

Novel Phenyl-s-triazine-Bearing Polymers

Jin Y. Wang, Zong Lishuai, Dong Nannan, Xi G. Jian¹

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China

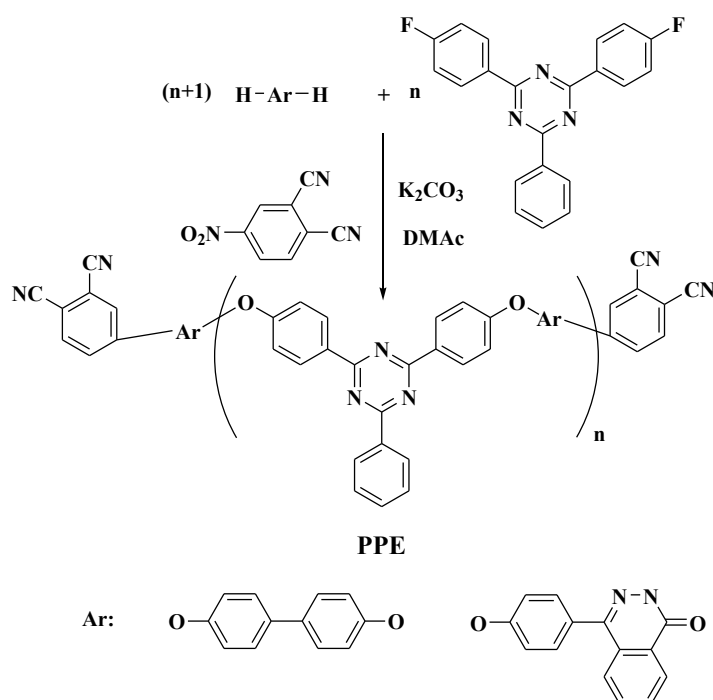
Department of Polymer Science & Materials, Dalian University of Technology, Dalian 116024, China

Email: wangjinyan@dlut.edu.cn

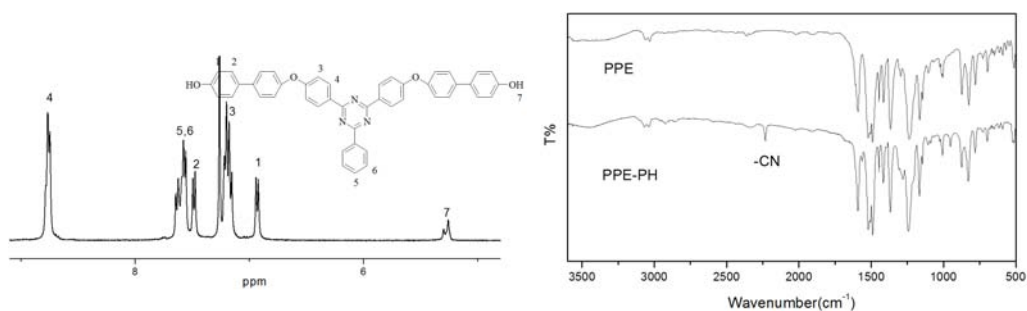
Keywords: phthalonitrile; phenyl-s-triazine; curing; heat resistance

Phthalonitrile resins, by the virtue of the cyano trimerization to form highly thermostable phenyl-s-triazine structures, are well-known for an attracting balance of many desirable properties such as excellent heat-resistance, good flame retardancy and mechanical properties, high chemical resistance and void-free processing, which make them attractive matrix materials or molding materials in marine, aerospace and electronic industries [1-3]. Our group has described the crosslinking of poly(arylene ether amide)s and poly(arylene ether nitrile)s to give insoluble products with excellent thermal stability, most possibly by the cyclization of activated terminal cyano groups [4, 5]. Very recently, we presented the synthesis of four functional aromatic ethers bearing cyano ends and their polymerization in the presence of terephthalonitrile via trimerization, resulting in s-triazine resins with decreased crystallinity and increased thermal stability [6, 7]. To further improve phthalonitrile resins' toughness without sacrifice of their outstanding thermal stability, introduction of phenyl-s-triazine into phthalonitrile monomers or polymers is expected to a unique efficiency method for raising s-triazine concentration and improving the chain length of the phthalonitrile monomers or polymers rather than crosslinking point in the networks of phthalonitrile resin. This paper extends a recent announcement that a novel bisphthalonitrile monomer was readily prepared via of the nucleophilic displacements of various bisphenol with 2-phenyl-4, 6-bis(4-fluorophenyl)-1, 3, 5-triazine, named as PPE, subsequently endcapped by 4-nitrophthalonitrile, referred as PPE-PH, in a dipolar aprotic solvent utilizing a base as catalyst (See Scheme 1). The structures of the resulting oligomers were characterized by FT-IR, ¹H NMR, ¹³C NMR and MODL-TOF (Fig. 1). Their curing behaviors were then investigated in details. This end-capped PPE was polymerized in their melt phase to form green prepolymers Po-PPE with or without the charge of promoting additives, such as aromatic diamines. The amorphous Po-PPE's chemical structure approves to be analogous to that of poly(iminoisindolenine)s. Both Ph-PPE and Po-PPE exhibit good solubility in common solvents (e.g., DMSO, DMF, DMAc, NMP, chloroform, etc) and hence can be processed from the melt or from solution. The insoluble networks Th-PPE prepared by direct curing of Ph-PPE or by post-curing of Po-PPE exhibited excellent thermal properties together with superior long-term thermo-oxidative stabilities with char yield of over 70 %, or upper to 80% after filled with boron carbide. The adhesives from PPE filled with boron carbide showed good mechanical property at 800 °C, the results were shown in Table 1.

¹ Corresponding to Xigao Jian, E-mail: jian4616@dlut.edu.cn, Phone: 86-411-83639223, 84986109
Fax:86-411-83639223, 84986109



Scheme 1. Synthesis of bisphthalonitrile containing phenyl-s-triazine segment



(a) ¹H NMR of PPE-BP

(b) FT-IR of PPE-BP and PPE-BP-PH

Figure 1 Spectra of bisphthalonitrile containing phenyl-s-triazine segment

Table 1 The Shear strength of the adhesives after heating at various temperature for 1 h

Adhesives	Shear Strength (MPa)*					
	r. t.	400 °C	500 °C	600 °C	700 °C	800 °C
PPE-BP-Ph	46.7	46.2	22.5	9.4	9.0	12.6
PPE-DHPZ-Ph	32.1	30.4	10.6	8.4	7.6	10.8

*The adhesive sample was treated in oven at certain temperature for 1 hour and then taken out to put into desiccators to cool down. The sample was measured at room temperature.

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