



# Controlling the growth of polycarbazole within the silicate galleries using peroxides via microwave-assisted green synthesis

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## HIGHLIGHTS

- Benign synthesis of poly(carbazole)/clay nanocomposites via microwave irradiation.
- Influence of peroxide on the morphology.
- Controlled morphology of PCz extracted from clay.
- Controlled growth within confined clay gallery.

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## ABSTRACT

The scientific challenges involved in the creation of organic–inorganic hybrid materials based on layered silicates with controlled morphological, optical and electronic properties have evolved considerable interest during the last few decades. The interlayer gap in the Bentonite clay provides an interesting, confined environment for the accommodation of the guest molecule at the nanoscale. Moreover, solid state reactions carried out using the reactants confined in clays, zeolites, silica, alumina or other matrices via microwave irradiation not only produce structures of controlled growth but bring down the handling costs due to simplification of experimental procedure which is important in terms of environmentally benign large scale industrial synthesis. This article highlights for the first time the effect of peroxides in controlling the properties of polycarbazole (PCz) within the Bentonite clay interlayer space in terms of morphology, spectral, and fluorescent properties synthesized through microwave-assisted solid-state intercalation. The orientation of the polymer within such restricted nanoscale environment is expected to be a significant solution for obtaining a better control of the molecular architecture.

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## 1. Introduction

The preparation, characterization, and study of polymer-layered silicate nanocomposites constitutes one of the most promising research fields in materials chemistry. These nanocomposites often possess enhanced mechanical, thermal, gas-barrier, and flame-retardant properties, as compared to the pristine polymer or clay [1]. Another important aspect is the possibility of conferring synergistic properties through guest–host interaction via intercalation of functional organic moieties into the inorganic layered hosts. Polymer intercalated structures are formed when polymer chains are intercalated between the silicate layers. This results in the formation of a well ordered structure of the polymer within the inorganic layers. Most of the conducting polymer based clay nanocomposites such as polypyrrole (Ppy) and polyaniline-(PANI) have been

synthesized either by chemical methods or by electrochemical methods [2–4].

The facile chemistry of synthesis of conducting polymer (CP) can broadly be classified as electrochemical and chemical oxidative polymerization methods. The oxidizing agent traditionally employed for the polymerization of CPs is ammonium persulfate, which yields an insoluble and infusible polymer. Moreover, the removal of inorganic byproducts from the synthesized polymer is also difficult. Several other oxidizing agents such as  $K_2Cr_2O_7$ ,  $FeCl_3$ ,  $KMnO_4$ ,  $KBrO_3$ , and  $KClO_3$ , have been reported in literature for the synthesis of CPs [5]. Another oxidant that has also been used for the synthesis of CPs, especially, PANI is hydrogen peroxide [6–9]. Recently attempts have been made to synthesize CPs using milder oxidizing agents such as benzoyl peroxide and metal/enzyme catalyzed  $H_2O_2$  [10]. Although nanofibers have been obtained in some  $Fe_{2+}/H_2O_2$  systems, in many instances, there is loss of nanofiber morphology and a significant reduction in bulk conductivity as a result of defects introduced along the polymer backbone. Benzoyl peroxide (BPO) and hydrogen peroxide ( $H_2O_2$ ) can be used as

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effective oxidants to achieve the desired growth of CPs resulting in controlled morphology. Among the extensively studied CPs such as PANI and Ppy, the intense interest in carbazole containing polymers developed with the discovery of polymeric light emitting diodes [11,12]. Polycarbazole (PCz) can be synthesized using chemical and electrochemical methods. PCz and its derivatives are being extensively studied as the electro-photographic photoreceptors, light-emitting diodes, and photovoltaic devices [13,14]. The application of microwave irradiation for polymerization and intercalation in clays has been developed because they offer a green and inexpensive route for synthesis that also results in higher yields within short reaction time [15,16]. Compared to the conventional heating methods, microwave irradiation has significant advantages of microwave dielectric and molecular selective heating without hysteresis effect. Microwave irradiation can provide specific effects pertaining to the selective absorption of microwave energy by polar materials [17,18]. The use of microwave irradiation for solid state intercalation of organic moieties in clays has been reported by several authors [19–24]. The results of these studies have shown that the reactions are very rapid at controlled temperatures with significant reduction of the activation energy.

The present study reports for the first time the influence of peroxides on the controlled growth of nanoscale polycarbazole (PCz) synthesized by microwave-assisted solid state intercalation and polymerization in Bentonite clay galleries. Varying amounts of benzoyl peroxide (BPO) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were used as oxidants for the intercalation of PCz. The polymerization of PCz within the clay galleries was confirmed by FT-IR analysis while the electronic structure was confirmed by UV-visible spectroscopy. The extent of intercalation and the morphology of the PCz in Bentonite galleries was determined by XRD and TEM analyses respectively. Fluorescence spectroscopy was used to delineate information about the variation in the fluorescent characteristics with the change in the oxidant.

## 2. Experimental section

### 2.1. Materials

Bentonite (Sigma Aldrich, USA), carbazole (Cz) (Sigma Aldrich, USA), Benzoyl peroxide (BPO) (Sigma Aldrich) hydrogen peroxide (30%) (Merck, India), N-methyl-2-pyrrolidone (NMP) (Merck, India), and methanol (Merck, India) were used without further purification.

### 2.2. Synthesis of bentonite-PCz nanocomposites using peroxides

The microwave irradiation was carried out for 180 s in a Ladd Research Laboratory microwave oven (MW frequency, 2500 MHz; power source, 230 V to 50 Hz; energy output, 800 W; input power, 1200 W). Prior to the synthesis, the microwave oven time was set to 180 s, temperature to 35 °C, ramp rate to 15.0, the cycle time to 4.0, and proportional band to 10.0. Bentonite clay (1 g) was mixed with different loadings of carbazole (0.25, 0.5, and 1 g), BPO (0.36, 0.7 and 1.47 g) and  $\text{H}_2\text{O}_2$  (0.005, 0.1 and 0.2 g) respectively using agate mortar and pestle as reported in our earlier studies [24]. The mole ratio of oxidant ( $\text{BPO}/\text{H}_2\text{O}_2$ ): Monomer (carbazole) was taken to be 1:1. During microwave synthesis, the color of Bentonite clay changed from cream to green which indicated the polymerization of carbazole within the Bentonite galleries. The nanocomposites obtained were then washed with distilled water and methanol several times and dried in a vacuum oven at 70 °C for 72 h to ensure complete removal of impurities, methanol, and water. The color of the nanocomposites was green. However, the intensity of the color was dependent upon the amount of carbazole initially taken.

In the case when carbazole was taken in the ratio Bentonite: carbazole, 1:0.25, the color was lighter as compared to the ratio Bentonite: carbazole, 1:0.5. The nanocomposites were designated as Bentonite:PCz:Oxidant ( $\text{BPO}$ ,  $\text{H}_2\text{O}_2$ )-1:0.25, 1:0.5, and 1:1 based on the weight ratios of Bentonite:carbazole initially taken.

### 2.3. Polymer extraction

PCz present in the Bentonite galleries was extracted by refluxing the polymer/clay nanocomposite in methanol overnight while stirring. The PCz was separated from the solid clay nanoparticles by centrifugation.

## 3. Characterization

FT-IR spectra of nanocomposites were taken in the form of KBR pellets on FT-IR spectrophotometer model Shimadzu IRA Affinity-1. The integrated absorption coefficient,  $\int ad\bar{\nu}$ , of the NH absorption peak between  $3420\text{ cm}^{-1}$  and  $3350\text{ cm}^{-1}$  for PCz and the peak of the SiO stretching vibration at  $1047/1042\text{ cm}^{-1}$  were determined using the IRA Affinity-1 software. UV-visible spectra were taken on a UV-visible spectrophotometer model Shimadzu UV-1800 using NMP as solvent.

In precision analytical determinations, the integrated absorption coefficient,  $\int ad\bar{\nu}$ , is used in place of the absorption coefficient at the maximum wavelength,  $\lambda_{\text{max}}$ .  $\int ad\bar{\nu}$ , was obtained from the area under the transition peak when the spectra were plotted as an absorption coefficient vs wavenumber. The area under the peak was obtained using Origin 6.1 which was standardized to the Gaussian-Lorentzian shape. For the determination of oscillator strength of the UV-visible peaks of each nanocomposite, the molar mass, Mw, of four Cz units were taken into account for obtaining a normalized molarity. X-ray diffraction patterns of the nanocomposites were recorded on a Philips PW 3710 powder diffractometer (nickel-filtered  $\text{Cu K}\alpha$  radiation).

Transmission electron micrographs (TEM) were recorded on Morgagni 268-D TEM, FEI, USA. The sample were prepared by placing an aqueous drop on a carbon-coated copper grid and subsequently drying in air before transferring it to the microscope, operated at an accelerated voltage of 120 kV. GPC measurements were carried out on 148 a Viscotek GPC Max AUTO sampler system consisting of a 149 pump, a Viscotek UV detector, and a Viscotek differential 150 refractive index (RI) detector. A Viscogel GPC column 151 (G2000HHR) (7.8 mm internal diameter, 300 mm length) was used. The effective molecular weight range of the column used was 456–42,800. THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. Both detectors were calibrated with 155 polystyrene (PS) standard having narrow molecular weight distribution. The data were analyzed using Viscotek OmniSEC 157 Omni-01 software. Molecular weights were calculated with the help of polystyrene standard.

## 4. Results and discussion

Polymerization of Cz has been well documented in literature which is a two step reaction [25]. The initial step is a one-electron oxidation of the monomer to form a radical cation. The second step is a coupling reaction of two radical cations to form a dihydro-dimer dication, which is followed by the elimination of two protons to form the dimer [26]. As the oxidation of dimer is easier than that of monomer, a radical cation of dimer undergoes further coupling reactions with other radical cations [26]. Microwave irradiation provides abundant thermal energy to carbazole and oxidant molecules to diffuse into the basal spacing of the Bentonite, and polymerization occurs under solid state conditions in pres-

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