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Synthesis of Polyolefin/Layered Silicate Nanocomposites via Surface-Initiated Ring-Opening Metathesis Polymerization

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ABSTRACT: Here we report the synthesis and characterization of block copolymer/layered silicate (BCPLS) nanocomposites via the surface-initiated ring-opening metathesis polymerization (SI-ROMP) of norbornene and cyclopentene from montmorillonite clay (MMT). The MMT particle surfaces were functionalized with a norbornene-terminated alkylammonium surfactant through ion exchange. Block copolymer brushes of norbornene and cyclopentene were polymerized directly from the surface of these functionalized clay platelets, yielding highly exfoliated nanocomposites. A fraction of the polymer brushes were removed from their substrate by reverse ion exchange and characterized in parallel with their corresponding nanocomposite analogues. The thermal, mechanical, and morphological characteristics of the BCPLSs and their neat analogues were then compared directly. This enabled us to assess the role of the MMT filler in the thermal properties, solid/melt state rheology, and morphology.

INTRODUCTION

Since the 19th century, polymer composites have been widely investigated because of significant improvements in various properties (typically mechanical) of the composite material compared to its constituents. A polymer nanocomposite is distinct from traditional composites in that at least one characteristic dimension of the filler material is mesoscopic. A number of factors influence the suitability of a particular nanofiller, such as its surface to volume ratio, the character of its interactions with the matrix, and the available processes by which it may be dispersed. Clays have been studied widely because of their abundance in nature, good dispersion properties, and established intercalation chemistry. Clays such as montmorillonite (MMT) are comprised of stacks of high-aspect-ratio sheets of silicate material roughly 1 nm in thickness. Each sheet has a net negative charge, and so cationic species (in nature, aqueous Na⁺) maintain charge neutrality within the 1−2 nm gap in between layers. The polar nature of MMT and the nonpolar nature of common polymers, especially polyolefins, make the sorption of polymer onto naturally occurring clays difficult. In the late 1980s, Okada et al. of Toyota reported a series of polymer/layered silicate nanocomposites (PLSNCs) comprised of a dispersion of MMT into a polyamide matrix. Favorable filler/matrix interactions were achieved via ion exchange of the native Na⁺ cations with long alkylammonium surfactants. These surfactants have very long carbon chains which reduce the clay surface energy and increase the d-spacing, making it easier to form nanocomposites.

Kojima et al. demonstrated that key mechanical properties in completely exfoliated nylon−clay hybrids with 4.2 wt % filler were elevated by as much as 50% with respect to the neat resin. Moreover, significant elevation in the service temperature, barrier properties, and resistance to oxidative degradation have been observed in PLSNCs. The degree of these improvements is strongly correlated to the degree of interfacial contact between the reinforcing filler and polymer matrix; this in turn is dictated by the quality of the filler dispersion. PLSNCs typically feature a mixture of three distinct filler morphologies: micrometer to submicrometer sized aggregates (minimal polymer/clay interaction); intercalated structures, tens of nanometers thick, where polymer has diffused into the interlayer gallery but significant interactions remain between clay layers; and exfoliated structures where maximal contact is achieved by the complete encapsulation of isolated clay layers with polymer. Many researchers have demonstrated that complete exfoliation is especially desired because of the highest possible contact between filler and matrix and the attendant improvements in many of the properties. Nanocomposites can be formed by melt processing, in situ polymerization, and surface-initiated polymerization (SIP); each method produces a different degree of dispersion. For complete exfoliation of platelets in the polymer matrix, surface-initiated polymerization is a desired route and is also expected to yield composites with superior properties.

The (SIP) route to polymer-modified surfaces is often preferred in the study of polymer brushes on macroscopic surfaces, e.g., polymer films or surface-modified glass/
Scheme 1. Synthesis of 5,6-Di(11-(N,N,N trimethylammonium)undecoxycarbonyl)norbomene (NbnN2+).

This is primarily due to the ease of achieving graft densities sufficient to force the polymer conformations into the "brush" regime, where crowding forces chains to extend far beyond their unperturbed dimensions. Analogously, SIP from clay platelets can potentially yield a graft density as high as ≈1 chain/nm. Moreover, if chain growth is uniform throughout the clay surfaces, steric forces will quickly push neighboring particles apart from each other, yielding highly exfoliated PLSNCs. This important caveat can pose a hurdle to the successful SIP-based dispersion of nanoclays due to the tight confinement imposed by the closely placed layered silicates.

Behling et al. illustrated using surface-initiated atom transfer radical polymerization (SI-ATRP) that limiting the polymerization rate was crucial to the synthesis of fully exfoliated structures. When the kinetics were properly controlled, Behling showed essentially complete exfoliation in poly(ethylene-block-tert-butyl acrylate) brushes produced an array of microphase-separated morphologies clearly influenced by the MMT substrate. Moreover, the glass transition temperature of the poly(tert-butyl acrylate) block varied between its bulk value of \( T_g \approx 43 \, ^\circ\text{C} \) and as high as \( T_g \approx 68 \, ^\circ\text{C} \) depending upon the sample morphology, while the 100 \( ^\circ\text{C} \) polystyrene \( T_g \) remained more or less constant across all of the specimens examined. While these studies were important to understand the nature of self-assembly in block copolymer/layered silicate nanocomposites, the model system employed is well-suited for morphological characterization but is far from ideal in understanding the influence of structure on mechanical properties.

In principle, any "living" polymerization scheme may be adapted to the SIP fabrication of PLSNCs. Ring-opening metathesis polymerization (ROMP), a type of catalyzed olefin metathesis reaction, is of particular interest to us for the access it provides to commercially relevant elastomers and plastics such as polyethylene. A ROMP catalyst is based on a transition metal center and a "cocatalyst" ligand system that has a pronounced effect on many of the kinetic steps that can ultimately produce polymers with living character. ROMP is especially an important polymerization route to form living polymers with cyclic olefins and opens a new arena for producing thermoplastic elastomers.

In this article we report the controlled surface-initiated ROMP (SI-ROMP) of norbornene (Nbn) and cyclopentene (CPE) from appropriately functionalized MMT clays based on the first-generation Grubbs' catalyst \((\text{PCy}_3)_2(\text{Cl})_2\text{Ru=CHPh}\). These monomers are interesting from a perspective of commercial relevance since hydrogenation of polycyclopentene gives perfectly linear polyethylene, a highly crystalline thermoplastic; hydrogenated substituted polynorbornenes yield low-\( T_g \) rubbers; together these monomers offer an appealing route to thermoplastic elastomeric PLSNCs. Moreover, Nbn is a canonical monomer for ROMP because of its commercial availability, high ring strain, and ability to form living polymers. The successful synthesis of block copolymers employing norbornene and cyclopentene using Shrock's catalyst has been reported in the literature. Schrock-type ROMP catalysts are very effective for polynorbornene (PNbn) synthesis but give polymers with less syndiotacticity and moreover are intolerant to air, moisture, and protic solvents. Because of low ring strain, the ROMP of CPE is a more difficult process; a major hurdle is the competing acyclic diene metathesis (ADMET), a major side reaction which increases oligomer concentration. Sanford et al. have shown that the addition of "cocatalyst" (excess ligand) to the polymerization is necessary to shift the equilibrium toward polymer propagation. On the other hand, with excellent moisture/air tolerance though with less activity, Ru-based Grubbs' catalysts give high-\( \text{trans} \) polymers with good isotactic bias. Unfortunately, Ru-based ROMPs of norbornenes have not been as extensively studied as compared to Shrock’s catalyst. In the present article, we first explain how to conduct SI-ROMP to form PLSNCs with good exfoliation and reproducible molecular weight distribution using the first-generation Grubbs’ catalyst, which is ideal for PLSNCs due to the intrinsic incompatibility with less tolerant systems. We then show PLSNCs characterization data exploring the thermal, mechanical, and morphological properties. In order to directly assess
the influence of the filler particles in these materials, the polymer brushes were removed from the MMT surface via reverse ion exchange and characterized along with its counterparts.

**EXPERIMENTAL DETAILS**

**Materials Synthesis. MMT Surface Modification.** Chemicals used for synthesis of organic surfactant modifier are 5-norbornene-2,3-dicarboxyl dichloride, 11-bromo-1-undecanol, diethyl ether, pyridine, magnesium sulfate, deionized water, hexanes, trimethylamine, and ethanol. All chemicals were purchased from Sigma-Aldrich and used as received. Montmorillonite clay (Cloisite-Na+) was generously supplied by Southern Clay Products Inc. Based on the cation exchange capacity of 92 mequiv/100 g and specific surface area,14 MMT clay contains ≈1 exchange site/Å². The synthesis (Scheme 1) is closely related to that employed by Behling14 and can be summarized as the addition of norbornene dicarboxyl chloride to bromoundecanol to form a norbornene ester; the addition of trimethylamine and extensive purification yield 1, 5,6-di(11-bromoundecoycarbonyl)norbornene. In a typical synthesis, 4 g of bromoundecanol in 2.6 mL of pyridine and 60 mL of diethyl ether is added dropwise to 2.58 mL (equimolar) of norbornene dicarboxyl chloride in 10 mL of diethyl ether and stirred for 6 h. The mixture is concentrated with rotary evaporation prior to liquid–liquid extraction (LLE) with diethyl ether. The norbornene diester is then mixed with 15.3 mL of 30 vol % trimethylamine and extensive evaporation, purified using LLE with diethyl ether, and dried under dynamic vacuum for 96 h to achieve maximal graft density.14 NbnN2⁺-MMT (3) was recovered by filtration and dried under dynamic vacuum at room temperature for 24 h. According to the TGA data presented in Figure 1, the difference in mass loss due to water adsorbed (around 170 °C) and that due to dehydroxylation of MMT (around 700 °C) gives 25% of organic content in the clay; this corresponds to nearly 80% of the ion-exchange capacity. X-ray diffraction spectra (Figure 2) show an increase of the intergallery spacing of clay platelets from 11 to 21 Å after the ion exchange of Na⁺-MMT with NbnN2⁺.

**Bulk Polymerization of Norbornene and Cyclopentene.** Reagent grade norbornene and cyclopentene (Sigma-Aldrich) were dried over calcium anhydride, subjected to three freeze/pump/thaw cycles, and stored and handled in an Ar-filled glovebox. The ROMP of norbornene is reported elsewhere in the literature.13,15,35 The procedure is similar to some modifications to be described in more detail in the Results section. A typical ROMP of norbornene consists of the addition of the required amount of monomer in MeCl (1 g:7 mL) to a solution of first-generation Grubbs’ catalyst in MeCl (1 mg:1 mL) at 20 °C; after 1 h the polymerization is terminated with ethyl vinyl ether and precipitated in methanol. In an exemplar with monomer/catalyst (M/C) ratio of 50, 0.45 g of norbornene in 7 mL of MeCl was added at a rate of 0.03 g/min to a solution of 9 mg of Grubbs’ catalyst, 9 mL of MeCl, and 36 mg of PCy3 at 20 °C for 1 h. The number-average molecular weight (Mn) was 46 800 Da, and the PDI was 1.067. ROMP of cyclopentene is performed as in literature and with same modifications as used for synthesis of norbornene. The reaction was terminated at 5 h, corresponding to 30% conversion, to minimize unwanted side reactions. In bulk polymerizations, block copolymers were synthesized by sequential addition of the second monomer after the first monomer is polymerized. The molecular weight distribution of all polymers was determined with size exclusion chromatography (SEC).

**PLSNC Synthesis.** Surface-modified clay platelets were used for synthesizing nanocomposites. Also, block copolymer nanocomposites were formed by sequential addition of monomers. All nanocomposites analyzed here in the article are block copolymer nanocomposites with poly(norbornene) as first and poly(cyclopentene) as second block. ROMP-active Nbn⁺-MMT substrates were prepared by the dispersion of 75 mg of Nbn⁺-MMT in 16 mL of dichloromethane for 4 h with ultrasonication at 20 °C, followed by the addition of 50 mg of Grubbs’s catalyst and 200 mg of PCy3 (Scheme 2). The mixture was vigorously stirred with ultrasonication for 1 h to form 4. The first polymerizable group (Nbn) radiating outward from clay surface gets initiated for polymerization and becomes active propagating species. The remainder of the SI-ROMP process is analogous to the bulk synthesis, with the polymers propagating from the active catalyst that is now attached to the surface of clay. A norbornene/MeCl solution (1 g:7 mL) was introduced to ultrasonicated mixture containing 4 at 0.03 g of Nbn/min with a syringe pump. After 1 h neat cyclopentene was then added at a rate of 0.5 mL/min. Neat polymer was recovered from PLSNCs for characterization and direct comparison with the PLSNC parent material via reverse ion exchange. In a typical reverse ion exchange procedure, 1 g PLSNC and 1 g LiCl are dissolved in 100 mL MeCl; the mixture is stirred under water for 90 h, filtered, and centrifuged, and vacuum distilled prior to use. Methylene chloride (MeCl, Sigma-Aldrich) was purified by three freeze/pump/thaw cycles. All chemicals were used within 1 week of purification in order to ensure there is no autopolymerization. Methanol, ethyl vinyl ether, first-generation Grubbs’ catalyst ((PCy3)2(Cl)2Ru═CHPh), and tricyclohexylphosphine (PCy3, Sigma-Aldrich) were used as received. All reactants were stored and handled in an Ar-filled glovebox. The ROMP of norbornene is reported elsewhere in the literature.13,15,35 Our

**Figure 1.** TGA thermogram showing pristine MMT and functionalized MMT.

**Figure 2.** XRD spectra for neat MMT, NbnN2⁺-MMT, and mNP1.
X-ray Diffraction (XRD). Increase in intergallery spacing of modified MMT and exfoliation of nanocomposites were analyzed with a Siemens D-500 powder diffractometer using a copper Kα source (λ_{avg} = 1.54 Å) operating in variable slit mode. Scattering angles varied in the interval 2θ ∈ [2°, 10°] or q ∈ [0.14, 0.71] Å⁻¹, where q ≡ 4π/θsinθ. Clay d-spacing is reported as d = 2π/q*, where q* corresponds to the peak in scattering intensity. X-ray diffraction patterns are available in the Supporting Information.

Thermogravimetric Analysis (TGA). TGA measurements were conducted on polymer nanocomposite and reverse ion exchanged polymer brushes. Analysis was done on TA Instruments thermal analysis system from 50 to 800 °C at 15 °C/min in an inert atmosphere. Data were analyzed with TA Instruments data analysis software.

Differential Scanning Calorimetry (DSC). DSC was used to measure the glass transition temperature T_g of the polymers and PLSNCs presented in this study. Prior to DSC measurements, samples were dried above 150 °C under vacuum for at least 24 h to eliminate the effects of small molecule plasticizing. All measurements were obtained using a TA Instruments DSC Q2000 system scanning from −75 to 150 °C at 10 °C/min in N₂. Three complete heating/cooling cycles were collected for each specimen. Data were analyzed by using TA Instruments data analysis software, and glass transition temperatures were reported.

Dynamic Mechanical Analysis (DMA). Solid state viscoelastic properties of PLSNCs and analogous neat polymers were measured using a TA Instruments DMA Q800 system from −50 to 100 °C at 3 °C/min in an inert atmosphere. Rectangular samples of 1 mm thickness were prepared, and tensile testing was done with amplitude of 7% strain and a frequency of 1 Hz.

Transmission Electron Microscopy (TEM). To image nano-composites, polymer sections of 70−90 nm thick were cut by using a Leica cryo Ultramicrotome. Images were collected from multiple sections at various locations using a FEI-Tecnai 2-F20 STEM.
mass $M_n$ for Nbn1 as a function of time for a ROMP of norbornene at room temperature ($\approx 23 \ ^\circ C$, no temperature control) with a 500:1 molar norbornene:Grubbs' catalyst (M/C) ratio, corresponding to a target molecular weight of $\approx 50$ kDa.

The scatter in the $M_n$ vs $t$ data of Figure 3 indicates that the polymerization is complete in less than 5 min; allowed to proceed for longer times, the reversible nature of the reaction is clearly problematic. To produce well-defined block copolymers, and also to encourage dispersion in the production of exfoliated PLSNCs, it is necessary to limit the kinetics of this polymerization.

To achieve optimum conditions, we repeated ROMP reactions with a variety of combinations of reaction time, monomer/catalyst (M/C) ratio, cocatalyst/catalyst (Co/C) ratio, monomer addition rate, and temperature.

To decrease the reaction rate, we first repeated the polymerization at 0 $^\circ C$, 15 $^\circ C$ (Nbn2a-e), and 20 $^\circ C$ (Nbn3a-e). We observed that the ROMP of norbornene at 0 $^\circ C$ did not yield any polymer, evidently because the initiation rate is negligible at this temperature. Table 1 shows that the Nb3 series at 20 $^\circ C$ produces more consistent $M_n$ and PDI values than the other temperatures that we attempted, although the polymerization is essentially complete within 5 min. To limit the polymerization rate through the monomer concentration, we then produced Nbn4a by adding monomer at a rate of 0.03 g/min with a syringe pump; this semibatch process significantly reduced the polymerization rate although the polydispersity index (PDI) of the product remained $\approx 2$. The Nbn4a-c series explores the role of the M/C ratio and suggests that better control over polydispersity is realized at higher catalyst concentration.

A final reaction parameter that we investigated was the use of PCy$_3$, corresponding to the ligand system in the Grubbs' catalyst, as a cocatalyst. PCy$_3$, significantly reduces the polymerization rate and yields polymers with very narrow molecular weight distributions, e.g., Nbn5b at 46.8 kDa and PDI = 1.067 after 30 min as shown in Figure 4. Under these conditions the polymerization appears to be complete at 1 h; the molecular weight distribution remained stable for up to 2 h. SEC traces that show the influence of PCy$_3$, are available in the Supporting Information.

We also produced several bulk poly(cyclopentene)s via ROMP; again, semibatch monomer addition along with the use of PCy$_3$ as a cocatalyst appears to be crucial to produce well-defined polymers. As stated earlier, acyclic diene metathesis (ADMET) is a problematic side reaction that inhibits the preparation of high molecular weight polymers and broadens the molecular weight distribution. Figure 5 illustrates the influence of PCy$_3$, in the synthesis of CPE1 and CPE2 over time. Clearly, as the reaction proceeds the cosubstituted polymerization features monotonic chain growth over the course of 5 h, and the PDI is characteristic of a "living"
After 5 h, the monomer is nearly depleted, and depolymerization reactions severely broaden the molecular weight distribution. Based on our observations of controlling ROMP reactions for individual monomers, synthesis of block copolymers using norbornene as first block and cyclopentene as second block was carried out accordingly. An SEC trace for NP1 is shown in Figure 6, where we can see an increase in molecular weight of the polymer after subsequent addition of second monomer yielding an overall PDI of 1.11. We applied identical conditions to the surface-initiated polymerization of norbornene and cyclopentene to produce mNP1 from NbnN2⁺-MMT, a 189 kDa poly(norbornene-b-cyclopentene) diblock copolymer PLSNC. A portion of mNP1 was subjected to the reverse ion exchange process as described in the Experimental Details section to yield mNP1*, i.e., mNP1 with the MMT substrates removed. An SEC trace of mNP1* appears in Figure 6 and illustrates that the surface-initiated polymerization proceeds with kinetics identical to the solution polymerization under otherwise analogous conditions.

**Nanocomposite Characterization.** XRD patterns of mNP1 (Figure 2) show only background scattering, which indicate that the material is free of MMT aggregates sufficiently large to contribute to measurable Bragg scattering. Figure 7 shows representative TEM images that further support the nearly full exfoliation of MMT within the block copolymer matrix. Figure 7a shows at high magnification a typical region in which a dispersion of hairlike particles 1 nm in thickness is visible, corresponding to fully exfoliated MMT particles. In some sections, however, we found regions such as that depicted in Figure 7b, which shows a 1 μm² area containing a number of intercalated structures ≈10–50 nm in thickness.

The high degree of dispersion in clay particles throughout mNP1 corresponds to a large polymer/clay interphase region. Substantial differences between mNP1 and mNP1* in thermal and mechanical behavior indicate strong interactions between the MMT substrate and block copolymer brushes. The thermal degradation characteristics of mNP1 and mNP1* were compared with TGA; the data in Figure 8, summarized in Table 2, show that higher temperatures are required to achieve
the same level of mass loss in mNP1 compared to mNP1*. For example, 10% mass loss occurs at 314 °C in mNP1*, whereas for the parent nanocomposite the mass loss remains less than 10% until 407 °C. The difference in final residual mass for these two samples corresponds to the mass composition of clay in mNP1, ≈ 9%. The enhanced thermal stability of mNP1 is consistent with that of other highly exfoliated nanocomposite systems reported in the literature,38 where the stability enhancement is believed to be a direct consequence of the barrier properties imparted by the high aspect ratio filler.

MMT also appears to strongly influence the properties of the block copolymer brushes. Differential scanning calorimetry (Figure 9) shows a glass transition of 15.6 °C in mNP1*, corresponding to polynorbornene domains; this transition increases by nearly 20 °C, to 34.6 °C, in mNP1. This substantial elevation in the glass transition temperature is similar in magnitude to that reported by Behling et al. in polystyrene- tert-butyl acrylate) PLSNCs formed by surface-initiated atom transfer radical polymerization.18 Strongly stretched polymer brushes have been shown in the past, through both simulation39 and experiments,40,41 to dramatically retard the chain relaxation dynamics. This may be understood qualitatively through the steric restriction of the cooperative motions that are believed to underpin the nature of the glass transition.52 These factors suggest that the T_g elevation that we observe supports that mNP1 is comprised of highly exfoliated polymer brushes.

The solid state viscoelastic properties further support the altered dynamic behavior of mNP1 compared to its MMT-free analogue. Figures 10 and 11 show isochronal DMA temperature scan data collected in the linear viscoelastic regime (<10% strain) at 1 °C/min and 1 Hz for mNP1 and mNP1*. At temperatures below their softening points, the loss moduli of both materials are within 10% of each other and show no dependence on temperature; that is, they represent a plateau modulus G_0, characteristic of an elastic solid. The softening point, defined here as the temperature at which the loss modulus decreases to 0.8G_0, is −9 °C for mNP1* and 30 °C for mNP1. The temperature span of the softening transition in mNP1 is much narrower than that of mNP1*, 36 °C for the former and 89 °C for the latter. The peak in tan δ, often reported as a measure of T_g is 17 °C for mNP1*, in quantitative agreement with the T_g value from DSC. T_gDMA for mNP1, on the other hand, is significantly greater than the DSC value at 52 °C. The loss moduli, G″(T), of these two materials closely mirror the behavior of tan δ(T); interestingly though, G″(T) for mNP1 has a slight upward inflection at −18 °C, in the vicinity of the softening onset temperature for mNP1*. This similarity suggests that the confinement induced by the MMT particles are suppressing the onset of a relaxation process that precedes the glass transition.

Because of the high level of unsaturation in ROMP-based polymers, they are highly susceptible to cross-linking on exposure to ultraviolet radiation or elevated temperature. To assess the role of the clay substrate in this process, we conducted an isochronal temperature ramp at ω = 1 rad/s and dT/dt = 18.5 °C/h in the parallel plate configuration of an ARES strain-controlled rheometer. Figure 12 shows the complex dynamic modulus vs temperature and time. Remarkably, we note that the melt-phase modulus of mNP1 is 3–6 times lower than that of its analogous clay-free counterpart, mNP1* throughout the 12 h experiment. This contrasts the solid state DMA data of Figure 10 where the nanocomposite is of similar modulus far below the glass transition temperature and nearly an order of magnitude larger than mNP1* at room temperature.

### Table 2. Thermal Properties of mNP1 and mNP1*

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_10^a (°C)</th>
<th>T_50^b (°C)</th>
<th>T_{max}^c (°C)</th>
<th>Residual mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mNP1</td>
<td>407</td>
<td>452</td>
<td>491</td>
<td>14.5</td>
</tr>
<tr>
<td>mNP1*</td>
<td>314</td>
<td>434</td>
<td>490</td>
<td>6.2</td>
</tr>
</tbody>
</table>

*Temperature at 10% weight loss. †Temperature at 50% weight loss. §Temperature at maximal weight loss.
temperature. Thus, in the melt, polymer/clay brushes have substantially lower viscosities which is desirable from a processing perspective. The modulus of mNP1 and mNP1** both increase by \( \approx 2000\% \) over the course of the 12 h experiment. \( G^\prime_{\text{mNP1}} \) increases monotonically throughout the experiment; \( G^\prime_{\text{mNP1}^*} \) increases monotonically until 150 °C, where it plateaus through \( \approx 190 \) °C. This behavior is consistent with cross-linking which proceeds at essentially a constant rate until 150 °C. Over the plateau region, mNP1 exhibits behavior characteristic of an elastic solid. At 190 °C, \( G^\prime_{\text{mNP1}} \) increases monotonically once again, suggesting that a new process has been thermally activated allowing the material to cross-link further. We speculate that this two-phase cross-linking behavior is related to the relative immobility of chains tethered to the clay surface at low temperature, which are then liberated at high temperature. In the low temperature regime, chains may only cross-link with their neighbors, limiting the extent of cross-linking. At high temperature, the ionically bound chain ends become liberated from their substrate and cross-linking again continues unabated. Classical elasticity theory lends plausibility to this interpretation: The plateau modulus of mNP1 at 400 K is roughly 50 kPa; assuming a mass density of mNP1 of \( \rho \approx 0.9 \) g/cm\(^3\) yields an average molecular weight between cross-links of \( M_n = \rho RT / G^\prime = 75 \) kDa, or approximately 1–2 cross-links per chain given \( M_n = 189 \) kDa.

**CONCLUSION**

In this work we have demonstrated that well-defined homopolymers and block copolymers of norbornene and cyclopentene can be synthesized via surface-initiated ring-opening metathesis polymerization from montmorillonite functionalized with first-generation Grubbs’ catalyst. Polydispersity indices less than 1.2 and reproducible molecular weights were achieved by the semibatch addition of monomer and the use of cocatalyst to suppress the polymerization rate. Under the polymerization conditions that we employed, 150 kDa polymers were produced over the course of 1 h. These conditions for solution polymerizations produced identical results as surface-initiated polymerizations NbnN\(^2\)^+–MMT. The resultant nanocomposites were free of aggregates as determined by X-ray diffraction and electron microscopy. Electron microscopy showed that the materials are highly exfoliated, although we found some regions where intercalated structures were present. This indicates that further reduction of the polymerization rate is necessary to achieve full exfoliation. We found substantial differences in the thermal, dynamic, and viscoelastic behavior of the nanocomposites compared to the neat polymer recovered by reverse ion exchange, most remarkably a 20–35 °C elevation in the polynorbornene glass transition temperature. These results show that SI-ROMP may be an attractive route to a new family of high performance polyolefin thermoplastics and thermoplastic elastomers.

**ASSOCIATED CONTENT**

Supporting Information

Additional SEC data and NMR characterization of NbnN\(^2\)^+. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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