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In-situ preparation of poly(2-ethyl-2-oxazoline)/clay nanocomposites via living cationic ring-opening polymerization

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ABSTRACT

The present study reports for the first time the preparation of poly(2-ethyl-2-oxazoline)/clay nanocomposites. The tosyl-functionalized montmorillonite clay is utilized as initiator for the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline, which triggers the delamination of silicate layers in the polymer matrix and leading to nanocomposite formation. The living nature of the polymerization has been confirmed by kinetic studies. The morphology and thermal properties of nanocomposite have been evaluated using X-ray diffraction, transmission electron microscopy, differential scanning calorimeter and thermogravimetric analysis. All nanocomposite samples have a mixed exfoliated/intercalated silicate layers and an improved thermal stability compared to pure poly(2-ethyl-2-oxazoline).

1. Introduction

Polyoxazolines (POx)s are stimuli responsive, biocompatible, nonionic, and highly soluble polymers [1]. Based on their superior properties including low toxicity and stealth behavior they are currently investigated for various different applications such as drug delivery, protein adsorption and antibacterial materials [2]. Due to the amide functions in both the main and side chains, these polymers are structurally isomers of both polyacrylamides and polypeptides [3,4]. These polymers can be synthesized by cationic ring-opening polymerization of 2-alkyl-2-oxazolines by using various initiators such as methyl tosylate, methyl triflate, and benzyl bromide [5,6]. The living nature of the polymerization allows the synthesis of numerous well-defined functional polymers together with the access to both hydrophobic and hydrophilic monomers [7–14]. Water-soluble polymers are accessible using small aliphatic side chains such as methyl, ethyl and different variants of propyl, whereas larger aliphatic or aromatic substituents result in hydrophobic polymers [5,15]. These features result in different polymer properties that make them suitable for biomedical applications [1,16–18]. However, their films exhibit very poor mechanical properties and show sensitivity to atmospheric moisture that still need to be improved in order to extend their use in other engineering applications [19]. The addition of a very small amount of reinforcing nanoparticles into a continuous polymer matrices leads to polymer nanocomposite formation, which show significant improvements in both thermal and mechanical properties of the corresponding polymer [20–24]. Clay minerals such as bentonite, montmorillonite, hectorite

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and synthetic mica are layered silicates composed of alumina and silica nanosized sheets stacked on top of each other in different combinations [25]. Due to their structural features (van der Waals forces holding layers together) and surface energies (incompatibility of the hydrophilic clay with the hydrophobic polymer), the dispersion of individual layered silicates without agglomeration in the polymer matrix is difficult to achieve [26,27]. The cation exchange technique does not only change the surface chemistry of the silicate layers, but also expands the basal spacing of them. Thus, the layered silicates are compatible with polymer matrix by increasing intermolecular interactions between them. There are three different techniques that have been used for the preparation of polymer/clay nanocomposites; solution exfoliation, melt intercalation and *in-situ* polymerization. *In-situ* polymerization is the most commonly used technique as it enables chain growth of polymer molecules in the silicate layers of nanoclays, which leads to the better exfoliation and interaction between clay and polymer matrix.

The important aspect in nanocomposite preparation is to find an efficient method that ensures the complete exfoliation of silicate layers and, simultaneously, provides more control over the polymer molecular characteristics such as functionality, molecular weight, architecture, composition and dimension. Controlled and living polymerization techniques enable production of well-defined polymers, which improve the intermolecular interactions as well as the exfoliation of clay layers in the nanocomposite formation. In recent years, various polymerization techniques such as conventional free radical polymerization [28–32], controlled radical polymerization [27,33–40], ring-opening polymerization [33,41–48], living cationic polymerization [49], living anionic polymerization [50,51], and click reactions [49,52–54] have been described for the *in-situ* preparation of polymer/clay nanocomposites. To the best of the authors' knowledge, there is no example for the preparation of polyoxazoline-based clay nanocomposites in the literature. Here, we report an efficient living cationic ring-opening polymerization (CROP) of 2-ethyl-2-oxazoline that is initiated by functionalized initiator anchored nanoclays and allows for the *in-situ* preparation of poly(2-ethyl-2-oxazoline)/montmorillonite (PEtOx/MMT) nanocomposites. The living nature of polymerization has been examined by kinetic studies. The morphologies and thermal properties of obtained PEtOx/MMT nanocomposites have been characterized by spectroscopic, microscopic and thermal analyses.

2. Experimental

2.1. Materials

Organo-modified montmorillonite clay modified by methyl bis(2-hydroxyethyl) tallow alkyl (containing ~65% C18; ~30% C16; ~5% C14 atoms) and ammonium ions, commercially known as Cloisite 30B (MMT-($CH_2CH_2OH)_2$), was purchased from Southern Clay Products (Gonzales, TX). Its organic content was calculated from thermogravimetric analysis and was found as 21 wt%. The clay was dried under vacuum at 110 °C for 1 h prior to use. Tosyl-functionalized montmorillonite clay (tosyl-MMT) was synthesized according to reported literature [11,13]. 2-Ethyl-2-oxazoline (Aldrich, ⩾99%), acetonitrile (J.T. Baker, ⩾99%) and triethylamine (Aldrich, HPLC grade) were purified by distillation prior to use. *p*-Toluenesulfonyl chloride (Alfa Easer, 98%) were used as received. All other solvents (methanol, dichloromethane and cold diethyl ether) were purchased commercially and used fresh from the apparatus or stored with drying agent.

2.2. In-situ preparation of poly(2-ethyl-2-oxazoline)/montmorillonite (PEtOx/MMT) nanocomposites

All nanocomposites were prepared by using slightly modified literature procedure [55]. A monomer 2-ethyl-2-oxazoline (EtOx) and with the tosyl-MMT initiator (1, 5 and 10 wt% with respect to EtOx) dissolved in acetonitrile (ACN) under an inert atmosphere at room temperature. The sealed vial was heated to 130 °C in an oil bath for 16 h at 130 °C, the reaction mixture was again cooled at room temperature and methanolic potassium hydroxide solution (0.1 N KOH/MeOH) was added to terminate the polymerization. After termination for 24 h at the room temperature in the dark media, the solvent was removed under reduced pressure. Then, the product was dissolved in dichloromethane and precipitated in cold diethyl ether and dried under vacuum for overnight.

2.3. Characterization

The resulting exfoliated polymer/clay nanocomposites have been characterized by X-ray diffraction (XRD) spectroscopy, Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The FT-IR spectra were recorded on a Perkin-Elmer FT-IR System Spectrum BX over the range 4000–500 cm^{-1}. Gel permeation chromatography (GPC) measurements were performed on an Agilent 1260 Infinity Multi-Detector GPC/SEC system with viscometer (390-MDS), light scattering (390-MDS 15/90 LS) and refractive index (Agilent 1260 Infinity MDS RID) detectors with a PL Aquagel-OH Mixed H column (7.5 × 300 mm^2; 8 μm; Agilent Technologies). The mobile phase used was deionized water consisted of 0.02% (w/w) sodium azide and the flow rate adjusted to 1.0 mL min^{-1} at 30 °C. All polymer samples prepared by previously reported procedure, they were cleaved from MMT nanoclay by refluxing with lithium bromide in THF for 24 h and then isolated by centrifugation and filtration. The DSC analyses were performed with a SEIKO DSC 6200 instrument under inert atmosphere at a heating rate of 5 °C/min between −20 and 300 °C. The TGA measurements were carried out with a SEIKO ExStar 6300 instrument under inert atmosphere at a heating