154 *Macromolecules* **2007,** *40,* 154−156

Rate Enhancement in Controlled Radical Polymerization of Acrylates Using Recyclable Heterogeneous Lewis Acid

Rong Luo and Ayusman Sen*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received October 11, 2006
Revised Manuscript Received November 30, 2006

The growing demand for functionalized, structurally well-defined, polymeric materials has been a driving force for the development of controlled ("living") radical polymerization (CRP) techniques,[1] two notable examples of which are nitroxide-mediated polymerization (NMP)[2−5] and reversible addition−fragmentation transfer (RAFT) polymerization.[5−10] However, in order to have good control over the polymerization, the concentration of propagating radicals must be kept low to minimize bimolecular termination reactions. The price paid for this is the slow polymerization rate, which diminishes the practical utility of such systems. Clearly, strategies must be developed that allow CRP to be conducted at lower temperatures, in shorter time periods, and with higher monomer conversions.

One approach to increasing the radical polymerization rate of acrylate monomers is to use a Lewis acid as a complexation agent. The Lewis acid coordinates to the ester carbonyl group of the acrylate monomer and reduces the electron density in the conjugated C═C bond, thereby increasing the reactivity of the radical generated. Although rate acceleration in acrylate polymerizations by added Lewis acids has been previously reported, most Lewis acids employed thus far are relatively expensive materials that are soluble in the reaction medium and, therefore, not easily recycled.[11−16] From the standpoint of practical "green chemistry", the ideal Lewis acid should be insoluble and can be separated by filtration and reused. At first glance, this appears to be a difficult problem because the radical polymerization would be expected to occur in the liquid monomer phase and the insoluble Lewis acid would be expected to have a minimal influence on the polymerization. However, as discussed above, the bonding of the acrylate monomer to the Lewis acid significantly increases the reactivity of the corresponding radical. Thus, under ideal conditions, the acrylate monomer units that participate in the polymerization would be predominantly those that are bound to the heterogeneous Lewis acid.[17] Herein, we report significant rate enhancement in NMP and RAFT polymerizations in the presence of a *catalytic* amount of solid acidic alumina (Al_2O_3) as Lewis acid. The acidic alumina can be recycled repeatedly without loss of activity.

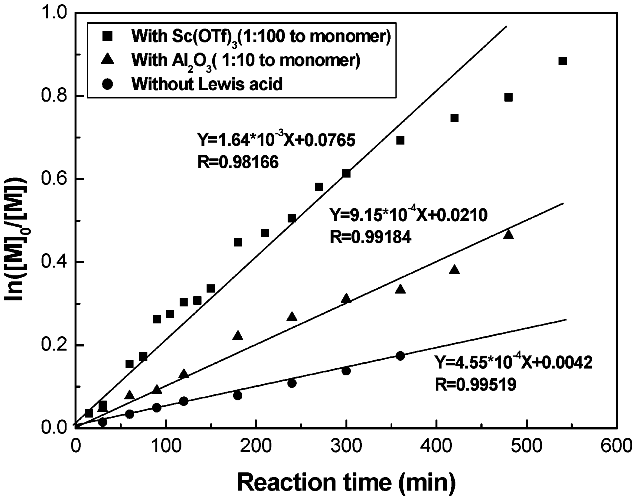

Figure 1. Polymerization kinetics for *n*-butyl acrylate (monomer, M) in the presence and absence of Lewis acids ($Sc(OTf)_3$, 1 mol %; Al_2O_3, 10 mol %). Conditions: nitroxide-mediated polymerization (NMP) initiator (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane), 0.6 mmol; NMP control agent (2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide), 0.03 mmol; BA, 75 mmol; tetrachloroethane, 0.5 g; PhCl, 20 mL; 125 °C.

Nitroxide-Mediated Polymerization in the Presence of Alumina. The first-order plots in Figure 1 illustrate the rate enhancement in the presence of Lewis acids for the polymerization of *n*-butyl acrylate. While the rate enhancement was much higher in the presence of soluble $Sc(OTf)_3$, a significant deviation from linearity was observed at longer reaction times, and the polydispersity (PDI) of the resultant polymers was high (2.3−3.6). However, the polymerization was well-behaved in the presence of acidic alumina (Aldrich, acidic, Brockmann I, standard grade, ∼150 mesh, pH = 4.5 ± 0.5 in aqueous solution) and proceeded at a rate (k_{obs}, observed polymerization rate constant) significantly faster than that without the Lewis acid. Furthermore, the polymerization rate increased with increasing amount of added alumina, eventually reaching an asymptote, presumably due to saturation coordination at the alumina surface (see Supporting Information, Figure S1). The polydispersity of the polymers obtained in the presence of alumina remained low in every case (1.10−1.15). The latter indicates that the polymerization is well-controlled and that alumina was increasing the reactivity of the propagating radicals rather than increasing their concentration (which would result in higher polydispersity). In contrast to the observation with *n*-butyl acrylate, the rate of NMP-mediated polymerization of styrene, a monomer that cannot coordinate to a Lewis acid, was nearly unaffected by the addition of alumina (see Supporting Information, Figure S2). This latter observation also suggests that there is no change in propagating radical concentration through the interaction of alumina with NMP.

The living nature of the *n*-butyl acrylate (BA) polymerization in the presence of alumina is further illustrated by the close correspondence between the theoretical molecular weight based on monomer/initiator ratio and the observed molecular weight. This is shown in Figure 2; all of the PDI values were below 1.15.

More importantly, the nitroxide-terminated polymers made from these systems can be retreated with a different monomer for chain extension to form block copolymers. For example, an alkoxyamine-functionalized poly(*n*-butyl acrylate) block (0.5 g; M_n, 15 000; PDI, 1.11) was initially grown in the presence of 10 mol % alumina, and the resultant macroinitiator was employed to polymerize styrene (1.5 g) at 125 °C under N_2 for 8 h. This resulted in 61% conversion of styrene and gave a block copolymer, GPC analysis of which revealed the expected increased molecular weight (M_n, 55 000; PDI, 1.16) and no detectable amount of unreacted starting block (see Supporting Information, Figure S3).

Finally, the alumina used for accelerating the NMP reactions can be readily removed by simple filtration and reused. As an

---

* Corresponding author. E-mail: asen@psu.edu.

10.1021/ma062341o CCC: $37.00

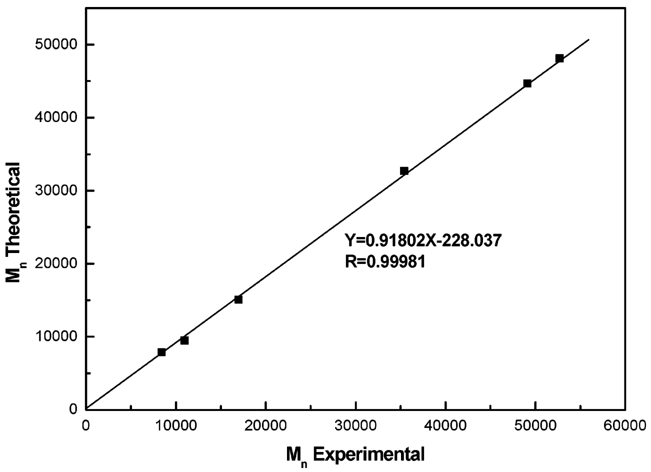

Figure 2. Relationship between experimental number-average molecular weight (M_n) and theoretical molecular weight for the nitroxide-meditaed polymerization (NMP) of *n*-butyl acrylate in the presence of alumina (10 mol % relative to monomer). Conditions: NMP initiator (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane), 1.0 equiv; NMP control agent (2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide), 0.05 equiv; 125 °C (see Table S1, Supporting Information for additional data).

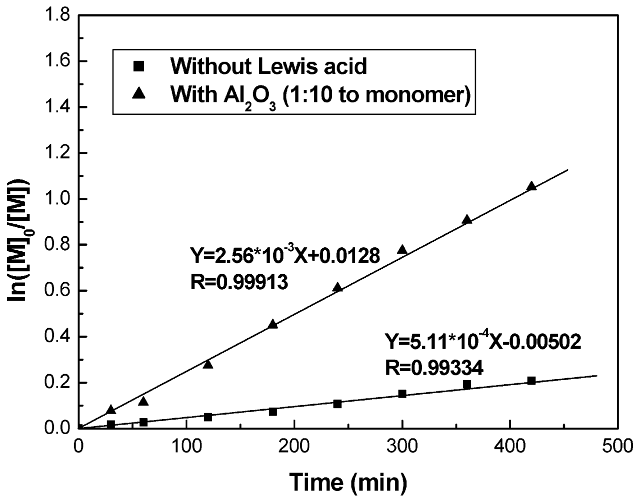

Figure 3. Polymerization kinetics for methyl acrylate (monomer, M) in the presence and absence of acidic alumina (10 mol % relative to MA). Conditions: reversible addition−fragmentation transfer (RAFT) agent (benzyl 1-pyrrolcarbodithioate), 0.29 mmol; AIBN, 0.058 mmol; MA, 23.3 mmol; 60 °C.

example, the same sample of alumina was used for successive *n*-butyl acrylate homopolymerizations. Typically, 96−98% of the alumina was recovered, and for each polymerization cycle there was good agreement between theoretical and experimental M_n values (cf. Table S1 and Figure 2) and the polydispersity remained below 1.15.

RAFT Polymerization in the Presence of Alumina. Figures 3 and 4 summarize our results on RAFT homopolymerization of methyl acrylate (MA) in the presence and absence of added alumina (10 mol % relative to monomer). A 5-fold increase in polymerization rate (k_{obs}) is observed in the presence of alumina. Furthermore, the linear relationship between molecular weight evolution and total monomer conversion, as well as the narrow polydispersities (Figure 4), is consistent with a polymerization that is “living”.

In summary, the addition of insoluble acidic alumina to controlled radical NMP and RAFT polymerizations of acrylate monomers results in significantly higher reaction rates and conversions. Parallel experiments with monomers that can and cannot interact with the Lewis acid suggest that the observed effect is not due to a change in the concentration of propagating radicals in the system. The accelerating effect is particularly dramatic since only a small fraction of the Lewis acid sites that are present on the alumina surface can actually interact with the acrylate. Preliminary NMR studies on the coordination of soluble Lewis acids to the ester carbonyl of acrylate monomers and polymers suggest that the interaction with the monomer is significantly stronger than that with the polymer,[14] thus explaining why only a catalytic amount of Lewis acid is required for polymerization rate enhancement. The Lewis acid-enhanced polymerizations have “living” characteristics, allowing the synthesis of block copolymers. The alumina can be quantitatively removed by filtration and recycled with no significant loss in efficacy.

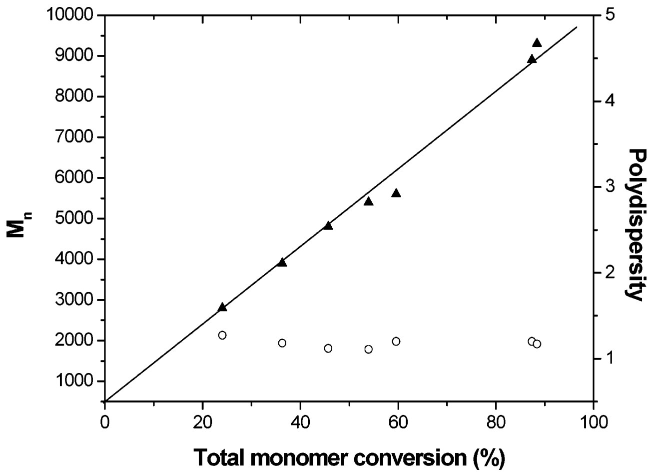

Figure 4. Dependence of number-average molecular weight (M_n) and polydispersity on total monomer conversion for the reversible addition−fragmentation transfer homopolymerization of methyl acrylate in the presence of Al_2O_3 (10 mol % relative to MA). Conditions: RAFT (benzyl 1-pyrrolcarbodithioate), 0.29 mmol; 2,2′-azobis(isobutyronitrile) (AIBN), 0.058 mmol; MA, 23.3 mmol; Al_2O_3, 2.3 mmol; 60 °C.

Acknowledgment. This research was supported by the National Science Foundation and Rohm & Haas Co. We thank Dr. Megan Nagel for helpful discussions.

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Matyjaszewski, K., Ed. *Advances in Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2003; Vol. 854.

(2) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(3) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.

(4) Gu, B.; Liu, S.; Leber, D.; Sen, A. *Macromolecules* **2004**, *37*, 5142−5144.

(5) Liu, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6175−6192.

(6) Chong, Y. K.; Kristina, J.; Le, T. P. L.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(7) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283.

(8) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.

(9) Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P. L.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(10) Liu, S.; Gu, B.; Rowlands, H. A.; Sen, A. *Macromolecules* **2004**, *37*, 7924−7929.

(11) Lutz, J. F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986−6993.

(12) Lutz, J. F.; Kirci, B.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 3136−3145.

(13) Lutz, J. F.; Jakubowski, W.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2004**, *25*, 486−492.

(14) Isobe, Y.; Nakano, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1463−1471.

(15) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamato, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702−1710.

(16) Nagel, M.; Poli, D.; Sen, A. *Macromolecules* **2005**, *38*, 7262−7265.

(17) Luo, R.; Sen, A. *Macromolecules* **2006**, *39*, 7798−7800.

MA062341O