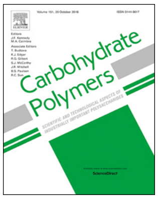
Carbohydrate Polymers 199 (2018) 603–609

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Convenient characterization of polymers grafted on cellulose nanocrystals via SI-ATRP without chain cleavage

Zhen Zhang[a,b], Kam C. Tam[c,*], Gilles Sèbe[a,d,*], Xiaosong Wang[b,*]

[a] Université Bordeaux, LCPO, UMR 5629, F-33600 Pessac, France
[b] Department of Chemistry, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada
[c] Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, N2L3G1, Canada
[d] CNRS, LCPO, UMR 5629, F-33600 Pessac, France

ARTICLE INFO

Keywords:
Cellulose nanocrystals
SI-ATRP
DLS
DSC
TGA
Polystyrene

ABSTRACT

Cleaving is usually required to characterize the molecular weight of grafted polymers on substrates. Here, we report on a technique to estimate the molecular weight of grafted polystyrene (PS) ($M_n^{\text{grafted PS}}$) in PS-grafted cellulose nanocrystals (PS-*g*-CNCs) without chain cleavage. PS-*g*-CNCs were prepared from brominated CNC (CNC-Br) by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) in the presence of sacrificial initiators. Differential scanning calorimetry (DSC), dynamic light scattering (DLS), and thermogravimetric analysis (TGA) of PS-*g*-CNCs revealed that $M_n^{\text{grafted PS}}$ increased proportionally with monomer conversion. By comparing the mass of grafted PS, deduced from TGA curves, with initiating sites on CNC-Br, $M_n^{\text{grafted PS}}$ was calculated. The resultant $M_n^{\text{grafted PS}}$ was the same as M_n of free PS initiated by sacrificial initiators and matched theoretical values calculated according to monomer conversion. Therefore, grafting polymerization from CNC-Br and free polymerization were progressing in a controlled manner with the same propagating rates.

1. Introduction

The grafting of polymers on nanoparticles is a promising “bottom-up” strategy to prepare well-designed nanocomposites with controlled properties.(Nicole, Laberty-Robert, Rozes, & Sanchez, 2014) In the “grafting-to” method, a pre-synthesized and characterized polymers are covalently attached to the nanoparticles, leading to a low grafting density due to high steric hindrance. This problem can be circumvented by using the “grafting-from” appr oach, also known as Surface-Initiated Polymerization (SIP), in which the polymerization of monomers is initiated from the surface of the nanoparticles.(Zuo et al., 2017) The SIP is generally preferred due to the much lower steric hindrance.(Huang, 2016) Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) is one of the most popular SIP methods because of its living radical polymerization characteristics. SI-ATRP has been widely used to graft polymers onto silica and metal nanoparticles,(Yan et al., 2016) and it has been recently applied to cellulose nanocrystal (CNC), a promising bio-based and biocompatible material.(Wei & McDonald, 2016; Yin, Tian, Jiang, Wang, & Gao, 2016) CNCs are renewable nanoparticles that possess many potential applications, such as reinforcing agents,(Sirviö, Visanko, Heiskanen, & Liimatainen, 2016; Yin et al., 2016; Zhang et al., 2018a) stabilizers for metal nanoparticles, (Lokanathan, Uddin, Rojas, & Laine, 2014; Zhang et al., 2018b) colloid stabilizers of Pickering emulsions,(J. Tang, Berry, & Tam, 2016; Zhang, Tam, Wang, & Sèbe, 2018) etc. However, the engineering of innovative nanomaterials from CNCs generally requires a fine control of their surface properties by chemical modification. In this context, the CNCs modification via SI-ATRP grafting is particularly promising, as it allows the preparation of hybrid polymer-grafted CNCs (polymer-*g*-CNCs) with tailored properties.

The properties of the polymer-*g*-CNCs obtained depend both on the chain length of the polymer and grafting density, hence controlled polymerization and precise characterization of the grafted polymer chains are necessary.(Dang et al., 2013) However, the characterization of the molecular weight of the grafted polymer ($M_n^{\text{grafted polymer}}$) is challenging and it generally requires the cleavage and subsequent analysis by Gel Permeation Chromatography (GPC), which is tedious and time-consuming.(Wang, Roeder, Whitney, Champagne, & Cunningham, 2015) The severe conditions used for the cleavage can also degrade the cellulosic material or denature the polymer, making subsequent analysis challenging.(Rosilo et al., 2014) In many cases, it is practically impossible to cleave grafted polymers in mild conditions without special modifications of nanoparticles.(Hansson, Antoni, Bergenudd, & Malmström, 2011; G. Morandi & Thielemans, 2012)

---

* Corresponding authors.
E-mail addresses: gilles.sebe@u-bordeaux.fr (G. Sèbe), xiaosong.wang@uwaterloo.ca (X. Wang), mkctam@uwaterloo.ca (K.C. Tam).

https://doi.org/10.1016/j.carbpol.2018.07.060
Received 13 April 2018; Received in revised form 17 July 2018; Accepted 18 July 2018

Alternatively, a sacrificial initiator is introduced into the SIP medium to produce free polymers necessary for M_n characterization.(Majoinen et al., 2011; G. Morandi & Thielemans, 2012) This method is based on the assumption that the molecular weights of the grafted polymers and free polymers ($M_n^{free\ polymer}$) are identical.(Hansson et al., 2011; G. Morandi & Thielemans, 2012) However, the accuracy of this method remains controversial. Indeed, the SI-ATRP reaction is influenced by the steric hindrance of grafted polymers, which is related to the grafting density and morphology of the substrate.(Xue et al., 2013) The relationship between grafted and free polymers is therefore not straightforward and needs to be verified for each particular case. Techniques to evaluate the molecular weight of the grafted polymers via a direct characterization of the polymer-*g*-CNC material have not been reported previously and hence, it should be very beneficial for researchers working in this field.

To explore the possibility of characterizing the $M_n^{grafted\ polymer}$ without chain cleavage, we reviewed several techniques on the determination of the length of grafted polymers. For example, the glass transition temperature (T_g) of polymer-grafted nanocomposites as measured by differential scanning calorimetry (DSC) may vary with $M_n^{grafted\ polymer}$ according to free volume theory.(Fox & Flory, 1950; Rudnick, Taylor, Litt, & Hopfinger, 1979) The hydrodynamic radius (R_h) of nanoparticles determined by dynamic light scattering (DLS) is related to the chain length of grafted polymers.(Mazurowski et al., 2013) The mass of grafted polymers relative to the nanoparticles can be measured using thermogravimetric analysis (TGA), which is expected to increase proportionally to the chain length of grafted polymers. Particularly, TGA technique can be used to measure the precise $M_n^{grafted\ polymer}$ by comparing the mass of grafted polymers with the number of initiating sites. By taking advantage of these widely-used techniques, it is possible to establish a technique to evaluate $M_n^{grafted\ polymer}$ without chain cleavage.

Herein, we report on the characterization of PS-grafted CNCs (PS-*g*-CNCs) using DLS, DSC and TGA techniques, allowing the direct determination of $M_n^{grafted\ PS}$ without PS chain cleaving. PS-*g*-CNC was prepared from brominated CNC initiators (CNC-Br) using SI-ATRP in the presence of a sacrificial initiator. PS was selected as a model polymer, as its surface grafting by ATRP has been performed on a wide variety of substrates as documented in the literature. The DLS, DSC and TGA analyses suggested that the grafted PS persisted with the monomer conversion. Particularly, the $M_n^{grafted\ PS}$ could be quantified without chain cleavage by comparing the mass of grafted PS, deduced from the TGA curves, with the initiating sites on CNC-Br. The calculated $M_n^{grafted\ PS}$ was identical to the $M_n^{free\ PS}$ measured using GPC and consistent with the theoretical $M_n^{free\ PS}$, indicating similar propagating rate for both grafting polymerization from CNC-Br and controlled radical polymerization in the bulk. DLS, DSC and TGA techniques provide a facile approach to estimate the $M_n^{grafted\ polymer}$ without chain cleavage.

2. Experimental section

2.1. Materials

CNCs were purchased from the University of Maine, which were prepared by sulfuric acid hydrolysis. Acetic acid, CuBr, $CuBr_2$, ascorbic acid, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), tris [2-(dimethylamino)ethyl]amine (Me_6TREN), calcium hydride, styrene, dimethylformamide (DMF), tetrahydrofuran (THF), diethyl ether, ethanol and other solvents were purchased from Sigma-Aldrich. Ethyl α-bromoisobutyrate (EBiB) and α-bromoisobutyryl bromide (BIBB) were purchased from Alfa Aesar. 4-dimethylaminopyridine (DMAP) and triethylamine (TEA) were purchased from Fisher. CuBr was purified by acetic acid at 80 °C under N_2 for 24 h, and then washed with acetic acid and dried under vacuum at 50 °C. All the other chemicals were used as received.

2.2. Preparation of the brominated CNC nano-initiators: CNC-Br

BIBB was used to modify CNCs and prepare the brominated CNC nano-initiators (CNC-Br), later used to initiate the SI-ATRP reaction. Firstly, CNCs (500 mg) were dispersed in DMF (50 mL) by sonication. TEA (4 mL) and DMAP (2 g) were added to the suspension. The suspension was evacuated under vacuum and backfilled with argon three times. Then BIBB (4 mL) was added dropwise to the suspension in an ice bath. After 24 h, EtOH was added, and the CNC-Br was recovered by centrifugation. CNC-Br was Soxhlet extracted with THF for 2 days, then dialyzed with deionized H_2O for 6 days. Finally, CNC-Br was obtained by freeze-drying. CNC-Br (10 mg) was re-dispersed in THF by sonication again, and the supernatant was dried and analyzed by ^1H NMR in CDCl3. The ^1H NMR results showed no residues were left.

2.3. Grafting PS from CNC-Br by SI-ATRP: PS-*g*-CNCs

In brief, the SI-ATRP of PS from CNC-Br was conducted at 100 °C, with the molar ratio of [Styrene]: [EBiB]: [CuBr]: [PMDETA]: [DMF] = 500: 1: 1: 1: 500. In detail, CuBr (72 mg) was transferred into the Schleck tube in the glove box. CNC-Br (50 mg) was dispersed in DMF (250 mmol) via sonication. Then styrene (250 mmol) and EBiB (0.5 mmol) were added to the suspension. After the suspension had been bubbled with argon for 20 min, the suspension was transferred to the Schleck tube under the protection of argon. The suspension was degassed by three freeze-pump-thaw cycles. After the addition of PMDETA (0.5 mmol) under Ar, the reaction was initiated at 100 °C. At a designed interval time (2 h, 4 h, 6 h, and 7.3 h), an amount of reaction mixture was withdrawn by a degassed syringe. The monomer conversion was calculated from the ^1H NMR analysis of the mixture in $CDCl_3$. The mixture was centrifuged to recover the PS-*g*-CNCs nanoparticles. PS-*g*-CNCs were washed with THF and EtOH three times respectively, to remove the free polymer and other unreacted chemicals. In the last washing cycle, the THF supernatant was recovered and dried. The ^1H NMR of the dried supernatant in $CDCl_3$ showed no PS or other residues. The PS-*g*-CNCs nanocomposites were obtained after drying at 50 °C under vacuum. The green supernatant became colorless after the catalyst was removed in an Al_2O_3 column. The colorless supernatant was then poured into excess MeOH, and the precipitated free PS was recovered through filtration and drying at 50 °C under vacuum.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of all the samples were obtained with the potassium bromide technique, using a Thermo Nicolet Avatar 970 FTIR spectrometer, at a resolution of 8 cm^{-1} (64 scans). Transmission electron microscopy (TEM) was conducted on Philips CM10 at an acceleration voltage of 60 keV. The TEM samples were prepared by drop coating the dispersion onto copper grids (200 mesh coated with copper) and allowing them to dry at ambient temperature overnight. The pristine CNCs dispersion for TEM samples was stained by $FeCl_3$. Thermogravimetric analysis (TGA) was performed on TGA-Q50 system (TA Instruments) at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out using a DSC Q100 apparatus (TA Instruments). All samples were first heated from 0 °C to 200 °C to remove the moisture, cooled down to 0 °C, and then heated to 200 °C. The T_g values were determined from the second heating run of the DSC curve. Dynamic light scattering (DLS) was performed using a particle size analyzer Vasco™ DL135 (Cordouan Technologies). Gel Permeation Chromatography (GPC) analysis was conducted in THF with LiBr, on a PL-GPC 50 plus Integrated GPC (Polymer Laboratories-Varian). The elution of the filtered samples was monitored using a simultaneous refractive index and UV detection system. The elution times were converted to molar mass using a calibration curve based on low dispersity (M_w/M_n) polystyrene standards. ^1H NMR spectra were recorded