



## Research paper

# Synthesis of palygorskite/polystyrene nanocomposites without crosslinked network via in-situ radical bulk polymerization technique

Peng Liu<sup>a,\*</sup>, Hongxing Wang<sup>a</sup>, Changou Pan<sup>a</sup>, Mingliang Pei<sup>a</sup>, Aiqin Wang<sup>b</sup>

<sup>a</sup> State Key Laboratory of Applied Organic Chemistry and Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

<sup>b</sup> Key Laboratory of Clay Mineral Applied Research of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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## ABSTRACT

Clay/polymer nanocomposites have attracted more and more attention owing to their superior performance for potential applications. The in-situ polymerization has been regarded as the promising strategy for the mass production of the clay/polymer nanocomposites with well-defined interfacial property. However, the gelation usually accompanies with the grafting reaction during the polymerization especially for the high aspect ratio nanomaterials, resulting to crosslinked network. In order to solve the problem, the thiol-modified palygorskite nanorods (Pal-SH) were prepared as clay-based chain transfer reagent for the radical bulk polymerization of styrene, as an example. With different dosages of the Pal-SH nanorods from 0.5% to 1.0% and 2.0%, well-defined polystyrene grafted palygorskite nanorods (Pal-PS) were obtained without crosslinked network, with high grafting percentage (PG%) of 40.0, 43.2, and 51.3% respectively. The proposed approach provides a promising technique for the mass production of high aspect ratio nanomaterials-based polymer nanocomposites with well-defined interfacial property, especially avoiding crosslinked network.

## 1. Introduction

Clay/polymer nanocomposites have attracted the growing interest of both academia and industry owing to their unexpected excellent properties, such as remarkably enhanced mechanical, thermal, dynamic mechanical, adhesion and barrier properties, flame retardancy, etc. (Bitinis et al., 2011). It is now well-known that the properties of the nanocomposites depend significantly on the chemistry of polymer matrices, nature and of modification clays, as well as the preparation methods. And the uniform dispersion of clays in polymer matrices is a general prerequisite to achieve improved physical and mechanical characteristics (Abate et al., 2008; Kotal and Bhowmick, 2015). On the other hand, the combination of enhanced properties, weight reduction, and low cost has led to interesting commercial applications such as automotive and packaging (Bitinis et al., 2011).

The physical blending technology seems a facile strategy for mass production of clay/polymer nanocomposites, in which the clay nanomaterials should be modified (usually with surfactants) to reduce their surface polarity in order to improve their dispersibility. However, the challenge is still remained on the impact of modifying clays by extracting the surfactant as most of the surfactants decompose very early to products which catalyze the degradation of the polymer matrix and

provoke earlier ignition resulting in deteriorating the fire retardance properties (Kotal and Bhowmick, 2015). Comparatively, the in-situ polymerization technique shows promising practical potential due to the better compatibility of clay nanomaterials in polymer matrices. It should be attributed to the better dispersibility in the monomers, which show much lower viscosity than the polymer melts or solutions in the physical blending technology. Furthermore, the better interfacial property could also be achieved in the in-situ polymerization technique, via the grafting polymerization of the monomers from the surface of the clay nanomaterials. The resulting polymer chains covalently bound to the clay nanomaterials tend to promote their dispersion into the polymeric matrix. To be specific, the polymerizable vinyl groups were immobilized on the surface of the clay nanomaterials, then they were copolymerized with the monomers to form the polymer brushes grafted on the clay nanomaterials (Zhao and Liu, 2008), which could significantly improve the interfacial property between the clay nanomaterials and the polymer matrices. Moreover, the problem resulted from the small-molecular surfactants could be perfectly solved.

However, the chemical crosslinking had been reported with the polymerizable group modified nanomaterials as crosslinkers via the in-situ polymerization technique (Liu et al., 2014a; Qi et al., 2011), due to the crosslinking role of the functional clay nanomaterials with more

\* Corresponding author.

E-mail address: [pliu@lzu.edu.cn](mailto:pliu@lzu.edu.cn) (P. Liu).

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than one polymerizable group. The crosslinking occurred in the systems with the 0- or 1-dimensional nanomaterials, but not the 2-dimensional layered nanomaterials because of the big space hindrance. It was also found to be independent of the polymerizing conditions (Liu et al., 2014b) but affected by the aspect ratio and modifying levels of the clay nanorods (Zhu et al., 2016a). Although such crosslinked structure was found to be beneficial to improve some properties of the composites, such as thermal property, hardness, and mechanical strength (Haraguchi et al., 2018; Liu et al., 2014b; Qi et al., 2011), it would lead to a fatal weakness, processability (Zhu et al., 2016a).

The radical chain transfer polymerization technique has provided another method to form the polymer-tethered surface for various applications (Chen et al., 2011; Huang et al., 2017; Khire et al., 2006; Liu et al., 2004a; Wang et al., 2008; Yang et al., 2017), based on the surface-modified chain-transfer agents. The approach had also been used to synthesis of polymer-grafted layered clay and clay/polymer composites. For example, Survant et al. recently prepared a polystyrene-organoclay composite by surface-initiated radical polymerization of styrene from the surface of thiol-functionalized layered organoclays synthesized in a one-step process (Survant et al., 2016). The direct covalent bonding between the polystyrene and the clay layers was found with a high PG% of 49.8%, as well as the essentially exfoliated structure of the layered clays. And the resulting polymer chains covalently bound to the inorganic layers tend to promote the dispersion of the organoclay layers into the polymeric matrix. Akat et al. prepared poly(methyl methacrylate) (PMMA) and polystyrene (PS) nanocomposites by in-situ free radical polymerization using intercalated chain transfer agent (diethyl octyl ammonium ethylmercaptan bromide) in the layers of montmorillonite (MMT) clay (Akat et al., 2008). And the exfoliation/intercalation structures were found to be related to the loading degree.

By now, to the best of our knowledge, there is no report on the radical chain transfer polymerization to synthesize clay/polymer nanocomposites containing 1-dimensional nanomaterials, such as nanorods or nanotubes, which would lead to crosslinked network during the radical copolymerization after being modified with polymerizable group. In the present work, the thiol-modified palygorskite nanorods (Pal-SH) were prepared as clay-based chain transfer reagent for the radical bulk polymerization of styrene. And the formation mechanism of the resultant clay/polymer nanocomposites, which were composed of free un-grafted polystyrene (PS) and the polystyrene grafted palygorskite nanorods (Pal-PS) nanorods, was speculated. Taking it as an example, a promising strategy was established for the mass production of the high aspect ratio nanomaterials-based polymer nanocomposites with well-defined interfacial property, but no crosslinked network.

## 2. Experimental section

### 2.1. Materials and reagents

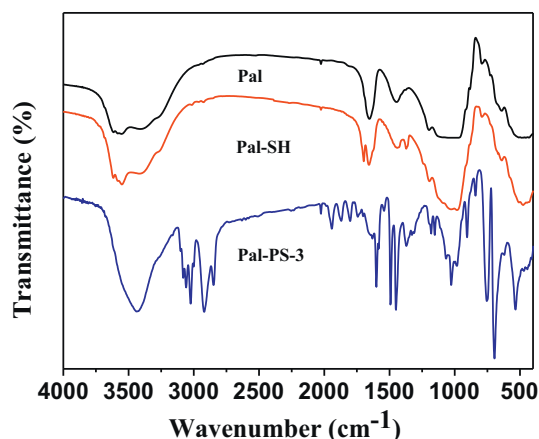
Palygorskite (Pal) nanorods (Jiangsu Goldstone Attapulgit R&D Center Co. Ltd., Xuyi, China) were dried at 120 °C for 24 h before use. 3-Mercaptopropyltrimethoxysilane (MPTMS, 97%) was purchased from J & K Scientific Co. Ltd., Beijing, China. Styrene was washed with dilute alkali solution, dried over barium oxide, and distilled under reduced pressure. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN) (Tianjin Chemicals Ltd. Co. Tianjin, China), was re-crystallized in methanol. Absolute ethanol, toluene and other reagents were analytical grade and used as received.

### 2.2. Preparation of pal-SH

The clay-based chain transfer reagent, Pal-SH nanorods, was prepared with the optimized condition to reduce as much as possible the covalent aggregation of the nanorods via locking effect and welding effect (Liu et al., 2018). Specifically, 1.00 g Pal nanorods were dispersed

**Table 1**  
Percentage of grafting (PG%) of the Pal-PS nanorods in the Pal/PS nanocomposites prepared with different Pal-SH amounts.

Samples	St (g)	Pal-SH (g)	PG (%)
Pal/PS-1	5.0	0.025	40.0
Pal/PS-2	5.0	0.050	43.2
Pal/PS-3	5.0	0.100	51.3



**Fig. 1.** FT-IR spectra of the pristine Pal, Pal-SH and Pal-PS nanorods.

into 20 mL absolute ethanol containing 0.10 mL MPTMS with ultrasonication for 2 h. After refluxing at about 70 °C for 8 h, the product was separated by centrifugation (10,000 rpm for 8 min), and washed with ethanol by ultrasonication for 30 min for three times. Finally, the Pal-SH nanorods were dried at 40 °C for 24 h.

### 2.3. In-situ polymerization

Pal-SH nanorods (0.025, 0.050 or 0.100 g, as 0.5%, 1.0% and 2.0% mass of styrene, Table 1) and azodiisobutyronitrile (AIBN, 0.50% mass of styrene) were ultrasonically dispersed into 5.0 g styrene in N<sub>2</sub> for 30 min. Then the mixture was heated at 80 °C for 3 h with stirring, and 100 °C for 5 days to achieve the monomer conversion near 100% (Liu et al., 2014b; Zhu et al., 2016a).

#### Table 1.

Parts of the resultant palygorskite/polystyrene (Pal/PS) nanocomposites were Soxhelt extracted with toluene for 3 days to separate the free un-grafted PS and the Pal-PS nanorods. And the grafted PS was cut off from the Pal nanorods by treating with HF, as reported previously (Liu et al., 2004a).

### 2.4. Analysis and characterization

Fourier Transform Infrared (FTIR) Spectrometer (NEXUS 670, Nicolet, Germany) was used to confirm the feature groups of samples in the range of 400–4000 cm<sup>-1</sup>, using KBr pellet method.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB 250Xi-XPS photoelectron spectrometer (ThermoFisher Scientific, USA) with an Al K $\alpha$  X-ray resource. The binding energies were calibrated by the C1s binding energy of 284.7 eV.

The morphological analysis of the Pal nanorods was carried out on a JEM-1200 EX transmission electron microscope (TEM, JEOL Ltd., Japan). The samples were dispersed in toluene. The carbon-coated copper grid was dip-coated in the dispersions of the samples, and dried at room temperature before observation.

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system (Perkin-Elmer, USA) at a scan rate of 10 °C/min from room temperature to 800 °C with nitrogen as the carrier gas at a

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