 70% char remained at 600 °C. TGA-FTIR studies suggested that the high char yield observed for this compound may be due to unreacted nitrile groups. Fifty percent of nitrile functional groups were consumed during the polymerization reaction, and the remainder was consumed during char formation at elevated temperatures. Laboratories of the Federal Aviation Administration (FAA) investigated the flame properties of neat resins employing micro-cone calorimetry. Polybenzoxazine **I** exhibited the lowest peak heat release rate and total heat release, with values of 100.9 W g⁻¹ and 4.97 KJ g⁻¹, respectively.

This research importantly demonstrated the use of reduced cure temperatures (250-252 °C) in the preparation networks from phthalonitrile resins with mechanical and flame properties comparable to resins cured at higher temperatures for extended periods.

¹⁹¹ Dargaville, T. R.; Guerzoni, F.; Looney, M. G.; Shipp, D.; Solomon, D. H.; Zhang, X. *J Polym Sci Pt A: Polym Chem* **1997**, *35*, 1399-1407.

¹⁹² Kopf, P.; Wagner, E. *J Polym Sci Chem Ed* **1973**, *11*, 939 - 960.

¹⁹³ Brunovska, Z.; Lyon, R.; Ishida, H. *Thermochimica Acta* **2000**, *357*, 195.

¹⁹⁴ Sastri, S.; Keller, T. *Journal of Polymer Science: Part A: Polymer Chemistry* **1999**, *37*, 2105.

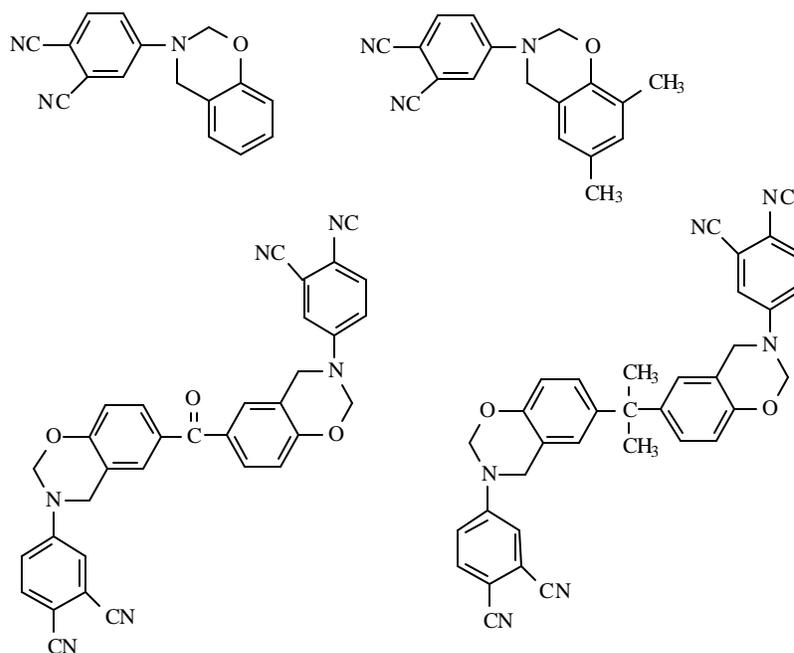


Figure 2.17: Phthalonitrile-functional benzoxazine monomers.¹⁹⁵

Brunovska and Ishida^{196,197} studied copolymers derived from phthalonitrile- and phenylnitrile- functional polybenzoxazines. Reportedly, the processability of polybenzoxazines was better than that of other phthalonitrile resins. In addition, ortho-phenylnitrile-functional polybenzoxazines had lower melt viscosities in comparison to standard polybenzoxazines. However, an investigation of the thermo-oxidative stability of phenylnitrile-functional polybenzoxazines revealed poor results. Brunovska and Ishida believed that preparing copolymers of phthalonitrile-functional polybenzoxazines and phenylnitrile-functional polybenzoxazines would allow them to exploit the attractive properties of each. Several

¹⁹⁵ Brunovska, Z.; Ishida, H. *Journal of Applied Polymer Science* **1999**, *73*, 2937-2949.

¹⁹⁶ Brunovska, Z.; Ishida, H. *Journal of Applied Polymer Science* **1999**, *73*, 2937-2949.

¹⁹⁷ Brunovska, Z.; Lyon, R.; Ishida, H. *Thermochimica Acta* **2000**, *357*, 195.

compositions were prepared by varying the weight fraction of each monomer. The monomers employed in this study are shown in **Figures 2.18** and **2.19**.

For the 30/70 w/w phthalonitrile-polybenzoxazine (**X**) /o-phenylnitrile polybenzoxazine (**I**) composition, DSC analysis revealed two exotherms, (250 and 315 °C) suggesting two reaction processes for this resin mixture. FT-IR studies at 240 and 300 °C were employed to identify structural changes during the curing reaction. These studies revealed that oxazine ring-opening polymerization occurred simultaneously with reaction of the phthalonitrile at 240-250 °C. The major difference in the spectra taken at 300 °C was the appearance of a carbonyl band at 1720 cm⁻¹, which was attributed to the degradation of the methylene groups in the Mannich Bridge, -CH₂-NR-CH₂-. This conclusion was also supported by the decrease in bands due to methylene groups at 2850-2900 cm⁻¹. Thermogravimetric analyses were performed in both inert and oxygen-rich atmospheres. In an inert atmosphere, the 30/70 w/w phthalonitrile-polybenzoxazine **VII** /o-phenylnitrile-polybenzoxazine **XI** copolymer exhibited the highest 5% weight loss temperature (490 °C) and highest char yield (80%) at 800 °C. Conversely, in air the 50/50 w/w phthalonitrile-polybenzoxazine **VIII** / phenylnitrile-polybenzoxazine **X** demonstrated the greatest performance, exhibiting a 5% weight loss temperature of 445 °C and 21% char at 700 °C. The o-phenylnitrile polybenzoxazine resin was believed to undergo “a special reaction providing a restricted Mannich bridge...during the polymerization of the resin” which led to improved thermo-oxidative stability.¹⁹⁸ In addition to predicting the thermal and oxidative stability of the copolymers, TGA analyses also revealed two broad maxima at 400 and 600 °C

¹⁹⁸ Brunovska, Z.; Ishida, H. *Journal of Applied Polymer Science* **1999**, *73*, 2937-2949.

suggesting two major decomposition processes. This correlated with DSC analyses in which two exotherms attributed to two different reactions were observed.

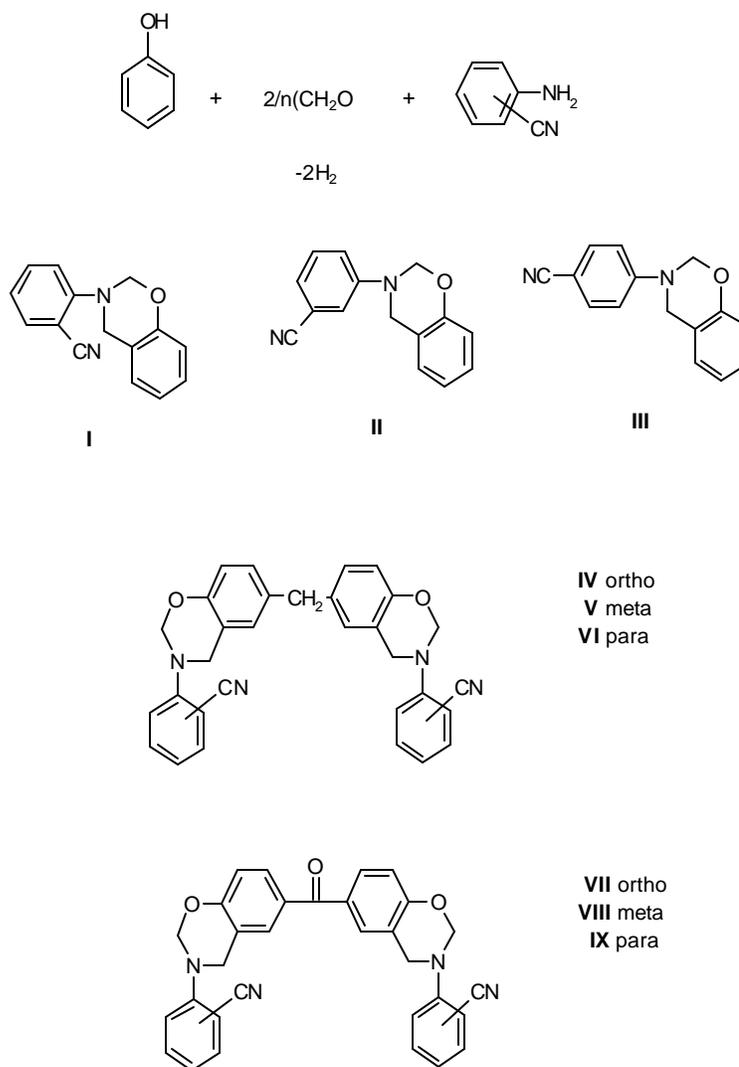


Figure 2.18: Synthesis of phenyl-nitrile polybenzoxazines I – IX.¹⁹⁹

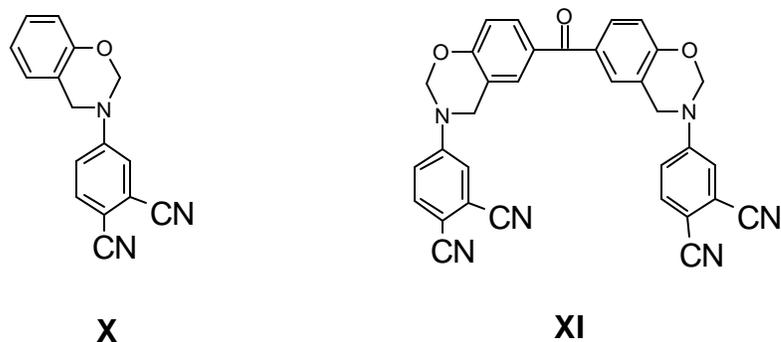


Figure 2.19: Phthalonitrile-functional polybenzoxazines X and XI.²⁰⁰

Neat phthalonitrile-polybenzoxazine resins have relatively high glass transition temperatures, 160 °C, and higher melt viscosities than benzoxazines with nitrile functionality. At room temperature, phenylnitrile monofunctional benzoxazines are very viscous, 6×10^5 Pa s, however, heating to ~80 °C significantly decreases their viscosity (~1 Pa s). Therefore, it was believed that the phenylnitrile component of the copolymer would reduce the melt viscosity of the phthalonitrile-polybenzoxazine resin. Indeed, this hypothesis was true, as was observed with the 30/70 w/w phthalonitrile-polybenzoxazine **X** / o-phenylnitrile-polybenzoxazine **I**, which exhibited a melt viscosity of 0.9 Pa s at 120 °C.

2.7.4 Networks of Novolacs cured with Phthalonitrile Monomers

Further progress was made in reducing the time and temperature required to cure phthalonitrile resins with the use of novolac oligomers.²⁰¹ Void-free, tough networks with

¹⁹⁹ Brunovska, Z.; Ishida, H. *Journal of Applied Polymer Science* **1999**, *73*, 2937-2949.

²⁰⁰ Brunovska, Z.; Ishida, H. *Journal of Applied Polymer Science* **1999**, *73*, 2937-2949.

²⁰¹ Sumner, M.; Sankarapandian, M.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 5069-5076.

excellent flame properties were synthesized from biphenoxyphthalonitrile resins (BPh) and a 700 g mol⁻¹ novolac oligomer. The cure reaction was monitored by FT-IR as a function of the decrease of the nitrile band at 2230 cm⁻¹. After curing for 1 hour at 200 °C and 20 minutes at 220 °C, 90% conversion was observed. Fracture toughness was measured to understand the toughness of the networks. Networks with 15, 20, and 25 wt % BPh exhibited K_{Ic} values ranging from 0.8 to >1MPa m^{1/2}. These networks had gel fractions of 0.9, suggestive of highly crosslinked networks, which were consistent with the high toughness demonstrated in K_{Ic} measurements. The network properties depended on the concentration of BPh. Networks with lower concentrations of BPh had lower crosslink densities, as indicated by high M_c values, and therefore diminished network properties. Thermo-oxidative stability and flame properties were studied using TGA and cone calorimetry. Significant differences between TGA degradation profiles in nitrogen versus air were not observed, suggesting that oxygen did not play a significant role the thermal degradation of these networks. All compositions exhibited 5% weight loss temperatures above 500 °C, and slow network degradation to 60-80% char at 800 °C. Cone calorimetry results were comparable to those of phenolic resole and polyetherimide networks. Reportedly,²⁰² polyetherimide exhibited a time to ignition of 70 seconds, total heat release of 128 MJ m⁻², PHHR of 128J g⁻¹ K⁻¹, 79% char, and CO/CO₂ ratio of 0.08 in cone calorimetry studies. The 80/20 w/w novolac/BPh composition exhibited the greatest flame properties with time to ignition of 102 seconds, total heat release of 49 MJ m⁻², PHHR of 137 J g⁻¹ K⁻¹, 54% char, and CO/CO₂ ratio of 0.019. This network out performed the commercial polyetherimide in nearly every category.

²⁰² Koo, J.; Venumbaka, S.; Cassidy, P.; Fitch, J.; Grand, A. *J Fire and Materials* **2000**, *24*, 209-218.

The novolac/BPh materials were advantageous in many regards. Void-free, tough networks were achieved with maximum post-curing temperatures of 220 °C within 3 hours, which was a significant improvement compared to amine cured systems, detailed earlier. However, the novolac/BPh resin mixtures were difficult to process into composites from the melt. A processing temperature of 140 °C was required to achieve sufficiently low melt viscosity to obtain good fiber wetting.²⁰³ The high melt viscosity was attributed to both the high melting point of the biphenoxyphthalonitrile resin (234 °C) and the glass transition temperature of the novolac oligomer, 95 °C.

In summary, phenol-formaldehyde based networks have proved effective in providing great mechanical strength and thermo-oxidative stability for advanced polymeric composites. With a heightened understanding of phenolic degradation mechanisms, flame properties have been significantly improved. Many approaches have been taken to further enhance the properties of phenolic networks including halogenation and the crosslinking of functionalized high-temperature polymers. One of the most effective approaches involves the use of phthalonitrile functional polymers. Phthalonitrile functional polymers may be polymerized into highly crosslinked networks possessing heterocyclic ring structures. As a result, high thermal and oxidative stability are characteristic of these materials. Research has shown that highly crosslinked networks are obtainable from phthalonitrile resins at moderate cure temperatures within rapid cure cycles. These networks are a great improvement compared to structural epoxy-based systems and even compared to polyetherimide networks. However, processability remains an issue due to the high melt viscosity of the resin mixtures. Composites are fabricated by

²⁰³ Sumner, M. High Performance Materials Containing Nitrile Groups. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2003.

conventional methods that require matrix materials with low melt viscosities. Phthalonitrile-polybenzoxazines/ortho-phenylnitrile-polybenzoxazine copolymers have offered some improvement in this regard.

CHAPTER 3: EXPERIMENTAL

3.1 Materials

In the synthesis 4-nitrophthalonitrile, the following reagents and solvents were used. Phthalimide (98%, FW 147.13, mp 232 °C) and thionyl chloride (99+%, FW 118.97, bp 79 °C, d 1.631), *N, N*-dimethylformamide (Biotech grade solvent, 99.9+%, FW 73.1, bp 153-155 °C, d 0.948) were purchased from Sigma Aldrich. Sulfuric acid (Reagent, ACS grade, FW 98.08 g/mol) and nitric acid (Reagent, ACS grade, FW 63.01g/mol) were purchased from VWR International. Ammonium hydroxide (33% ammonium solution, FW 35.03g mol⁻¹) was purchased from EM Science.

In the synthesis of novel phthalonitrile resins, the following materials were used. Dow Chemical generously supplied the DEN 431 and DEN 438 phenol-formaldehyde novolac resins. The number average molecular weight, M_n , and average functionality, f , was determined using ¹H NMR. For the DEN 431 precursor resin, $M_n \approx 348$ g mol⁻¹ and $f \approx 3.4$ were determined, while the DEN 438 resin had $M_n \approx 256$ g mol⁻¹ and $f \approx 2.54$. *N*-methyl-2-pyrrolidone (HPLC grade, FW 99.1, bp 202 °C) was purchased from Burdick and Jackson. Potassium Carbonate (FW 138.21 g mol⁻¹) was purchased from EM Science. Bis(4-hydroxyphenyl)methane, 2-allylphenol (98%, FW 134.18, bp 220 °C, d 1.028), 1,1,3,3,5,5-hexamethyltrisiloxane (95%, FW 208.48, bp 128 °C, d 0.834), 1,4-bis(dimethylsilyl)benzene (98%, FW 194.43), chloromethylphenylsilane (95%, FW 156.69, bp 113 °C, d 1.043), and chlorodiphenylsilane (95%, FW 218.76, bp 143 °C/10mm, d 1.118) were purchased from Aldrich. 1,1,3,3-tetramethyldisiloxane was obtained from Gelest, Inc. A platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4%

platinum concentration), which was used as a hydrosilation catalyst, was also purchased from Gelest, Inc.

Triphenylphosphine (99%, FW 262.29g mol⁻¹, mp 79-81° C, bp 377 °C) was purchased from Aldrich Chemical and employed as a catalyst for the novolac cure reactions.

All materials were characterized via ¹H NMR to confirm their chemical structure and purity. These materials were used as received with no further purification.

3.2 Synthesis and Sample Preparation

3.2.1 Synthesis of 4-nitrophthalonitrile

A three-step synthesis was developed in our laboratories for preparing 4-nitrophthalonitrile¹. In the first step, 4-nitrophthalimide was prepared by nitration of phthalimide. Nitric acid (15.1 mL, 0.272 mol) was slowly added to sulfuric acid (90.1 mL) (6:1 v/v) in a roundbottom flask cooled in an ice bath. The solution was stirred for approximately 20 minutes. Afterward, the ice bath was removed and the acidic solution was allowed to warm to room temperature. The phthalimide monomer was stirred into the acid solution and heated at 35°C until a clear, colorless, homogeneous solution was achieved. As the phthalimide monomer dissolved, the reaction solution became yellow. The reaction solution was stirred for 4 hours. A powdery white solid was precipitated from ice water (800 mL; 7:1 v/v), collected via vacuum filtration, and washed twice with 500 mL of deionized water. The precipitant was dried under ambient conditions for 12 hours. The reaction produced 7.8 g, a 60% yield. ¹H NMR in (CD₃)₂SO was used to confirm the chemical structure (ppm): 8.05 (m, 1H), 8.40 (d, 1H), 8.60 (dd, 1H), 11.80 (s, 1H).

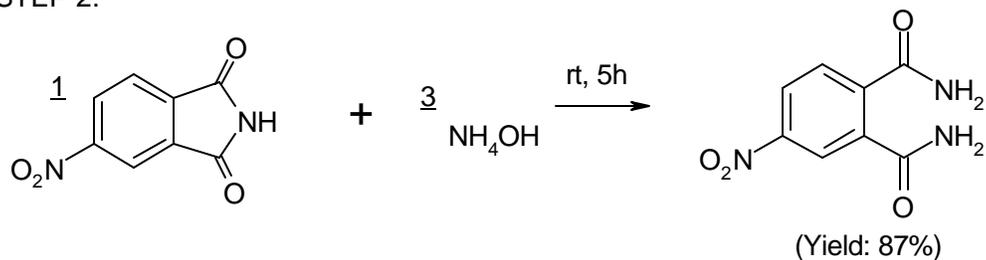
In a second step, the basic hydrolysis of 4-nitrophthalimide with ammonium hydroxide produced 4-nitrophthalamide. The 4-nitrophthalimide monomer (7.8 g, 0.0404 mol) was added to a two-neck roundbottom flask with ammonium hydroxide (25 mL). As ammonium hydroxide was added to the reaction flask, a yellow color change was observed. The resulting slurry was stirred at room temperature for approximately 5 hours. The slurry was vacuum filtered, and the filtrate was washed with cold deionized water and dried under ambient conditions. The reaction produced 7.4 g, an 87% yield. ^1H NMR in $(\text{CD}_3)_2\text{SO}$ revealed (ppm): 7.60 (s, 2H), 7.68 (dd, 1H), 7.98 (s, 1H), 8.04 (s, 1H), 8.26 (dd, 1H), 8.30 (dd, 1H).

The final step of the procedure involved the dehydration of the 4-nitrophthalamide with thionyl chloride, SOCl_2 , to produce 4-nitrophthalonitrile. In this reaction dry DMF (40 mL) was added to a two-neck roundbottom flask via a cannula, cooled in an ice bath and purged with nitrogen gas. Thionyl chloride (10.3 mL) was slowly syringed into the reaction flask and allowed to cool for approximately 20 minutes. The 4-nitrophthalamide monomer (7.4 g, 0.0352 mol) was added to the solution with stirring and was stirred at room temperature for 24 hours. The 4-nitrophthalonitrile monomer was precipitated from ice water (7:1 v/v) and collected via vacuum filtration. Drying was achieved under ambient conditions. 4-Nitrophthalonitrile was produced in an 85 % yield. ^1H NMR in $(\text{CD}_3)_2\text{SO}$ was used to confirm the chemical structure (ppm): 8.41 (dd, 1H), 8.67 (dd, 1H), 9.03 (dd, 1H). **Figure 3.1** illustrates the overall scheme for the synthesis of 4-nitrophthalonitrile.

STEP 1:



STEP 2:



Step 3:

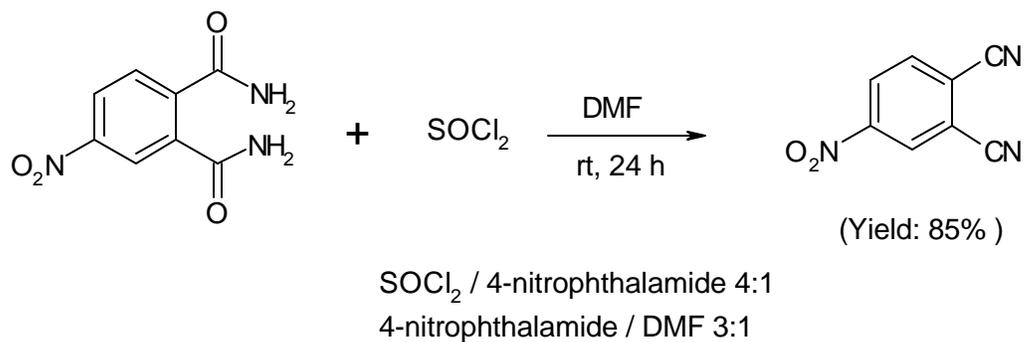
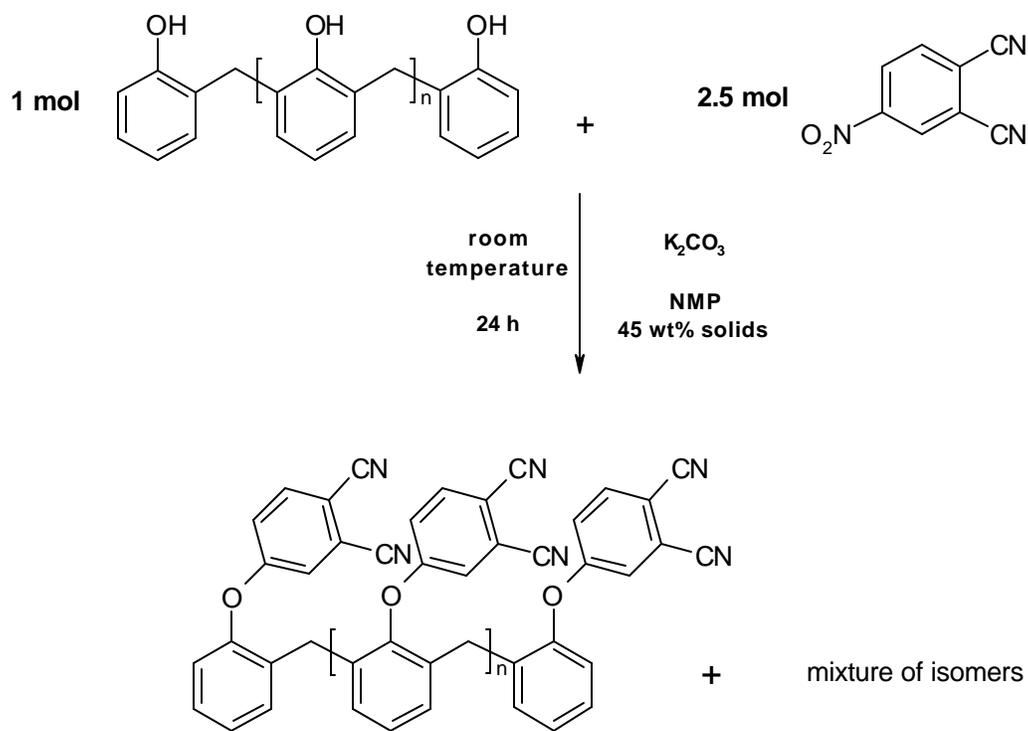


Figure 3.1: Three-step synthetic scheme for the preparation of 4-nitrophthalonitrile.

3.2.2 Novolac-Phthalonitrile Oligomers: Reaction of DEN 431 novolac resin with 4-nitrophthalonitrile (NOV-Ph)

Novel novolac-phthalonitrile oligomers were prepared from the reaction of phenolic novolac resins, Dow DEN 431 and DEN 438, and 4-nitrophthalonitrile. The synthetic scheme for this reaction is depicted in **Figure 3.2**. In a typical reaction using the DEN 431 precursor ($M_n = 256 \text{ g mol}^{-1}$ and $f = 2.54$), the novolac resin (0.984 g, 0.0038 mol) and the 4-nitrophthalonitrile monomer (1.702 g, 0.0098 mol) were weighed directly into a 100-mL roundbottom flask. *N*-methyl-2-pyrrolidone (NMP) was added to the reaction flask to achieve ~ 45 wt % solids. A slurry of potassium carbonate (1.720 g, 0.0124 mol), was employed to deprotonate the phenolic novolac resin, to produce a nucleophilic phenolate species. The reaction vessel was sealed and purged with nitrogen gas. Within 20 minutes, a color change from cloudy yellow to opaque amber/brown was observed. After 24 hours, the reaction solution was precipitated from a chilled (10-15 °C) dilute HCl aqueous solution rapidly stirring in a blender. Ten-milliliter aliquots were syringed into 1000 mL of the dilute HCl aqueous solution. The precipitant was agitated in the blender for ~10 min. A pale yellow powder was collected via vacuum filtration. The novolac-phthalonitrile oligomer (**260 NOV-Ph**) was dried under ambient conditions for 12 hours. The oligomer was then stirred in DI water to extract residual NMP, collected via vacuum filtration, and dried under vacuum. The novolac-phthalonitrile oligomer was produced in high yield, $\geq 85\%$, and the chemical structure was confirmed with ^1H NMR in $(\text{CD}_3)_2\text{SO}$ (ppm): 3.5-4.1 (m, 3.1H), 6.2-8.1 (m, 17.3H).



Molar ratio of K_2CO_3 to Novolac 3.2: 1

Figure 3.2: Synthesis of novel novolac-phthalonitrile oligomers.

3.2.3 Bis(3,4-dicyanophenoxyphenyl)methane Monomers: Reaction of Bis(4-hydroxyphenyl)methane and 4-nitrophthalonitrile (BisF-Ph)

Bis(4-hydroxyphenyl)methane was chemically modified to produce a novel phthalonitrile monomer, bis(3,4-dicyanophenoxyphenyl)methane (**BisF-Ph**), in a reaction similar to that employed in the synthesis of the novolac-phthalonitrile oligomers. In a typical reaction, bis(4-hydroxyphenyl)methane (1.02 g, 0.0051 mol) and 4-nitrophthalonitrile (1.858 g, 0.0108 mol) were weighed into a 100-mL roundbottom flask. NMP was added to the reaction flask to achieve ~45 wt % solids. A slurry of potassium carbonate (1.788 g, 0.0129 mol) was employed to deprotonate bis(4-hydroxyphenyl)methane to produce nucleophilic phenolate species. The reaction was stirred at room temperature for 24 hours under nitrogen. The resultant amber/brown solution was slowly poured into rapidly stirring DI water (1000 mL) to precipitate the monomer. The synthetic scheme is illustrated in **Figure 3.3**. The monomer was collected via vacuum filtration and recrystallized from methanol to remove residual starting materials and NMP. The purified bis(3,4-dicyanophenoxyphenyl)methane monomer was collected via vacuum filtration and dried under ambient conditions. The chemical structure of the resin was confirmed with ^1H NMR in $(\text{CD}_3)_2\text{SO}$ (ppm): 4.01 (s, 2H), 7.12 (d, 4H), 7.33-7.40 (2d, 6H), 7.75 (d, 2H), 8.05 (d, 2H).

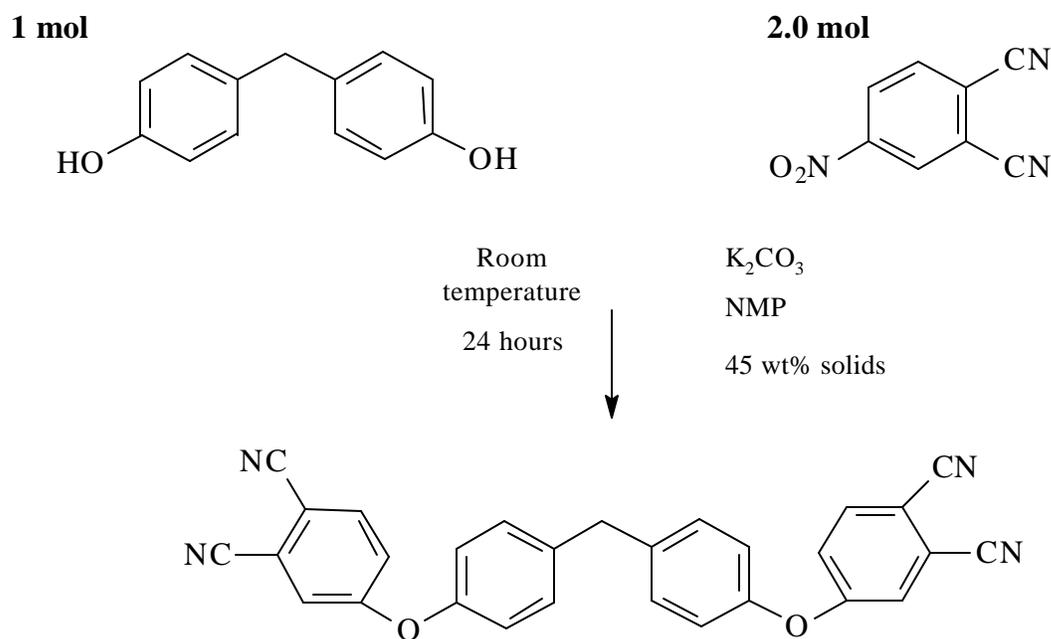


Figure 3.3: Synthesis of Bis(3,4-dicyanophenoxyphenyl)methane (BisF-Ph).

3.2.4 Syntheses of Novel Siloxane/Silane-Containing Phthalonitrile Monomers

Novel siloxane/silane containing phthalonitrile monomers were synthesized in a hydrosilation reaction of 2-allylphenoxyphthalonitrile with 1,1,3,3-tetramethyldisiloxane, 1,3-dimethyl-1,3-diphenyldisiloxane, 1,1,3,3-tetraphenyldisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, and 1,4-bis(dimethylsilyl)benzene. 1,1,3,3-Tetraphenyldisiloxane and 1,3-dimethyl-1,3-diphenyldisiloxane were prepared from hydrolysis reactions of chlorodiphenylsilane and chloromethylphenylsilane, respectively.

3.2.4.1 Synthesis of 2-(3,4-dicyanophenoxy)allylbenzene or (2-allylphenoxy-phthalonitrile)

The 2-(3,4-dicyanophenoxy)allylbenzene monomer was synthesized from 2-allylphenol and 4-nitrophthalonitrile. In a typical reaction, 2-allylphenol (11.5 g, 98%, 0.084 mol), potassium carbonate (K_2CO_3) (27.66 g, 0.200 mol), 4-nitrophthalonitrile (14.54 g, 0.084 mol), ~60 mL of NMP, and 4 mL of water were charged to a one-neck, 250-mL, roundbottom flask. The mixture was rapidly stirred for 24 h at ~25 °C. To precipitate the product, the reaction solution was slowly poured into water rapidly stirring in a blender at room temperature. The precipitation mixture was agitated for ~10 min in a blender and then 2-allylphenoxyphthalonitrile was collected and dried via vacuum filtration. To extract residual NMP, the 2-allylphenoxyphthalonitrile was stirred in water for 8-12 h. The 2-allylphenoxyphthalonitrile (20.15 g, 0.078 mol) was collected by vacuum filtration and dried under ambient conditions. The monomer was achieved in high yield, 92.3%. The chemical structure was confirmed using 1H NMR in $(CD_3)_2SO$ (ppm): 3.3 (d, 2H), 5.0 (dd, 2H), 5.8 (m, 1H), 7.0 (d, 1H), 7.2 (dd, 2H), 7.3 (m, 3H), 7.7 (d, 1H), 8.05 (d, 1H).

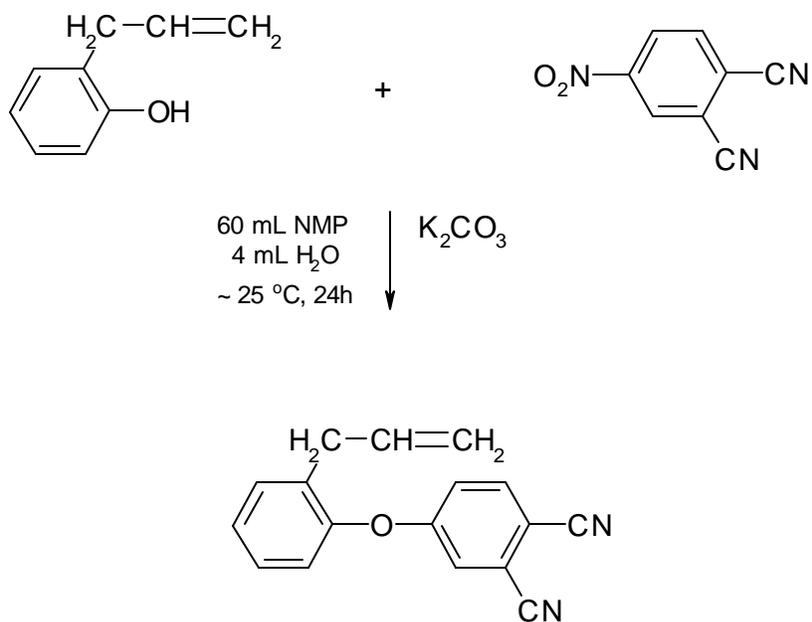


Figure 3.4: Synthesis of 2-(3,4-dicyanophenoxy)allylbenzene.

3.2.4.2 Synthesis of 1,3-di[2-(3,4-dicyanophenoxy)phenylpropyl]-1,1,3,3-tetramethyldisiloxane (TMDS-Ph)

A series of novel phthalonitrile monomers were prepared from hydrosilylation reactions of 2-(3,4-dicyanophenoxy)allylbenzene. In a typical reaction, 2-(3,4-dicyanophenoxy)allylbenzene (1.0 g, 0.0038 mol), 1,1,3,3-tetramethyldisiloxane (0.281 g, 0.0021 mol), and platinum-divinyltetramethyldisiloxane complex in xylene (2.1-2.4% platinum concentration) (0.0513 g, 0.08 wt % Pt) were charged to a 20-mL scintillation vial. The vial was capped and heated in an oil bath at 70 °C for 3 hours with continuous stirring. Initially, a slurry existed, however, as the reaction proceeded a homogeneous solution was achieved. After cooling to room temperature, a dark brown viscous material was obtained and analyzed by ¹H NMR (ppm): 0.0 (s, 12H), 0.5(t, 4H), 1.5 (m, 4H), 2.5 (t, 4H), 6.9 (d, 2H), 7.1-7.4 (m, 10H), 7.7 (d, 2H).

Several siloxane/silane-phthalonitrile monomers were prepared via analogous procedures. Using 1,1,3,3-tetraphenyldisiloxane, 1,3-di [2-(3,4-dicyanophenoxy)phenylpropyl]-1,1,3,3-tetraphenyldisiloxane was synthesized (**TPDS-Ph**). The structure was confirmed using ^1H NMR (ppm): 0.9 (t, 4H), 1.5 (m, 4H), 2.4 (t, 4H), 6.8-7.6 (m, 34H). Using 1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-di-[2-(3,4-dicyanophenoxy)phenylpropyl]-1,3-dimethyl-1,3-diphenyldisiloxane (**DDDS-Ph**) was prepared and the chemical structure was confirmed using ^1H NMR (ppm): 0.2 (s, 6H), 0.7 (t, 4H), 1.5 (m, 4H), 2.4 (t, 4H), 6.9-7.6 (m, 24H). Using 1,1,3,3,5,5-hexamethyltrisiloxane, 1,5-di{2-(3,4-dicyanophenoxy)phenylpropyl} -1,1,3,3,5,5-hexamethyltrisiloxane (**HMTS-Ph**) was prepared and the structure was confirmed using ^1H NMR (ppm): -0.05 (s, 6H), 0.0 (s, 12H), 0.5 (t, 4H), 1.55 (m, 4H), 2.5 (t, 4H), 6.95 (d, 2H), 7.2 (t, 4H), 7.3 (m, 6H), 7.7 (d, 2H). Using 1,4-bis(dimethylsilyl) benzene, 1,4-bis[2-(3,4-dicyanophenoxy)phenylpropyl-dimethylsilyl] benzene (**Silane-Ph**) was prepared and confirmed via ^1H NMR (ppm): 0.2 (s, 12H), 0.7 (t, 4H), 1.55 (m, 4H), 2.5 (t, 4H), 6.95 (d, 2H), 7.1(d, 2H), 7.2 (d, 2H), 7.3 (m, 6H), 7.4 (s, 4H), 7.7 (d, 2H).

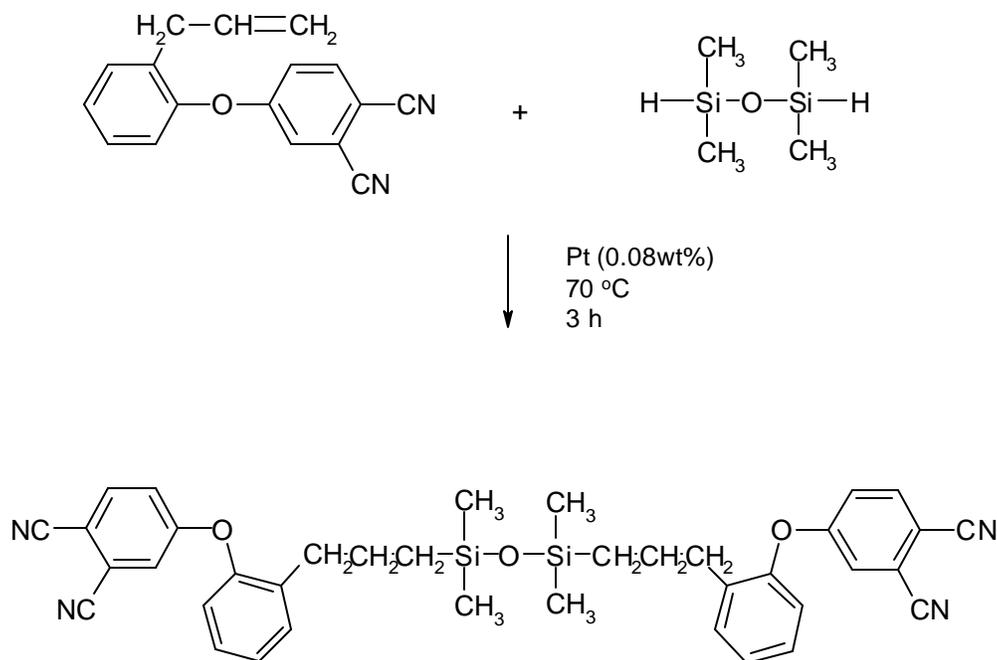


Figure 3.5: Hydrosilylation of 2-(3,4-dicyanophenoxy)allylbenzene with 1,1,3,3-tetramethyldisiloxane.

3.2.5 Resin Melt Mixing-Sample Preparation (FT-IR Model Curing Studies, Rheology Studies, DSC, TGA)

Model curing studies were performed to characterize the curing behavior of the phthalonitrile oligomers and monomers with various curing agents. A melt mixing procedure was employed to achieve homogeneous resin mixtures. The phthalonitrile monomer/oligomer was weighed into a 20-mL scintillation vial. By varying the weight of curing agent added, the resin mixture composition was varied. The viscosity of the resin mixture decreased with mild heating, and the samples were stirred to promote homogeneity. The duration of heating was limited to < 5 minutes to prevent premature curing. FT-IR model curing and rheology studies were conducted. For characterization via DSC and TGA, the resin mixtures were transferred to

aluminum weighing pans, quenched at room temperature and cured in a programmable temperature-controlled oven.

3.3 Measurements

3.3.1 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was conducted with a TA Instruments Model Q1000 to analyze the thermal transitions of the phthalonitrile derivatives and networks. The resin mixtures under investigation in the FT-IR model curing studies were ground into powder samples (3-8 mg). The samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. The midpoints of the specific heat increases in the transition region during the second heating scans were reported as the glass transition temperatures. For network analyses, the first heating scans were reported.

3.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (FT-IR) was utilized to confirm the structure of the monomers and polymers. Measurements were conducted on a Nicolet Impact 400 FTIR Spectrometer. Thin films cast from either chloroform or tetrahydrofuran were analyzed. In addition, model-curing studies were performed using FT-IR. Resin samples were prepared as described above. The disappearance of the peak at 2230 cm^{-1} , attributed to the nitrile functionality of the phthalonitrile monomer, was monitored as a function of time. After the spectra were normalized, the decreases in the nitrile peak heights were used to quantify the progress of the cure reactions. The progress was reported as the percent conversion of the nitrile

functional groups as a function of time. In the model curing studies, a ceramic heating cell and thermo-regulator were employed to control the reaction temperature.

3.3.3 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) was employed to qualitatively characterize the DEN precursor novolac resins. Samples (15-20 mg) were analyzed using three in-line 5 μ PL-gel MIXED-C columns and a Waters SEC 410 Refractive Index detector with an autosampler inline with a multi-angle laser light scattering (MALLS) with a Wyatt Technology MiniDAWN at 40 °C with a flow rate of 1.000 mL/min in tetrahydrofuran (ACS grade).

3.3.4 Nuclear Magnetic Resonance (NMR)

Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR) was employed to confirm the chemical composition of all solvents, monomers, oligomers and polymers utilized in this research. Samples were dissolved in the appropriate deuterated solvents, (CDCl_3 , DMSO-d_6 , $\text{CD}_6(\text{CO})$), at a typical concentration of 10% (0.1g/1 mL). The spectra were obtained using a Varian Unity Spectrometer operating at 400 MHz with a 29° pulse angle, acquisition time of 3.7s and a 1s relaxation delay. Quantitative ^{13}C NMR spectroscopy was employed to characterize the isomeric distribution of the DEN precursor resins. The analyses were performed from concentrated solutions of the resins in deuterated acetone. The spectra were obtained using a Varian Unity Spectrometer operating at 400 MHz with a 49.7° pulse angle, acquisition time of 1.2 s and a 1s relaxation delay.

3.3.5 Rheology Studies of Resin Mixtures: Time-Temperature-Viscosity Parameters

Rheology studies were conducted in an effort to predict the processability of the resin mixtures. Resin mixtures were prepared by the previously described melt mixing procedure. A TA Instruments AR1000 Rheometer, with a parallel plate-geometry and extended temperature module (ETM) were used in these studies. Steady state flow analysis, in which 25 mm aluminum plates and a 450 μm gap were used, was performed on < 0.5g resin samples treated with mild heat to promote efficient sample transfer. The percent torque required to rotate the spindle was measured and used to calculate shear stress, F' , according to **Equation 3.1**. Viscosity, reported in Pascal-seconds (Pa·s), was calculated from the ratio of shear stress, F' , to shear rate, S' , as is shown in **Equation 3.3**.

$$F\zeta = F_s M$$

F' = shear stress (Pa)

M = % torque

$$F_\sigma = 2 / \pi r^3$$

r = plate radius (cm)

Equation 3.1: Shear stress (Pa)

$$S\zeta = F_g \omega$$

S' = shear rate (s^{-1})

$$F_\gamma = r / d$$

d = gap distance between plates

ω = angular velocity of drive shaft (rad/sec)

$$\omega = (2\pi/60)N$$

N = spindle speed (RPM)

Equation 3.2: Shear rate (s^{-1})

$$h = F\dot{\gamma} / S\dot{t}$$

η = viscosity (Pa·s)

Equation 3.3: Viscosity (Pa·s)

The resin mixtures were subjected to temperature-scan and isothermal analyses. In the temperature-scan analysis, the sample viscosity was initially evaluated at temperatures between 50 and 70 °C. The temperature was increased incrementally, 3-10°, and multiple data points were recorded at shear rates between 4 and 10 s⁻¹. The temperature ramp analysis was pursued until the viscosity was sufficiently below 1000 mPa·s (1000 centipoises), and the temperature at which this was observed was regarded as the processing temperature. A plot of viscosity versus temperature was reported for the temperature scan analysis. The time-dependences of the resin viscosities were investigated isothermally at the processing temperature over an hour, at a set shear rate, 5.1 s⁻¹.

3.3.6 Thermogravimetric Analysis

The thermal and thermo-oxidative stability of the phenolic-novolac resins and phthalonitrile monomers and oligomers were analyzed by thermogravimetric analysis (TGA) utilizing a TA Instruments Model Q500. Networks were prepared from the resin mixtures investigated in the FT-IR model curing studies as described above. Cured networks were ground into powder samples. The powder samples were heated at 10°C/min from 25 to 800 °C in either nitrogen or air. The weight loss of the sample was measured as a function of temperature. The

temperature at which the sample exhibited a 5 % weight loss, $T_{5\%}$, and the weight % of the sample (char yield) remaining at 800 °C were reported.

3.3.7 X-ray Photoelectron Spectroscopy (XPS)

A Perkin-Elmer Model 5400 X-ray photoelectron spectrometer with a magnesium x-ray source was employed for the surface analysis of the phenolic networks pyrolyzed at 800 °C. Samples were loaded into a high vacuum chamber at approximately 1×10^{-7} torr. The samples were irradiated with x-rays and the photoelectrons ejected were captured with a hemispherical analyzer and amplified with a channel plate detector. Their energies were displayed on an Apollo DN3500 computer. The elemental composition of the first ~5 nanometers of the sample surface was determined by comparing the spectra obtained to that of standards.

CHAPTER 4: RESULTS / DISCUSSION

4.1 Characterization

4.1.1 4-Nitrophthalonitrile

The synthesis of 4-nitrophthalonitrile was achieved in good yield (85%) and confirmed with the use of ^1H NMR. Three chemically distinct protons were identified (9.03 ppm, 8.67 ppm, 8.41 ppm) and integration revealed a 1:1:1 ratio, as expected. The ^1H NMR spectrum did not reveal residual NMP, reaction solvent, or water.

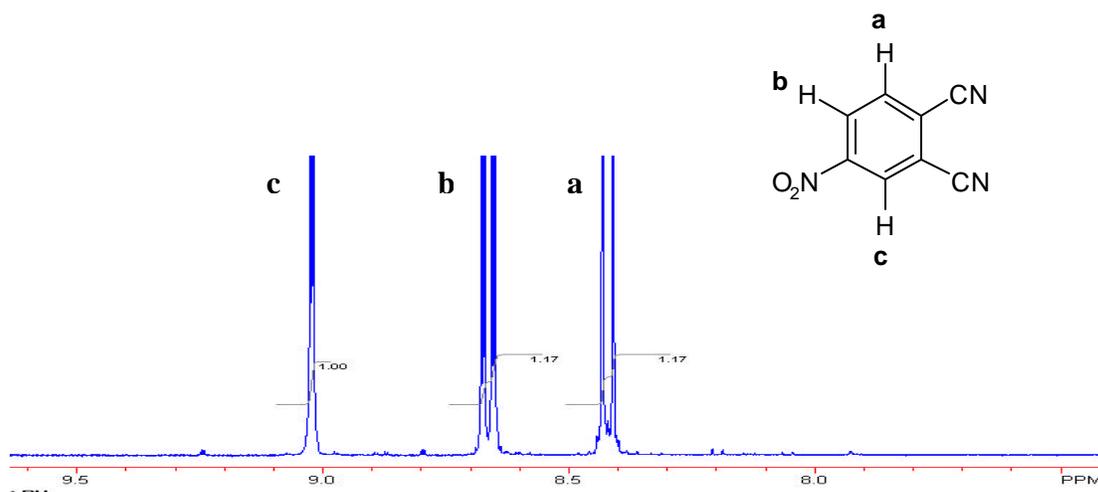


Figure 4.1: ^1H NMR of 4-nitrophthalonitrile monomer.

4.1.2 Phenol Formaldehyde Novolac Resins (DEN 431 and DEN 438 precursors)

Dow Chemical generously supplied the novolac resins employed in this research. The resins were characterized with ^1H NMR from which the number average molecular weight, M_n , and average phenol functionality, f , were determined for each. ^1H NMR analyses were performed in deuterated DMSO, $(\text{CD}_3)_2\text{SO}$. Using the ratio of the integration of aromatic

resonances to aliphatic resonances, M_n was calculated from the ^1H NMR spectra (**Figure 4.2**). The number average molecular weight of the DEN 431 and DEN 438 novolac resins was 348 g mol^{-1} with $f = 3.40$, and 256 g mol^{-1} with $f = 2.55$, respectively. Employed in a similar manner, ^1H NMR was also useful in characterizing the phthalonitrile derivatives of these resins.

It was anticipated that the DEN precursors, isomeric mixtures of low molecular weight novolac oligomers, would afford low melt viscosity resin mixtures. Low melt viscosity resins were targeted to produce network prepolymers with sufficiently low viscosity ($< 1000 \text{ mPa}\cdot\text{s}$) to be employed in composite fabrication processes such as vacuum assisted resin transfer molding (VARTM). It was also important that these materials contribute mechanical strength to the resulting thermoset matrix material. The isomeric distribution of the resins was investigated quantitatively with ^{13}C NMR spectroscopy.

The NMR absorption pattern of methylene carbons in the resin is most sensitive to positional isomerism.²⁰⁴ The ^{13}C NMR chemical shifts of numerous bis(hydroxyphenyl)methane and bis(hydroxybenzyl)phenol isomers have been reported.^{205,206,207} From the ^{13}C NMR spectra of the DEN 431 precursor, the resin was determined to consist of 94.9% ortho-ortho (29.2 – 30.4 ppm), 3.6% ortho-para (35.3 - 35.5 ppm), and 1.5% para-para (40.6 – 40.8 ppm) methylene linkages (**Figure 4.3**). Although these results revealed a high ortho-structured novolac, the resonances attributed to ortho-ortho methylene linkages represent ten chemically distinct carbons and, therefore, ten different methylene bridges. The higher molecular weight novolac DEN 438 precursor was also determined to be an isomeric mixture with high ortho-ortho composition:

²⁰⁴ Bogan, L. J.; Graziano, K. *Proc SPIE-Internat Soc Opt Engng* **1990**, 1262, 180.

²⁰⁵ Sojka, S. A.; Wolfe, R. A.; Dietz, E. J.; Daniels, B. *Macromolecules* **1979**, 12, 767.

²⁰⁶ Dradi, E.; Casiraghi, G.; Satori, G.; Casanti, G. *Macromolecules* **1978**, 11, 1295.

²⁰⁷ Sojka, S. A.; Wolfe, R. A.; Guenther, G. D. *Macromolecules* **1981**, 14, 1539-1543.

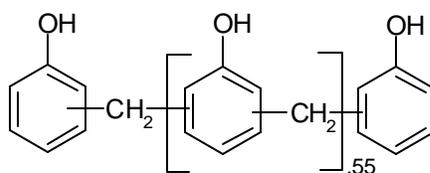
93.1% ortho-ortho, 4.7% ortho-para, and 2.2% para-para methylene linkages. ¹³C NMR supports an isomeric composition for the DEN precursor novolac resins.

As molecular weight increases, intra-molecular hydrogen bonding increases within novolac resins, and this phenomenon results in complex GPC elution behavior.²⁰⁸ Therefore, gel permeation chromatography in THF (**Figures 4.4 and 4.5**) only served as a qualitative characterization tool in the investigation of the oligomeric composition. The presence of dimer, trimer, and higher oligomeric species was evident in the multiple peaks seen in the chromatogram. Species with greater hydrodynamic volumes have shorter retention times and elude earlier. The chromatograms revealed that the smaller species, dimers and trimers, make up the majority of the resin composition. The use of ¹³C NMR and GPC analyses substantiated claims that the DEN precursors were low molecular weight isomeric mixtures.

The thermal properties of the novolac resins were investigated to predict their contribution to the mechanical strength of the network. Using DSC, it was determined that these materials possessed low glass transition temperatures, 8 and 32 °C for the DEN 431 and DEN 438 precursors, respectively. These low molecular weight novolac oligomers had significantly lower T_g s compared to the 740 g mol⁻¹ novolac resin ($T_g = 95$ °C) used in the study of novolac/biphenoxyphthalonitrile resins.²⁰⁹ The DEN novolac materials were expected to demonstrate improved melt processability compared to the biphenoxyphthalonitrile monomers previously studied.

²⁰⁸ Dargaville, T. R.; Guerzoni, F.; Looney, M. G.; Shipp, D.; Solomon, D. H.; Zhang, X. *J Polym Sci Pt A: Polym Chem* **1997**, *35*, 1399-1407.

²⁰⁹ Sumner, M.; Sankarapandian, M.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 5069-5076.



DEN 431 (260NOV)

$$\frac{\text{Aromatic protons} \quad (3n + 2)}{\text{Aliphatic protons} \quad (2n + 2)} =$$

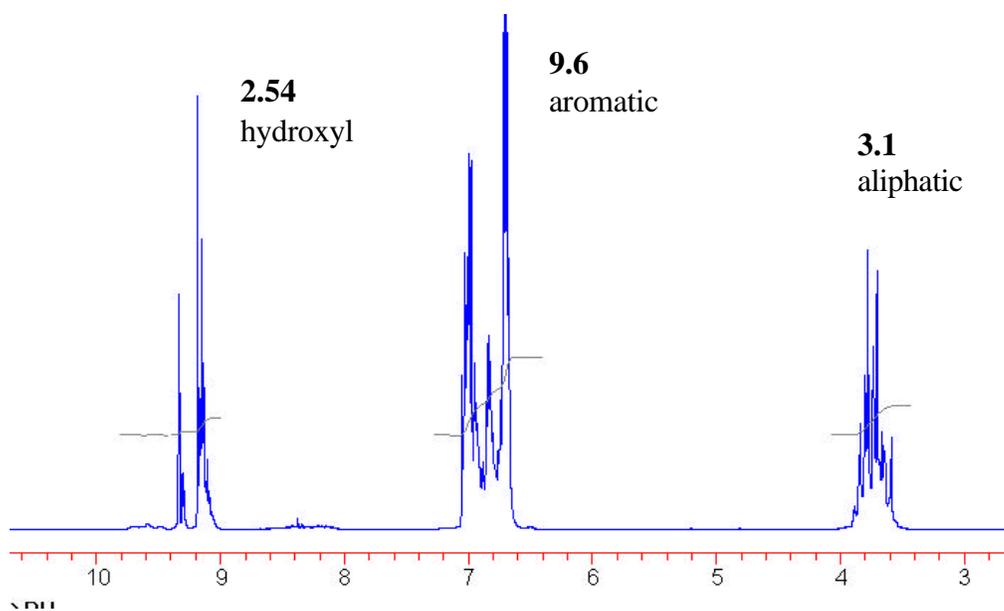


Figure 4.2: ^1H NMR integration of DEN 431 novolac resin for the determination of the number average molecular weight, M_n .

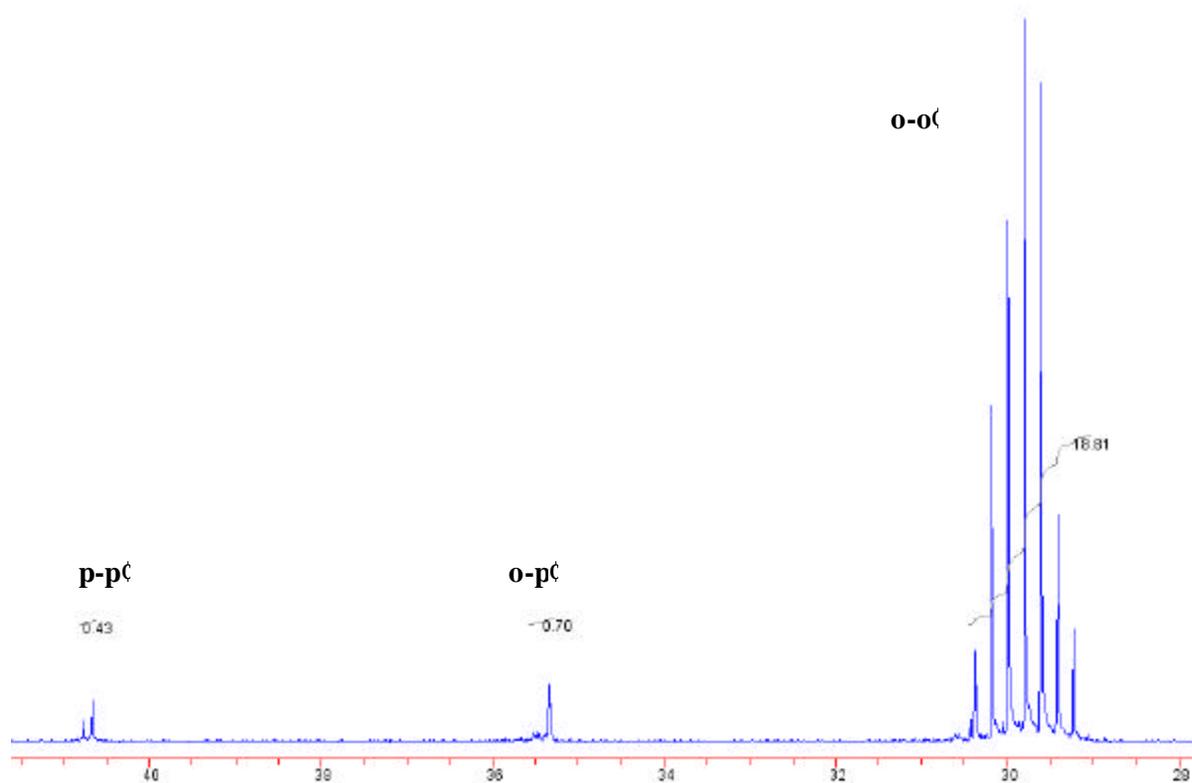


Figure 4.3: Ratio of ortho-ortho, ortho-para, and para-para isomeric methylene bridges identified in ^{13}C NMR analysis of the DEN 431 novolac resin.

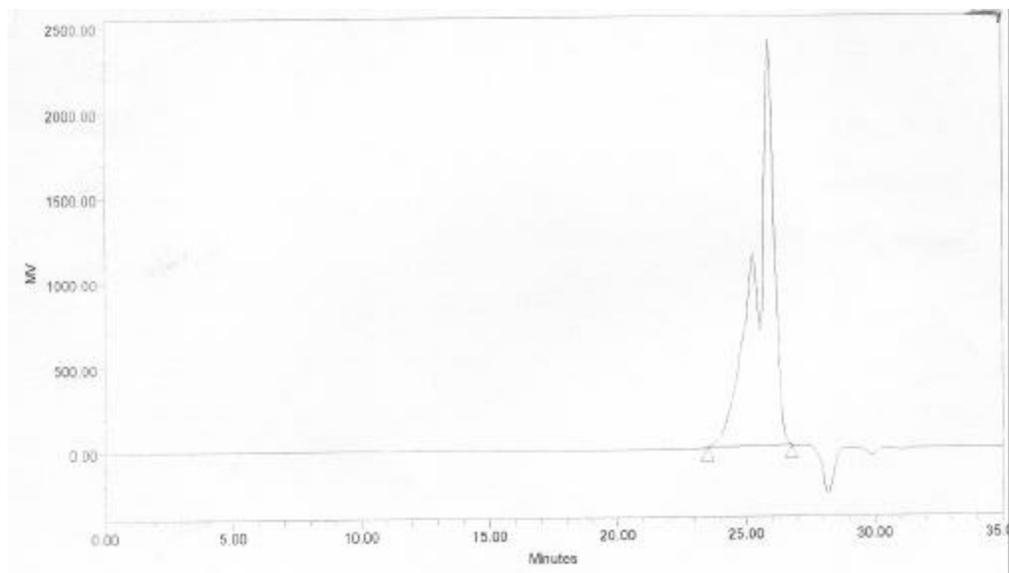


Figure 4.4: GPC Chromatogram of DEN 431 novolac resin in THF.

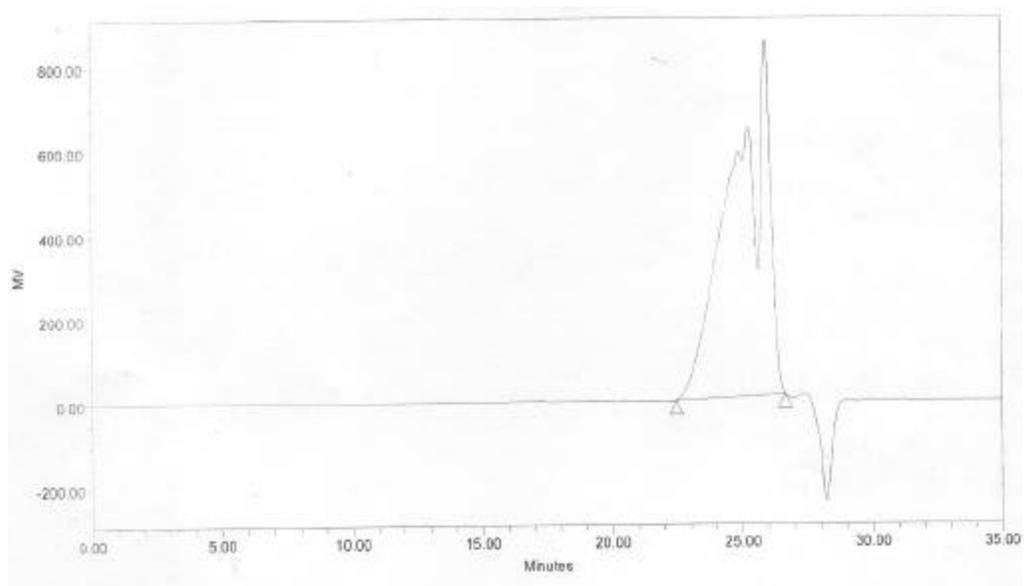


Figure 4.5: GPC Chromatogram of DEN 438 novolac resin in THF.

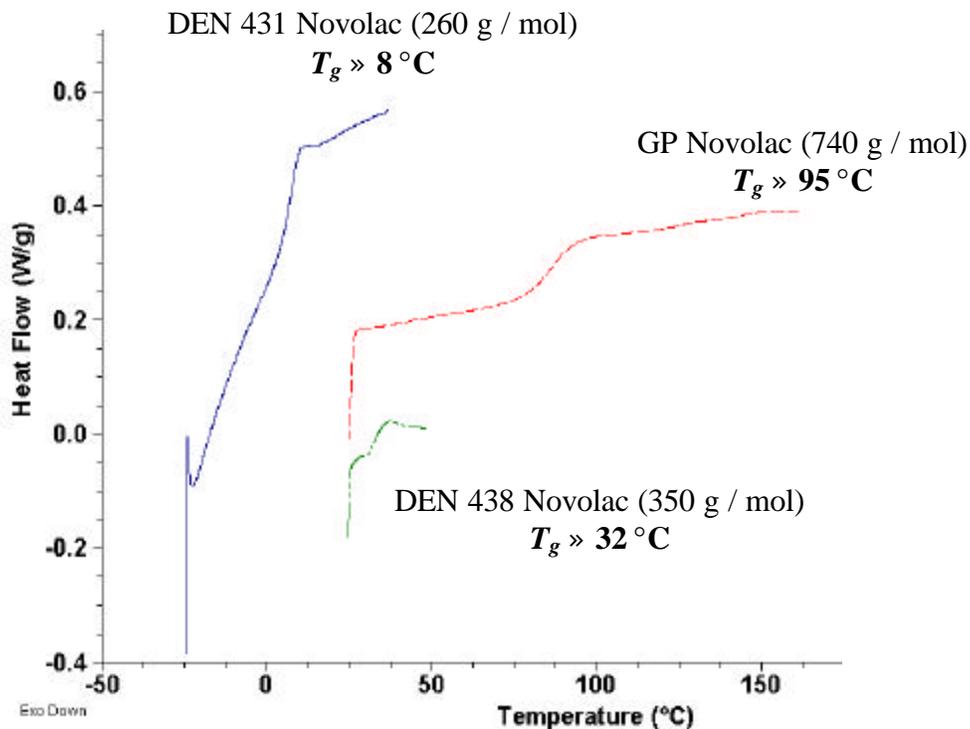


Figure 4.6: DSC analysis of novolac resins: DEN 431, DEN 438, and Georgia Pacific.

4.1.3 Novolac – phthalonitrile Oligomers

The DEN 431 and DEN 438 novolac resins were chemically modified with 4-nitrophthalonitrile to combine the low melt viscosity of the novolac resins and the high flame resistance inherent of networks prepared from the phthalonitrile moiety. ^1H NMR spectroscopy was used to confirm the structure of the modified novolac-phthalonitrile oligomers. The aromatic/aliphatic proton ratio was used to quantitatively confirm the chemical structure. In the case of the phthalonitrile derivative of DEN 431 (260NOV-Ph), the area under the aliphatic proton resonances between 3.5 and 4.1 ppm was set to 3.1, representative of the theoretical number of methylene protons in the phthalonitrile derivative of the novolac resin, where the number of repeat units, n , was 0.55. The experimental aromatic/aliphatic ratio was compared to

the theoretical ratio for each oligomer prepared. ^1H NMR spectrum of 260NOV-Ph is shown in **Figure 4.7**.

DSC analysis was performed on the novolac-phthalonitrile oligomers and revealed T_g s of 53 °C and 76 °C, for the 260NOV-Ph and the 350NOV-Ph, respectively (**Figure 4.8**). Chemical modification with the phthalonitrile moiety increased the glass transition temperature of the novolac resins significantly. Crystallinity was not observed, which was an important aspect to achieve melt processability.²¹⁰ In addition, each of the novolac-phthalonitrile oligomers possessed T_g s below that of the 740g mol⁻¹ novolac resin employed in novolac/BPh resin studies.

The phthalonitrile derivatives were analyzed by TGA to evaluate their thermal and thermo-oxidative stability. Powder samples were heated at 10 °C/min to 800 °C in both air and nitrogen. The TGA results (**Figure 4.9**) confirm that the modified novolac-phthalonitrile resins were relatively stable. The 260NOV-Ph resin exhibited a 5% weight loss temperature, $T_{5\%}$, of 339 °C and ~71% char at 800 °C in nitrogen and $T_{5\%}$ of 348 °C and ~18% at 800 °C in air. TGA studies of the 350NOV-Ph resin revealed similar trends. In nitrogen, $T_{5\%}$ of 368 °C and 78% char at 800 °C, and in air, $T_{5\%}$ of 348 °C and 18% char at 800 °C were observed. This level of thermal stability suggested that these resins would result in flame retardant networks after curing.

²¹⁰ Sumner, M. High Performance Materials Containing Nitrile Groups. Ph.D., Virginia Polytechnic Institute and State University, Blacksburg, VA, 2003.

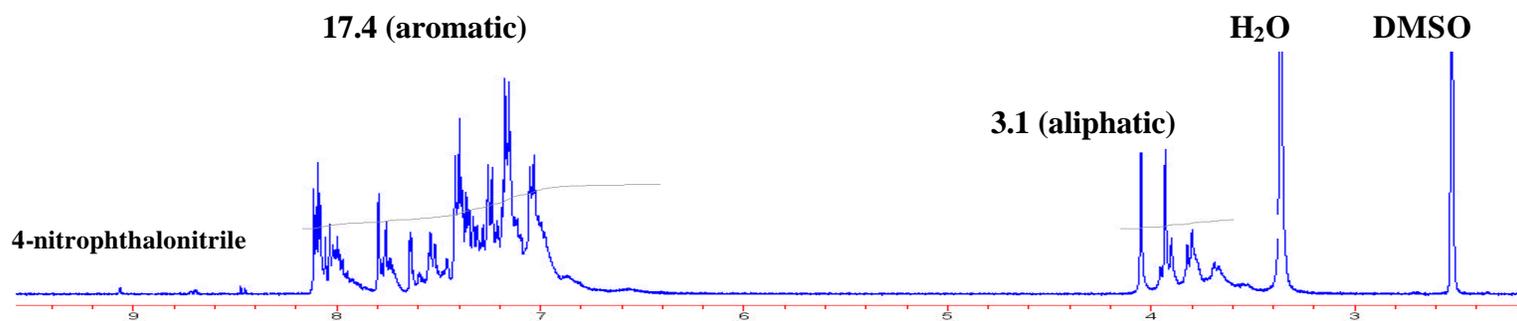
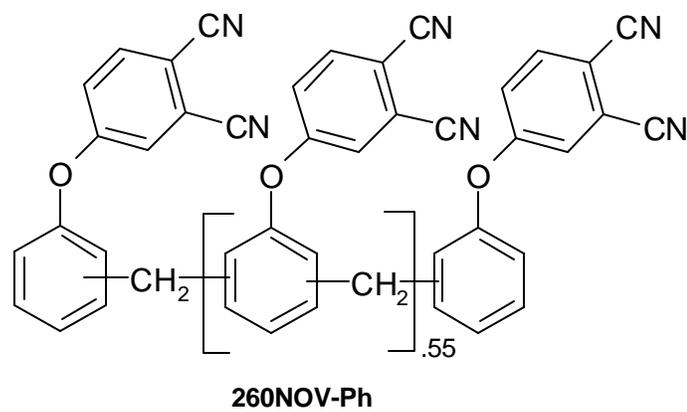


Figure 4.7: ^1H NMR of the phthalonitrile derivative of 260 g mol^{-1} DEN 431 novolac resin (260NOV-Ph).

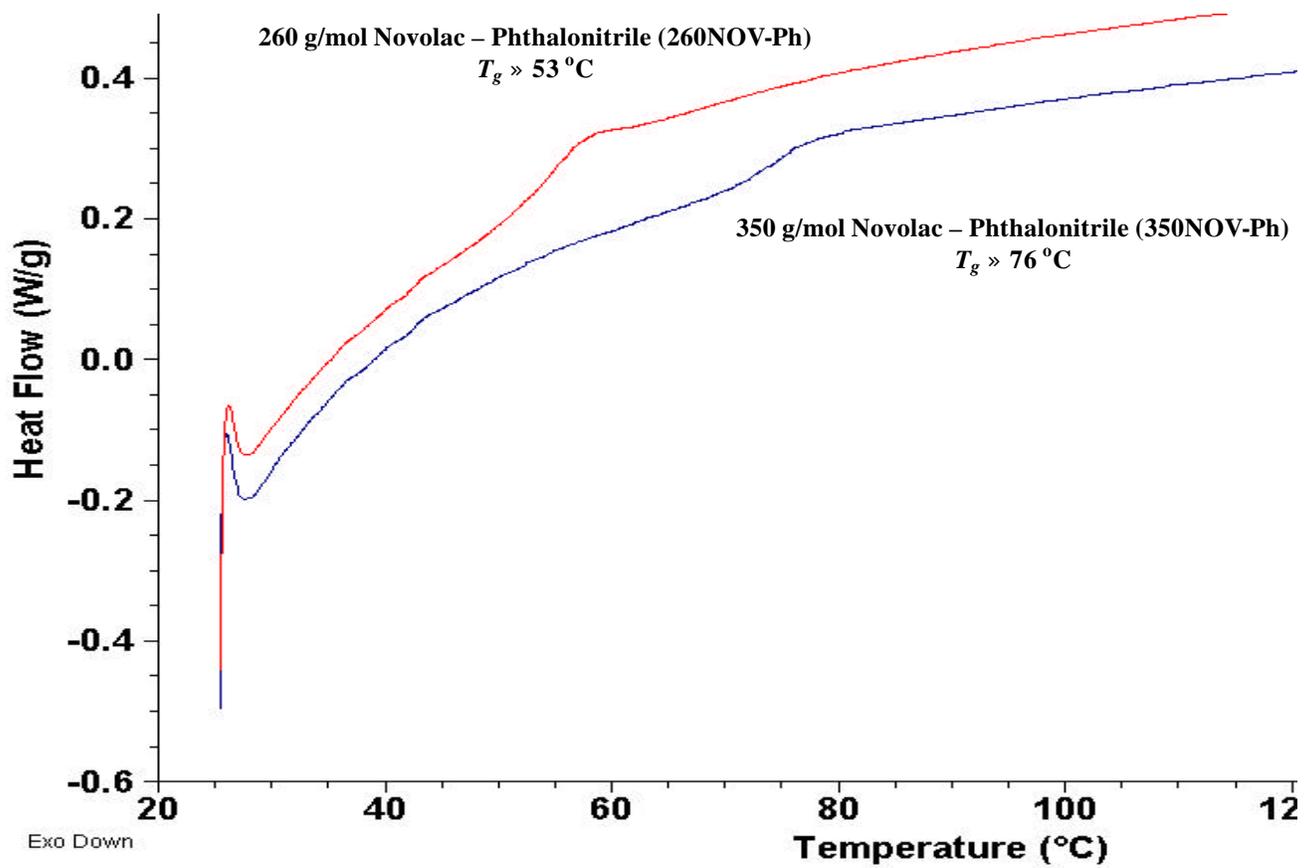


Figure 4.8: DSC thermograms of 260NOV-Ph and 350NOV-Ph resins.

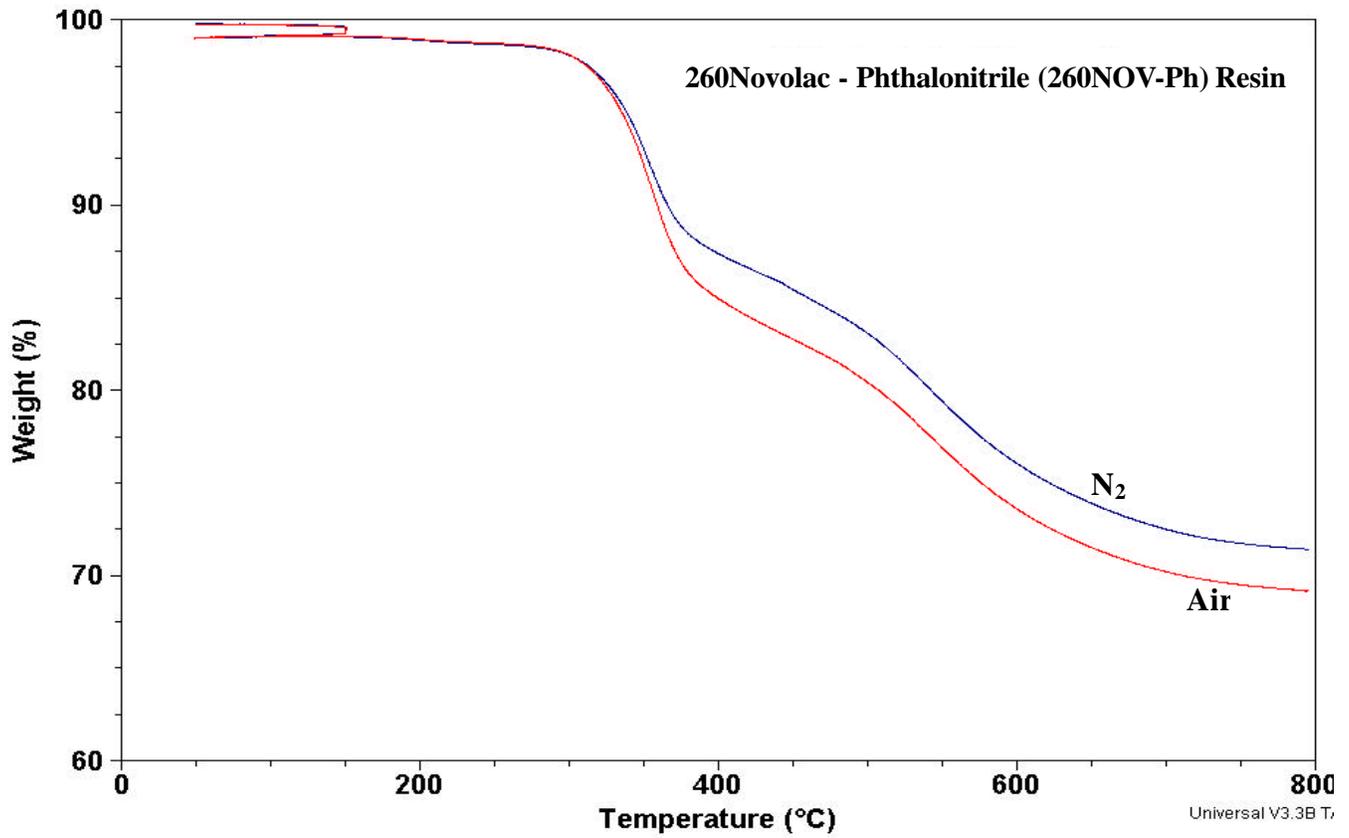


Figure 4.9: Thermogravimetric analysis of 260NOV-Ph resin in Nitrogen and Air.

4.1.4 Bis(3,4-dicyanophenoxyphenyl)methane

Bis(3,4-dicyanophenoxyphenyl)methane (Bis F-Ph) was prepared from the chemical modification of bis(4-hydroxyphenyl)methane with 4-nitrophthalonitrile. The flexible methylene linkage of the bisphenol monomer in conjunction with the high flame resistance of the phthalonitrile moiety was expected to afford highly flame resistant, processable resins. ^1H NMR was used to confirm the structure of the phthalonitrile monomer (**Figure 4.10**).

DSC analysis revealed a T_g of 43 °C and T_m of 190 °C. Although the Bis F-Ph monomer had a lower glass transition temperature than the novolac-phthalonitrile derivatives, its crystallinity mirrored that of the biphenoxyphthalonitrile monomer (**Figure 4.11**). Therefore, it was speculated that this resin would have similar limitations in melt processing procedures, requiring elevated temperatures to achieve sufficient fiber wetting. The Bisphenol F phthalonitrile derivative was also analyzed using TGA to evaluate its thermal stability. The Bis F-Ph monomer exhibited a $T_{5\%}$ of 357 °C and ~ 63% residue remained at 800 °C in nitrogen.

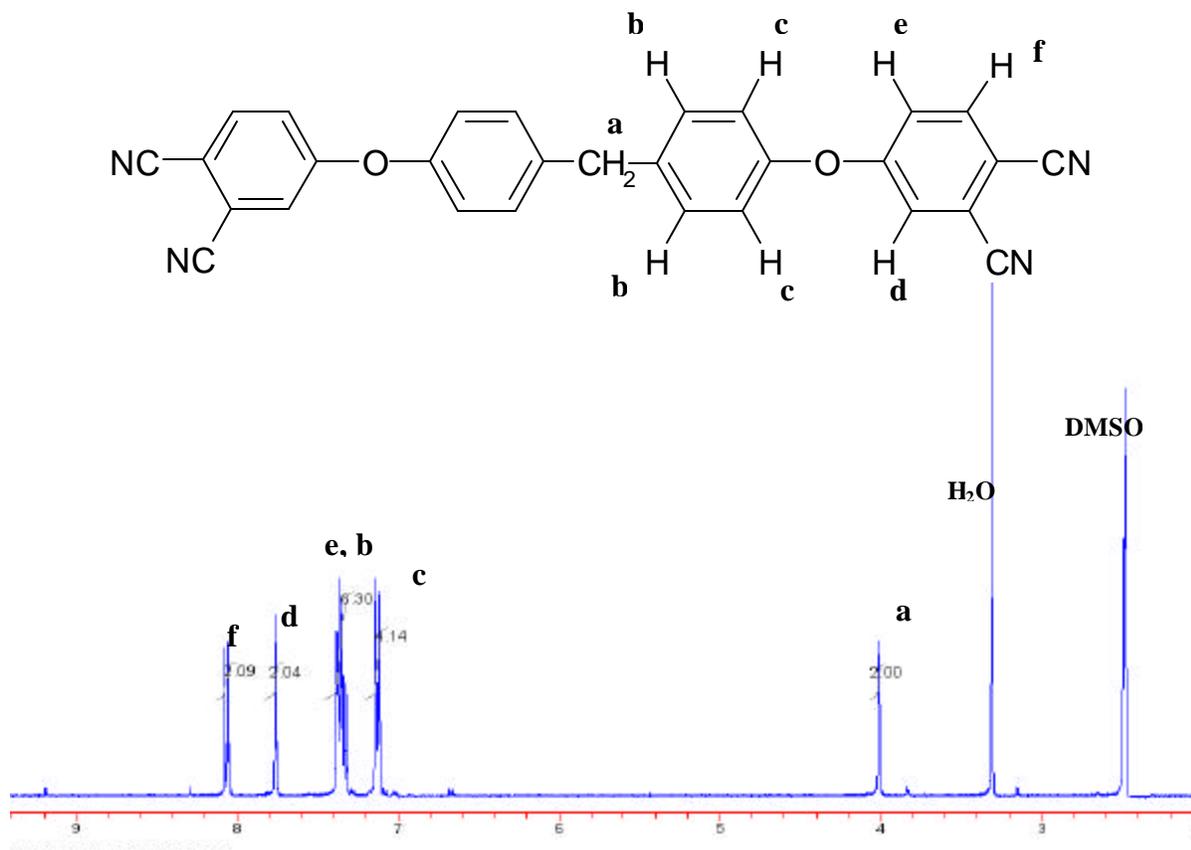


Figure 4.10: ^1H NMR of bis(3,4-dicyanophenoxy)methane (BisF-Ph) monomer.

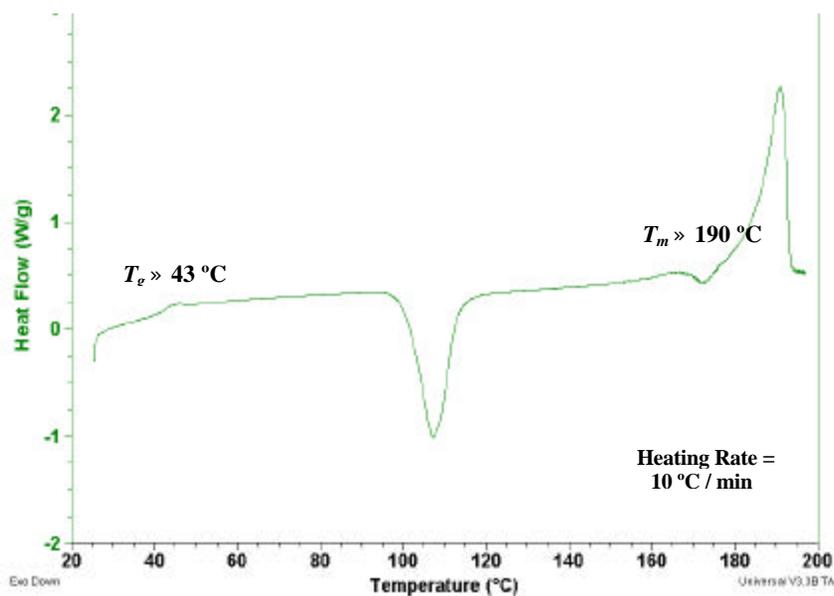


Figure 4.11: DSC thermogram of Bisphenol F phthalonitrile derivative (BisF-Ph) monomer.

4.1.5 Novel Siloxane/Silane-Containing Phthalonitrile Monomers

The synthesis of 2-(3,4-dicyanophenoxy)phthalonitrile, or 2-allylphenoxyphthalonitrile, was confirmed using ^1H NMR spectroscopy (Figure 4.12). A sharp melting temperature, 49 °C, was observed via DSC indicating high purity.

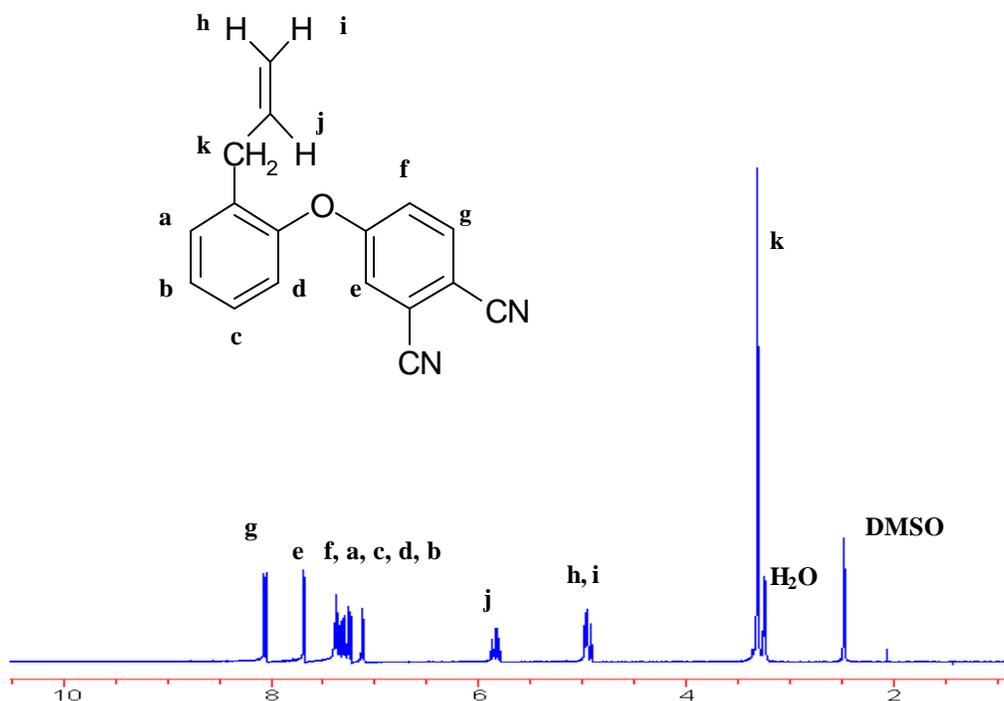


Figure 4.12: ^1H NMR of 2-(3,4-dicyanophenoxy)allylbenzene.

The hydrosilylation reaction of 2-(3,4-dicyanophenoxy)allylbenzene was monitored with ^1H NMR spectroscopy. Completion of the hydrosilylation reaction was indicated by the disappearance of the peaks at 5.0 and 5.8 ppm, representative of the protons from the unsaturated allyl group, and the peak at 4.5- 4.7 ppm, which represented the methine protons of Si-H groups, and the appearance of the three new peaks around 0.5 to 2.5 ppm. Anti-Markovnikov addition

was observed due to steric hinderance. However, small peaks (0-2.5 ppm) attributed to the Markovnikov addition product were also observed.

A series of novel phthalonitrile monomers was prepared using this method: 1,3-di[2-(3,4-dicyanophenoxy)phenylpropyl]-1,1,3,3-tetramethyldisiloxane (**TMDS-Ph**), 1,3-di[2-(3,4-dicyanophenoxy)phenylpropyl]-1,3-dimethyl-1,3-diphenyldisiloxane (**DDDS-Ph**), 1,3-di[2-(3,4-dicyanophenoxy)phenylpropyl]-1,1,3,3-tetraphenyldisiloxane (**TPDS-Ph**), 1,5-di[2-(3,4-dicyanophenoxy)phenylpropyl]-1,1,3,3,5,5-hexamethyltrisiloxane (**HMTS-Ph**), and 1,4-bis[2-(3,4-dicyanophenoxy)phenylpropyl-dimethylsilyl]benzene (**Silane-Ph**). In **Figure 4.13**, the structure and T_g s are listed for each compound of the series. The series of siloxane and silane containing phthalonitrile derivatives was prepared to produce low melting resins with high mechanical strength. It was hypothesized that the flexibility and bond strength of the Si-O, and in the case of the silane containing monomer, the Si-C bond, would promote the desired properties. By tailoring the chemical structure, siloxane and silane containing phthalonitrile resins with T_g s varying from -25 to +7 °C were prepared. As expected, the T_g of the resulting monomer increased as the aromatic character of the starting materials was increased.

The low glass transition temperatures observed in DSC studies support the theory that siloxane and silane moieties may be incorporated to achieve low viscosity resins that may be further polymerized into tough, flame retardant networks.

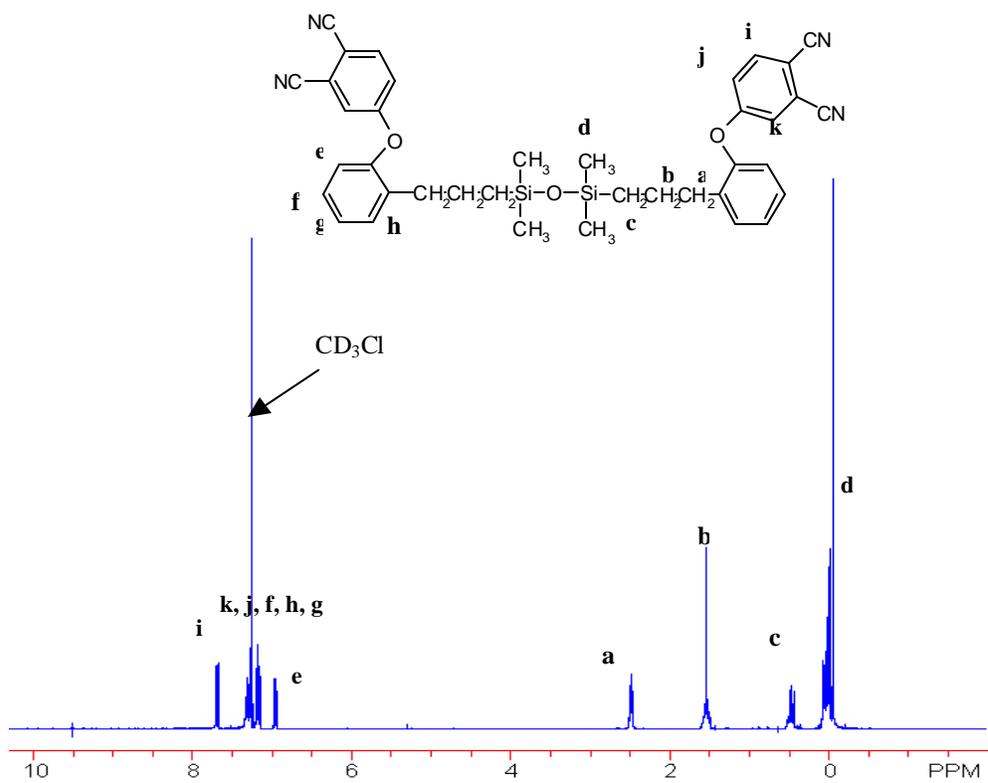
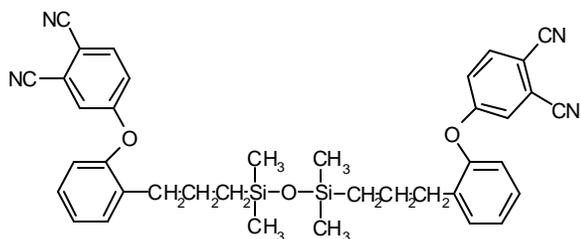
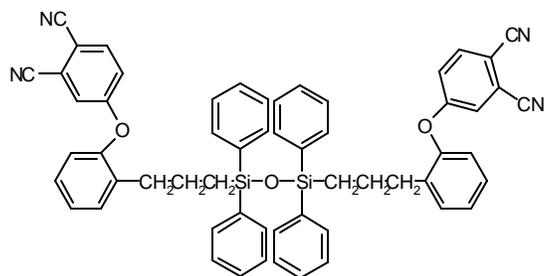


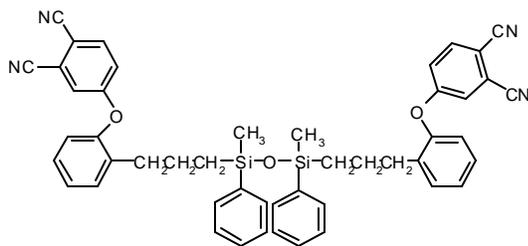
Figure 4.13: ¹H NMR of Hydrosilylation product of allylphenoxyphthalonitrile and TMDS (TMDS-Ph).



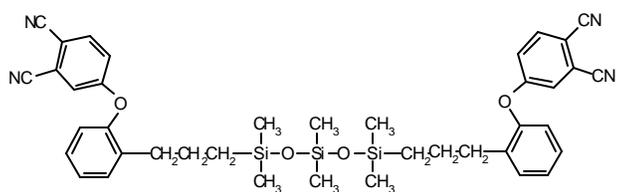
**Tetramethyldisiloxane-phthalonitrile
(TMDS-Ph)**
 $T_g = -11\text{ }^\circ\text{C}$



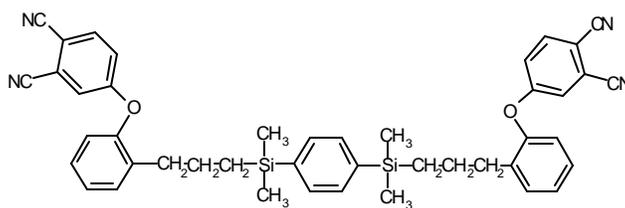
**Tetraphenyldisiloxane-phthalonitrile
(TPDS-Ph)**
 $T_g = 7\text{ }^\circ\text{C}$



**Dimethyldiphenyldisiloxane-Phthalonitrile
(DDDS-Ph)**
 $T_g = -7\text{ }^\circ\text{C}$



**Hexamethyltrisiloxane-phthalonitrile
(HMMS-Ph)**
 $T_g = -25\text{ }^\circ\text{C}$



**Silane-phthalonitrile
(Silane-Ph)**
 $T_g = 4\text{ }^\circ\text{C}$

Figure 4.14: Novel siloxane and silane containing phthalonitrile monomer series.

4.2 FTIR Model Curing Studies

The main objective of this research was to identify low viscosity resin mixtures that could be cured at low to moderate temperatures. Curing profiles of resin mixtures containing a high molecular weight novolac oligomer, $M_n \approx 740 \text{ g mol}^{-1}$, and biphenoxyphthalonitrile monomer (740NOV/BPh) were investigated previously.²¹¹ These resin mixtures were cured at 200 °C for 1 hour and post cured at 220 °C for 3 hours, and void-free, tough (K_{Ic} 0.8 to >1 MPa m^{1/2}), flame resistant (PHHR 137 kW/m²) networks were achieved. On the contrary, 740NOV/BPh resin mixtures required elevated temperatures, $\approx 140 \text{ °C}$, to achieve homogeneous mixtures and efficient fiber wetting in melt fabrication procedures. The high melt viscosity was attributed to both the melting point of the biphenoxyphthalonitrile resins, 234 °C, and the glass transition temperature of the novolac oligomer, 95 °C.

In an effort to prepare highly flame retardant networks and improve the processability of the resin mixtures, novel novolac and siloxane/silane containing phthalonitrile monomers and oligomers were cured with a low molecular weight novolac oligomer (256 g mol^{-1} , $f = 2.54$) in an equivalent weight ratio (50/50 w/w). Samples were prepared by the melt mixing procedure previously described. The kinetics of the cure reaction were investigated using FT-IR spectroscopy at 200 °C for each phthalonitrile/novolac resin composition. Each FT-IR data series was normalized and the progress of the reaction was signified by the decrease in the intensity of the peak attributed to nitrile stretch at 2230 cm^{-1} .

²¹¹ Sumner, M.; Sankarapandian, M.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 5069-5076.

Figure 4.15 depicts the FTIR reaction series for TMDS-Ph/260NOV, in which the stretch at 3030 cm^{-1} attributed to an aromatic C-H stretch was used to normalize each spectrum of the series.

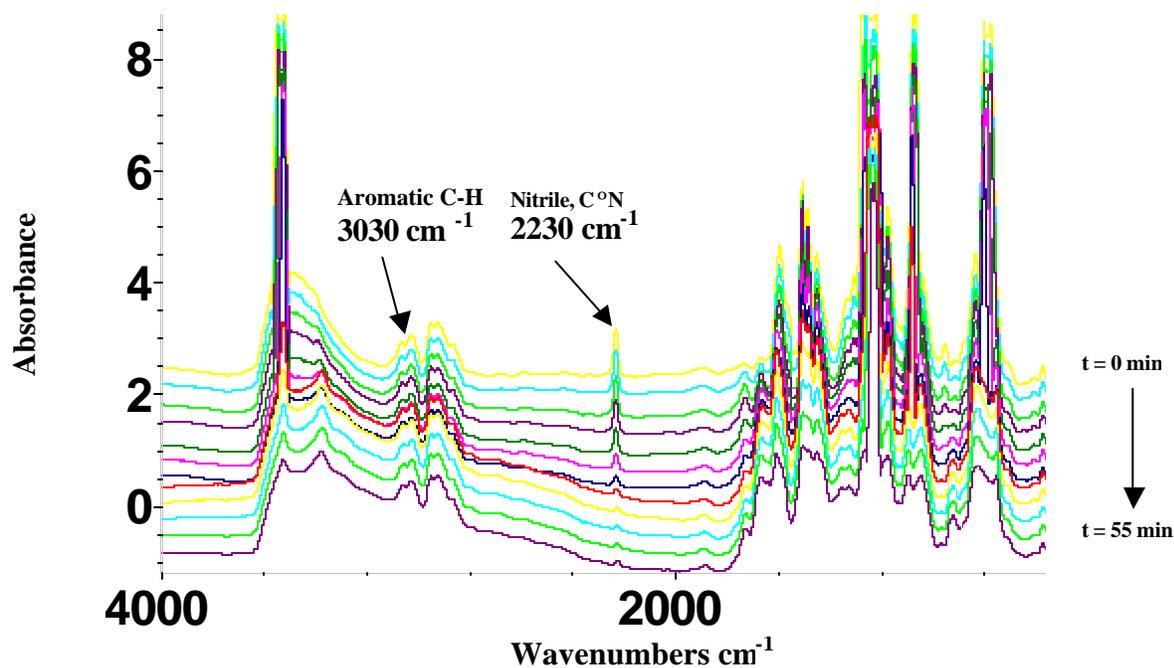


Figure 4.15: FT-IR series of the cure reaction of TMDS-Ph/260NOV resin blend at 200°C .

The 50/50 w/w TMDS-Ph /260NOV resin mixture was cured at 200°C for an hour.

Figure 4.16 illustrates the percent nitrile conversion as function of time for this system. Ninety percent conversion was achieved within 40 minutes. Similar results were observed for the 740NOV/BPh resin mixtures cured for 1 hour at 200°C and post cured at 220°C for 20 minutes.²¹² The TMDS-Ph/260NOV resin composition demonstrated a significant improvement

²¹² Sumner, M.; Sankarapandian, M.; McGrath, J.; Riffle, J. S.; Sorathia, U. *Polymer* **2002**, *43*, 5069-5076.

compared to BPh monomers cured with diamine curing agents reported by Keller et al., which required 8-24h curing cycles at temperatures above 300 °C.²¹³

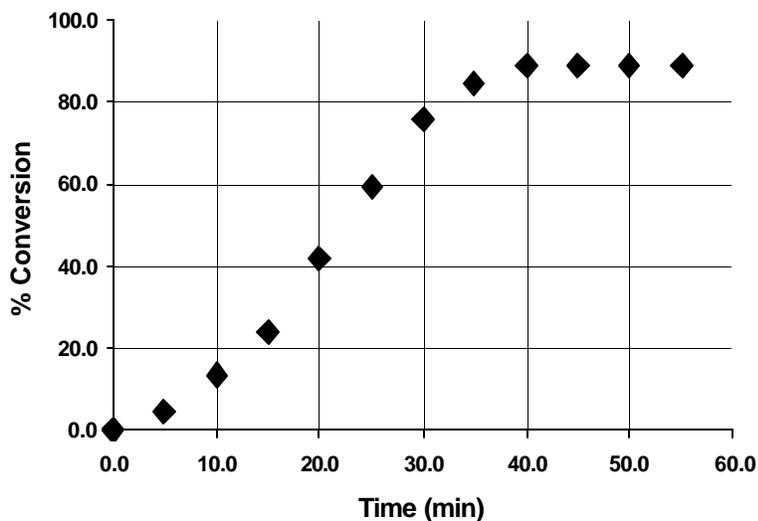


Figure 4.16: 50/50 w/w TMDS-Ph/ 260NOV resin Cure Behavior at 200°C.

The 50/50 w/w TMDS-Ph /260NOV resin mixture was cured at 200 °C for 1 hour in an aluminum weighing dish and the product network was analyzed using DSC. Crosslinking was evidenced by an increase in the glass transition temperature, 95 °C (**Figure 4.17**). Post-curing was investigated as a means to increase the degree of crosslinking and target networks of high mechanical strength. The 50/50 w/w TMDS-Ph /260NOV networks, previously cured at 200 °C for 1 hour, were post cured at 225 °C for 4 hours. DSC analysis of the post-cured networks

²¹³ Keller, T.; Price, T. *Journal of Macromolecular Science - Chemistry* **1982**, A18, 931.

(**Figure 4.18**) did not reveal a T_g below 250 °C. Therefore, it was concluded that the post-curing procedure did increase the degree of crosslinking.

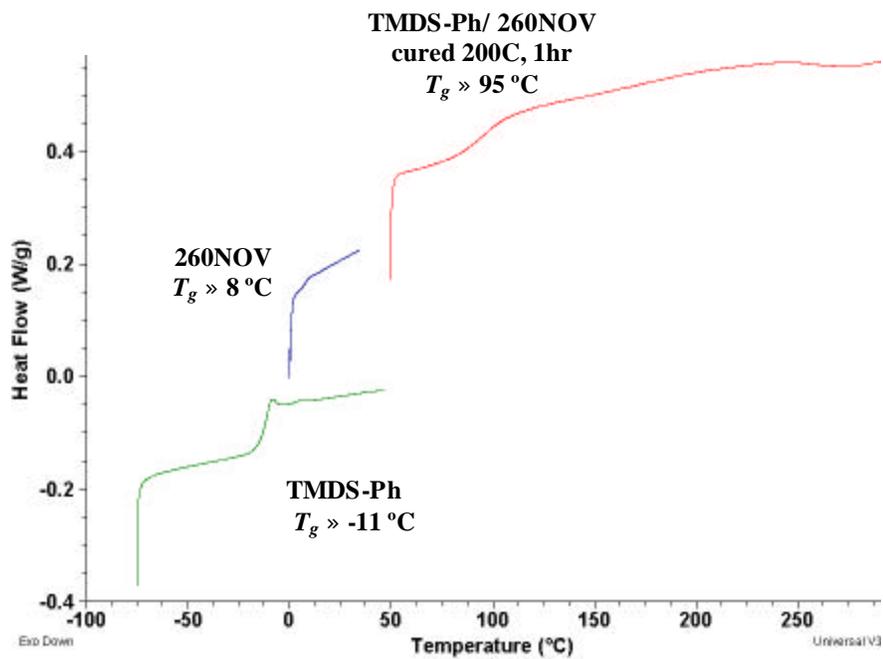


Figure 4.17: DSC analysis of TMDS-Ph/260NOV network cured at 200 °C for 1 hour.

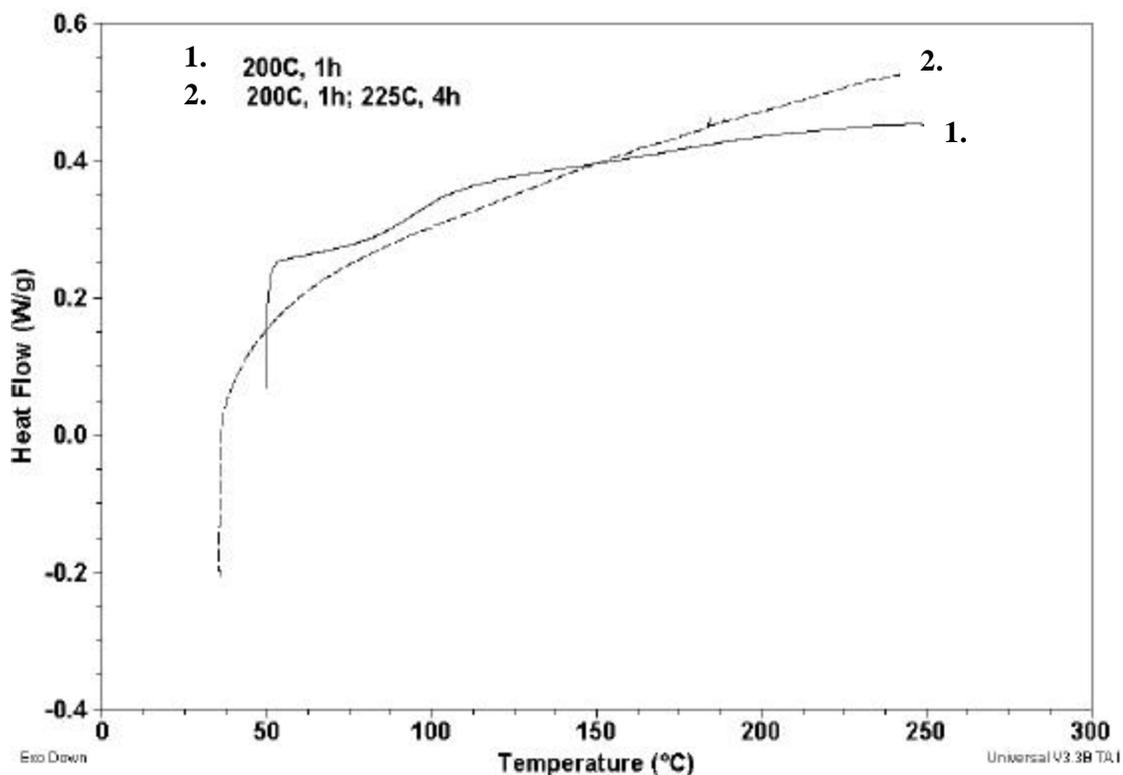


Figure 4.18: DSC thermograms of TMDS-Ph/260NOV networks.

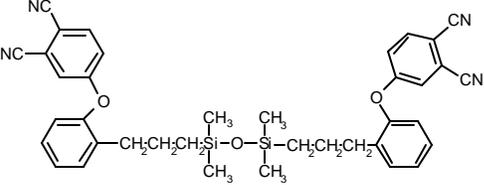
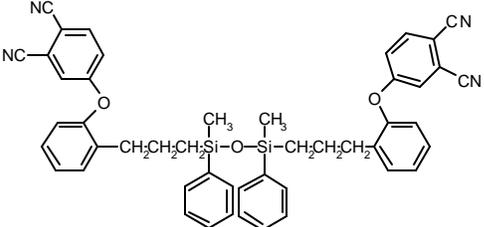
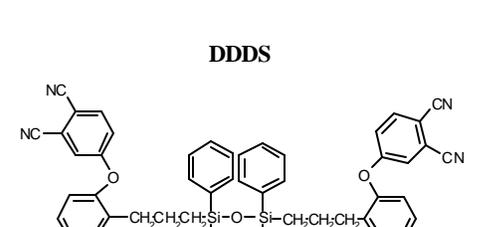
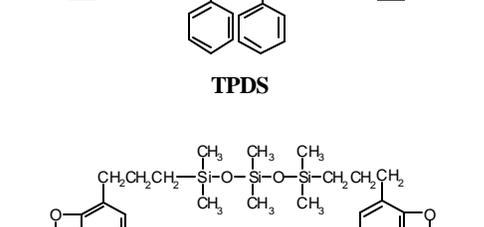
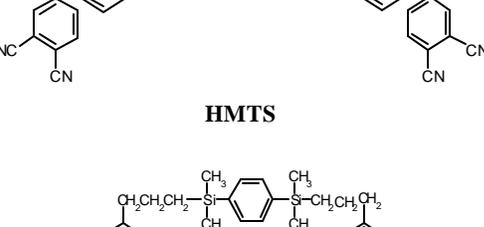
A summary of the results of the model curing studies of the siloxane- and silane-phthalonitrile derivatives is provided in **Table 4.1**. All of the siloxane-based phthalonitrile monomers exhibited high conversion, $\geq 88\%$, within 40 minutes at $200\text{ }^{\circ}\text{C}$. The silane-based phthalonitrile resins were comparable to the siloxane derivatives with 91% conversion achieved in 30 minutes. The TPDS-Ph/260NOV resin mixture exhibited the highest percent conversion (93%) achieved in the most rapid cure cycle (25 minutes).

Model curing studies were also investigated for novolac-phthalonitrile oligomers. In the FT-IR studies of 50/50 w/w 260NOV-Ph/260NOV, only 40 % conversion was achieved at $200\text{ }^{\circ}\text{C}$ over a two-hour cure cycle. Increasing the cure temperature to $250\text{ }^{\circ}\text{C}$ resulted in 90% conversion within 30 minutes. Further investigations employed a nucleophilic initiator,

triphenylphosphine, to catalyze the reaction between novolac-phthalonitrile resins and phenol functional groups on the novolac curing agent. A small amount of triphenylphosphine, 1.5 mol % based on the amount of phenolic novolac, was added to a 260NOV-Ph /260NOV (50:50 w/w) sample (NOV/NOV/TPP). Curing studies of the NOV/NOV/TPP resin composition resulted in 90% conversion within one hour at 200 °C. The curing reaction of the catalyzed NOV/NOV/TPP resin mixture was comparable to that of the siloxane-containing phthalonitrile derivatives.

Networks of NOV/NOV/TPP resin mixtures cured at 200 °C for one hour were investigated using DSC at a heating rate of 10 °C/minute. No glass transition could be detected below 250 °C (**Figure 4.19**). Thus, this catalyzed reaction was significant with regard to cure kinetics and thermo-mechanical studies. The results of the model curing studies of the novolac- and bis F-phthalonitrile derivatives are listed in **Table 4.2**. The bis F-phthalonitrile derivative did not demonstrate comparable results in these studies.

Table 4.1: Cure Kinetics of Siloxane-/Silane-phthalonitrile resins cured with 50% 260-NOV at 200 °C.

PHTHALONITRILE MONOMER	% CONVERSION	TIME (MIN)
 <p style="text-align: center;">TMDS</p>	89	40
 <p style="text-align: center;">DDDS</p>	88	30
 <p style="text-align: center;">TPDS</p>	93	25
 <p style="text-align: center;">HMTS</p>	89	30
 <p style="text-align: center;">Silane</p>	91	30

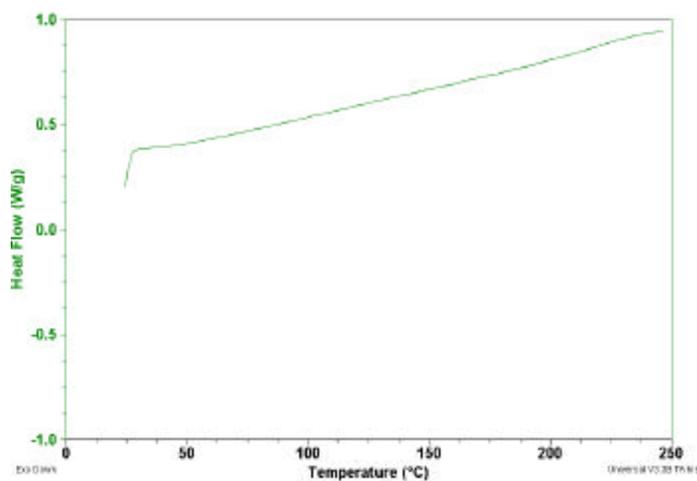
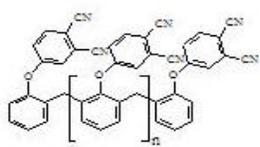
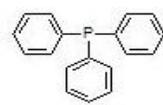
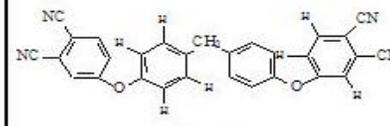


Figure 4.19: DSC thermogram of 260NOV-Ph/260NOV/TPP network cured at 200 °C for 1 hour.

Table 4.2: Curing Kinetics of Novolac- and Bisphenol F-phthalonitrile derivatives cured with 50 wt % 260NOV.

Phthalonitrile Derivative	Nucleophilic Initiator	% Conversion	Time (min)
 <p>NOV</p>	 <p>TPP</p>	88	50
 <p>Bis-F</p>	NA	55	170

4.3 Thermal Analysis of Networks

As candidates for use in structural applications, it is important that the networks under consideration possess high thermal and thermo-oxidative stability. **Tables 4.3 and 4.4** summarize the results of the networks investigated by TGA. The TMDS-Ph/260NOV network (200 °C, 1h) demonstrated good thermal stability in an inert nitrogen atmosphere, with a 5% weight loss temperature, $T_{5\%}$, of 262 °C and 55% char yield at 800 °C. The thermal stability exhibited by this system was attributed to the highly aromatic nature of the network, as well as the formation of heterocyclic crosslinks. Thermo-oxidative stability was measured with TGA under an atmosphere of streaming air. In air, the network demonstrated a $T_{5\%}$ at 278 °C, a slight improvement over the analysis in nitrogen, which may be attributed to heterogeneity of the crosslink density of the sample. However, a sharp 10% weight loss was observed at 600°C and a mere 13% char remained at 800 °C. The resulting char was observed to be a fine white powder, which differed greatly from the shiny, black, graphite-like char produced in the analysis performed under nitrogen. The white powder, believed to be silica, was investigated by X-ray photoelectron spectroscopy (XPS). The sharp weight loss at 600 °C was attributed to the cleavage of the aliphatic -Si-CH₂- bonds of the networks. This ‘aliphatic’ segment was deemed the weakest site of the network, and it was proposed that a more highly crosslinked network may retard volatilization due to cleavage of the methylene linking groups. Therefore, the TMDS-Ph/260NOV networks were post cured at 225 °C for 4 hours to increase the crosslink density. As shown in **Table 4.4**, employing a post-cure step alleviated the drastic weight loss and increased the char yield at 800 °C in air threefold. In addition, post-curing increased the $T_{5\%}$ by 100 °C in both air and nitrogen for the TMDS-Ph/260NOV resin. Post-curing the networks at

225 °C for 4 hours increased the degree of crosslinking within the networks, which served to protect the labile aliphatic segments of the network structure. TGA studies also revealed that the thermo-oxidative stability was improved with increasing aromatic character of the respective networks. This phenomenon can be demonstrated in the comparison of the thermal analyses of the TMDS-Ph/260NOV and TPDS-Ph/260NOV systems. The TPDS-Ph/260NOV system exhibited a $T_{5\%}$ at ~230 °C and ~50% char at 800 °C, behavior which was consistent in both nitrogen and air. These results differed from the TMDS-Ph/260NOV system, wherein the behavior was greatly influenced by the atmosphere under which it was analyzed.

A general trend was observed among the siloxane-based phthalonitrile/ novolac networks. Upon curing at 200 °C for 1 hour, the $T_{5\%}$ ranged comparatively from 230 to 273 °C, with char yields at 800 °C within a 50 to 56 % range for the inert analyses. For samples subjected to the same curing conditions and analyzed in air, the $T_{5\%}$ ranged from 235 to 280 °C, with char yields ranging between 13 and 51% confirming an oxidative degradation process. In every case, the post-cured networks had greater thermal and oxidative stabilities than those prepared without the post-curing step. All of the post-cured (200 °C, 1h; 225 °C, 4h) siloxane-containing networks exhibited $T_{5\%}$ between 285 and 418 °C, and char yields between 54 and 66% at 800 °C in nitrogen. In an oxygen-rich atmosphere, the $T_{5\%}$ ranged from 327 °C to 397 °C, with char yields between 8 and 42%. The thermal stability of the silane-based network was comparable to the siloxane-based networks, however, the silane materials fall short when thermo-oxidative stability is considered, $T_{5\%} \approx 178^\circ\text{C}$ with 5% char at 800 °C was observed for the post-cured networks studied in air.

The thermal and thermo-oxidative stability of the NOV/NOV/TPP networks was also studied by TGA. A $T_{5\%}$ of 350 °C and 70% char yield was observed at 800°C in the thermal

analysis of the networks cured at 200 °C for 1 hour. The networks were thermo-oxidatively stable up to 377 °C, but exhibited comparatively low char yields, ~13%. The networks after post-curing at 225 °C for 4h had increased thermal and thermo-oxidative stabilities. In nitrogen, the networks were stable up to 386 °C and exhibited ~70% char. In air, the networks were stable up to 447 °C and 50% char remained at 800 °C. The NOV/NOV/TPP network exhibited the highest thermo-oxidative stability of all the networks investigated. This network has high aromatic character and, therefore, the cleavage of labile aliphatic chains was not an issue as it was in the case of the siloxane-based phthalonitrile networks.

Table 4.3: Thermogravimetric analysis of phthalonitrile/novolac (50/50 w/w) networks in nitrogen.

Network Composition	Cured Networks (200°C, 1hr)		Post-Cured Networks (200°C, 1hr; 225°C, 4hr)	
	$T_{5\%}$	wt % Char at 800°C	$T_{5\%}$	wt % Char at 800°C
TMDS-Ph/260NOV	262	55	360	59
DDDS-Ph/260NOV	273	56	285	54
TPDS-Ph/260NOV	230	50	396	66
HMTS-Ph/260NOV	257	55	418	66
Silane-Ph/260NOV	243	54	393	64
NOV-Ph/NOV/TPP	350	70	386	70

Note: NOV-Ph/NOV (50/50 w/w) with 1.5 mol% TPP (based on NOV)

Table 4.4: Thermogravimetric analyses of phthalonitrile/novolac (50/50 w/w) networks in air.

Network Composition	Cured Networks (200°C, 1hr)		Post-Cured Networks (200°C, 1hr; 225°C, 4hr)	
	$T_{5\%}$	wt % Char at 800°C	$T_{5\%}$	wt % Char at 800°C
TMDS-Ph/260NOV	278	13	383	42
DDDS-Ph/260NOV	-	-	327	42
TPDS-Ph/260NOV	235	51	391	30
HMTS-Ph/260NOV	242	14	397	14
Silane-Ph/260NOV	202	6	178	5
NOV-Ph/NOV/TPP	377	13	447	50

Note: NOV-Ph/NOV (50/50 w/w) with 1.5 mol% TPP (based on NOV)

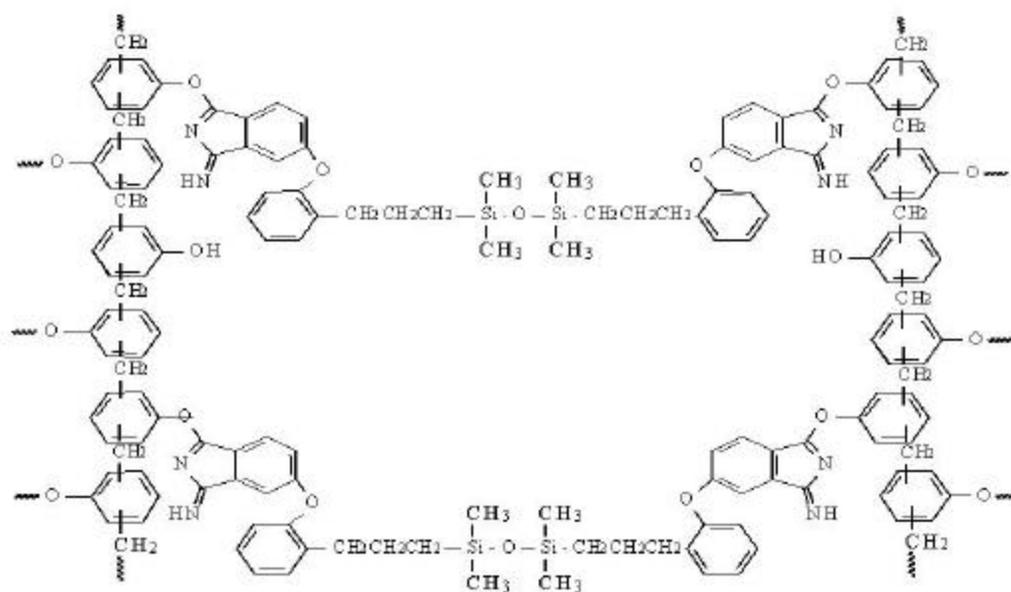
TGA studies of the NOV-Ph/NOV/TPP post-cured network resulted in high char yields (50-70 wt%) at 800 °C. This degree of char formation makes these materials appealing for use in carbon-carbon composites. In carbon-carbon composites, a carbon or graphite fiber reinforcement is embedded in a carbon or graphite matrix, which is pyrolyzed. Typically, these materials possess low weight and density, have high strength and stiffness, and retain strength as temperature increases up to 2000 °C.²¹⁴ These properties make the materials attractive for use in high temperature aerospace applications.

4.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), a powerful tool for gaining insight to the elemental composition of a surface, was utilized to examine the char produced in TGA studies of

the TMDS-Ph/260NOV networks. By analyzing the surface of the char produced in thermo-oxidative studies, a better understanding of the sharp weight loss observed at 600 °C was achieved. This phenomenon was not observed in the analysis of networks performed in nitrogen nor was it observed in the analyses of the post-cured networks performed in air. Therefore, the char from these analyses were investigated for comparison. The networks cured at 200 °C for 1h under nitrogen produced a shiny black graphite-like char. XPS results of the shiny black char revealed 72.1% Carbon, 19.7% Oxygen, 1.1% Nitrogen, and 7.1% Silicon on the surface. Conversely, the same networks analyzed in air produced a fine white powder. The white powder was studied with XPS which revealed 13.6% Carbon, 60.1 % Oxygen, 0 % Nitrogen, and 26.3 % Silicon on the surface. A significant decrease in carbon and increase in silicon content was observed for the samples from the air analysis. Consideration of a proposed network structure lead to the belief that the three-carbon aliphatic chain bonded to the silicons was the most vulnerable segment. Cleavage of this aliphatic chain would lead to separation of the silicon moiety and the aromatic character of the network. TGA analyses of post-cured TMDS-Ph/260NOV networks were performed in air and resulted in shiny black char. The surface possessed 50.3% Carbon, 34.9 % Oxygen, 1.6 % Nitrogen, and 13.3 % Silicon. The increase in carbon content and the decrease in silicon content on the surface supported the premise that post-curing the networks, and thus increasing the degree of crosslinking, protected the labile aliphatic chain. In addition, the post-cured networks displayed enhanced thermal and thermo-oxidative stability.

²¹⁴ Ngai, T. Carbon-carbon composites. In *International Encyclopedia of Composites; Volume 1*. Lee, S, Ed. VCH: New York, 1990. 158-187.



200 °C, 1hr
TGA - Nitrogen

Element	%
C	72.1
O	19.7
N	1.1
Si	7.1

200 °C, 1hr
TGA - Air

Element	%
C	13.6
O	60.1
N	0
Si	26.3

200 °C, 1hr; 225 °C, 4hrs
TGA - Air

Element	%
C	50.3
O	34.9
N	1.6
Si	13.3

Figure 4.20: XPS analyses of char from TGA studies of TMDS-Ph/260NOV networks.

4.5 Rheology Studies of Resin Blends Predict Processability

The viscosity of the TMDS-Ph/260NOV (50/50 w/w) resin mixture was investigated as a means to predict the processability of the resin via fabrication processes such as vacuum assisted resin transfer molding (VARTM), which requires viscosities <1000 mPa·s. In a temperature ramp (dynamic) analysis, the resin viscosity was studied as a function of temperature to determine the processing temperature, defined as the lowest temperature at which the resin viscosity was <1000 mPa·s. The TMDS-Ph/260NOV resin mixture had a viscosity of ~ 5000 mPa·s at 60 °C, and as the temperature was increased the viscosity decreased exponentially to ~ 650 mPa·s at 80 °C (**Figure. 4.21**). The processing temperature was determined to be 80 °C for the TMDS-Ph/260NOV resin. An isothermal analysis was performed to predict the resin processing window, the length of time for which the viscosity remained stable at its processing temperature. In an isothermal analysis at 80 °C, the TMDS-Ph/260NOV resin viscosity was measured over one hour. As is shown in **Figure 4.22**, the resin viscosity remained relatively constant at ~ 560 mPa·s, which would make the resin an excellent candidate for this process.

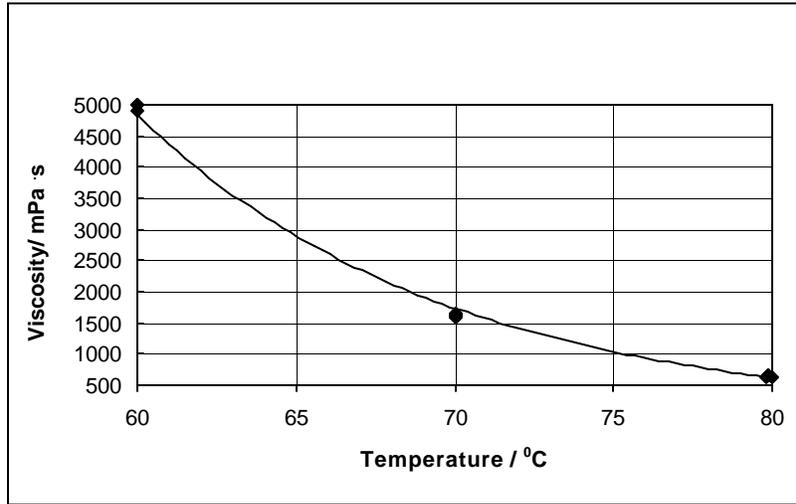


Figure 4.21: Rheological temperature-ramp analysis of TMDS-Ph/NOV resin blend.

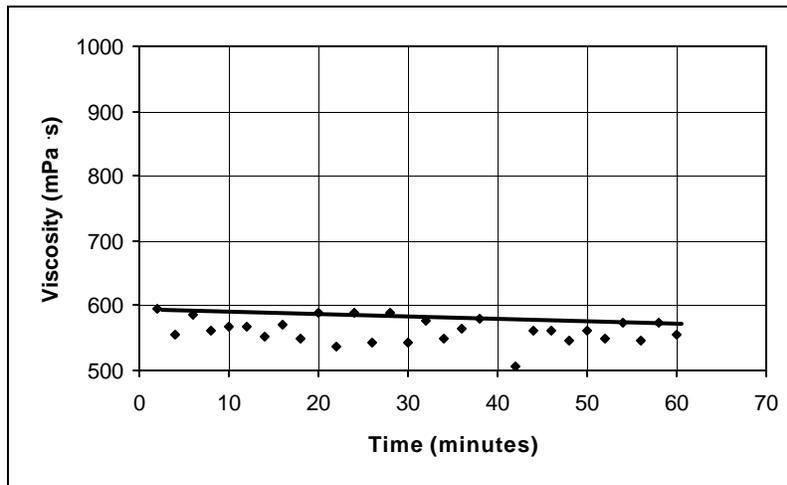


Figure 4.22: Rheological isothermal analysis of TMDS-Ph/260NOV resin blend at 80 °C.

Rheological studies were performed on the TPDS-Ph/260NOV resin mixture to investigate the influence of the increased aromatic character of the TPDS-Ph resin compared to the TMDS-Ph. At 70 °C, the viscosity of the TPDS-Ph/260NOV resin mixture was much higher (~ 6200 mPa·s) than that of the TMDS-Ph/260NOV resin mixture (1600 mPa·s) at the same temperature. As shown in **Figure 4.23**, the TPDS-Ph/260NOV resin mixture required heating to 87 °C to achieve a viscosity < 1000 mPa·s. In an isothermal analysis, the TPDS-Ph/260NOV resin mixture maintained a viscosity of ~ 944 mPa·s over an hour (**Figure. 4.24**). Thus, the increased aromatic character of the TPDS-Ph/260NOV had a substantial effect on the resin viscosity, as predicted.

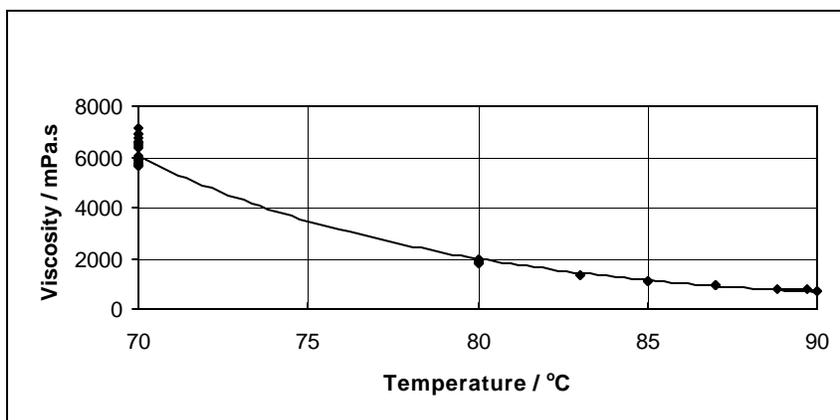


Figure 4.23: Rheological temperature ramp analysis of TPDS-Ph/260NOV resin blend.

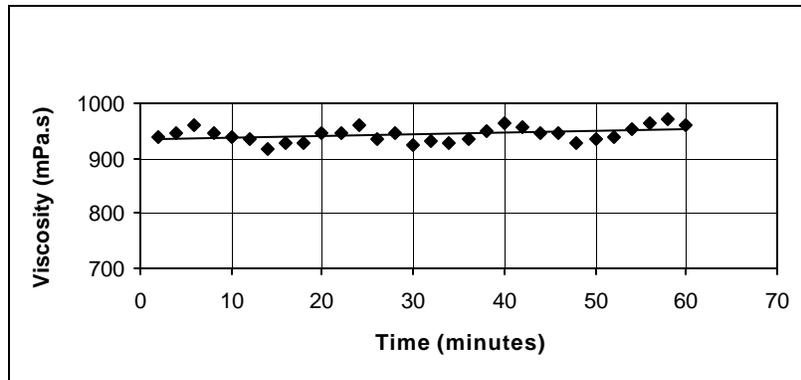


Figure 4.24: Rheological isothermal analysis of the TPDS-Ph/260NOV resin blend at 87°C.

The viscosity of the novolac-phthalonitrile resin mixture (NOV/NOV/TPP) was also investigated using rheology studies. As was observed in the comparison of the TPDS-Ph and TMDS-Ph resins, the highly aromatic nature of this system results in high resin viscosity. The NOV/NOV/TPP resin mixture exhibited a viscosity of 7000 mPa·s at 70 °C. Although an exponential decrease was observed with increasing temperature, the target viscosity of < 1000 mPa·s was not achieved with heating up to 115 °C. The analysis was terminated at 115 °C to avoid curing the resin. The high viscosity of the NOV/NOV/TPP resin was attributed to the use of constituents with high T_g s (260-novolac-phthalonitrile T_g 53°C) and the presence of the triphenylphosphine catalyst, which in FTIR curing studies has been demonstrated to increase the kinetics of the cure reaction. A small amount of progress of the curing reaction leads to significant increases in viscosity.

Rheology studies of the resin mixtures revealed that those with less aromatic nature had lower viscosities at lower temperatures. The TMDS-Ph/260NOV and TPDS-Ph/260NOV resins exhibited processing temperatures of 80 and 87 °C respectively. In addition, the siloxane-containing resins were stable at their respective processing temperatures for at least one hour. In

contrast, the viscosity target (<1000 mPa·s) was not accomplished with heating up to 115 °C for the NOV/NOV/TPP resin mixture, which suggested that this resin was not, at present, suitable for VARTM processing (**Figure 4.25**).

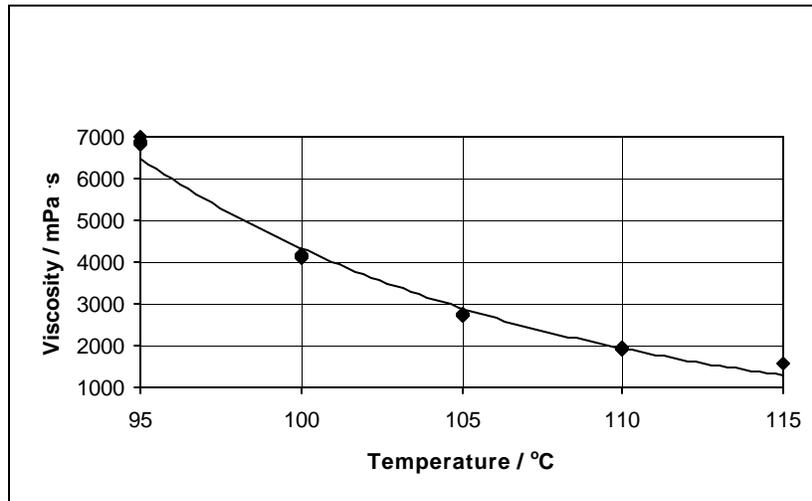


Figure 4.25: Rheological temperature ramp analysis for NOV/NOV/TPP resin blend.

CHAPTER 5: SUMMARY AND CONCLUSIONS

Novel phthalonitrile derivatives were prepared from the chemical modification of novolac oligomers with 4-nitrophthalonitrile and hydrosilation of 2-(3,4-dicyanophenoxy)allylbenzene with siloxane/silane-containing monomers. These new phthalonitrile derivatives afford resins with decreased softening points as compared to the biphenoxyphthalonitrile resins reported in previous studies. In addition, they can be cured with a low molecular weight novolac resin in a 50/50 w/w ratio at 200 °C. In FTIR studies, ~ 90% conversion of nitrile functionality was observed within 30 – 60 minutes. These materials demonstrated the rapid cure schedules desirable in composite processing at temperatures much lower than other phthalonitrile resins previously reported.

Thermal analysis of siloxane-phthalonitrile/novolac networks cured at 200 °C for 1h and 225 °C for 4h did not exhibit glass transition temperatures, T_g s, below 250 °C. Networks from these materials exhibited 5% weight loss temperatures, $T_{5\%}$, between 285 and 418 °C with high char yields (50-56%) at 800 °C in nitrogen. Networks from novolac-phthalonitrile oligomers blended with a 260 g mol⁻¹ novolac resin and 1.5 mol% triphenylphosphine (based on novolac) were cured at 200°C for 1h and did not exhibit T_g s below 250 °C. High thermal stability was observed in both nitrogen ($T_{5\%} \approx 350^\circ\text{C}$ and 70% char) and air ($T_{5\%} \approx 377^\circ\text{C}$ and 13% char). Post-curing (225 °C, 4h) the NOV/NOV/TPP networks resulted in improved thermo-oxidative stability with $T_{5\%} \approx 450^\circ\text{C}$ and 50 % char at 800 °C. The high thermal stability and degree of char formation observed with these materials makes them appealing as composite matrices, including use in carbon-carbon composites.

Rheology studies were performed on the resin blends to predict time-temperature-viscosity parameters. The TMDS-phthalonitrile/260NOV resin had a viscosity of 560 mPa·s at 80 °C, and the viscosity was stable at this temperature for a minimum of one hour. By contrast, comparable viscosities were not observed for the NOV/NOV/TPP resin with heating up to 115 °C. The viscosity of the TMDS-phthalonitrile/260NOV resin at 80 °C meets the requirements for processing via vacuum assisted resin transfer molding.

In summary, these novel phthalonitrile derivatives emerge as viable candidates for highly flame resistant structural thermosets.

CHAPTER 6: FUTURE RESEARCH

Further investigation of the physical properties of the novolac and siloxane/silane-phthalonitrile networks may be performed to determine their mechanical strength. Sol-gel studies can be performed to determine the degree of crosslinking within the networks. Such studies will provide information that may be used to better understand the mechanical and thermal properties. Scanning Electron Microscopy (SEM) may be used to investigate the network structure for defects or voids. This tool will prove useful in explaining deficiencies in the network mechanical strength due to the evolution of volatiles or the presence of ambient water during the curing reaction. Dynamic mechanical analysis (DMA) may be used to obtain accurate glass transition temperatures, which would provide further insight into the performance capabilities of these materials. It would be beneficial to investigate flame properties using cone calorimetry measurements for comparison of the novolac and siloxane/silane-phthalonitrile networks with other flame resistant networks.

Thermally stable, high T_g networks were produced with novolac-phthalonitrile/novolac resins cured with a triphenylphosphine catalyst at 200 °C for 1 hour; however, in the rheology studies the targeted processing viscosity (1000 mPa s) was not achieved with heating up to 115 °C. It may prove worthwhile to investigate novolac-phthalonitrile oligomers of varying compositions of the phthalonitrile functionality (25, 50, 75%) and cure the neat resins. This approach may alleviate the need for a catalyst and impede the reaction just enough to achieve the target viscosity at reasonable temperatures (80-90 °C).

VITA

Shauntrece Nicole Hardrict

On March 7, 1976, in Saint Louis, Missouri, Shauntrece Nicole Hardrict was born to William P. and Karen D.(Merkson) Hardrict. As her parents pursued careers in their respective military fields, Shauntrece received primary care from her grandmother, Odessa Koonce Hardrict. Shauntrece lived the first eighteen years of life in suburban Saint Louis. She matriculated through the Hazelwood School District, to eventually attend Hazelwood East High School. Her family of college-educated professionals instilled the importance of academics in her at a young age. Shauntrece spent her time away from academics at Pelagie Greene Wren Academy of Dance, where she studied and fell in love with dancing. Dance has served as a cathartic form of expression for her for many years. Upon graduating from high school, she attended Howard University in Washington, DC where she received a Bachelor of Science in Chemistry. In Fall 2000, Shauntrece entered the Chemistry program at Virginia Tech and joined the Riffle research group in the Polymer Division. Shauntrece plans to pursue a Doctorate in Organic-Polymer Chemistry, with goals of pursuing a career in the Cosmetics Industry.