Poly(methyl methacrylate)/Laponite Nanocomposites: Exploring Covalent and Ionic Clay Modifications

Paul A. Wheeler, Junzuo Wang, and Lon J. Mathias*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406

Laponite clay was modified with combinations of organic ammonium surfactant and/or covalently bound poly(methyl methacrylate) (PMMA). Two polymer attachment methods were explored, one through reaction of a methacrylate compound with the clay's silanol group followed by in situ free-radical polymerization of methyl methacrylate (MMA), and the other through attachment of an ATRP initiator followed by brush polymerization. The free-radical method yielded clays with ca. 75 wt % of polymer bound though multiple attachment sites to the clay, whereas the ATRP method yielded ca. 68 wt % of bound polymer attached only at the chain end. The PMMA-modified clays were very dispersible in organic solvents and were solvent-blended with commercial PMMA at 1, 3, 5, and 10 wt % concentrations. The resulting nanocomposites were optically transparent and homogeneous. TEM images showed mixed intercalated and exfoliated dispersions. DMA analysis showed an increase in room temperature modulus of 50% at 5 wt % concentration for the clay with no surfactant and PMMA free-radical attachment.

Introduction

Research in the area of polymer/clay nanocomposites has been quite vigorous over the past decade,[1−3] beginning with Toyota researchers' discovery that nylon 6, when produced in situ in the presence of aminolauric acid-treated montmorillonite, yielded materials with an 80 °C increase in heat distortion temperature and nearly double the modulus with a clay content of only 5 wt %.[4,5] Since then, polymer/clay nanocomposites have been evaluated for applications as flame retardants, mechanical property enhancers, and permeation barriers.[6−9] Generally, the critical part of creating such a system is exfoliating the clay sheets and dispersing them throughout the polymer matrix to maximize interaction between the clay surface and the polymer.

Since clay is naturally hydrophilic and inherently incompatible with most organic polymers, several methods have been studied to make clay compatible with polymer. The most popular involves surface ion exchange, in which the metal cations on clay's surface are exchanged for organic cationic surfactants, typically ammonium or phosphonium compounds with long alkyl chains.[10−12] Imidazolium surfac-

tants have also been studied for this purpose because they offer superior thermal stability.[13,14] Another method uses complexation of the surface sodium cations with poly-(ethylene glycol),[15,16] while another involves reaction of trialkoxysilanes as the silicon source during clay synthesis.[17,18] Sol−gel reaction in the presence of dispersed organically modified montmorillonite was also found to form delaminated clay structures.[19] All of these clays, modified in some form, can then be used in polymer matrix nanocomposites. The typical methods of exfoliating clay in a polymer matrix include in situ polymerization, polymer mixing by melt compounding, and solvent casting.[3] These generally involve organically surface-modified clays that are mixed at less than 10 wt %.

Recently, covalent reaction of silane coupling agents to the silanol groups of clay has been reported, and the silanol groups are assumed to be on the edge of the clay sheets.[20,21] For example, the treatment of montmorillonite with trichloro- and trialkoxysilanes has been reported, resulting in organic

* Corresponding author. Phone: 601-266-4871. Fax: 601-266-5635. E-mail: lon.mathias@usm.edu.

(1) LeBaron, P.; Wang, Z.; Pinnavaia, T. *Appl. Clay Sci.* **1999,** *15,* 11.
(2) Carrado, K. A. Polymer-Clay Nanocomposites. In *Advanced Polymeric Materials: Structure Property Relationships;* Advani, S., Shonaike, G., Eds.; CRC Press: Boca Raton, FL, 2003; pp 349−396.
(3) Ray, S.; Okamoto, M. *Prog. Polym. Sci.* **2003,** *28,* 1539.
(4) Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993,** *8,* 1174.
(5) Gilman, J.; Jackson, C.; Morgan, A.; Harris, R. *Chem. Mater.* **2000,** *12,* 1866.
(6) Morgan, A.; Harris, R.; Kashiwagi, T.; Chyall, L.; Gilman, J. *Fire Mater.* **2002,** *26,* 247.
(7) Zhang, J.; Wilkie, C. *Polym. Degrad. Stab.* **2003,** *80,* 163.
(8) Giannelis, E. *Appl. Organomet. Chem.* **1998,** *12,* 675.
(9) Chaiko, D.; Leyva, A. *Chem. Mater.* **2005,** *17,* 13.
(10) Vaia, R.; Teukolsky, R.; Giannelis, E. *Chem. Mater.* **1994,** *6,* 1017.

(11) Xie, W.; Gao, Z.; Pan, W.; Hunter, D.; Singh, A.; Vaia, R. *Chem. Mater.* **2001,** *13,* 2979.
(12) Xie, W.; Xie, R.; Pan, W.; Hunter, D.; Koene, B.; Tan, L.; Vaia, R. *Chem. Mater.* **2002,** *14,* 4837.
(13) Gilman, J.; Awad, W.; Davis, R.; Shields, J.; Harris, R.; Davis, C.; Morgan, A.; Sutto, T.; Callahan, J.; Trulove, P.; DeLong, H. *Chem. Mater.* **2002,** *14,* 3776.
(14) Awad, W.; Gilman, J.; Nyden, M.; Harris, R.; Sutto, T.; Callahan, J.; Trulove, P.; DeLong, H.; Fox, D. *Thermochim. Acta* **2004,** *409,* 3.
(15) Loizou, E.; Butler, P.; Porcar, L.; Kesselman, E.; Talmon, Y.; Dundigalla, A.; Schmidt, G. *Macromolecules* **2005,** *38,* 2047.
(16) Shemper, B.; Morizur, J.; Alirol, M.; Domenech, A.; Hulin, V.; Mathias, L. *J. Appl. Polym. Sci.* **2004,** *93,* 1252.
(17) Carrado, K.; Xu, L.; Csencsits, R.; Muntean, J. *Chem. Mater.* **2001,** *13,* 3766.
(18) Minet, J.; Abramson, S.; Bresson, B.; Sanchez, C.; Montouillout, V.; Lequeux, N. *Chem. Mater.* **2004,** *16,* 3955.
(19) Letaief, S.; Ruiz-Hitzky, E. *Chem. Commun.* **2003,** 2996.
(20) Manufacturer's Laponite Literature. http://www.laponite.com/pdf/broch/science.pdf (accessed May 12, 2004).
(21) Song, K.; Sandi, G. *Clays Clay Miner.* **2001,** *49,* 119.

loadings of up to 25 wt %, with the intended application of hazardous material remediation.[21] No increase in the clay's basal spacing was observed, suggesting that the organic compounds are bound to the outer clay edges. Methacrylate-terminated alkoxysilanes were also used to treat the edge of Laponite for applications in emulsion polymerizations.[22,23] The trialkoxysilanes apparently linked the clay sheets together, making them nondispersible, while monoalkoxy-silane-treated clays were dispersible in water. In another report, protonated amino alkoxysilanes and end-terminated alkoxysilanes were used to create clay monoliths by cross-linking clay particles together through their edges.[24] Also, the surface of magadiite, a layered sodium polysilicate containing silanol groups, was reacted with different lengths of aliphatic alcohols and was able to be cast into transparent nanocomposite films.[25] Surfactant-treated montmorillonite was further modified with a trialkoxysilane-terminated epoxy to improve clay compatibility and properties of poly(L-lactide) and poly(L-lactide)/poly(butylene succinate) blends.[26-28]

Laponite was chosen for this study because it is a relatively uniform, disc-shaped synthetic clay 25 nm in diameter and 1 nm thick, as claimed by the manufacturer.[20] It has an empirical formula of $0.7Na^+[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$ and a cation exchange capacity of 50-55 mmol/100 g.[20] Its high ratio of edge-to-surface area (0.07) makes it an ideal candidate for further investigating edge modification, since easily observed amounts of organic material can be attached. We have been exploring synthesis of edge-modified Laponite clay using alkoxysilanes possessing additional reactive groups such as primary amines, methacrylates, benzo-phenones, and tertiary bromines.[29] With such structures, polymer chains can be grafted to, or grown from, clay edges, creating starlike or fringed polymers with a nanosized inorganic core. We have previously reported preliminary work in the synthesis of polymer grown from covalently bound atom transfer radical polymerization (ATRP) initiators on Laponite.[30] The present work combines both edge and surface modification of clay via different synthetic routes, opening up possibilities for a broad range of multifunctional nanomaterials, an area we are actively exploring.

Combining ion exchange and covalent attachment allows a wide range of tailorability for inorganic clays. With methacrylate and ATRP initiating sites, covalent polymer attachment to clay is possible. Here we explore combining surfactant treatment with covalently attached poly(methyl methacrylate) (PMMA) polymer on Laponite clay and blending with commercial PMMA to create nanocomposites. PMMA was grown from or attached to Laponite through free-radical or ATRP polymerizations. The resulting polymer-
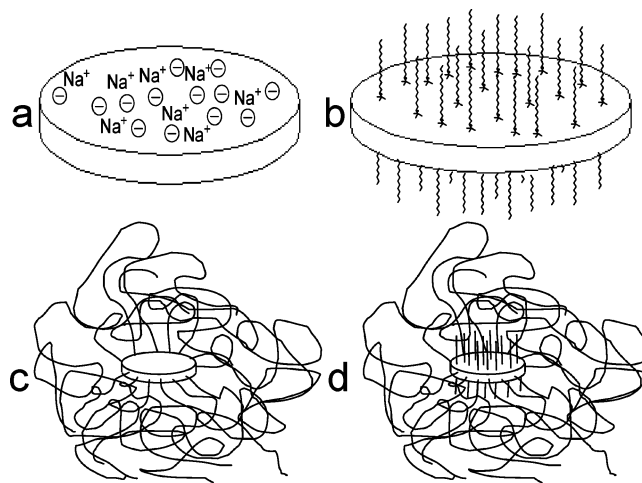

Figure 1. Four different types of clay blended into PMMA: (a) no modification, (b) surface surfactant ion exchange, (c) covalent polymer grafting, and (d) surfactant and polymer grafting.

treated clay was then solvent-blended with commercial PMMA and cast into films. The resulting films were evaluated with DSC, DMA, and TEM to study the effectiveness of the clay treatments as they relate to clay dispersion quality and the resulting mechanical properties.

Results and Discussion

In this study, four types of clay were evaluated for use in PMMA nanocomposites, as shown in Figure 1: (a) non-modified sodium Laponite, (b) Laponite surface treated with a 16-carbon ammonium surfactant, (c) Laponite with co-valently attached PMMA, and (d) Laponite with surfactant treatment combined with attached PMMA. Two methods of attaching PMMA to the clay were studied: attachment of a methacrylate group followed by free-radical bulk polymerization with methyl methacrylate (MMA), and attachment of an ATRP initiator followed by MMA ATRP polymerization. The two methods should yield different structures. Attaching methacrylate groups to the clay could lead to crosslinked structures surrounding the clay and could also link the sheets together, whereas ATRP polymerization should produce linear chains attached to an inorganic core.

Synthesis of Methacrylate-Functionalized Clays. Figure 2 shows the overall scheme for clay treatment and polymerization. A compound terminated on one side with an ethoxysilane and on the other side by a methacrylate group was synthesized by a Michael addition reaction of the amine of aminopropylethoxydimethylsilane to an acrylate/methacrylate compound. The compound was then deposited onto the clay via an acidic aqueous ethanol procedure. Ethanol was used in this procedure to dissolve the silane and acid to hydrolyze the ethoxy groups; this has been successful in previous work.[29] After treatment, some of the clay was subsequently surface-treated with cetyltrimethylammonium bromide (CTAB) via an ion-exchange reaction.

The presence of organic content on the clay was constantly monitored with TGA. After methacrylate treatment, there was approximately 7.4 wt % organic on the clay, corresponding to 20 mmol/100 g of clay, which is nearly twice as much as

(22) Herrera, N.; Letoffe, J.; Putaux, J.; David, L.; Bourgeat-Lami, E. *Langmuir* **2004**, *20*, 1564.
(23) Herrera, N.; Letoffe, J.; Reymond, J.; Bourgeat-Lami, E. *J. Mater. Chem.* **2005**, *15*, 863.
(24) Bourlinos, A.; Jiang, D.; Giannelis, E. *Chem. Mater.* **2004**, *16*, 2404.
(25) Mitamura, Y.; Komori, Y.; Hayashi, S.; Sugahara, Y.; Kurada, K. *Chem. Mater.* **2001**, *13*, 3747.
(26) Chen, G.; Yoon, J. *Macromol. Rapid Commun.* **2005**, *25*, 899.
(27) Chen, G.; Kim, H.; Shim, J.; Yoon, J. *Macromolecules* **2005**, *38*, 3738.
(28) Chen, G.; Kim, H.; Kim, E.; Yoon, J. *Polymer* **2005**, *46*, 11829.
(29) Wheeler, P.; Wang, J.; Baker, J.; Mathias, L. *Chem. Mater.* **2005**, *17*, 3012.
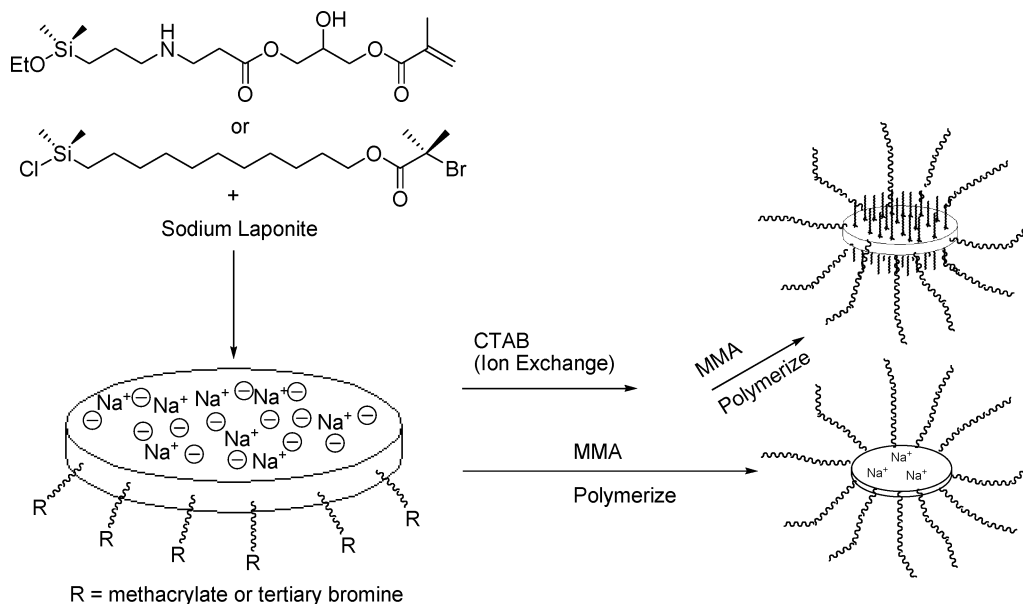(30) Wheeler, P.; Mathias, L. *Macromol. Synth.* **2004**, *13*, 1.

Figure 2. Scheme showing process of covalently attaching polymer to Laponite.
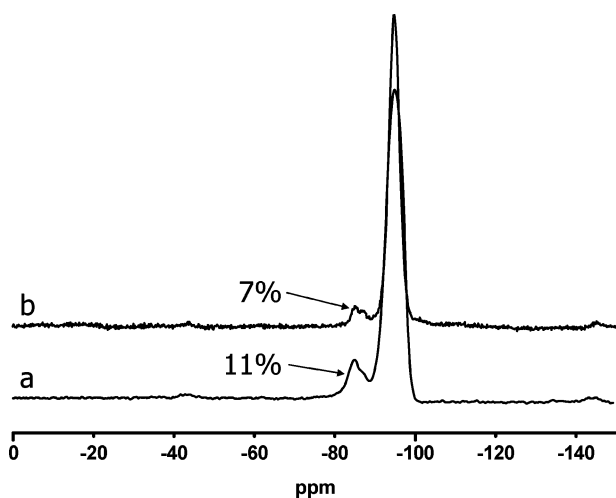

Figure 3. Quantitative ^{29}Si spectra of Laponite: (a) unmodified sodium Laponite RD as received, and (b) Laponite after ATRP initiator treatment.

was found in previous work.[23,29,31] After CTAB treatment, there was 13.7 wt % organic, equating to a cation exchange capacity of 22 mmol/100 g if one subtracts the material previously deposited in the silane reaction. This is in poor agreement with the reported CEC of Laponite, 55 mmol/ 100 g. Most likely, ion exchange of the silane compound is taking place, replacing some of the sodiums on the clay's surface during the first step. This reaction will likely take place because of the presence of a secondary amine in the silane compound and the presence of acetic acid. This explains the presence of excess silane agent after the first step and the apparently poor ion-exchange reaction in the second step.

Two types of polymer-bound clays were then synthesized: one without surface CTAB treatment and one with the treatment. The covalent polymer binding was achieved by in situ polymerization of MMA with the free-radical

initiator AIBN followed by extraction of all unbound polymers. During extraction, it was noted that the clay with CTAB treatment was much more viscous and swelled more in chloroform than the one without CTAB.

Synthesis of ATRP-Functionalized Clays. A chlorosilane-terminated ATRP initiator was synthesized and linked to the clay via a nonaqueous reaction in toluene using triethylamine as catalyst. Several other procedures were attempted, including heating in toluene,[32] stirring in methylene chloride,[21] and stirring in anhydrous alcohol;[33] however, the toluene/triethylamine procedure resulted in the most binding. Some of the treated clay was subsequently surface-treated with CTAB via ion-exchange reaction. Figure 3 shows quantitative ^{29}Si solid-state NMR spectra of unmodified Laponite and ATRP initiator-modified Laponite. The NMR spectrum of unmodified Laponite shows a large peak at −95 ppm which represents the condensed silicons and a smaller peak with a shoulder at −85 ppm from the uncondensed silicons.[34,35] On the basis of peak integration, the unmodified Laponite contains approximately 11% uncondensed silicons. After treatment with the ATRP initiator, the peak at −85 ppm decreases to 7% of the silicons, suggesting successful reaction. The silicon peak from the ATRP initiator is not seen, probably due to its low concentration. TGA showed an organic content of 1.4 wt %, or approximately 3 mmol/100 g of clay, significantly less than 11 mmol/100 g that was found previously.[29] However, it is important to note that, in this case, the reactant is a chlorosilane which is deposited in nonaqueous toluene versus an alkoxysilane reacted in water. Success of the CTAB treatment was also monitored with TGA and resulted in binding of 12.9 wt %, which equates to a CEC of 45 mmol/100 g, in good agreement with Laponite's published CEC.

(31) Park, M.; Shim, I.; Jung, E.; Choy, J. *J. Phys. Chem. Solids* **2004**, *65*, 499.

(32) Boyes, S.; Brittain, W.; Weng, X.; Cheng, S. *Macromolecules* **2002**, *35*, 4960.
(33) Applying a silane coupling agent. Gelest Library. http://www.gelest-.com/Library/09Apply.pdf.
(34) Mandair, A.; Michael, P.; McWhinnie, W. *Polyhedron* **1990**, *9*, 517.
(35) Delevoye, L.; Robert, J. L.; Grandjean, J. *Clay Miner.* **2003**, *38*, 63.
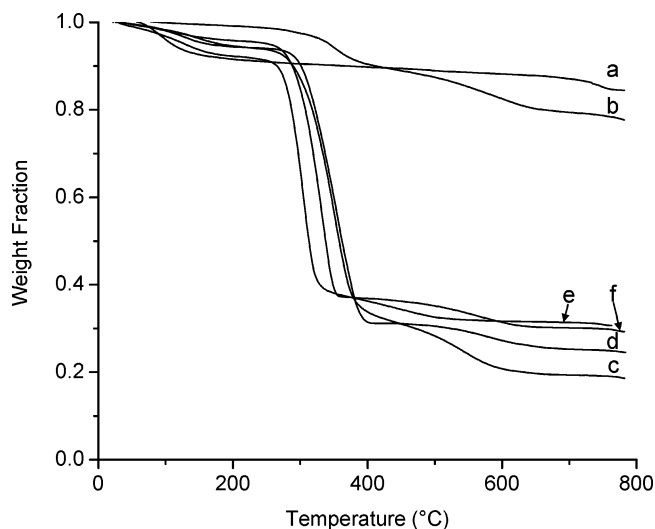
Figure 4. TGA degradation curves of clays with various treatments: (a) none (sodium Laponite RD), (b) CTAB, (c) methacrylate/PMMA, (d) methacrylate/CTAB/PMMA, (e) ATRP/PMMA, and (f) ATRP/CTAB/PMMA.

Figure 5. Clays dispersed in chloroform after allowing to settle for 2 h: (a) sodium Laponite, (b) CTAB, (c) MA/PMMA, (d) MA/CTAB/PMMA, (e) ATRP/PMMA, and (f) ATRP/CTAB/PMMA.

Table 1. Amount of Polymer Binding on the Treated Clays before and after Methanolysis Cleaving Reaction

clay description	after polymerization (%)[a]	after cleaving reaction (%)[a]	% polymer removed
MA/PMMA	80	76	5
MA/CTAB/PMMA	73	66	10
ATRP/PMMA	66	31	53
ATRP/CTAB/PMMA	69	41	41

[a] Data obtained from TGA analysis of clay/polymer materials before and after cleaving reaction.

ATRP polymerizations were carried out on the treated clays in bulk. The presence of CTAB on the clay did not seem to affect the polymerizations. Similar to the methacrylate clays, it was observed that the presence of CTAB on the clay made the clay/polymer material much more swollen and viscous in chloroform.

Analysis of Treated Clays. The amount of organic binding to the clay was quantified with TGA analysis, and the curves for all six clays are shown in Figure 4. Curve (a) is for sodium Laponite and shows a small weight loss below 200 °C due to bound water along with a steady weight loss up to 800 °C as more water of inorganic reaction is eliminated. After surface ion exchange with CTAB, a 16% weight loss is observed between 200 and 600 °C for curve (b), which corresponds to a CEC of 56 mequiv/100 g. In contrast, the polymer attachment methods achieved between 66 and 80% organic bound to the clay. Curve (c) corresponds to methacrylate-treated clay followed by free-radical polymerization, while curve (d) is the same reaction except the clay had CTAB on its surface. They show organic contents of 80 and 73%, respectively. It is somewhat surprising that the polymerization with CTAB-treated clay resulted in less organic binding, as it was theorized that the CTAB helps the clay disperse better during the polymerization, yielding more polymer attachment, along with the extra organic content due to the CTAB itself. As discussed earlier, it is believed that, during deposition of the methacrylate compound onto the clay, some ion exchange occurred as well. In this way, some methacrylate groups were probably exchanged onto the clay's surface, increasing the resulting amount of polymer attachment. The ATRP polymerizations yielded similar amounts of polymer binding, from 66 to 69%, as seen in curves (e) and (f).

After attaching 70−80% organic on clay, one would expect a large increase in dispersibility in organic solvents. Figure 5 shows all six clays dispersed in chloroform after being stirred for 24 h followed by 2 h of no stirring. The sodium Laponite quickly settles to the bottom of the test tube, as does CTAB-treated Laponite but to a lesser degree.
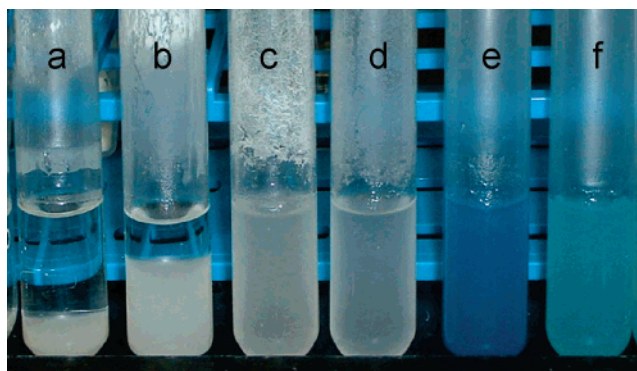
The four polymer-treated clays, however, do not settle out appreciably over the course of several hours. Upon standing for days, however, some clay will float to the top of the solvent and some will settle to the bottom. This is due to the density of the resulting polymer/clay material, with density decreasing as more polymer is attached. Since some clay floats and some sinks within a single sample, there is obviously a range of polymer attachment. In some cases, especially with clay (c), the clay would float to the top of chloroform during centrifugation, necessitating addition of THF to decrease the density of the solvent to facilitate clay separation.

Analysis of Bound and Solution Polymer. Because both routes of polymer attachment to clay involve an ester linkage, it is possible to remove the polymer for analysis. The polymer was removed via methanolysis in the presence of methanol, toluene, and catalytic *p*-toluene sulfonic acid. The success of the cleaving reaction is detailed in Table 1, and these data give indications on the mechanism of polymer binding. It is proposed that growing polymer from clay via ATRP and binding via free-radical polymerization would yield different structures. ATRP polymerizations should give linear chains grown from an inorganic clay core, while free-radical polymerization would yield an uncontrolled, possibly cross-linked structure around the clay sheets. The information in Table 1 shows that the cleaving reaction for the free-radical clays was much less successful than that for the ATRP clays. Approximately 5−10% of the bound polymer was able to be removed from the free radical-generated materials, whereas 40−50% from the ATRP-generated structures was cleaved. This is consistent with ATRP polymers being attached by a single linkage while free-radical polymers are attached by multiple linkages. It is difficult to say whether the multiple attachment points are on the same clay sheet or between clay sheets, although attachments on the same sheet

Table 2. Analysis of MMA Polymerizations in the Presence of Treated Clays

reaction temp (°C)	initiator	surfactant treatment	polymer in solution			polymer bound to clay			% organic bound to clay[a]	ave chains per sheet[b]	
			$M_n \times 10^{-3}$	PDI	yield	$M_n \times 10^{-3}$	PDI	yield		M_n	M_w
60	AIBN	no	52	3.14	46	258	2.20	40	80	30	14
60	AIBN	yes	56	3.67	47	200	2.82	27	73	26	9
$0 \rightarrow 23$	ATRP	no	163	2.34	62	159	2.01	21	66	24	12
$0 \rightarrow 23$	ATRP	yes	187	1.90	52	133	2.54	24	69	32	13

[a] Calculated from TGA data. [b] Calcuated on the basis of the approximated weight of one clay sheet, amount of bound polymer, and weight of polymer chains.

should be more common since intramolecular reactions are generally faster than intermolecular reactions.

The cleaved polymer, as well the polymer formed in solution during the polymerizations, was analyzed with SEC, and the results are summarized in Table 2. In both free-radical and ATRP systems, there was no appreciable effect from CTAB treatment on the molecular weights of solution or bound polymer. For the ATRP polymerizations, similar molecular weights and polydispersities were observed for both the solution and bound polymers, as expected. This behavior has been observed by others in ATRP polymerizations from various substrates when comparing polymer grown from a surface versus in solution under the same conditions.[36] The polydispersities of the ATRP polymers are quite high, from 2 to 2.5, which is not consistent with a controlled polymerization. It is believed that lack of control could be due to excess amounts of catalyst relative to initiator, or catalyst binding to the clay, which was clearly seen as blue or green color in the isolated clay materials. It is also possible that the polymerization was simply carried out for too long and for too high of a conversion. Zhao et al. observed molecular weights of more than 138 000 and a polydispersity of 2.14 when growing polystyrene from the surface of montmorillonite by ATRP when the reaction was carried out for longer times.[37]

Polymer made by free-radical polymerization with clay-bound methacrylate groups led to much higher molecular weight for the bound polymer versus solution material. Both AIBN polymerizations produced ca. 50 000 molecular weight PMMA in solution and 200 000−250 000 molecular weight for bound polymer. It is hypothesized that restricting the growing polymer chain on the clay lowers its mobility, decreasing termination events, thus increasing molecular weight, similar to a Trommsdorff effect. This same effect could also occur if isolated cross-linked phases form around clay aggregates.

Table 2 also contains calculations for the average number of polymer chains per clay sheet. If the mass of a single sheet of Laponite, the mass of a single polymer chain, and the mass of total polymer binding are known, it is possible to calculate an average number of polymer chains bound to each sheet of clay. The mass of a sheet of Laponite was estimated previously.[29] All polymerization methods yield a similar number of chains for this calculation, ca. 30 chains

Table 3. Glass Transition Temperatures (from DSC) of Polymer Formed in Solution, Polymer Bound to Laponite, and Polymer after Cleaving from Laponite

	unbound PMMA	PMMA bound to clay	PMMA cleaved from clay
MA	121.2	126.6	110.6
MA/CTAB	124.8	124.9	106.6
ATRP	129.7	124.9	128.5
ATRP/CTAB	128.8	126.3	130.1

per sheet based on M_n and ca. 12 based on M_w. Using the same type of calculation, it is also possible to estimate the number of methacrylate and ATRP initiating groups originally present on the clay. For ATRP clays, assuming 1.4 wt % of initiator, there are about 50 sites per sheet. This is in reasonable agreement with the chains-per-sheet calculations. On the other hand, for the methacrylate clays, with an assumed methacrylate binding of 7.4 wt %, there should be 350 sites per sheet. This is not in agreement with the estimate of 10−30 chains per sheet. These data, along with the cleaving studies, indicate that there are multiple binding sites for free radical-generated polymer chains and possibly some unreacted methacrylate groups.

The thermal properties of the unbound, bound, and cleaved polymers were analyzed with DSC, and the glass transition temperatures are listed in Table 3. The T_g of unbound polymer is similar for all polymerizations, ranging from 121 for the lower molecular weight PMMA formed free radically to 130 °C for the higher molecular weight PMMA from ATRP. Interestingly, there is almost no difference in T_g between free PMMA and bound PMMA. The T_g for PMMA while bound to Laponite ranges from 125 to 127 °C for all four polymerizations. Once cleaved, the polymer formed via ATRP has a T_g from 129 to 130 °C, similar to free polymer. However, PMMA cleaved from the free radical-generated materials shows considerably lower T_g's of 107−111 °C. This is consistent with copolymer formation, again indicating that polymerization through clay-bound methacrylate groups occurred.

Formation of PMMA/Laponite Nanocomposite Blends. Since the treated clays exhibited excellent dispersion in methylene chloride, this was used as a solvent for blending with commercial PMMA. Six different clays were solvent-blended with PMMA in inorganic concentrations of 1, 3, 5, and 10 wt %. It is important to note that the amount of attached organic was taken into account when calculating the amount of clay needed to achieve the desired weight percent of inorganic. For example, the 10 wt % sample using sodium Laponite has the same inorganic clay content as the 10 wt % sample with polymer-treated clay, even though total

(36) Husseman, M.; Malmstrom, E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D.; Hedrick, J.; Mansky, P.; Huang, E.; Russel, T.; Hawker, C. *Macromolecules* **1999**, *32*, 1424.
(37) Zhao, H.; Argoti, S.; Farrell, B.; Shipp, D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 916.
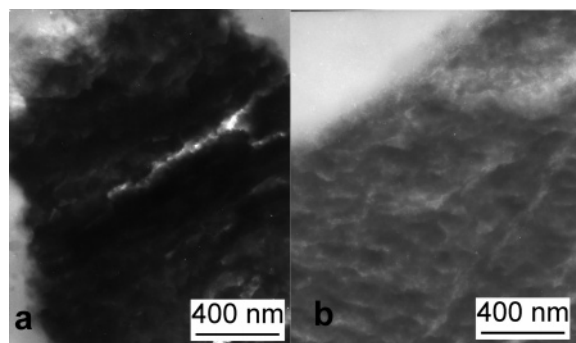
Figure 6. TEM images of PMMA blends: (a) sodium Laponite @ 5 wt % and (b) CTAB Laponite @ 5 wt %.

Figure 7. TEM images of PMMA blends: (a) MA/PMMA @ 5 wt % and (b) MA/CTAB/PMMA @ 5 wt %.

added polymer-plus-clay was greater. After mixing the PMMA with the clay for 24 h, we poured the mixture into pans and allowed to evaporate. This was followed by melt pressing to achieve a solvent-free film.

Optical Appearance of Films. Before running any analytical tests, one can visually look at the sample and obtain an idea of the quality of clay dispersion. PMMA is ideal for this purpose since it is normally optically clear. The sodium and CTAB-treated clays showed visible clay particles at all clay concentrations, indicating poor dispersion. All of the other samples appeared homogeneous and transparent with no visible particles, even at 10 wt % clay. The methacrylate clays showed a slight brown color after melt-pressing that progressively got worse as clay concentration increased. The origin of this color is unknown and may be due to oxidation or clay-induced degradation. Neither the CTAB-treated nor the sodium clays exhibited any color formation. The ATRP clays exhibited a blue color characteristic of the copper catalyst used for polymerization. The catalyst seems to bind strongly to the clay and cannot be easily removed.

TEM Analysis of Films. One of the best ways to analyze clay dispersion is with TEM. At lower magnification levels (images not shown), there is a lack of good microscale dispersion in all of the samples. This poor dispersion may be improved with high energy mixing during the solvent-blending step, which was found to be important to exfoliate clay in polystyrene.[38] Differences in nanoscale dispersion between the samples at high magnification are evident. Figures 6−9 show TEM micrographs of the prepared films. Figure 6 shows images of the sodium and CTAB clay dispersions in PMMA. The pictures look similar, showing nondispersed clay aggregates. Figure 7 shows images of the methacrylate/PMMA treated clays, with and without CTAB treatment. Part (a) shows a much better dispersion, with individual sheets visible at higher magnification, than that seen in part (b). Figure 8 shows the ATRP clays with and without CTAB treatment. Figure 9 shows an enlarged view of MA/PMMA and ATRP/CTAB/PMMA clays. The MA/PMMA clay shows excellent dispersion at this level, with mostly individual sheets and few aggregates, whereas ATRP/CTAB/PMMA clay showed some separated sheets but mostly aggregates. This is a surprising finding, as it was expected that surfactant-treated clay would disperse better.
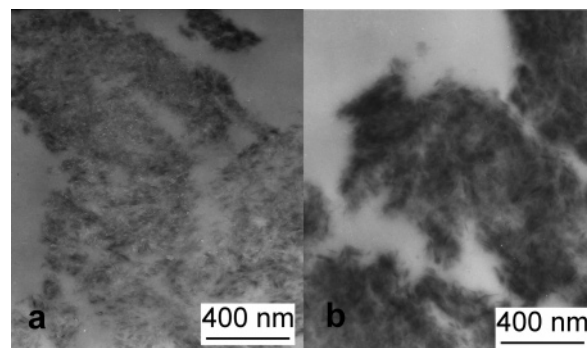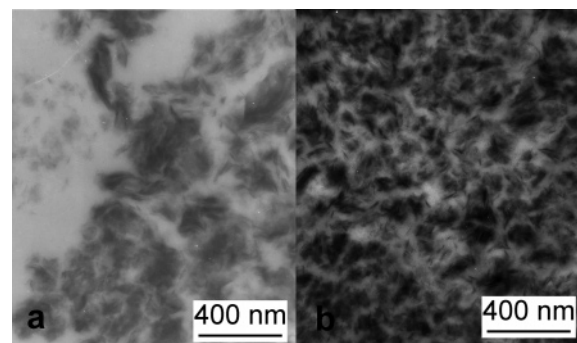

Figure 8. TEM images of PMMA blends: (a) ATRP/PMMA @ 5 wt % and (b) ATRP/CTAB/PMMA @ 5 wt %.
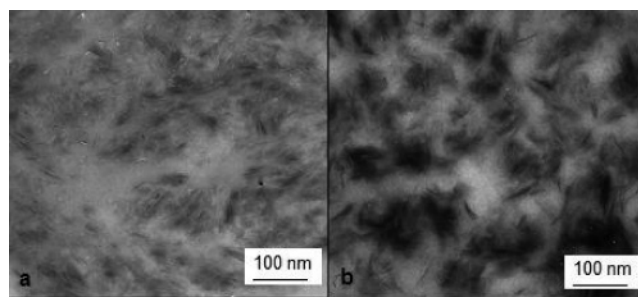

Figure 9. TEM images of PMMA blends: (a) MA/PMMA @ 5 wt % and (b) ATRP/CTAB/PMMA @ 5 wt %.

Thermal Analysis. TGA was used to observe the effect of the different clays on the composite's thermal stability and degradation characteristics. The sodium and CTAB clays caused no change in the degradation curve of PMMA compared to the neat material. On the other hand, all of the PMMA-modified clay composites exhibited a slight decrease in thermal stability by approximately 10 °C, consistent with the lower thermal stability of PMMA attached to the clay versus the commercial polymer. The differences in thermal stability of these two components can be attributed to different polymerization conditions[39] and the fact that the commercial PMMA contains a small amount of comonomer.

Mechanical Properties. DMA and DSC were used to study differences in mechanical and thermal properties caused by inclusion of the clay, and the data is summarized in Table 4. Figure 10 plots room temperature modulus versus clay content of the PMMA blends whose clay does not contain CTAB treatment. Neat PMMA has a modulus of 2.4 GPa as measured for the control. Sodium Laponite with

(38) Morgan, A.; Harris, J. *Polymer* **2004**, *45*, 8695.

(39) Hu, Y.; Chen, Y. *Polym. Degrad. Stab.* **2003**, *82*, 81.

Table 4. Modulus and Glass Transition Data for PMMA/Clay Blends from 1 to 10 wt % Clay Concentration[a]

clay type	storage modulus @ 23 °C (GPa)				T_g from DSC (°C)			
	1%	3%	5%	10%	1%	3%	5%	10%
sodium	2.53	2.69	2.23	2.82	94.6	96.4	95.9	99.1
CTAB	2.68	2.79	2.77	3.17	96.0	95.5	96.6	98.5
MA	2.49	2.71	3.56	2.91	93.9	93.4	94.2	91.7
MA/CTAB	2.46	3.01	2.69	3.35	95.6	95.5	93.7	96.2
ATRP	3.34	2.73	3.36	3.04	94.5	97.3	95.2	95.1
ATRP/CTAB	2.76	3.03	2.59	2.84	90.2	93.6	93.5	95.0
pure PMMA	2.39				90.3			

[a] Clay concentration is total amount of inorganic material in the sample. Organic grafting to the clay was taken into account.
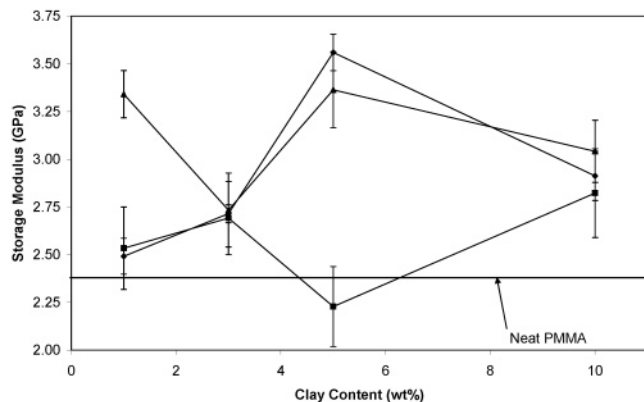
Figure 10. Storage modulus (23 °C) of PMMA blends at various concentrations of clays: (■) sodium Laponite, (◆) methacrylate/PMMA, and (▲) ATRP/PMMA. Error bars represent ±1 standard deviation for three measurements.
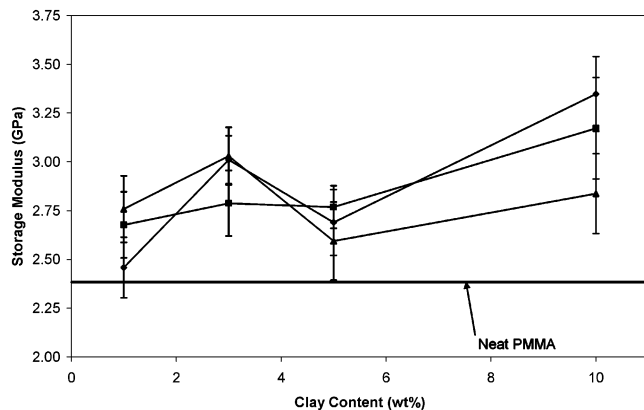
Figure 11. Storage modulus (23 °C) of PMMA blends at various concentrations of clays: (■) CTAB Laponite, (◆) methacrylate/CTAB/PMMA, and (▲) ATRP/CTAB/ PMMA. Error bars represent ±1 standard deviation of three measurements.

no organic treatment did not show any major improvements in modulus. The PMMA-treated clays, however, showed a modulus improvement of ca. 50%, up to 3.5 GPa, at a clay concentration of 5 wt %, followed by a decrease as clay content rose to 10 wt %. Figure 11 shows modulus data for the CTAB-treated clays. There appears to be a small maximum at 3 wt-%, corresponding to a modulus increase of ca. 25%, followed by a larger modulus increase at 10 wt-% incorporation. Others have reported an increase in modulus for PMMA nanocomposites with montmorillonite. Qu et al. report a 50% increase in tensile modulus with only 1 wt % clay, also improving toughness and maintaining transparency.[41] Li et al. report a progressive increase in modulus from incorpora-
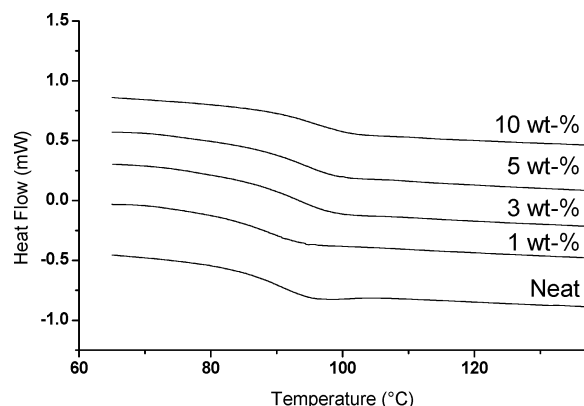
Figure 12. DSC plots of ATRP/CTAB/PMMA blends at various clay concentrations.

tion of 1−10 wt % clay.[42] Zhao and Samulski demonstrate a modulus of increase of 50% with 5−10 wt % of clay loading.[40] It is evident from this wide variation in mechanical properties with vastly different clay concentrations that the quality of clay dispersion, surfactant choice, and processing methods to synthesize the nanocomposites greatly affect the properties of the end product.

DSC was used to study changes in glass transition temperatures due to the presence of clay. The neat PMMA that was used exhibited a T_g at 90.3 °C, which is quite low and indicates copolymer formation. Solution NMR analysis showed that the commercial PMMA is, indeed, a copolymer with a slight amount of another repeat unit, probably butyl methacrylate, explaining the decrease in T_g, which for pure PMMA synthesized in these experiments is around 125 °C. Incorporation of clay into the PMMA produced a slight increase of T_g in almost all cases. The T_g increase was more pronounced for the incompatible clays (sodium and CTAB), which showed an increase of 8 to 9 °C at 10 wt % incorporation. The treated clays showed less of an increase in T_g, with the largest increase of 6 °C at 10 wt %. Figure 12 shows DSC plots of the final composites using ATRP/CTAB clay from 1 to 10 wt %, which are representative of all of the DSC plots obtained. No real trends correlating clay content to T_g were observed here, as has been seen in PMMA/montmorillonite nanocomposites. Correlations between T_g and montmorillonite content have been previously demonstrated in these systems, with a maximum T_g increase of 15 °C at 10 wt % clay.[41−43] The absence of such a trend could be due to the relatively small size of the Laponite sheets or to the heterogeneous morphology seen in the TEM images.

Conclusions

Covalently grafting polymer onto Laponite clay improved its dispersibility in PMMA, allowing the formation of intercalated nanocomposites. All of the polymer-compatibilized clay PMMA nanocomposites exhibited optical transparency, up to 10 wt % clay, whereas nontreated and surfactant-treated

(40) Zhao, Q.; Samulski, E. *Macromolecules* **2005**, *38*, 7967.
(41) Qu, X.; Guan, T.; Liu, G.; She, Q.; Zhang, L. *J. Appl. Polym. Sci.* **2005**, *97*, 348.
(42) Li, Y.; Zhao, B.; Xie, S.; Zhang, S. *Polym. Int.* **2003**, *52*, 892.
(43) Xie, T.; Yang, G.; Fang, X.; Ou, Y. *J. Appl. Polym. Sci.* **2003**, *89*, 2256.

clay composites contained visible particles at all concentrations. The clays with only polymer edge treatment displayed modulus increases of 50% at 5 wt % clay concentration, whereas the combined surfactant and polymer-treated clays showed a modulus increase of 25% at 3 wt % concentration, indicating that this particular surfactant treatment of clay may be unnecessary and even detrimental to mechanical properties. Although property enhancements were observed, the TEM images showed poor microscale dispersion that might be improved by high-shear mixing during the solvent-blending process or afterward as a melt-blending procedure (not done here). The techniques explored in this research may be applied to other clays such as montmorillonite and mica to improve their compatibility in polymer networks through covalent grafting of functional groups. Thus, this approach may provide a general one for modifying and enhancing clay miscibility and nanocomposite properties.

Experimental Section

Materials. Laponite (RD grade) was purchased from Southern Clay Products, Inc. AIBN, 3-(acryloyloxy)-2-hydroxypropyl methacrylate, CTAB, MMA, anhydrous toluene, triethylamine (TEA), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), CuBr, and $CuBr_2$ were all purchased from Aldrich Chemical Co. 3-Aminopropylethoxydimethylsilane was purchased from Gelest. Atactic poly(methyl methacrylate) (100 000 MW) was obtained from Polysciences, Inc. Solvents used were purchased from Aldrich or Fisher. MMA was vacuum-distilled and stored in a freezer prior to use. TEA was vacuum-distilled and stored over potassium hydroxide and molecular sieves. All other compounds were used as received.

Characterization. TGA analyses were performed on a TA Instruments SDT 2960 simultaneous DTA-TGA, at a rate of 20 °C/min up to 800 °C under an air atmosphere. DSC analyses were performed on a TA Instruments DSC 2920 with the following procedure. The samples were heated to 180 °C at a rate of 10 °C/min, held for 5 min, cooled at 10 °C/min to 45 °C, then heated to 180 °C at 10 °C/min. DMA analysis was performed on a Polymer Laboratories DMTA Mk III in single cantilever bending mode at 1 Hz with a heating rate of 2 °C/min. For TEM analyses, small pieces of composite samples were cast into epoxy matrixes, which were subsequently sectioned on a Porter-Blum MT-2B microtome using a diamond knife at room temperature. The sections were placed on 100-mesh copper grids and images were obtained on a Zeiss 109-T transmission electron microscope at 80 kV accelerating voltage. SEC was performed on a system using a HP 1037A RI detector with a constaMetric pump flowing THF at 100 mL/min through five American Polymer Standards separation columns with porosities ranging from 100 to 1 000 000 Å. The SEC runs were calibrated using polystyrene standards. Melt-pressed films were produced on a Carver melt press at 180 °C.

Solution NMR spectra were obtained on a Varian Mercury 300 MHz spectrometer. Solid-state NMR spectroscopy was performed on a Varian UNITYINOVA 400 spectrometer using a standard Chemagnetics 7.5 mm PENCIL-style probe. Samples were loaded into zirconia rotor sleeves, sealed with Teflon caps, and spun at a rate of 4 kHz. For quantitative ^{29}Si acquisitions, direct polarization/magic angle spinning (DP/MAS), or Bloch Decay, techniques were used. The acquisition parameters were as follows: ^{29}Si pulse width was 4 μs, acquisition time was 45 ms, and recycle delay time was 180 s.

Synthesis.

Synthesis of Methacrylate-Terminated Ethoxysilane Compound. To a scintillation vial were added 3-aminopropylethoxy-

dimethylsilane (1.0 g, 6.2 mmol) and 3-(acryloyloxy)-2-hydroxypropyl methacrylate (1.3 g, 6.2 mmol), and the mixture was stirred at room temperature for 1 h. The product was used without further purification. Yields were quantitative based on NMR. ^{13}C NMR (75 MHz, ppm, CDCl$_3$): 172.72 (s, 1C, $-NH-CH_2-CH_2-CO-O-$), 167.39 (s, 1C, $-O-CO-C(CH_3)=CH_2$), 136.06 (s, 1C, $-CO-C(CH_3)=CH_2$), 126.34 (s, 1C, $-CO-C(CH_3)=CH_2$), 67.58 (s, 1C, $-NH-CH_2-CH_2-CO-O-CH_2-CH(OH)-CH_2-$), 65.52 (s, 1C, $-NH-CH_2-CH_2-CO-O-CH_2-CH(OH)-CH_2-$), 65.34 (s, 1C, $-NH-CH_2-CH_2-CO-O-CH_2-CH(OH)-CH_2-$), 58.45 (s, 1C, $CH_3-CH_2-O-Si(CH_3)_2-$), 52.79 (s, 1C, $-Si(CH_3)_2-CH_2-CH_2-CH_2-NH-$), 45.35 (s, 1C, $-NH-CH_2-CH_2-CO-O-$), 34.92 (s, 1C, $-NH-CH_2-CH_2-CO-O-$), 23.40 (s, 1C, $-Si(CH_3)_2-CH_2-CH_2-CH_2-NH-$), 18.70 (s, 1C, $CH_3-CH_2-O-Si(CH_3)_2-$), 18.51 (s, 1C, $-CO-C(CH_3)=CH_2$), 13.92 (s, 1C, $-Si(CH_3)_2-CH_2-CH_2-CH_2-NH-$), and -1.95 (s, 1C, $-Si-(CH_3)_2-$).

Deposition of Methacrylate-Terminated Ethoxysilane Compound. To a 250-mL Erlenmeyer flask were added Laponite (10 g) and an ethanol/water mixture (50/50 vol/vol, 100 mL), and the mixture was stirred until the clay dispersed. The pH was adjusted to 5 by addition of acetic acid. In a separate scintillation vial was added the methacrylate/ethoxysilane compound (2.3 g) to an ethanol/water solution (50/50 vol/vol, 10 mL). This solution was added to the clay dispersion, and the mixture was stirred for 2 d. The clay was collected on a Buchner funnel and redispersed by stirring in methanol (100 mL) for 2 h, collected again, and stirred again in methanol (100 mL) for 2 h. The clay was collected on a Buchner funnel and air-dried in a hood for 16 h.

Surfactant Treatment of Clay (Ion Exchange). Laponite with attached methacrylate (3.0 g) was dispersed in an acetone/water mixture (50/50 vol/vol, 50 mL). CTAB (1.0 g) was added to the mixture and stirred for 16 h at room temperature. The clay was collected on a Buchner funnel, then dispersed in ethanol (100 mL) for 2 h, collected again, and washed again in ethanol (100 mL). The clay was collected on a Buchner funnel and air-dried in a hood for 16 h.

Free-Radical Polymerizations. To a 50-mL round-bottom flask were added either methacrylate-treated Laponite or methacrylate/CTAB-treated Laponite (1.0 g), methyl methacrylate (10 g, 100 mmol), and AIBN (0.16 g, 1 mmol). The flask was sealed with a septum, and the mixture was purged with argon for 5 min. It was then placed in an oil bath at 60 °C with magnetic stirring for 16 h to give a solid plug of polymer. Following polymerization, chloroform was added to dissolve unbound polymer. The clay was removed via centrifugation followed by at least three washings with chloroform, two washings with THF, and one washing with methanol. Unbound polymer was recovered via precipitation of the chloroform supernatant in methanol. The product was then dried in a vacuum oven at room temperature.

Synthesis of ATRP Initiator. The ATRP initiator, [11-(2-bromo-2-methyl)propionyloxy]undecylchlorodimethylsilane, was synthesized on the basis of literature procedures.[44,45] The exact procedure used has been reported previously.[30]

Deposition of ATRP Initiator. To a 100-mL round-bottom flask were added Laponite (10.0 g), toluene (50 mL), [11-(2-bromo-2-methyl)propionyloxy]undecylchlorodimethylsilane (2 mL, 4.8 mmol), and 4 to 5 drops of triethylamine.[46] The mixture was stirred at 23 °C

(44) Boyes, S.; Granville, A.; Brittain, W. *Macromol. Synth.* **2004**, *13*, 15.
(45) Matyjaszewski, K.; Miller, P.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B.; Siclovan, T.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(46) Prucker, O.; Naumann, C. A.; Ruhe, J.; Knoll, W.; Frank, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 8766.

for 4 d. The clay was collected on a Buchner funnel, then dispersed with stirring in ethanol (100 mL) for 2 h, collected again, and stirred in ethanol for 2 h (100 mL). The clay was collected on a Buchner funnel and air-dried in a hood for 16 h.

Surfactant Treatment of Clay (Ion Exchange). Laponite with attached ATRP initiator (3.0 g) was dispersed in an acetone/water mixture (50/50 vol/vol, 50 mL). CTAB (1.0 g) was added, and the mixture was stirred for 16 h at room temperature. The clay was collected on a Buchner funnel, then stirred in ethanol (100 mL) for 2 h, collected again, and stirred again in ethanol for 2 h (100 mL). The clay was collected on a Buchner funnel and air-dried in a hood for 16 h.

ATRP Polymerizations. To a 25-mL round-bottom flask were added ATRP initiator-treated Laponite, ATRP initiator/CTAB-treated Laponite, or sodium Laponite (as a control) (1.0 g), CuBr (51.3 mg, 0.36 mmol), CuBr$_2$ (9.3 mg, 0.042 mmol), and MMA (9.4 g, 94 mmol). The flask was sealed with a septum and purged with argon for 30 min. The flask was then placed in an ice bath under magnetic stirring for at least 5 min. PMDETA (80 μL, 0.36 mmol), which was previously purged with argon, was added with an argon-purged syringe. The solution was stirred for 16 h, during which time the ice bath melted and slowly warmed to 23 °C.

Following polymerization, chloroform was added to the flask to dissolve unbound polymer. The clay was removed via centrifugation followed by at least three washings with chloroform, two washings with THF, and one washing with methanol. Unbound polymer was recovered via precipitation of the chloroform supernatant into methanol. The clay was then dried in a vacuum oven at room temperature. In the control experiment, no polymer formation or organic binding to the clay was observed.

Preparation of Films. The appropriate amount of clay was added to a test tube with a stir bar and magnetically stirred in dichloromethane (2 mL) for 24 h. Commercial PMMA (2.0 g) and additional dichloromethane (8 mL) were added, and the mixture was stirred for 24 h. The clay/PMMA solutions were poured into aluminum pans and evaporated in a hood for 1 week. The product composites were then melt-pressed into films approximately 0.5-mm thick.