

Synthesis of Magnesium Dihydroxide Hybrid Nanocomposites via ATRP

Jeongbin Ok^{1,2} and Krzysztof Matyjaszewski^{1,3}

Several hybrid nanocomposites consisting of a magnesium dihydroxide (MDH) core and tethered poly(meth)acrylate chains were synthesized via atom transfer radical polymerization (ATRP). The hydroxyl groups on the surface of the MDH particles were modified by reaction with 2-bromopropionyl or 2-bromoisobutyryl bromide to attach ATRP initiator moieties to the particle. *n*-Butyl acrylate, methyl methacrylate, dodecyl methacrylate and octadecyl methacrylate were polymerized from the functionalized MDH particles using the “grafting-from” technique. MDH is a representative of flame retardants which release water when heated. The polymer chains attached to MDH particles will provide the composites with enhanced compatibility in blends with common polymers. The efficiency of attachment, and the molecular weights and polydispersity of the polymers attached to the nanoparticles were investigated by GPC and TGA after post-polymerization cleavage from the particles. AFM was used to analyze morphologies and structure of the composites.

KEY WORDS: Magnesium dihydroxide; ATRP; nanocomposite; poly(methacrylates); poly(*n*-butyl acrylate); grafting; fire retardancy.

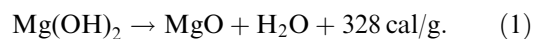
1. INTRODUCTION

Magnesium dihydroxide (MDH) is a versatile inorganic material finding use in many industrial applications, including pharmaceuticals and materials for water treatment [1–3]. MDH is also a powerful and safe flame retardant [4–6]. Although various compounds are employed for suppressing flame and smoke, MDH has been regarded as a superior agent due to its inherent high performance, lack of halogen, low toxicity, low corrosivity and relatively low cost [7].

Fire results from the availability of heat, fuel and oxygen. During combustion of polymers, the heat

produced by the fire is both spread out to the atmosphere (ΔH_1) and fed back (ΔH_2) to the substrate. In this cycle, the polymer continues to act as a fuel, and combustion continues (Fig. 1). In order to extinguish the fire, one or more of the ingredients should be removed from the cycle [8, 9].

When heated above 330 °C, MDH decomposes endothermically according to reaction 1



The water released from this reaction can block the flame and exclude oxygen by diluting the concentration of the flammable gases in the contacting atmosphere. In addition, char formed on the surface of the polymer works as a heat-insulating barrier interrupting the flow of flammable decomposition products [10, 11]. To increase the efficiency of MDH as a flame retardant, MDH is incorporated into a polymer matrix. However, in many cases, inorganic particles can aggregate and act as defects in the polymer composite/blend that deteriorate physical properties

¹ Department of Chemistry, Center for Macromolecular Engineering, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA.

² LG Cable Research Lab., 555 Hogye, Dongan, Anyang, Gyeonggi, 431-749, Korea.

³ To whom correspondence should be addressed.
E-mail: km3b@andrew.cmu.edu

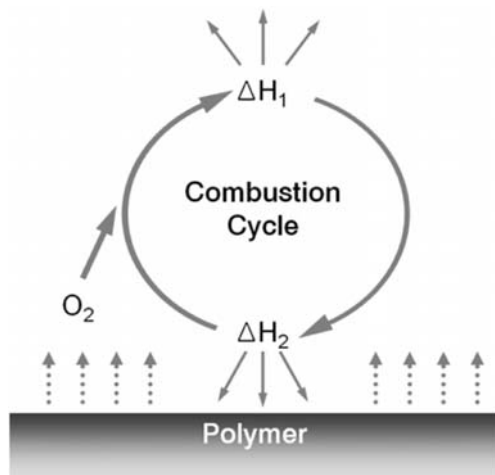


Fig. 1. Scheme for polymer combustion.

of blends. The modifications of MDH particles proposed in this study should overcome this problem. Coating the MDH particles with polymers should increase the compatibility of the particles with matrix polymers. However, there are some fundamental limitations to enhance the compatibility at the boundaries between inorganic particles and the matrix polymers. Recently developed nanocomposites might overcome such problems and are promising substitutes for conventional fillers [12]. With nanoscale core particles and organic-inorganic hybrid structures, the nanocomposites have higher affinity for a polymer matrix maintaining inherent reinforcing characteristics [13, 14].

Atom transfer radical polymerization (ATRP) [15–17] provides convenient and effective ways to synthesize nanocomposites [18–22]. The synthesis of various nanocomposites with well-defined polymers grown from the surface of silica particles using ATRP, were reported for the functionalization [23–26]. Several monomers such as acrylates, methacrylates, styrenes, and acrylonitrile were successfully attached to particle surfaces by grafting-from, grafting-through and grafting-onto methods. These techniques enabled effective synthesis of organic/inorganic composite structures via functionalization of inorganic surfaces. In this paper, novel (meth)acrylates-MDH nanocomposites were synthesized by ATRP. *n*-Butyl acrylate (BA), methyl methacrylate (MMA) and octadecyl methacrylate (ODMA) were used as monomers and grafted from functionalized sites on the MDH particles. Sacrificial initiators were added to the reaction to follow progress of polymerization. The properties of the “free”

polymers were compared with those of polymer chains cleaved from the composite structures. Atomic force microscope (AFM) and thermogravimetric analysis (TGA) were used for analyses of synthesized nanocomposites.

2. EXPERIMENTAL

2.1. Materials

MDH ($d = 50\text{--}100\text{ nm}$) was purchased from Sakai Chem. and used after thorough drying in a convection oven. Polymerization inhibitors from (meth)acrylate monomers were removed by passing through a column packed with basic alumina. Other reagents were purchased from Aldrich and introduced to the reactions without further purification.

2.2. Attachment of Initiators to MDH

MDH (8.5 g, 100 mM), triethylamine (13.93 mL, 100 mM) and anhydrous tetrahydrofuran (THF; 150 mL) were added to a 250 mL flask that had been placed in an ice bath. To prevent MDH particles from aggregating during reactions, thorough pre-drying was crucial. 2-Bromopropionyl bromide (15.71 mL, 150 mM) was then added drop-wise using a dropping funnel, with caution since it is a violent exothermic reaction. After stirring for 2 h in the ice bath, the reaction was stirred for a further 24 h at room temperature. The mixture was diluted with additional THF, then centrifuged. After centrifugation, the solvent was decanted from the solids and replaced with fresh THF. These steps were repeated until the liquid became clear and colorless (Fig. 2).

A similar method was used for attachment of 2-bromoisobutyryl initiator to MDH particles. In this procedure, MDH (8.5 g, 100 mM), triethylamine (13.93 mL, 100 mM) and 2-bromo-2-methylpropionyl (2-bromoisobutyryl) bromide (18.54 mL, 150 mM) were introduced to the reaction flask (Fig. 3).

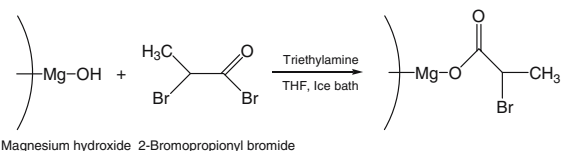


Fig. 2. Attachment of 2-bromopropionyl bromide to MDH particles.

Magnesium Dihydroxide Nanocomposites via ATRP

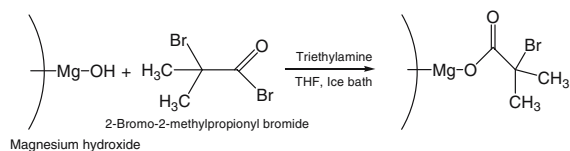


Fig. 3. Attachment of 2-bromoisobutyryl bromide to MDH particles.

2.3. Polymerization of *n*-Butyl Acrylate from MDH

The functionalized initiator-attached MDH (1.839 g, 0.3 mM of presumed initiator moiety), 4,4'-dinonyl-2,2'-bipyridine (dNbpy; 0.245 g, 0.6 mM), and purified *n*-butyl acrylate monomer (10.97 mL, 75 mM) were placed in a 50 mL Schlenk flask. MDH particles were slowly added into reactors with constant and vigorous stirring to prevent aggregation. After purging with nitrogen gas, methyl 2-bromopropionate (0.033 mL, 0.3 mM), CuBr (0.043 g, 0.3 mM) and CuBr₂ (0.0034 g, 0.015 mM) were added to the flask. Impurities were removed by conducting three “freeze–pump–thaw” cycles. The reactor then was placed in an oil bath preheated to 70 °C and the reaction was performed under nitrogen. Samples were taken periodically to determine changes in molecular weights and monomer conversion. After 30 h, the polymerization was terminated by exposure to air, and then reaction mixture was poured into a vial and vigorously mixed with THF. The slurry was centrifuged and the complex of dNbpy and CuBr₂, dissolved in THF, was decanted and remaining particles were again dispersed in THF. This slurry/centrifugation process was repeated five times. After reactions, polymer-grafted particles were dried on large pans to preclude agglomeration. For larger quantity, jet driers were used.

2.4. Polymerization of Methyl Methacrylate from MDH

The initiator-attached MDH particles (1 g; 0.17 mM of presumed initiator moiety), ethyl 2-bromoisobutyrate (0.025 mL, 0.17 mM), dNbpy (0.07 g, 0.17 mM), purified methyl methacrylate (36.4 mL, 340 mM) and MEK (30 mL) were added to a 50 mL Schlenk flask. After purging with nitrogen gas, impurities in the reactants were removed via three repeated freeze–pump–thaw cycles. CuBr (0.012 g, 0.083 mM) and CuBr₂ (0.00094 g, 0.0042 mM) were added to the flask and then the reactor was placed into an oil bath preheated to 70 °C. The progress of

the reaction was estimated by following the molecular weight evolution of the free polymer by periodic sampling. After 24 h, the reaction was terminated by exposure to air. The white sticky mixture in the flask was poured into a centrifuge tube and mixed with fresh THF. After vigorous shaking, the mixture was centrifuged and the clear solution was decanted from the particles to remove the free polymer as well as formed dNbpy and CuBr₂ complex dissolved in the THF. This step was repeated five times to ensure removal of all impurities.

2.5. Polymerization of Dodecyl Methacrylate from MDH

The initiator-attached MDH particles (1 g; presumed initiator moiety: 0.17 mM), ethyl 2-bromoisobutyrate (0.025 mL, 0.17 mM), dNbpy (0.07 g, 0.17 mM), dodecyl methacrylate (12.44 mL, 42.5 mM) and toluene (30 mL) were placed in a 100 mL Schlenk flask. After purging with nitrogen gas, impurities in the reactants were removed via three freeze–pump–thaw cycles. CuBr (0.012 g, 0.083 mM) and CuBr₂ (0.0009 g, 0.004 mM) were added to the flask and the reactor was placed into an oil bath preheated to 70 °C. The progress of the reaction was following by periodic sampling and measuring the molecular weight of the free polymer. After 50 h, the reaction was terminated by exposure to air. The product was isolated as for the polymerization of MMA.

2.6. Polymerization of Octadecyl Methacrylate from MDH

ODMA monomer was purified by dissolving in hexane and extracting four times with 5% aqueous NaOH. After drying the organic phase over anhydrous magnesium sulfate, the solution was passed through a neutral alumina column and then the solvent was removed under reduced pressure [27]. Previously prepared initiator-attached MDH particles (1 g; presumed initiator moiety: 0.17 mM), ethyl 2-bromoisobutyrate (0.025 mL, 0.17 mM), dNbpy (0.07 g, 0.17 mM), octadecyl methacrylate (16.64 mL, 42.5 mM) and toluene (30 mL) were placed in 100 mL Schlenk flask. Repeated freeze–pump–thaw cycles were followed by purging with nitrogen gas to remove air from the reaction mixture. CuBr (0.012 g, 0.083 mM) and CuBr₂ (0.0009 g, 0.004 mM) were added into the flask. All other

procedure was identical to those for the polymerization of MMA. Reaction time was 57 h.

2.7. Cleavage of Attached Polymer Chains

The MDH-polymer nanocomposite (50 mg), THF (30 mL), 1-butyl or methyl alcohol (15 mL) and concentrated sulfuric acid (1 mL) were added sequentially to a 50 mL round-bottomed flask. The flask was fitted with a water condenser, and the mixture was stirred at 95–100 °C for 5 days [28, 29]. The solvent was removed under vacuum, and then the residual solid was dispersed in chloroform. After an extraction of sulfuric acid moiety with a small amount of water, the organic phase was isolated and the solvent distilled off. The remaining solid was dispersed in anhydrous THF. The MDH particles were removed by filtration through a PTFE membrane. The molecular weight of the cleaved polymer chains was measured using GPC and compared with original values from free polymer synthesized using sacrificial initiators.

2.8. Analyses of Synthesized Nanocomposites

Conversion of monomers was measured using a Shimadzu GC14-A gas chromatograph with a FID detector equipped with a J&W scientific 30m DB WAX Megabore column. Molecular weight was measured using a GPC system consisting of a Waters 510 HPLC pump, three Waters Ultrastaygel columns (10^5 and 10^3 Å) and a Waters DRI detector, with a THF flow rate of 1.0 mL/min. PMMA was used as standard. The efficiency of the attachment of initiator to the MDH particle was determined by elemental analysis (Midwest Microlab Inc.). Tapping mode AFM was performed using a Multimode Nanoscope III system (Digital Instruments). The analysis was carried out under ambient conditions using commercial Si cantilevers with 40 N/m of nominal spring constant and 300 kHz of resonance frequency. TGA analysis was performed over a range of 30–800 °C using SDM/5600H and TG/DTA 300 machines from Seiko.

3. RESULTS AND DISCUSSION

3.1. Attachment of Initiators to MDH

Suitable ATRP initiator moieties were attached to the surface hydroxyl groups on MDH particles for

a “grafting-from” ATRP by conducting an esterification reactions with 2-bromopropionyl bromide and 2-bromo-2-methylpropionyl bromide. A mixture of initiator-attached particles and unreacted MDH particles might be present if the modification was not quantitative. Elemental analysis was used to estimate the portion of reacted particles. The content of initiator moiety attached to MDH particles was 0.153 mM/g [30]. Since the surface area of the MDH particles was 44 m²/g (Sakai Chemicals), the surface density of initiators is 2.1 molecules/nm².

TGA traces for pure MDH and initiator-attached MDH are shown in Fig. 4. The TGA curves show some differences between the samples. It is known that typical MDH powders can release 27–30% of water when heated [31, 32]. There is about 1.8% difference in volatiles between MDH and initiator-attached particles in the curves, indicating attachment of initiating functionality.

3.2. Grafting Polymers from MDH via ATRP

(Meth)acrylate monomers were used to prepare MDH hybrid nanocomposites using ATRP for the “grafting-from” technique. Monomers were chosen because of their intrinsic facility for polymerization, their potential to enhance dispersability and their compatibility with a range of polymer blends.

First, *n*-butyl acrylate was polymerized from the initiator-attached MDH particles. Kinetics for the polymerization, and evolution of molecular weight and polydispersities with conversion during the experiment, are shown in Fig. 5. The final molecular weight, measured from free polymer chains,

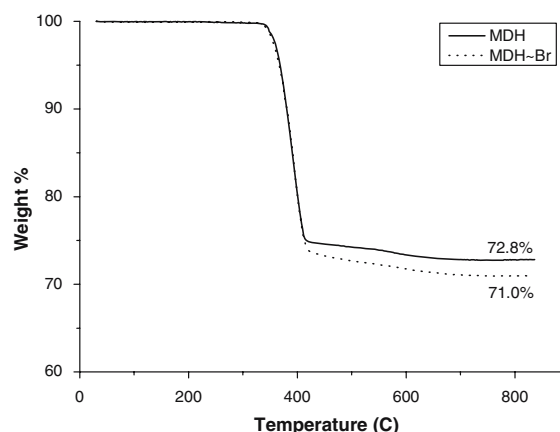


Fig. 4. TGA diagrams of MDH and initiator-attached MDH.

Magnesium Dihydroxide Nanocomposites via ATRP

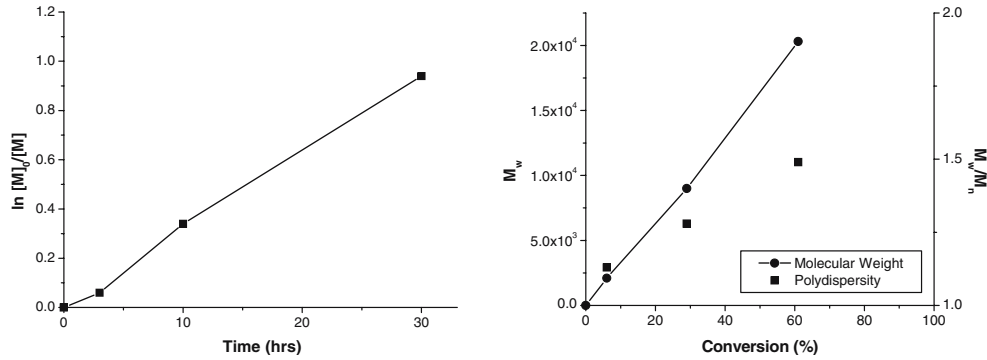


Fig. 5. Kinetics and evolution of molecular weights, polydispersities with conversion for ATRP of *n*-butyl acrylate grafted from MDH.

was $M_n = 20,300$ and polydispersity was $M_w/M_n = 1.49$.

Next, methyl methacrylate was grafted from the MDH particles. It was of interest to synthesize PMMA–MDH hybrid nanocomposites since methyl methacrylate is readily polymerized by ATRP, and the polymer mixes well with a diverse range of commodity resins. The progress of the reaction was followed by measuring conversion and molecular weight evolution of free polymer, synthesized using a sacrificial initiator (Fig. 6). The final sample of the free poly(methyl methacrylate) had a $M_n = 127,000$ and polydispersity $M_w/M_n = 1.40$.

Nanocomposites with tethered poly(methacrylates) containing longer alkyl side chains could have better compatibility and better mixing with non-polar polymers such as polyolefins. Controlled polymerization of dodecyl methacrylate from MDH particles was confirmed by following the kinetics and evolution of molecular weight and polydispersity with conversions in the series of GPC traces shown below (Fig. 7). It is anticipated that the longer alkyl side chains in octadecyl methacrylate could further

enhance compatibility and properties of blends with polyolefins [33, 34].

The resulting GPC traces, kinetics and evolution of molecular weight and polydispersity with conversion are shown in Fig. 8. The reaction was well-controlled and the final polymer with $M_n = 38,400$ and polydispersity $M_w/M_n = 1.26$ was prepared.

3.3. Selected Properties of the Synthesized Nanocomposites

3.3.1. Colloidal Stability

Inorganic particles with covalently bonded polymer chains should maintain stable suspensions in solvents for the tethered chains for a longer time than mere mixture of two components. Two vials, respectively, filled with bare MDH and MDH-poly(butyl acrylate) particles dispersed in THF were placed side by side for comparison of stabilities, as illustrated in Fig. 9. The slurry with bare MDH particles began to sediment after 30 min and they were fully precipitated after 5 h. On the other hand,

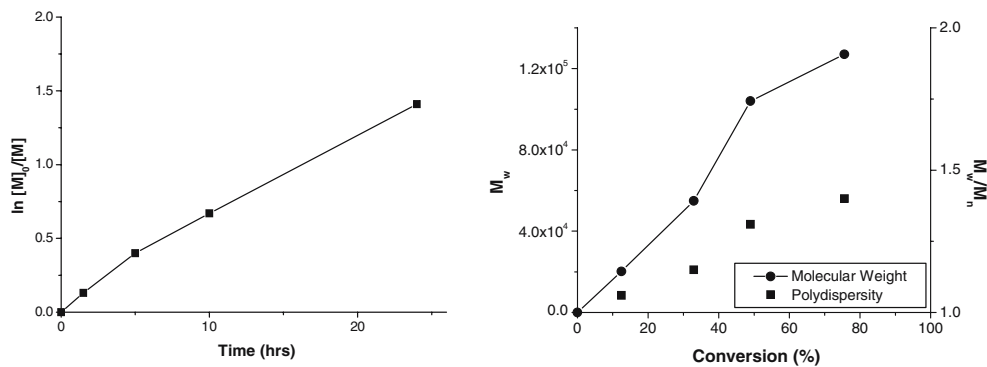


Fig. 6. Kinetics and evolution of molecular weights, polydispersities with conversion for ATRP of methyl methacrylate from MDH.

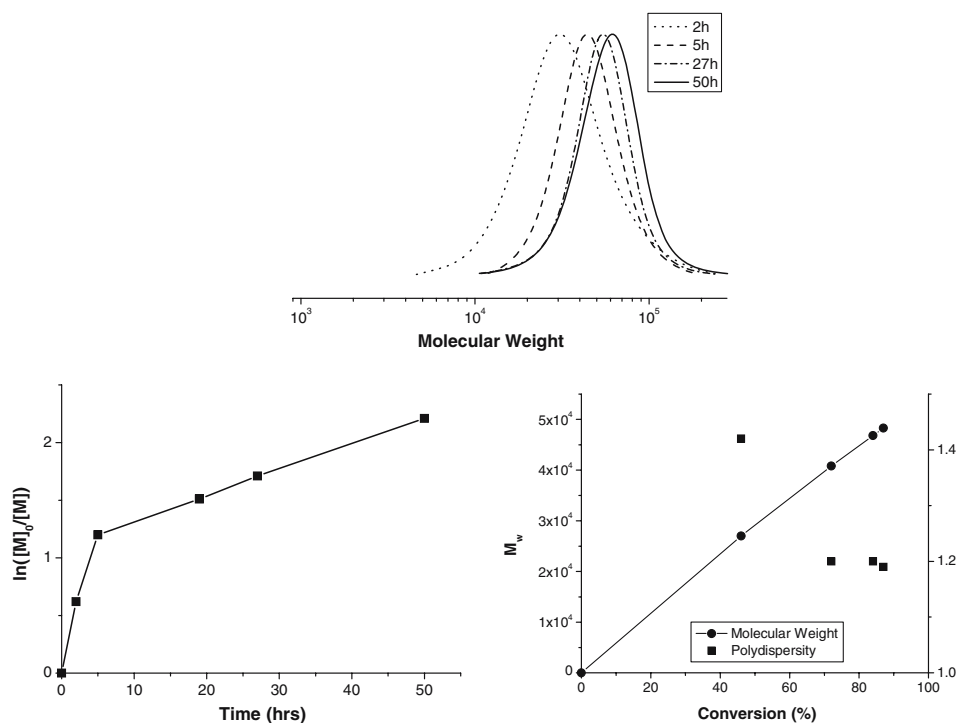


Fig. 7. GPC traces, kinetics and evolution of molecular weights, polydispersities with conversion for ATRP of dodecyl methacrylate from MDH.

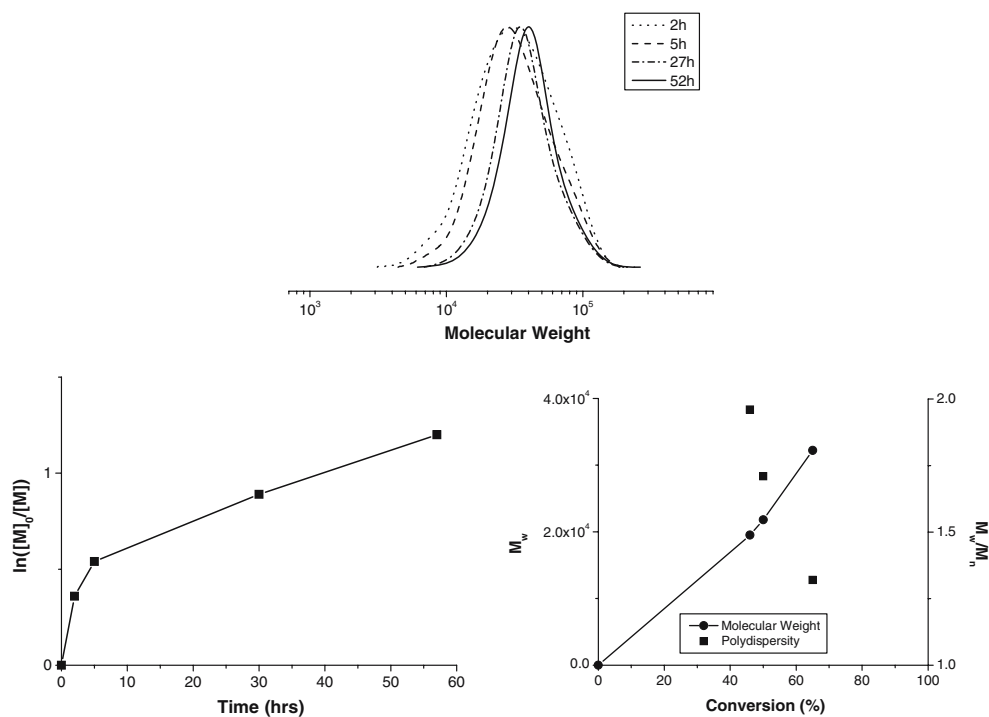


Fig. 8. GPC traces, kinetics and evolution of molecular weights, polydispersities with conversion for ATRP of octadecyl methacrylate from MDH.

Magnesium Dihydroxide Nanocomposites via ATRP



Fig. 9. Comparison of colloidal stabilities of bare MDH particles (left vial) and MDH-poly(*n*butyl acrylate) particles in THF (Initial, after 2 h and 2 weeks; from left).

MDH-poly(*n*-butyl acrylate) nanocomposite particles showed stable dispersion even after 2 weeks. This phenomenon indirectly proves the attachment of polymer chains to the MDH particles.

3.3.2. Uniformity of Attached Chains

The poly(*n*-butyl acrylate) chains attached to MDH particles were cleaved from the particles in order to determine their molecular weight. The molecular weight and polydispersity of the free polymer formed at the same time as the grafting from polymerization were 20,300 and 1.49 while those values of the cleaved polymer chains were 19,100 and 1.16, respectively. The shape of the GPC traces of the cleaved polymer and the free polymer synthesized using a sacrificial initiator, were similar, differences between the two molecular weights were small and could have originated by fractionation during the cleavage process,

Using the same method, poly(methyl methacrylate) chains were cleaved from MDH particles and molecular weight measured. The molecular weight and polydispersity of the cleaved polymer (124,000 and 1.23) were close to those of the free polymer (127,000 and 1.40, respectively) as illustrated by the GPC traces in Fig. 10.

3.3.3. AFM Analysis

AFM was used to visualize poly(methyl methacrylate) chains attached onto MDH particles (Fig. 11). The white areas around bright spots (MDH particles) show the attached polymer chains. A small amount of free polymer formed from sacrificial initiator is also observed.

Figure 12 shows a larger area of MDH-poly(octadecyl methacrylate) hybrid nanocomposites prepared by drop casting a dilute chloroform solution of the composite structures onto the substrate. The measurements were performed under ambient conditions using commercial Si cantilevers with a nominal

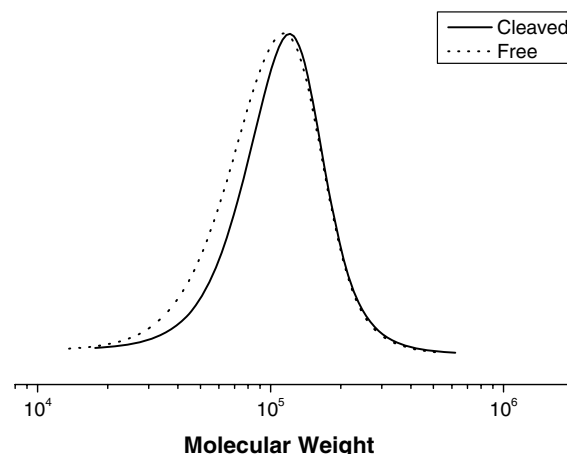


Fig. 10. Comparison of molecular weights of poly(methyl methacrylate). Cleaved polymer ($M_n = 124,000$, PDI = 1.23) shows traces similar to free polymer ($M_n = 127,000$, PDI = 1.40).

spring constant and resonance frequency, respectively, equal to 10 N/m and 300 kHz. The height and phase images were acquired simultaneously at set-point ratio $A/A_0 = 0.7$, where A and A_0 refer to the “tapping” and “free” cantilever amplitude, respectively. All polymer films were prepared through the “drop-cast” method or “spin coating” method from polymer solutions, followed by vacuum drying overnight at room temperature. There is no aggregation of the polymer-coated particles and the particles appear to be well-dispersed at the distance exceeding 100 nm.

Mechanical, thermal and flame retardancy studies, as well as compatibilities with various polymer blends, are in progress and will be reported in a forthcoming paper.

4. CONCLUSIONS

Br-containing ATRP initiators were attached to MDH particles by esterification of surface hydroxyl groups. Several (meth)acrylates were polymerized

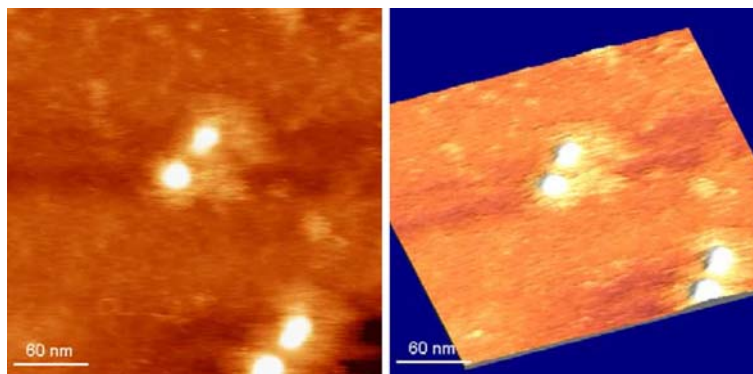


Fig. 11. AFM micrographs of MDH-poly(methyl methacrylate) (Height 2D and 3D).

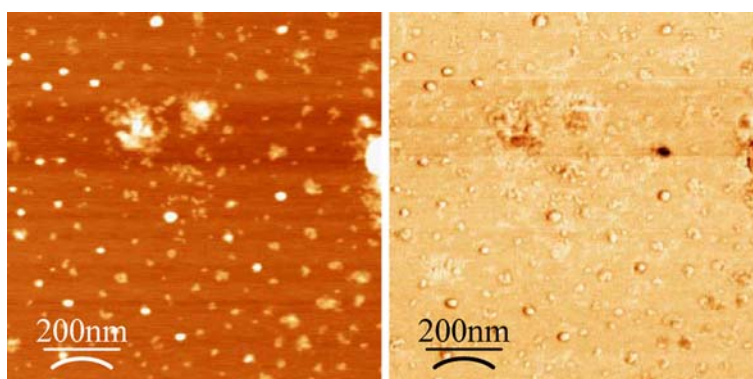


Fig. 12. AFM micrographs of MDH-poly(octadecyl methacrylate) (height and phase images).

from the initiator-attached MDH by ATRP. Molecular weights in the range up to $M_n = 100,000$ and low polydispersities $M_w/M_n \sim 1.2$ indicated a controlled “grafting from” polymerization process. The molecular weights and polydispersities of the attached polymers and those formed from added sacrificial initiator were very similar. The resulting hybrid nanocomposites formed stable suspensions and showed good dispersability in solvents.

ACKNOWLEDGMENTS

Support from NSF (DMR-0549353) is acknowledged. JO appreciates financial support from Korea Research Foundation. Dr. Jung Kwon Oh and Hyung-il Lee are acknowledged for helpful discussions and experimental assistance and Wei Wu for AFM analysis.

REFERENCES

- V. A. Shaposhnik, N. N. Zubets, I. P. Strygina, and B. E. Mill, *Desalination* **145**, 329 (2002).
- Y. Zhao, Y. Tan, F. -S. Wong, A. G. Fane, and N. Xu, *Separ. Purif. Technol.* **44**, 212 (2005).
- R. Giorgi, C. Bozzi, L. Dei, C. Gabbiani, B. W. Ninham, and P. Baglioni, *Langmuir* **21**, 18 (2005).
- O. Grexa and H. Lübke, *Polym. Degrad. Stabil.* **74**, 427 (2001).
- Y. Ding, G. Zhang, H. Wu, B. Hai, L. Wang, and Y. Qian, *Chem. Mater.* **13**, 435 (2001).
- A. Bobovitch, E. Gutman, M. Schenker, L. Utevski, and M. Muskatel, *Mater. Lett.* **23**, 317 (1995).
- J. Zhang, X. Wang, F. Zhang, and A. R. Horrocks, *Polym. Test.* **23**, 225 (2004).
- H. Qin, S. Zhang, C. Zhao, G. Hu, and M. Yang, *Polymer* **46**, 8386 (2005).
- P. M. Hergenrother, C. M. Thompson, J. G. Smith Jr, J. W. Connell, J. A. Hinkley, R. E. Lyon, and R. Moulton, *Polymer* **46**, 5012 (2005).
- F. Carpentier, S. Bourbigot, M. Le Bras, R. Delobel, and M. Foulon, *Polym. Degrad. Stabil.* **69**, 83 (2000).
- S. Vyazovkin, *Anal. Chem.* **74**, 2749 (2002).
- B. N. Jang, D. Wang, and C. A. Wilkie, *Macromolecules* **38**, 6533 (2005).
- T. D. Fornes and D. R. Paul, *Macromolecules* **37**, 7698 (2004).
- S. Choi, K. M. Lee, and C. D. Han, *Macromolecules* **37**, 7649 (2004).
- (a) J. -S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.* **117**, 5614 (1995); (b) J. -S. Wang and K. Matyjaszewski, *Macromolecules* **28**, 7901 (1995); (c) K. Matyjaszewski, *Macromolecules* **28**, 7572 (1995).
- (a) K. Matyjaszewski, *J. Macromol. Sci., Pure App. Chem.* **A34**, 1785 (1997); (b) K. Matyjaszewski, *Chemistry – Europ. J.* **5**, 3095 (1999); (c) K. Matyjaszewski, M. J. Ziegler, S. V. Arehart, D. Greszta, and T. Pakula, *J. Phys. Org. Chem.* **13**,

Magnesium Dihydroxide Nanocomposites via ATRP

- 775 (2000); (d) K. Matyjaszewski and J. Xia, *Chem. l Rev. (Washington, D. C.)* **101**, 2921 (2001).
17. (a) T. E. Patten, J. Xia, T. Abernathy, and K. Matyjaszewski, *Science (Washington, D. C.)* **272**, 866 (1996); (b) T. E. Patten and K. Matyjaszewski, *Adv. Mat.* **10**, 901 (1998); (c) T. E. Patten and K. Matyjaszewski, *Acc. Chem. Res.* **32**, 895 (1999).
18. J. Pyun, S. Jia, T. Kowalewski, G. D. Patterson, and K. Matyjaszewski, *Macromolecules* **36**, 5094 (2003).
19. (a) J. Pyun and K. Matyjaszewski, *Chem. Mater.* **13**, 3436 (2001); (b) K. Matyjaszewski, *Prog. Pol. Sci.* **30**, 858, (2005); (c) J. Pyun, S. Jia, T. Kowalewski, and K. Matyjaszewski, *Macromol. Chem. Phys.* **205**, 411 (2004); (d) J. Pyun, T. Kowalewski, and K. Matyjaszewski, *Macromol. Rapid Commun.* **24**, 1043 (2003). (e) T. Kowalewski, R. D. McCullough, and K. Matyjaszewski, *Europ. Phys. J. E: Soft Matter* **10**, 5 (2003); (f) T. Kowalewski, K. Matyjaszewski, T. Endo, and H. Nishida, *Mirai Zairyo* **3**, 12 (2003); (g) J. Pyun, K. Matyjaszewski, T. Kowalewski, D. Savin, G. Patterson, G. Kickelbick, and N. Huesing, *J. Amer. Chem. Soc.* **123**, 9445 (2001); (h) V. Coessens, T. Pintauer, and K. Matyjaszewski, *Prog. Polym. Sci.* **26**, 337 (2001); (i) J. Qiu, B. Charleux, and K. Matyjaszewski, *Prog. Polym. Sci.* **26**, 2083 (2001); (j) K. A. Davis and K. Matyjaszewski, *Adv. Polym. Sci.* **159**, 2 (2002).
20. T. Kowalewski, N. V. Tsarevsky, and K. Matyjaszewski, *J. Am. Chem. Soc.* **124**, 10632 (2002).
21. T. Liu, S. Jia, T. Kowalewski, K. Matyjaszewski, R. Casado-Portilla, and J. Belmont, *Langmuir* **19**, 6342 (2003).
22. (a) I. I. Potemkin, A. R. Khokhlov, S. Prokhorova, S. S. Sheiko, M. Moller, K. L. Beers, and K. Matyjaszewski, *Macromolecules* **37**, 3918 (2004); (b) K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick, and S. Diamanti, *Macromolecules* **32**, 6526 (1999); (c) K. Matyjaszewski, D. A. Shipp, J. L. Wang, T. Grimaud, and T. E. Patten, *Macromolecules* **31**, 6836 (1998); (d) P. J. Miller and K. Matyjaszewski, *Macromolecules* **32**, 8760 (1999); (e) K. Matyjaszewski, P. J. Miller, N. Shukla, B. Immaraporn, A. Gelman, B. B. Luokala, T. M. Siclovan, G. Kickelbick, T. Vallant, H. Hoffmann, and T. Pakula, *Macromolecules* **32**, 8716 (1999); (f) Y. Nakagawa, P. J. Miller, and K. Matyjaszewski, *Polymer* **39**, 5163 (1998).
23. M. Kruk, B. Dufour, E. B. Celer, T. Kowalewski, M. Jaroniec, and K. Matyjaszewski, *J. Phys. Chem. B.* **109**, 9216 (2005).
24. N. Saleh, T. Sarbu, K. Sirk, G. V. Lowry, K. Matyjaszewski, and R. D. Tilton, *Langmuir* **21**, 9873 (2005); N. Saleh, T. Phenrat, K. Sirk, B. Dufour, J. Ok, T. Sarbu, K. Matyjaszewski, R. D. Tilton, and G.V. Lowry, *Nanoletters* **5**, 2489 (2005).
25. K. Ohno, T. Morinaga, K. Koh, Y. Tsujii, and T. Fukuda, *Macromolecules* **38**, 2137 (2005).
26. C. Li and B. C. Benicewicz, *Macromolecules* **38**, 5929 (2005).
27. S. Qin, K. Matyjaszewski, H. Xu, and S. S. Sheiko, *Macromolecules* **36**, 605 (2003).
28. H. G. Börner, K. Beers, K. Matyjaszewski, S. S. Sheiko, and M. Möller, *Macromolecules* **34**, 4375 (2001).
29. S. Qin, D. Qin, W. T. Ford, D. E. Resasco, and J. E. Herrera, *J. Am. Chem. Soc.* **126**, 170 (2004).
30. (a) K. Matyjaszewski, *Progr. Polym. Sci.* **30**, 858 (2005); (b) C. W. Macosko, H. K. Jeon, and T. R. Hoye, *Progr. Polym. Sci.* **30**, 939 (2005); (c) Y. Shen, H. Tang, and S. Ding, *Progr. Polym. Sci.* **29**, 1053 (2004); (d) I. Luzinov, S. Minko, and V. V. Tsukruk, *Progr. Polym. Sci.* **29**, 635 (2004); (e) A. Bhattacharya, and B. N. Misra, *Progr. Polym. Sci.* **29**, 767 (2004).
31. J. C. Yu, A. Xu, L. Zhang, R. Song, and L. Wu, *J. Phys. Chem. B.* **108**, 64 (2004).
32. B. V. L'vov, A. V. Novichikhin, and A. O. Dyakov, *Thermochim. Acta* **315**, 135 (1998).
33. (a) L. Zheng, A. F. Xie, and J. T. Lean, *Macromolecules* **37**, 9954 (2004); (b) K. Matyjaszewski, M. Teodorescu, P. J. Miller, and M. L. Peterson, *J. Polym. Sci., Part A: Polym. Chem.* **38**, 2440 (2000); (c) S. C. Hong, S. Jia, M. Teodorescu, T. Kowalewski, K. Matyjaszewski, A. C. Gottfried, and M. Brookhart, *J. Polym. Sci., Part A: Polym. Chem.* **40**, 2736 (2002); (d) H. Kaneyoshi, Y. Inoue, and K. Matyjaszewski, *Macromolecules* **38**, 5425 (2005); (e) Y. Inoue and K. Matyjaszewski, *J. Polym. Sci., Part A: Polym. Chem.* **42**, 496 (2004); (f) Y. Inoue, T. Matsugi, N. Kashiwa, and K. Matyjaszewski, *Macromolecules* **37**, 3651 (2004); (g) L. Okrasa, T. Pakula, Y. Inoue, and K. Matyjaszewski, *Coll. Polym. Sci.* **282**, 844 (2004).
34. Z. M. Wang, H. Nakajima, E. Manias, and T. C. Chung, *Macromolecules* **36**, 8919 (2003).