

Bergman cyclopolymerization within the channels of functional hybrid nanocomposites formed by co-assembly of silica and polymerizable surfactant monomer†

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The Bergman cyclopolymerization of polymerizable surfactant monomer was carried out within the hexagonal channels of functional hybrid nanocomposite formed by co-assembly with silica.

Ordered periodic mesoscopic materials allow the construction of composites with many guest types like organic molecules or polymers. Inclusion of dye molecules such as Coumarin 40, Rhodamine BE50, Oxazine 1 inside the nanopores has been demonstrated.^{1–3} Nanocomposites that contain conjugated polymers confined within a silica matrix show enhanced conductivity, mechanical strength, processability, environmental stability, and other unique properties⁴ that allow for potential use in light emitting diodes, information storage devices, optical signal processors, and sensors. To name a few, nanocomposite formation of polymers such as poly(phenylene vinylene),⁵ polyaniline,⁶ polydiacetylene,⁷ poly(2,5-thienylene ethynylene),⁴ polythiophene, polypyrrole, and polyacetylene^{8,9} have been reported. Several synthetic efforts to obtain such nanocomposites used mainly slow procedures like monomer or polymer infiltration of inorganic nanostructures^{5,10–13} or sequential deposition.^{14,15} Such nanocomposites are heterogeneous, exhibiting two distinct conjugated polymer environments, that is, polymers inside and outside the hexagonally arranged pore channels of the silica particles. However, self-assembly, one of the few practical strategies for making ensembles of nanostructures provides one solution to the fabrication of ordered aggregates from components with sizes from nanometers to micrometers.¹⁶ It typically employs asymmetric molecules that are pre-programmed to organize into well-defined supramolecular assemblies.

The use of polymerizable surfactants as both structure-directing agents and monomers in various evaporation-driven self-assembly schemes represents a general, efficient route to the formation of robust and functional nanocomposites.⁷ In this research we utilize this self-assembly⁴ route to form mesostructured polynaphthalene/silica nanocomposites. One of the many approaches to form the polynaphthalenes (PN) is through Bergman cycloaromatization,^{17,18} a remarkable isomerization in which an endiyne forms an arene 1,4-diradical. Here, we make use of this approach with a

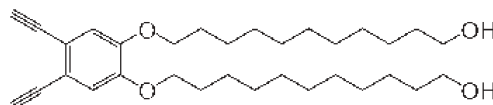


Chart 1 Chemical structure of amphiphilic surfactant monomer.

materials synthesis view-point. Amphiphilic polymerizable surfactant monomer was synthesized (Chart 1).

It has two long alkyl chains with hydrophilic hydroxyl head groups at one end and the phenyl ring with two terminal acetylene groups *ortho* to each other at the tail end. (see Supplementary Information† for synthetic details).

Beginning with a homogeneous solution of soluble silica—tetraethoxy orthosilicate (TEOS), acid catalyst, and surfactant monomer in ethanol–water solvent, thin films were drawn by dip-coating or spin-coating. Solvent evaporation during the coating process enriches nonvolatile components and induces their co-assembly into liquid crystalline mesophases.⁴ Polymerization of silica during the coating process freezes the mesophases and spatially organizes the monomer surfactant into mesostructures. These films were vacuum-dried overnight and kept immersed in benzene in thick-walled screw cap glass tubes which were capped in the glove box under nitrogen atmosphere prior to heating (see Supplementary Information for experimental details†).

Fig. 1 A and B show scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the nanocomposite formed after the evaporative self-assembly from the gel solution mounted on the substrate, respectively. The highly ordered nanocomposite shows a center-to-center spacing of 53 Å.

X-ray diffraction (XRD) patterns of the nanocomposites before (solid lines) and after (dashed lines) the Bergman cyclopolymerization are shown in Fig. 1D. Along with an intense diffraction peak at around $2\theta = 1.93$, additional higher order diffraction peaks are ‘clearly’ observed at $2\theta = 3.3, 3.8,$ and 5 . The intense one is attributed to the [100] orientation of the hexagonal mesophase. There was no change in the XRD peak position for the heat-treated (polymerized) sample, except a decrease in the intensity of the spectrum which indicates that the nanocomposite is intact even after heat-treatment (polymerization). Energy dispersive spectroscopy (EDS) elemental analysis identified carbon, silicon and oxygen as expected for the nanocomposite prepared and is shown in Fig. 1C.

The topochemistry generated during the co-assembly favors the Bergman cyclopolymerization. Formation of polymer within the hexagonal channels of the nanocomposite was verified by UV-vis

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† Electronic supplementary information (ESI) available: Scheme, synthetic and experimental details. ¹H NMR and EI-MS data of surfactant monomer (S1–S7). See DOI: 10.1039/b603195a

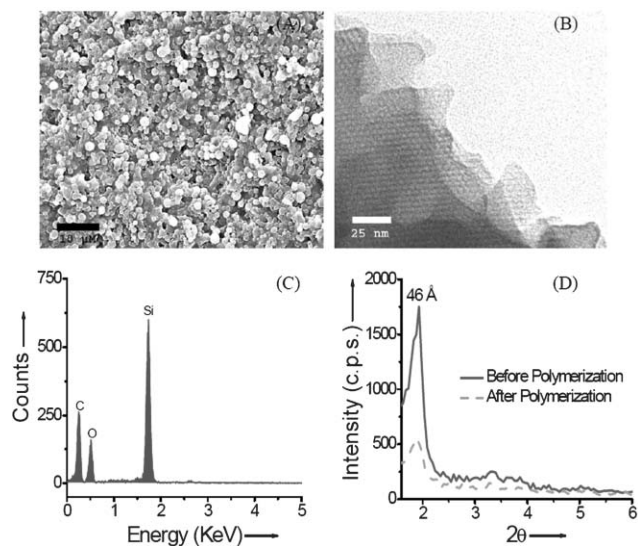


Fig. 1 (A) SEM (B) TEM (C) EDS and (D) XRD of the monomer/silica nanocomposite formed.

and photoluminescence spectroscopy. UV-vis spectroscopy has been used previously to relate the degree of polymerization and absorbance.⁴ Fig. 2A shows the absorption spectra of the nanocomposite before and after the polymerization. Monomer nanocomposite showed maximum absorbance at about 285 nm, whereas polymer nanocomposite showed absorbance between 345 to 390 nm tailing up to 450 nm, indicating extensive conjugation of the polymer backbone.¹⁹ Direct molecular weight determination of such type of polymer/nanocomposite films is difficult.⁴ Monomer nanocomposite showed photoluminescence (PL) in UV-blue region with maximum peak at 353 nm. After polymerization, the photoluminescence was red-shifted with a maximum peak at 415 nm and a shoulder at around 483 nm.

Bergman cyclopolymerization of the monomers with terminal acetylene groups, as in the present case, generally gives insoluble polymers,²⁰ making their characterization difficult. We carried out the polymerization of surfactant monomer dissolved in benzene as described in literature.²⁰ Heating the monomer at about 140 °C for one day indeed afforded insoluble red brown solid. Monomer and

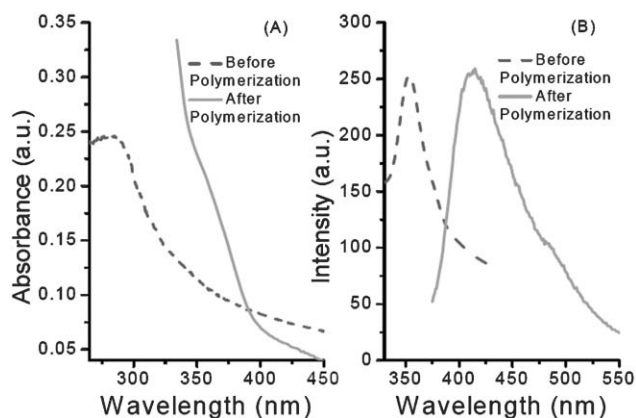


Fig. 2 (A) UV-vis absorbance and (B) normalized PL spectra of the nanocomposites formed.

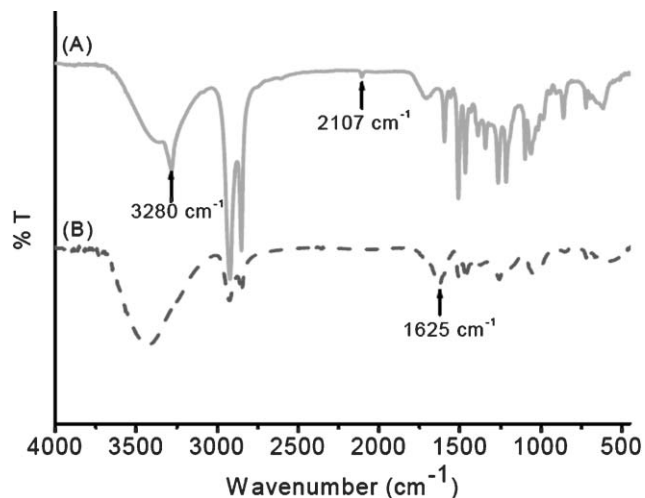


Fig. 3 FTIR spectra of (A) monomer and (B) polymer formed by heating monomer in benzene.

polymer were characterized by infra-red (IR) spectra for comparison, as shown in Fig. 3. The characteristic alkyne triple bond C–H and C=C stretching bands at 3280 and 2107 cm^{-1} , respectively, present in the monomer disappeared after the polymerization.²¹ A new broad and strong band at 1625 cm^{-1} , due to C=C stretching was observed, indicating formation of polymer with extensive conjugation.¹⁹ The degree of polymerization in thin film and in bulk might be different as these are two different environments and should affect the extent of conjugation. There are controversies regarding the structure of the polymer formed by Bergman cyclization of monomer with terminal triple bonds, as presence of five-membered ring and terminal triple bonds has been reported recently.²² However, from the IR spectra shown above, the possibility of presence of terminal triple bonds in the final product is ruled out in this case. Enhanced topochemistry due to the self-assembly and orientation of the surfactant monomers within the inorganic framework limits the formation of unidentified polymeric by-products, thereby giving small chain polynaphthalenes or their oligomers. We envisage formation of low molecular weight PN obtained by Bergman cyclization of polymerizable surfactant monomer within the hybrid nanocomposites formed by evaporative self-assembly. The polymers thus obtained could be soluble and be applied in opto-electronic devices. This route to polynaphthalenes (or polyphenylenes) and their derivatives is most attractive since it requires no exogenous chemical catalysts or reagents for the polymerization.

In summary, we have demonstrated Bergman cyclopolymerization of polymerizable surfactant monomer within the hexagonal channels of functional hybrid nanocomposite formed by evaporative self-assembly. Such a technique allows the patterned polymerization of the polymer precursor material directly onto a surface, thus avoiding solubility related problems that may be encountered when attempting to directly coat the pristine polymeric material, which is often insoluble,²⁰ thereby facilitating its use in device fabrication.

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