Preparation and Characterization of Clay-polymer Nanocomposite Having Covalently-bound poly(norbornenes) with Pendant Cholesterols

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We have successfully prepared a clay-based polymer nanocomposite having grown cholesterol bearing poly(norbornene) brushes end-tethered from a naturally-occurring montmorillonite clay template. The synthesis of this hybrid material involved the treatment of the clay with first generation Grubbs catalyst, a ruthenium alkylidene, which induced a ring-opening metathesis and subsequent surface initiated polymerization of the cholesterol bearing monomer. This results in an inorganic/organic hybrid functional nanomaterial where the inclusion of the clay particles in a liquid crystalline domain modifies the thermal transitions.

Keywords: *surface initiated polymerization, nanocomposite, liquid crystalline polymer, tethered polymer.*

1. Introduction

Cholesterol-bearing polymers belong to a class of polymeric system called liquid crystalline polymers (LCPs). LCPs exhibit remarkable properties such as high heat resistance, remarkable electrical tolerance and excellent chemical stability LCPs have found applications in opto-electronics, color information technology, and biotechnology[1-3].

In the area of nanocomposites, one interesting synthetic approach to prepare such materials is through surface initiated polymerizations (the "**grafting from**" approach) to produce complex materials with well-defined structures[4-8]. The growth of polymers directly from the surface-immobilized initiators using controlled polymerization techniques such as atom transfer radical polymerization (ATRP)[9-14], reversible addition-fragmentation transfer polymerization (RAFT)[15-17] and ring opening metathesis polymerization (ROMP)[18-21], among others, had become a powerful strategy for anchoring well-defined polymers to substrates.

The rationale for using surface initiated polymerizations is to control the density of surface grafting *a priori* as well as the chain length for a variety of polymers. The current study marks the beginning of explorations of functional nanocomposites where the inclusion of the particles in a liquid crystalline domain modifies the thermal transitions.

2. Materials and Methods

Silylation of the host silicate clays. A commercial organoclay, Cloisite15A, from the Southern Clay Products, Inc. was used as a surface polymerization template. The organoclay was vacuum-dried at 50 ºC prior to silylation.

A silane coupling agent having a norbornene moiety, [(bicycloheptenyl)ethyl] dimethylchlorosilane, was used to functionalize the clay. A 5.0 g sample of the organoclay was placed in an air-free three-neck round bottom flask and flushed with nitrogen for few minutes. 150 mL of dry hexane was then added to the sample and the mixture was stirred under static nitrogen for 10 minutes.

Then, 5 mL of norbornene-chlorosilane was added to the flask and the mixture was refluxed under nitrogen for 48h. The final product (silylated organoclay) was then filtered off and repeatedly washed with hexane, before being dried at 60 °C for 24h under vacuum. (Yield = 91%)

Synthesis of Cloisite15A/polyNBCh9 nanocomposite. Synthesis was done inside a glovebox. A 100 mg Cloisite_sil was placed in a 20-mL scintillation vial and was brought inside glovebox. Five mL of distilled THF (stabilized with TCP, 0.69 g TCP per 150 mL THF) was used to disperse the clay. Fifteen mg of Grubbs 1st generation catalyst was then added to the clay solution and stirred for 5 minutes. The clay solution was then washed with 15 mL hexane to get rid of unbound catalyst, sealed with parafilm wax and brought outside the glovebox for centrifugation. After centrifugation, clay solution was brought back inside the glovebox, and the supernatant was pipetted off. Then the clay was dispersed in 5 mL THF. Washing with hexane was done two more times. After the last wash, the clay was redispersed in 5 mL of THF.

In a separate 20 mL scintillation vial, 470 mg of NBCh-9 monomer was placed. Saturated solution of this monomer was prepared by adding anhydrous THF stabilized with tricyclohexylphosphine (TCP) drop by drop until all monomers were dissolved. The prepared cholesterol-norbornene solution was then added to the solution of activated silica particles and stirred for one hour. The polymerization was terminated by

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adding 1 mL of ethyl vinyl ether (EVE). The nanocomposite material was precipitated in cold methanol. The precipitate was then recovered by filtration and was vacuum dried for 24 hours prior to analysis. (Yield = 85%)

3. Instrumentation

Fourier transform infrared (FTIR) spectroscopy. To monitor the growth of the polymer chains from the clay template, infrared spectroscopy was employed. Fourier transform infrared (FTIR) spectra of the samples in KBr pellets were collected using a Nicolet Magna-560 FTIR spectrometer.

Thermogravimetric analysis (TGA). Thermogravimetric analysis was utilized to determine the organic (polymer and modifier) and the inorganic (clay) components of the nanocomposites. Samples were placed in alumina pan and were heated up to 800 ºC under nitrogen atmosphere with a heating rate of 10 ºC/min. TGA analyses of the clay and clay-polymer nanocomposites were carried out on a TA Instruments SDT Q600 Simultaneous TGA/DSC.

Differential scanning calorimetry (DSC). Differential scanning calorimetric (DSC) measurement was utilized to determine the thermal transition properties of the prepared nanocomposite as compared to that of the polymer only. Samples were placed in alumina pan and were heated up from -5 ºC to 150 ºC under nitrogen atmosphere with a heating rate of 10 ºC/min at three heating/cooling cycles. DSC analyses of the nanocomposite and the bare polymer were carried out on a TA Instruments DSC Q-20.

4. Results and Discussion

4.1 Preparation of clay-polyNBCh9 nanocomposite

This work describes the preparation of hybrid materials composed of an outer layer of cholesterol-bearing poly(norbornenes) covalently bound from an inorganic substrate. In our approach, the nanocomposite was prepared in the following manner: (1) the inorganic surface (Cloisite15A) was initially functionalized with norbornenyl initiator ligands via a silane coupling reaction; and then, (2) a ruthenium-based metal alkylidene catalyst (first generation Grubbs catalyst) was used to activate the surface-bound norbornenyl ROMP initiators; and a chain growth polymerization of the norbornene derivative was directly conducted from the inorganic surface resulting in the formation of surface-tethered chains containing cholesteric mesogens. A schematic diagram outlining the two-step process as described above is shown in Figure 1. The nanocomposite was prepared by the addition of the norbornenyl-bearing inorganic template activated by the first generation Grubbs catalyst to a solution of the norbornene derivative dissolved

in tetrahydrofuran (THF). The THF solvent was spiked with tricyclohexylphosphine (TCP) to increase the stability of the metal alkylidene catalyst bound on the surface of the host silicate clay template. Also, the presence of the free TCP ligand in the solution slows down the polymerization rate of norbornene in THF. Jordi and Seery (2005)[19] observed that the bound ruthenium catalysts on the silica nanoparticles surfaces were found to polymerize norbornene too rapidly when THF was not added with TCP. The polymerization was terminated by the addition of ethyl vinyl ether (EVE).

4.2 Characterization of clay-polyNBCh9 nanocomposite

To confirm the growth of the poly(norbornene) chains bearing cholesterol moieties on the clay template, FTIR and TGA measurements of the clay template and the resulting nanocomposites were done.

FTIR spectroscopy. Figure 2 shows the FTIR spectra of (a) a poly(norbornene) chain having pendant cholesterol groups, (b) the clay template used for the SI-ROMP, silylated organoclay Cloisite15A and (c) the clay-polymer nanocomposite prepared from the SI-ROMP of norbornene monomers bearing a cholesterol moiety. The silylated Cloisite 15A has characteristic peaks at 1045, 525 and 467 cm^{-1} originating from the Si-O group. Also, the clay has IR peaks at 2919 and 2852 cm^{-1}, referring to the assymetric and symmetric C-H stretching bands, respectively, associated with the alkyl chains of the modifier (Figure 2b). Meanwhile, the following IR peaks are observed in the cholesterol-bearing poly(norbornenes), polyNBCh9: (=CH$_2$), 3066 cm^{-1}; (aliphatic C-H), 2929-2852 cm^{-1}; (C=O), 1734 cm^{-1}; and (C-O), 1173 cm^{-1} (Figure 2a).
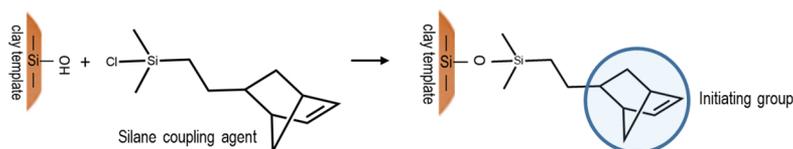
The presence of the peaks at 1734 cm^{-1} (C=O), that is inherent to the carbonyl group of the poly(norbornene) derivative and the peaks at 1045, 525 and 467 cm^{-1} originating from the Si-O group in the FTIR spectrum of the nanocomposite (Figure 2c) confirms the growth of the polymer chains from the host silicate clay.

Thermogravimetric analysis. We ran TGA experiments on the clay, the unfilled polyNBCh9 and the nanocomposite to compare mass loss. The purpose of the TGA was to determine the composition of the nanocomposite using TGA data obtained from the clay template and the polymer.

Figure 3 shows the TGA thermograms of the (a) clay template, Cloisiste15A_sil; (b) nanocomposite, Cloisite15A-polyNBCh9 and (c) an unfilled polymer prepared from the same norbornene derivative, polyNBCh9.

For the clay template (Figure 3a), the decomposition of the organic substance (modifiers in the clay that includes the alkyl ammonium and norbornene-bearing silane) takes place in the range 200-450 ºC and the total mass loss after heating to 800 ºC is 41%. Meanwhile, the unfilled polyNBCh9 (Figure 3c) thermally degrades around 400 ºC and registers

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1. Modifying clay template to covalently attach the initiating group

2. End-tethered poly(norbornene) chains from the clay template via metal-mediated polymerization
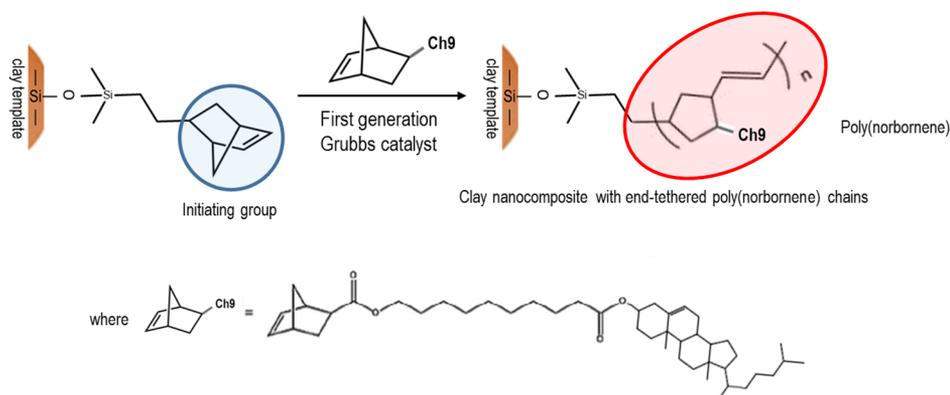

Figure 1. Schematic representation of the preparation of clay-based liquid crystalline polymer nanocomposite with end-tethered polymer having cholesterol pendant chains

100% mass loss after heating at 800 ºC. Further, different decomposition steps can be identified. The decomposition profiles can be associated with the degradation of the cholesterol side chains and the subsequent degradation of the poly(norbornene) backbone as established by Ahn, Le and Kasi (2009)[1] where they characterized different side-chain liquid crystalline polymers bearing cholesterol mesogens. To prepare these liquid crystalline polymers, a series of norbornene carboxylic cholesteryl ester monomers using various alkyl spacers were synthesized.

The nanocomposite exhibited a much higher mass loss relative to the clay template at 17% confirming the presence of the polymer in the nanocomposite. This result also complements the FTIR data. It is interesting to note however, that the nanocomposite degrades at a much lower temperature, around 310 ºC as compared to the unfilled polyNBCh9. In the studies involving nanocomposites, some papers indicated the decrease of thermal stability of polymer nanocomposites[22-24] while other studies indicated otherwise[25-27].

Differential scanning calorimetric (DSC) study of the homopolymer and the nanocomposite. All thermal transition temperatures of the polymer and the inorganic-polymer nanocomposite were determined using the 2nd heating scans from -50 ºC to 150 ºC at 10 ºC/min. The glass transition temperature, T_g, of the homopolymer polyNBCh9 was determined at 40 ºC (Figure 4). Growing these chains from the MMT clay surfaces via surface initiated polymerization decreased the T_g to 12 ºC, respectively. It has been reported

in the literature that the addition of nanofiller can change by as much as ±30 °C of the T_g of a polymer[28-29]. Bansal and co-researchers (2006)[29] found out the matrix polymers that wetted the nanoparticles showed an increase in glass transition temperature, and those that were non-wetting showed a decrease in glass transition temperature. Their study established the direct correlation between polymer wetting behavior and changes in the glass transition temperature. The study involved the use of poly(styrene) brushes having silica spheres. Further, in the work of Bandi and Schiraldi (2006)[30] where they studied the T_g behavior of clay aerogel/ poly(vinyl alcohol) composites, the change in T_g is a result of two competing processes: (1) enhanced surface interaction resulting in a decrease in the chain mobility of the polymer architecture and (2) increased free volume at the interface due to lowered crystallinity of the chains, leading to increased chain mobility.

Aside from the glass transition, another thermal transition occurs at 88 ºC for the homopolymer, but is observed at a much lower temperature for the clay-polyNBCh9 nanocomposite, at 12 ºC. This temperature is where the side-chain crystallization occurs (T_s). The observation of a side-chain crystallization for the homopolymer, polyNBCh9, can be attributed to the flexibility of the 9-carbon spacer connecting the cholesterol mesogens to the poly(norbornene) network[1-2,31].

Another strong, sharp exothermic transition was also observed at 106 ºC for the polyNBCh9 referring to the clearing temperature, T_{cl}, the temperature at which the mesophase of the liquid crystalline polymer becomes isotropic.
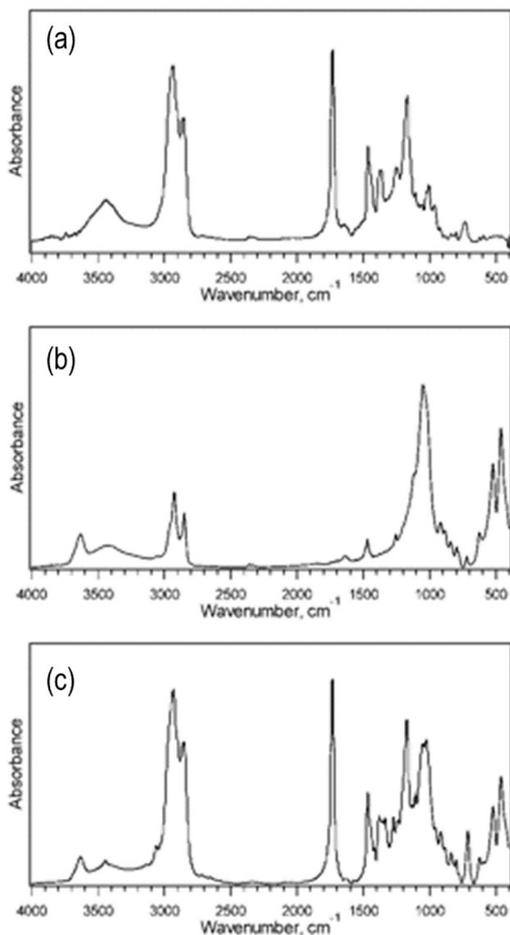
Figure 2. FTIR spectra of the (a) poly(norbornene) with cholesterol-bearing pendant group, polyNBCh9, (b) silylated organomodified MMT clay, Cloisite15A (Cloisite15A_sil) and a (c) clay-polyNBCh9
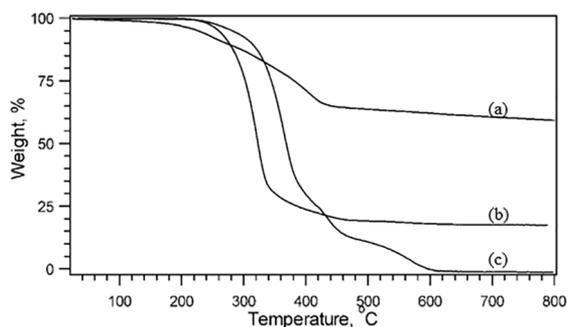

Figure 3. TGA thermograms of the (a) clay template (Cloisite15A_sil) and (b) a clay- polyNBCh9 nanocomposite obtained from the surface-initiated polymerization of NBCh9 monomers using Cloisite15A-sil clay as the template and (c) a poly(norbornene) with cholesterol-bearing pendant groups, polyNBCh9

In summary, tethering the polymer containing cholesteric moieties changes the thermal properties of the prepared nanocomposites as compared to the bare (unfilled) homopolymer prepared from the same derivatized monomer.
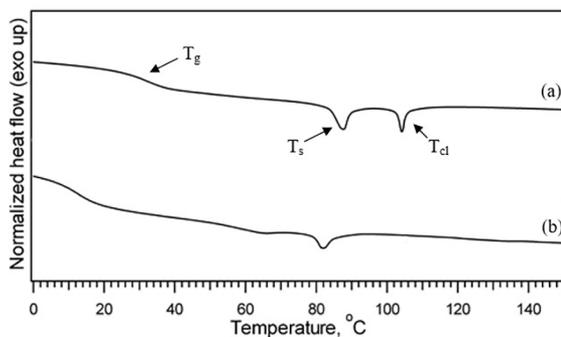

Figure 4. DSC thermograms (10 ºC/min, second heating scans) of (a) homopolymer polyNBCh9 and (b) MMT-polyNBCh9. T_g, T_s and T_{cl} refer to the glass transition temperature, side-chain crystallization temperature and clearing temperature, respectively

5. Conclusion

We have successfully grown cholesterol-bearing poly(norbornene) brushes covalently attached from surfaces of silicate clays. The synthesis of these composites involved the treatment of inorganic host with first generation Grubbs catalyst, a ruthenium alkylidene, that induced a ring-opening metathesis and subsequent surface initiated polymerization of the cholesterol bearing monomer. Nanocomposites of this nature can serve as models for testing theories of polymer brushes in confined geometries. In the synthesis of these model systems, control over aspects of the polymer brushes such as brush density, molecular weight, and polydispersity is essential. Varying the organic moieties, *i.e.* the monomer used to grow the polymer chains, is one method of controlling these variables. Work is presently being done to further characterize the growth of these polymer chains formed in this fashion and their behavior as LCPs.

6. Acknowledgments

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