

Intercalation behavior of hydroxylated dendritic polyesters in polymer clay nanocomposites prepared from aqueous solution

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ARTICLE INFO

Article history:

Received 1 June 2011

Received in revised form

7 July 2011

Accepted 10 July 2011

Available online 23 July 2011

Keywords:

Hyperbranched polymer

Clay

Intercalation

ABSTRACT

Second and fourth generations of hydroxylated dendritic polyesters based on 2,2-bis-methylpropionic acid (bis-MPA) with an ethoxylated pentaerytriol (PP50) core were combined with unmodified sodium montmorillonite clay (Na⁺MMT) in water to generate a broad range of polymer clay nanocomposite films from 0 to 100% wt/wt. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to investigate intercalation states of the clay galleries. Intercalation was the dominant state in these nanocomposites. Significant exfoliation was only observed within 0–5% wt/wt of mineral composition range. It was shown that interlayer spacing changed within the composition range 5–95% wt/wt from 0.5 nm to up to 3.5 nm in a step-like fashion with 0.5 nm increments which corresponded to a flattened conformation of confined hyperbranched polymers (HBP). Second and fourth generations exhibited the same layer-by-layer intercalation of completely flattened HBPs. No dependence of interlayer spacings on generation number was found. XRD and TEM revealed the presence of mixed intercalated populations with interlayer spacings at multiples of 0.5 nm.

Published by Elsevier Ltd.

1. Introduction

Research has intensified in the area of dendritic polymers due to their highly branched structures which possess high end group functionality, structures, and unique properties [1,2]. In addition, due to their highly branched structures, dendritic polymers are almost exclusively amorphous in character. From a processing perspective, dendritic polymers often exhibit lower melt and solution viscosities, as compared to their linear analogues with the same molecular weights. This is attributed to a lack of entanglements in solution. Dendritic macromolecules are comprised of two classes: dendrimers and hyperbranched polymers. Both are macromolecular compounds built from multifunctional monomers AB_n, where the A and B functionalities couple to form branched structures. Dendrimers are characterized by monodispersity and perfect branching from a central core with multistep synthetic routes, whereas hyperbranched polymers (HBPs) are made by one-pot synthesis and possess less perfect structures and incomplete branch coupling. Hyperbranched polymers, due to their ease of manufacture (relative to dendrimers), offer similar properties, at

greatly reduced cost. This has led to increased research of these materials in recent years.

Perhaps due to their ease of accessibility, dendritic hyperbranched polyester polyols based on 2,2-bis-methylpropionic acid (bis-MPA) with an ethoxylated pentaerytriol (PP50) core became a popular model system in a number of studies investigating the chemical structure and physical properties of these systems [3–9]. The pseudo-one-step, divergent synthesis of these aliphatic-ester dendritic polymers, was first described by Malmström et al. in 1995 [10]. The creation of these hyperbranched polymers involves the sequential addition of monomer during synthesis and was further investigated in a number of publications [11–13]. Although characterized by imperfect branching and significant polydispersity, these polymeric structures preserve the essential features of dendrimers, namely, high end group functionality and a globular architecture. Importantly these HBP's are water soluble due to the strong influence of their hydroxylated end groups [14].

A novel nanocomposite study was conducted with these particular HBPs by Månson's group [15]. It was followed by a series of papers further exploring the behavior of these novel nanocomposites [16–18]. In these studies they prepared HBP/clay nanocomposites via a solution-intercalation method using the hyperbranched polyesters and unmodified sodium montmorillonite

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clay with water as the solvent to yield nanocomposite films. Previous work with water soluble linear polymers, such as PEO, PVA, PVP, had successfully demonstrated intercalation of polymer into unmodified clay galleries using this type of methodology [19,20]. With the HBP nanocomposite work, it was anticipated that intercalation of these globular HBPs would lead to larger interlayer spacings than with linear polymers, as collapse of the dendritic structures onto silicate layers could be sterically restricted. So, novel nanocomposites using second, third, and fourth generations of HBPs were previously prepared and studied, and it was concluded that at intermediate Na^+ MMT contents, the interlayer spacings in the resulting intercalated nanocomposites correlated closely with estimates of the molecular diameters for the different generations of HBPs employed. However at larger mineral contents, the effects of nanoclay confinement led to a flattening of the HBPs. These conclusions were based upon XRD data.

The research carried out by Månson's group became a starting point for this investigation which was driven by our fundamental interest in exploring the confinement of polymeric structures, in particular dendritic polymers, on the nanoscale level. The adsorption behavior of dendrimers and HBPs on the substrate was in the past predominantly investigated by using the surface techniques such as AFM and ellipsometry [21,22]. However, these studies only allowed study of the adsorption behavior by deposition on a solid substrate. Another potential method to investigate adsorption and confinement of polymeric structures at the nanoscale level is through the utilization of polymer clay nanocomposites. These offer additional levels of confinement, via intercalated nanocomposite structures, which introduce polymers to multiple substrate interactions.

The main goal of the project described in this article was to revisit the nanocomposite work conducted by Månson's group with an emphasis on preparing a very broad, and very detailed, range of nanocomposites, using a very small 5% wt/wt step, from 0 to 100% wt/wt. The intercalation behavior of these hydroxylated dendritic polyesters as a function of clay content was then investigated by a tandem of X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was anticipated that XRD would be particularly revealing at larger mineral content and TEM at smaller mineral compositions. The confinement effects upon these flattened hyperbranched polymers are detailed in an accompanying publication utilizing differential scanning calorimetry and positron annihilation lifetime spectroscopy.

The practical rationale for this research can be stated as follows. Polymer clay nanocomposites have received significant attention in the recent decades because they often exhibit chemical and physical properties that differ from those of conventional composite materials [19,20,23]. Due to their inherent hydrophilicity, layered silicates such as sodium montmorillonite (Na^+ MMT) generally require surfactant modification to increase the organophilicity of the clays in order to promote dispersion in a polymer matrix. However, some hydrophilic polymers exhibit an affinity for the hydrophilic clay layers and therefore nanocomposites can be prepared by the aqueous blending of these polymers and clay without the introduction of surfactants. While hydrophilic polymers such as poly(vinyl alcohol) have been successfully used to prepare nanocomposites with Na^+ MMT, conventional polymer solutions often possess a high viscosity, and can require shear intensive processing procedures [24]. The utilization of hydrophilic hydroxylated hyperbranched polyesters, which possesses low solution viscosities, allows for easy processing of nanocomposites with Na^+ MMT up to very high clay contents. These nanocomposites may also potentially be used as an alternative to organoclays prepared by cation exchange reactions and dispersed into other polymer matrices [25].

2. Experimental

Sodium montmorillonite clay (Na -MMT) Cloisite[®] with a cation exchange capacity (CEC) of 92.6 meq/100 g was purchased from Southern Clay Products. As received clay powder was sifted through a 75 micron sieve, dried at 150 °C under vacuum overnight, and stored over desiccant prior to use. Two hydroxyl-functional dendritic (hyperbranched) polyesters, Boltorn[™] H20 and H40 (2nd and 4th pseudogenerations respectively), were obtained from Perstorp Specialty Chemicals AB, Sweden, in the form of pellets. HBP2 and HBP4 will henceforth be used to designate the second and the fourth pseudogenerations of these hydroxylated hyperbranched polyesters. A schematic representation of the idealized structure of the second pseudogeneration of the hyperbranched polyester is shown in Fig. 1.

Nanocomposites were prepared via a solution-intercalation method using deionized (DI) water as the solvent medium. The processing methodology was based upon that proposed by Plummer et al [15]. The required amount of Na^+ MMT clay was first dispersed in DI water at 50 °C temperature and stirred for at least 8 h to optimize clay delamination. The concentration of clay in the deionized water was kept below 1% (wt/wt) in order to ensure that individual clay layers were well dispersed. Sufficiently diluted, sodium montmorillonite particles delaminate into single layers [26].

The required amount of Boltorn[™] polyols was then dissolved in boiling DI water. The concentration of polymer in water was kept at or below 10% (wt/wt) as this concentration was seen to effectively disperse and dissolve the HBP at or near 100 °C. This solution was then quantitatively transferred into the clay dispersion. This combined solution was then rapidly stirred in open air at 50 °C until the dispersion approached the level of the stir bar but remained in a liquid state. It was then transferred to Teflon trays and dried for 2 days in a convection oven at 50 °C. Two further days of drying followed, under vacuum, at 120 °C. This temperature was demonstrated as optimal for removing water from Boltorn[™] polyols [27]. The resulting nanocomposite films were stored over desiccant at room temperature.

One dimensional X-ray diffraction spectra were collected on a Rigaku Ultima III diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.542\text{\AA}$) at room temperature using Bragg-Brentano parafocusing geometry (reflection mode XRD). XRD information was obtained from samples powdered in an analytical mill, and from intact nanocomposite films. Powdered samples ensured that the Debye-

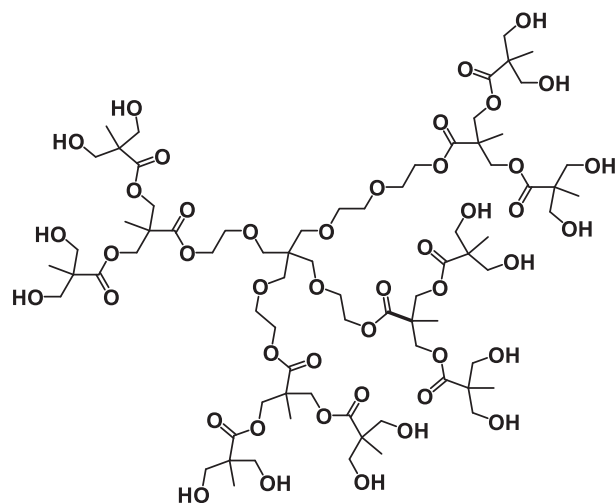


Fig. 1. Schematic representation of the idealized structure for the second pseudogeneration HBP.

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