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One component propargyl phthalonitrile novolac: Synthesis and characterization

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ABSTRACT

Novolac polymers bearing varying proportions of propargyl and phthalonitrile groups on the same backbone and capable of self and co-curing to a thermally stable matrix have been synthesized. Spectral and thermal studies gave evidence for both homopolymerization of propargyl groups and its co-reaction with nitrile groups during thermal curing. Propargyl groups promoted curing of phthalonitrile groups through the hydroxyl and chromene intermediates formed from the thermal cyclization reactions of this group. Resins rich in propargyl groups showed higher crosslink density and higher modulus values. Among the copolymers, phthalonitrile rich systems exhibited relatively higher thermal stability with initial decomposition temperature at around 435 °C. All the cured compositions showed anaerobic char yields of 73–76% at 900 °C.

1. Introduction

Easily processable matrix resins with high temperature performance are highly demanding for advanced composites used for aerospace and marine applications. Among the class of high performance thermosets, phthalonitrile systems are of much interest owing to their excellent mechanical properties, high glass transition temperature, exceptional thermal stability and chemical resistance and high flame retardancy [1–7]. Studies have revealed that the polymers with pendant phthalonitrile units form different heterocyclic aromatic structures via addition polymerization depending upon the reaction conditions. These thermally and chemically stable network structures make phthalonitrile systems promising candidates for high temperature applications. However, their general features such as small processing window, brittle nature and prolonged cure conditions at elevated temperatures are unacceptable for many practical applications [8–12]. Blending and copolymerization are reportedly effective ways for overcoming the afore-mentioned concerns [13,14]. For crosslinking, phthalonitrile polymers require the aid of either external or internal curing groups. Generally, phenol, aromatic amines, metals, metallic salts and complexes are used as catalysts for nitrile polymerization [15–25]. However in such cases, volatile nature of external curatives adversely affects the structural integrity of polymer network and results in void containing composites.

In our recent studies on bisphenol-based phthalonitrile systems, we have investigated addition curable propargyl resins as possible phthalonitrile curatives [26]. Addition curable groups are much compatible and could aid the polymerization and amend the properties of phthalonitrile resins in terms of thermal and chemical stability [27]. In the previous paper, we had reported a thermosetting blend of propargyl ether resin and phthalonitrile resin. Evidences were obtained for the possible

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reaction between C≡N and propargyl groups. In this paper, we report a unique prepolymer bearing both phthalonitrile and propargyl groups on the same backbone. Its synthesis and cure characteristics are described.

2. Experimental

2.1. Raw materials

Propargyl bromide (80% w/w solution in toluene, Alfa Aesar, Britain), benzyl triethyl ammonium chloride (Spectrochem, Mumbai), and 4 – nitro phthalonitrile (Acros Organics, New Jersey) were used as received. Potassium carbonate was procured from SRL Mumbai and was dried at 120 °C for 5 h. N-methyl pyrrolidone (NMP), N,N-dimethyl acetamide (DMAc), Tetrahydrofuran (THF) and acetone (AR grade) were all received from SRL Mumbai and used as received.

2.2. Synthesis of control oligomers

Control oligomers were realized by the complete conversion of free hydroxyl groups in the novolac backbone into crosslinking active sites of interest. Both Novolac phthalonitrile (NPN) and Novolac propargyl (NPR) oligomers were synthesized according to the procedures in reported literatures [28,29]. The polymers were characterized by –OH value estimation and elemental analysis. They were cured and were compared with resins derived from curing of the control oligomers.

2.3. Synthesis of phthalonitrile–propargyl oligomers (NPN-PR)

NPN-PR oligomers of different compositions were obtained as described here typically for the case of NPN-PR1. In a 250 mL three necked R.B. flask were taken a mixture of novolac phthalonitrile oligomer with free hydroxyl groups (NPN-OH1) (10 g) dissolved in acetone, dried potassium carbonate (15 g) and benzyl triethyl ammonium chloride (0.2 g) and were heated with mechanically stirring under nitrogen purge. When the temperature of reaction mixture reached 45 °C, 5 mL of propargyl bromide was added dropwise and then the temperature was raised and maintained at 60 °C for 5 h. The reaction mixture was cooled to room temperature and the potassium salts were removed by suction filtration. The filtrate was flash evaporated to obtain the resin.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 2.5 (≡CH), 3.96 (Ar–CH_2–Ar), 4.68 (propargyl CH_2) and 7, 7.18, 7.58 (Ar–H). ^{13}C NMR (300 MHz, $CDCl_3$, δ ppm): 76 (≡CH), 78 (C≡C), 57 (propargyl CH_2), 30 (Ar–CH_2–Ar), 150 and 162 (Aromatic C–O–C), 115.5, 121.4, 122.5, 129 and 131 (Aromatic carbon), 115.8 (CN). FT-IR (KBr, cm^{-1}): 3280 (≡CH), 2231 (–CN), 2120 (C≡C), 1025 and 1118 (C–O), 1490, 1500, 1592 and 1660 (Ar–H).

2.4. Curing of NPN-PR oligomers

NPN-PR oligomers were heated in a step-wise manner at different dwell temperatures up to 350 °C. Cure cycle adopted for the present study is represented in Fig. 1.

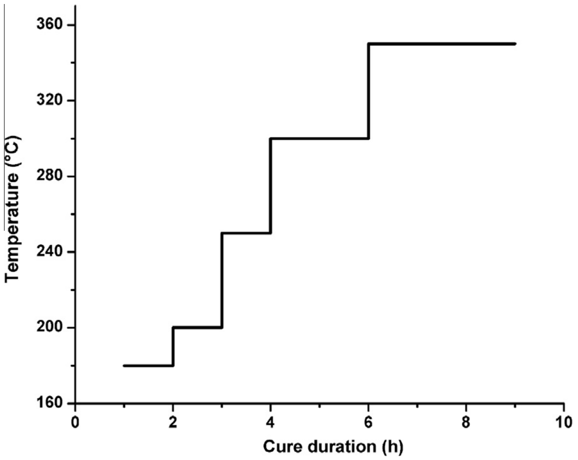

Fig. 1. Cure schedule adopted for one component propargyl–phthalonitrile systems.