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Grafting of poly[(methyl methacrylate)-*block*-styrene] onto cellulose *via* nitroxide-mediated polymerization, and its polymer/clay nanocomposite

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ABSTRACT

For the first time, nitroxide-mediated polymerization (NMP) was used for synthesis of graft and block copolymers using cellulose (Cell) as a backbone, and polystyrene (PSt) and poly(methyl metacrylate) (PMMA) as the branches. For this purpose, Cell was acetylated by 2-bromoisobutyryl bromide (BrBiB), and then the bromine group was converted to 4-oxy-2,2,6,6-tetramethylpiperidin-1-oxyl group by a substitution nucleophilic reaction to afford a macroinitiator (Cell-TEMPOL). The macroinitiator obtained was subsequently used in controlled graft and block copolymerizations of St and MMA monomers to yield Cell-*g*-PSt and Cell-*g*-(PMMA-*b*-PSt). The chemical structures of all samples as representatives were characterized by FTIR and ^{1}H NMR spectroscopies. In addition, Cell-*g*-(PMMA-*b*-PSt)/organophilic montmorillonite nanocomposite was prepared through a solution intercalation method. TEM was used to evaluate the morphological behavior of the polymer–clay system. It was demonstrated that the addition of small percent of organophilic montmorillonite (O-MMT; 3 wt.%) was enough to improve the thermal stability of the nanocomposite.

1. Introduction

Since the discovery and introduction of cellulose (Cell) in 1838 by Anselme Payne (Payen 1838), this natural polymer has considered as a promising material in numerous fields ranging from industrial to biomedical applications (Budtova & Navard 2016; Mokhothu & John 2015; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Wang, Lu, & Zhang, 2016). Cellulose is a liner and semi-crystalline polysaccharide composed of several D-glucose moieties connected together by β,1-4-glycosidic bond (AGU units). Furthermore, cellulose molecule chains attach to each other through hydrogen bonds (intramolecular and intermolecular) and van der Waals interactions. Due to this network structure cellulose remarkably exhibited high strength, stiffness, and high thermal stability (Budtova & Navard 2016; Moon et al., 2011; Wang et al., 2016). Cellulose is the most ubiquitous and abundant organic compound in nature, and can be produced from bacteria (BC; synthesized by *Gram-negative* bacteria such as *Gluconacetobacter xylinus*) or plants (Habibi, Lucia, & Rojas, 2010; Lin et al., 2013). Cellulose and its derivatives (*e.g.*, hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and carboxymethyl cellulose (CMC)) have been applied in various fields including biofuels (Álvarez-Murillo et al., 2016), bio/chemical sensors (Rull-Barrull, D'Halluin, Le Grognec, & Felpin, 2016), biomedical sciences (*e.g.*, tissue engineering and drug delivery) (Abeer, Mohd Amin, & Martin, 2014; Saber-Samandari, Saber-Samandari, Kiyazar, Aghazadeh, & Sadeghi, 2016), as a filler in polymer composites (Dormanns et al., 2016), environmental sciences (Huang et al., 2016), as well as energy source, building materials, paper, textiles, and clothing (Budtova & Navard 2016; Moon et al., 2011; Wang et al., 2016).

However, some drawbacks of cellulose such as poor solubility (in both organic and aqueous solvents), high moisture absorption, incompatibility with hydrophobic polymers, and low dimensional stability restrict its industrial applications (Giese, Blusch, Khan, & MacLachlan, 2015; Hufendiek, Trouillet, Meier, & Barner-Kowollik, 2014). Thus, the chemical modification of this natural polymer is an important step for extending the range of industrial applications. Several strategies such as oxidation, esterification, etherification, silylation, and polymer grafting have been adopted for the chemical modification of cellulose (Liu, Chen, Li, Lin, & Shen, 2014; Salimi,

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Aryanasab, Banazadeh, Shabanian, & Seidi, 2016). Among these, the polymer grafting approach with tailored surface properties is of great interest due to their wide range of potential industrial applications such as antibacterial surfaces (Joubert et al., 2015), membrane materials (Goetz, Jalvo, Rosal, & Mathew, 2016), ion-exchange materials (Dods, Hardick, Stevens, & Bracewell, 2015), reinforcing agents in composite materials (Ng et al., 2015), and many more. In this context, three grafting approaches including "grafting to", "grafting from" and "grafting through" can be employed (Joubert, Musa, Hodgson, & Cameron, 2014). It should be pointed out that, the "grafting from" approach is the most common way toward the synthesis of cellulosic copolymers using a cellulosic macroinitiator (Joubert et al., 2014; Moreira et al., 2015; Tang et al., 2015).

It is well established that the physicochemical properties of polymers are strongly depended on their molecular parameters such as molecular weight, molecular weight distribution (MWD), and the type, number and spatial locations of functional groups in the polymer chain (Abbasian, Masoumi, & Rashidzadeh, 2016; Hatamzadeh & Jaymand 2014; Wang & Matyjaszewski 1995). On the other hands, the physicochemical properties of the copolymers are far different from those of blends of the same corresponding homopolymers (Abbasian, Jaymand, & Shoja Bonab, 2012; Jaymand, Hatamzadeh, & Omidi, 2015). From this conceptual point of view, reversible deactivation radical polymerization (RDRP; otherwise known as controlled or 'living' radical polymerization) approaches including reversible addition of fragmentation chain transfer (RAFT) polymerization (Abbasian, Masoumi, Masoudi, & Rashidzadeh, 2014; Moad, Rizzardo, & Thang, 2008), atom transfer radical polymerization (ATRP) (Davis, Matyjaszewski, & Höcker, 2002; Tizpar & Ghasemi 2006), and nitroxide-mediated polymerization (NMP) (Abbasian, Pakzad, & Amirmanesh, 2015; Nicolas et al., 2013) have been developed as powerful tools for the synthesis of copolymers with controlled molecular weight, narrow dispersity, and complex macromolecular architectures.

To the best of our knowledge, ATRP is the most widely used method for the synthesis of cellulosic copolymers, and the use of NMP is neglected for this purpose (Yin, Tian, Jiang, Wang, & Gao, 2016; Yu, Wang, Wang, & Chu, 2016). Among the mentioned techniques, NMP is historically the first and represents perhaps the easiest RDRP technology to apply. This technique is based on the use of traditional radical initiator (*e.g.,* benzoyl peroxide) in the presence of a stable nitroxide or alkoxyamine radical, that allows the synthesis of complex macromolecular architectures (*e.g.,* star and graft copolymers) with controlled molecular weight of final polymer under mild conditions (Abbasian, Bonab, Shoaeifar, & Entezami, 2012; Hawker, Bosman, & Harth, 2001). In this technique, the activation–deactivation equilibrium is reached by a simple temperature increase and the polymerization can be quenched efficiently by cooling. There is no need for a transition metal activator such as in the case of ATRP, or for a radical initiator such as in the reversible transfer techniques (Nicolas et al., 2013). Thus, the system is not suffer from metal trace contamination, and is based on all-organic components.

In the past few decades, the emergence of nanotechnology has provided exciting new possibilities for development of new functional materials with improved physicochemical properties in different multidisciplinary fields such as biology, chemistry, engineering, and many more. Polymer/clay nanocomposites (PCNs) are one of the advances and innovations results in the field of nanotechnology (Abbasian, Jaymand et al., 2012; Abbasian et al., 2015; Chiu, Huang, Wang, Alamani, & Lin, 2014). It is well accepted that the properties of polymer (*e.g.,* mechanical, thermal stability and flame retardancy, and gas barrier) are significantly improved and new unexpected features may appear after the addition of only a small amount of clay (Farmahini-Farahani et al., 2015; Kotal & Bhowmick 2015; Madusanka, De Silva, & Amaratunga, 2015; Zare & Garmabi 2015).

The PCNs can be prepared by three main methods including solution exfoliation, melt intercalation, and *in situ* intercalative polymerization (Kotal & Bhowmick 2015; Suter, Groen, & Coveney, 2014). On the other hand, depending on the strength of the interfacial interactions between the polymer matrix and the silicate layers, three distinct structures are thermodynamically achievable (Chiu et al., 2014; Kotal & Bhowmick 2015). If the polymer chain does not enter the silicate galleries, d_{001} of clay remains unchanged, and a conventional microcomposite is formed. If there is some affinity between the clay and the polymer, the polymer chains tend to penetrate between the platelets, causing an increase in d_{001}, but the clay layers remain stacked, the composite is an intercalated microstructure. Finally, if the interaction between the clay and the polymer is proper, and the silicate layers are completely pushed apart to create a disordered array, an exfoliated morphology can be obtained (Chiu et al., 2014; Chu, Chiang, Tsai, & Lin, 2005; Kotal & Bhowmick 2015).

In present investigation, a novel and efficient strategy for the chemical modification of cellulose by the incorporation of PSt and PMMA segments through the NMP technique is reported. To the best of our knowledge, this methodology is not reported yet. In addition, Cell-*g*-(PMMA-*b*-PSt)/O-MMT nanocomposite was prepared through a solution intercalation method. The chemical structures of all samples as representatives were characterized by means of FTIR and ^{1}H NMR spectroscopies. The morphologies of the pure Cell, Cell-*g*-PSt, and Cell-*g*-(PMMA-*b*-PSt) were studied by atomic force (AFM), and scanning electron (SEM) microscopies. The thermal behaviors of the Cell-*g*-(PMMA-*b*-PSt) and its nanocomposite were investigated by differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Microcrystalline cellulose with a degree of polymerization (DP) 200 was purchased from Beijing Fengli Jingqiu Commerce and Trade Company (China), and dried in vacuum at 50 °C for about 24 h before use. Methyl methacrylate (MMA), and styrene (St) monomers from Merck (Darmstadt, Germany) were dried over calcium hydride, vacuum-distilled, and then stored at −20 °C prior to use. Benzoyl peroxide (B.P.O; Merck) was recrystallized from ethanol and then dried under vacuum at room temperature. Tetrahydrofuran (THF; Merck) was dried by refluxing over sodium, and distilled under argon atmosphere before use. 4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) was synthesized in our laboratory. Hexadecyl trimethyl ammonium chloride salt, pyridine, and 2-bromoisobutyryl bromide (BrBiB) were purchased from Merck and were used as received. Sodium montmorillonite (Na^+-MMT) was purchased from Southern Clay Products (Gonzales, TX, USA) under the trade name Cloisite NaC, which possesses the idealized chemical formula $Na_{0.33}[Mg_{0.33}Al_{11.67}Si_4O_{10}](OH)_2$ and a cation exchange capacity (CEC) of 95 meq 100 g^{-1}. All other reagents were purchased from Merck and purified according to standard methods.

2.2. Pretreatment of cellulose

In order to break down the extensive hydrogen bonding between the hydroxyl groups of cellulose and to open up the ordered regions, cellulose (2.0 g) was first washed with ethanol, and subsequently immersed into an aqueous solution of NaOH (150 mL; 10 wt.%). The mixture was stirred for about 24 h at room