



## Macromolecular Nanotechnology

# Monomer self assembly and organo-gelation as a route to fabricate cyanate ester resins and their nanocomposites with carbon nanotubes



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## ABSTRACT

A novel method is described for the preparation of porous cyanate ester networks by using the self-assembly and organo-gelation of the monomers and subsequent curing of the xerogels. Dicyanate esters (CE) were synthesized by the reaction of dihydroxy aromatic compounds (OH) with cyanogen bromide (CNBr) in the presence of triethylamine. Structures of the cyanate esters were confirmed by FT-IR, NMR and elemental analyses. Organo gels were prepared from the cyanate ester monomers with a polar aprotic solvent. Introducing single wall carbon nanotubes (CNT) in the monomer solution prior to gelation led to nano-composite gels. The morphology of the gels was studied by optical and scanning electron microscopies. The polymerization of the gels and the gel/single walled CNT composites was studied by differential scanning calorimetry. Polymerization temperature of the cyanate esters decreased with increasing weight percentage (1–5%) of CNT loading. The curing time of the cyanate esters also decreased with an increase in CNT loading. The xerogels were polymerized at 120 °C for 3 h, 170 °C for 1 h and post cured at 210 °C for 1 h. The morphology of the gels of the monomers, as well as those of cured cyanate esters and CNT–cyanate ester nanocomposites were investigated by scanning electron microscope. The morphology of the polycyanurate network consisted of porous fibrous network. The thermal properties of the cyanate ester and CNT–cyanate ester nanocomposites were studied by thermogravimetric analysis. Although the synthesis of cyanate ester resin is a mature area, we present gelation as a way of fabricating porous resins.

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## 1. Introduction

Cyanate ester resins (CE) have recently attracted increasing attention as the next generation thermosetting polymer matrices because of their high thermal stability, excellent mechanical properties, flame resistance, low outgassing, and radiation resistance [1,2]. Applications of cyanate esters include structural, aerospace, electronics, microwave-transparent composites, encapsulates, and adhesives. Cyanate ester resins are superior to conventional epoxy, polyimide, and BMI resins. For example, the moisture absorption of cyanate esters is lower than those of epoxy, polyimide, and BMI resins. High glass

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transition temperatures of cyanate esters fill a temperature regime intermediate between that of epoxy resins and the hazardous/difficult to handle polyimide or BMI resins. Cyanate ester resins are easy to process in a manner similar to epoxy resins. Cyanate esters undergo thermal or catalytic cyclotrimerization to form triazine rings during curing. However, cyanate esters tend to be brittle and have reduced impact resistance like most highly cross-linked thermosets. Although polycyanurate or triazines (i.e., the thermoset network that results from trimerization of the cyanate monomers) can exhibit improved mechanical properties in comparison to other thermosetting polymers, significant improvements in fracture resistance are still needed for many applications [3,4]. Effective toughness enhancement in polycyanurate systems has been realized through the incorporation of thermoplastic additives [5–12] that can withstand higher temperatures than elastomeric species.

Attempts to toughen cyanate ester resins using various thermoplastics have almost always adversely affected one or more key physical properties [13–22]. Fortunately, some very recent developments have enabled overcoming of these problems. One such development is the availability of a wide variety of agents capable of being dispersed at the nanometer scale in thermosetting resin systems. These include polyhedral oligomeric silsesquioxane (POSS) [23,24] in the range of 1 nm in size, functionalized nanoclay particles, and more traditional additives such as the carbon nanotube with 12–30 nm [25,26]. Another development, which will be further explored herein, is the creation of new synthetic routes to cyanate esters that allow enormous diversity in the structure of the starting material, essentially allowing the structure to be tailored at the molecular level. When combined with the developments in nanotechnology and systematic examination of more traditional elastomeric and thermoplastic tougheners, the availability of these new atomically tuned cyanate esters serve as the cornerstone in the systematic design of improved polycyanurate systems. We had previously reported the synthesis and cure characteristics of a polycyanurate, 1,5-bis (4-cyanato phenyl) penta-1,4-dien-3-one (denoted as Pentyl-CE here) and its blends with a commercial bisphenol-A dicyanate ester [27]. In this present work, the effect of the position of carbonyl group and number of alkene carbons between two aromatic groups, including a cyclohexyl group in the spacer has been studied.

Molecular self-assembly mediated by non-covalent interactions such as hydrogen bonding, dispersion forces, and  $\pi$ - $\pi$  interactions has long been studied and emerged as a powerful tool for creating supramolecular architectures of desired dimensions and functionality. Organo- and polymer gels are a state of matter that exploits such self-assembly feature and several studies have been reported in this area [28,29]. Organo-gels of  $\pi$ -systems, with oligo-p-phenylenevinyls (OPV) were first reported by Ajayaghosh et al. [30,31]. Since then gels with perylene tetracarboxylic diimides (PTCDI) and phthalocyanines which are large  $\pi$ -systems have been discussed by us and others [32–40].

Conventional curing of the cyanate ester monomers is performed in the (solid) bulk. Since the cyanate ester monomers bear aromatic groups, in order to explore the applicability of the self-assembly mediated by  $\pi$  interaction, we prepared organo-gels of these monomers and then cured the gels to obtain the resin. We used the monomer 1,5-bis (4-cyanatophenyl) penta-1,4-diene-3-one the synthesis of which had been reported before [27]. In addition, two homologous monomers with a propyl spacer and a cyclohexyl substituent were used. The characteristics of the resins thus prepared are compared with the conventionally cured resins. Further, similar to our previous work [41] on two-component gels of poly (methyl methacrylate) (PMMA)/carbon nanotube (CNT) composites, gels of cyanate ester monomers with CNT were also prepared and cured to fabricate polycyanurate/ CNT composite material.

## 2. Experimental part

### 2.1. Materials

Cyclohexanone was purchased from Aldrich, USA. Acetone, 4-hydroxy benzaldehyde, 4-hydroxy acetophenone, boric acid and cyanogen bromide (CNBr) were purchased from SRL, (India). Triethylamine ( $\text{Et}_3\text{N}$ ) was purchased from E-Merck (India). All reagents were used as received. Triethylamine and acetone were distilled prior to use. The single walled carbon nanotubes (SWNT) were purchased from CarboLex (Batch AP8333). As described in our previous publication [42], the SWNTs were purified by refluxing with 35%  $\text{HNO}_3$  for 24 h followed by repetitive washing with distilled water and centrifuging until a neutral supernatant was obtained. After the removal of carbon species, residual catalysts etc. by this process, the yield was about 70%. These CNTs tend to bundle into ropes. TEM analysis showed the thickness of the SWNT to be approximately 1.4 nm and the average diameter of the bundles to be about 20 nm (TEM and SEM). Similar acid treatment on CarboLex AP series SWNT has been reported by Hu [43] and Hu et al. [44] and the number of acid sites was found to be 6 mol%. (The words CNT and SWNT are used interchangeably in the rest of the paper).

### 2.2. Measurements

Fourier Transform Infrared spectra (FT-IR) were obtained using a Perkin Elmer (spectrum-RX1) spectrometer with KBr pellet.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker SF-II spectrometer at an operating frequency of 500 MHz. The samples were dissolved in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  and TMS was used as internal standard. Elemental analysis (EA) was performed on a Vario micro cube analyzer. Melting points of the precursor and CE were determined on a melting point apparatus (IA 6304). The morphology of the gels was studied using a JEOL JSM-6460 scanning electron microscope. Dried gel samples were coated with gold (80%) and palladium (20%) alloy layer by Hummer VII sputtering system

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