Macromolecules **2003,** *36,* 539−542

Solid-State Metathesis Polycondensation

Garrett W. Oakley, Stephen E. Lehman, Jr.,
Jason A. Smith, Paul van Gerven, and
Kenneth B. Wagener*

The George & Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

Received October 15, 2002
Revised Manuscript Received December 4, 2002

Introduction. We report the first solid-state polycondensation of any kind to be done near room temperature by using acyclic diene metathesis (ADMET) chemistry. This equilibrium reaction is driven by the elimination of the highly volatile condensate, ethylene, which vents from the reacting solid to create high polymer.

Solid-state polymerization (SSP) traditionally has been divided into two classes: crystal-to-crystal polymerization[1] and equilibrium condensation polymerization.[2] The principles governing these two types of polymerization are quite different, for the former is topological chemistry, while the latter occurs in the amorphous state of semicrystalline polymers. Topological SSP (the polymerization of diacetylenes[1,3] and diolefins[4] are examples) relies on a suitable arrangement of the reactants in the monomer crystal to permit the necessary contact between reacting groups with only the slight vibrations allowed within a crystalline state. On the other hand, significant molecular motions occur in polycondensation SSP, mostly in the amorphous phase. This motion facilitates the release of a small condensate molecule (ethylene, in the case of ADMET chemistry), which can be removed at the surface of the solid to drive the increase in molecular weight.

Solid-state polycondensation first was observed more than 35 years ago[5] and is practiced in the polyester, polyamide, and polycarbonate industries. Polymerization begins in the liquid (bulk) state at high temperatures (usually above 250 °C), followed by cooling of the macromolecule to a temperature below its semicrystalline melting point. The polymer chemistry then is continued in the solid state above the glass transition temperature, but below the melting point. Solid-state polycondensations of this nature usually are done at temperatures above 150 °C.[6] This approach has distinct advantages over performing the polymerization completely in the melt state, advantages which are found both in terms of producing polymers of higher purity (fewer side reactions occur at these lower temperatures) and in the economics of the reaction (less energy is required). The ADMET reaction has the potential of operating in this manner, doing so at temperatures far below 150 °C, even as low as room temperature.

Removal of the condensate is the rate-determining factor in solid-state polycondensation, where greater surface area within the polymerizing solid favors faster evolution of the small molecule. The condensate can be removed from the solid by using static or dynamic vacuum or by exposure to a stream of inert gas. For semicrystalline polymers, operating above T_g enhances molecular translational mobility within the amorphous regions, while the regions of crystallinity maintain the shape of the particle during the polymerization.

We now report that the olefin metathesis mechanism can operate within these principles. Olefin metathesis is a superb tool for making carbon−carbon connections in both organic and polymer chemistry,[7] where the important reactions of the day are ring-opening metathesis polymerization (ROMP),[8] acyclic diene metathesis (ADMET) polymerization,[9] ring-closing metathesis (RCM),[10] and cross metathesis (CM).[11] ADMET, RCM, and CM all involve condensation steps, so in principle all of them could operate in the solid state, assuming some degree of amorphous character is present during the conversion. Of the three, acyclic diene metathesis chemistry leads to macromolecules, and in most examples, the small molecule released is ethylene. The high volatility of ethylene explains why this solid-state polycondensation can occur under such mild conditions. All other known SSP examples release high boiling condensates such as ethylene glycol (PET), water (nylon), or phenol (polycarbonate). Low-temperature solid-state polymerization can lead to the generation of highly pure, high molecular weight polymers at or near room temperature; further, the process may offer a new route to the direct preparation of intractable polymers, which presently are made via indirect techniques.

Key factors in any solid-state polycondensation are the nature and the lifetime of the catalyst employed, in this case, metathesis catalysts. Three of the most widely used metathesis catalysts are bis(tricyclohexylphosphine) benzylidine ruthenium(IV) dichloride (**1**),[12] tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidine] ruthenium(IV) dichloride (**2**),[13] and 2,6-diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-*tert*-butoxide) (**3**),[14] commonly known as the first (**1**) and second (**2**) generation Grubbs ruthenium catalysts and Schrock's molybdenum catalyst (**3**), respectively. Thus far, we have shown that the two Grubbs catalysts promote solid-state ADMET polymerization. Reported below are the results of our research on this topic to date.

Experimental Section. A typical experimental setup is trivial and consists of equipping a three-neck round-bottom flask with two vacuum adapters and a stopper. The apparatus is evacuated, flame-dried, and purged with argon; liquid monomer and catalyst are added at constant temperature (± 2 °C) under a positive argon pressure. Polymerization begins in the liquid state with subsequent crystallization of the growing macromolecule. This reactor then is left intact with argon flowing over the semicrystalline solid, which is sampled periodically for molecular weight determination by gel permeation chromatography (GPC) and/or NMR end group analysis. Sampling consists of dissolving the solid in a "quench" solution of ethyl vinyl ether (EVE), butylated hydroxytoluene (BHT), and the GPC solvent to minimize further reaction. Ethyl vinyl ether inhibits Grubbs metathesis catalyst activity,[15] and BHT is a free radical scavenger. Reagents were purchased from Aldrich and used as received unless noted otherwise. 1,9-Decadiene was distilled over CaH before use. First[12] and second[13] generation Grubbs catalysts were synthesized by known methods. Syntheses of other monomers are discussed herein.

Results and Discussion. Figure 1 shows several examples of ADMET solid-state polymerization. 1,9-

10.1021/ma0215924 CCC: $25.00

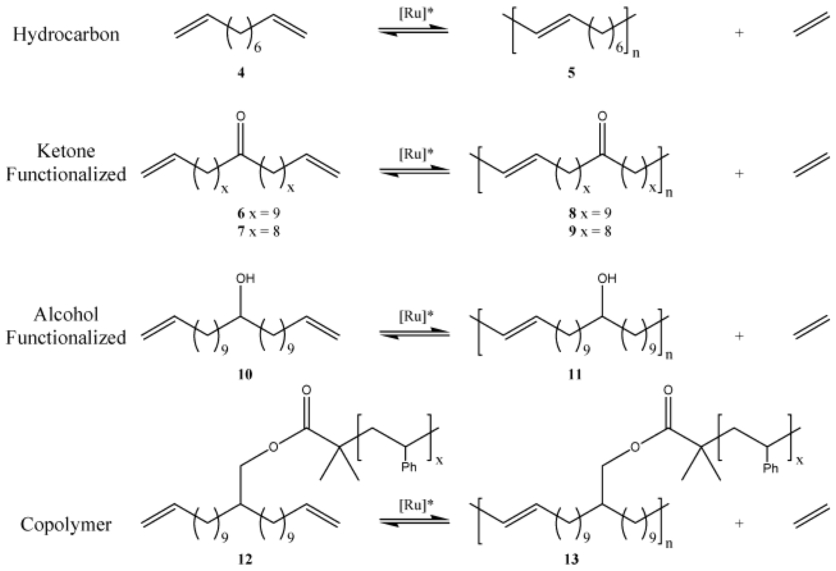

Figure 1. A variety of monomers that undergo solid-state ADMET polymerization.

Table 1. Results of Solid-State Polymerizations of Monomer 4 with Periodic Sampling

			number-average mol wts^a at specified reaction times							
catalyst	Mon:Cat. ratio	temp (°C)	3 h	6 h	12 h	24 h	48 h	72 h	96 h	168 h
1	500:1	30	2800	3700	6600	9400	9900	19000	20000	21000
		45	5400	6400	7200	16000^b	30000	30000	31000^c	
2	500:1	30	2200	5800	7000	7800	7900	8800^d		
		45	8900	12000	12000	15000	23000	23000	27000	27000

[a] M_n determined by GPC in chloroform verses polystyrene standards. [b] Actual time of sampling is 30 h. [c] Actual time of sampling is 107 h. [d] Actual time of sampling is 119 h.

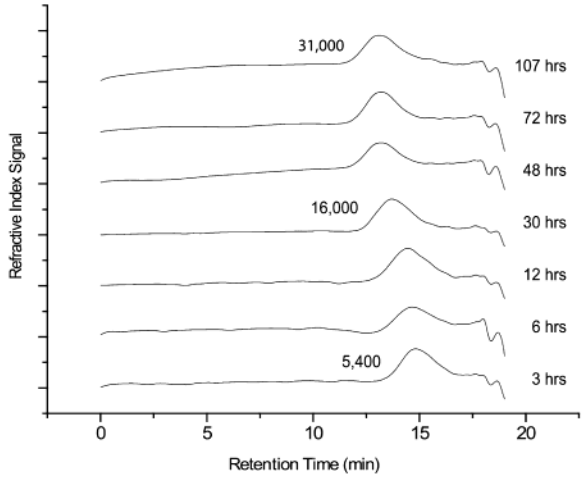

Figure 2. Gel permeation chromatography traces of the SSP of 1,9-decadiene with first generation Grubbs at 45 °C sampled periodically. The molecular weights listed at 3, 30, and 107 h are number-average molecular weights based on polystyrene equivalents.

Decadiene (**4**) was investigated first; all polymerizations shown in Table 1 produced semicrystalline solids before the first sampling was done.

These results demonstrate unequivocally that solid-state polycondensation is occurring at temperatures as low as 30 °C, with the possibility of the reaction occurring at even lower temperatures. Figure 2 shows the GPC traces for polymerizations done with first generation Grubbs catalyst at 45 °C. As the polymerization proceeds, the number-average molecular weight increases from 5400 to 31 000 g/mol, all while in the solid state. It should be noted that all the molecular weights reported herein are well within the range normally expected for equilibrium step polymerization chemistry. For example, polyester, nylon, and polycarbonate all exhibit useful properties with number-average molecular weights of less than 25 000.[16]

Both catalysts **1** and **2** promote ADMET solid-state polymerization. First generation Grubbs is the more active of the two, largely due to its higher reactivity at lower temperatures, reaching number-average molecular weights of 30 000 g/mol in 3 days at 45 °C. Second generation Grubbs, **2**, is slower but seems continue to promote polymerization at later stages of the reaction. This observation may be the result of the longer lifetime of complex **2** as compared with the first generation Grubbs complex, **1**. The half-life of second generation Grubbs is found to be 6 h at 55 °C in benzene[17] compared to 40 min for first generation Grubbs;[18] however, we suspect that the lifetimes of these complexes are longer in the solid state compared to those in solution.

When comparing polymerizations of the same catalyst at different temperatures, higher temperatures achieved higher molecular weights. For first generation Grubbs at 30 °C, a number-average molecular weight of approximately 20 000 g/mol was achieved in 3 days, while at 45 °C, it reached approximately 30 000 g/mol in the same amount of time. A similar effect was found for complex **2**. At 30 °C, the number-average molecular weight does not exceed 10 000 g/mol in 5 days, while reaching approximately 27 000 g/mol at 45 °C in the same amount of time.

Experiments also were conducted to increase the surface area of the solid mixture in order to facilitate escape of the condensate from the surface of the solid. 1,9-Decadiene (**4**) was polymerized in the melt with

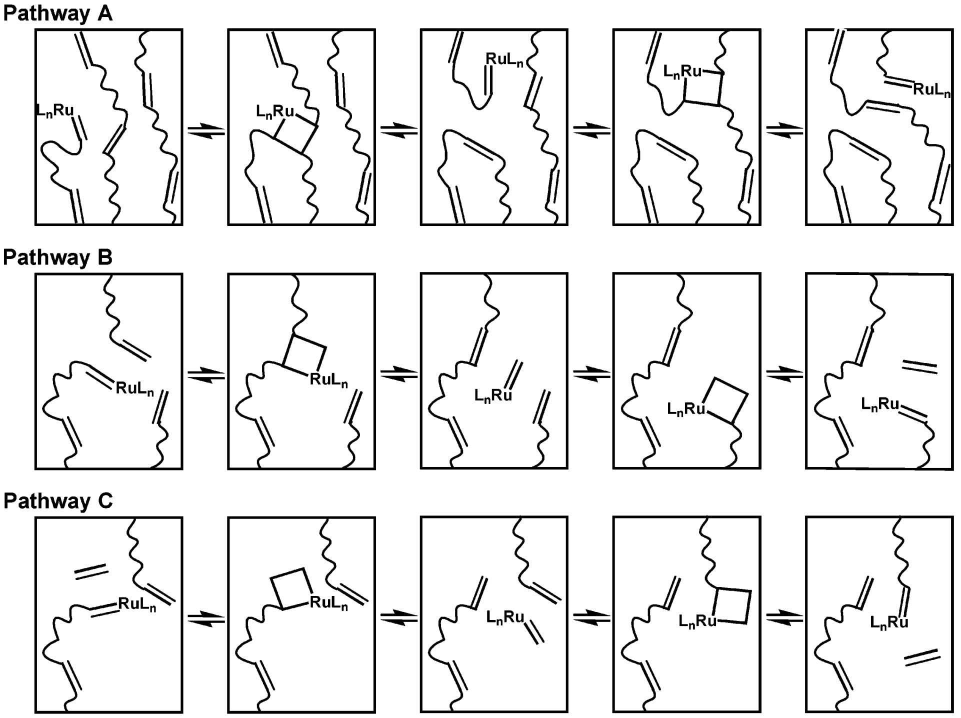

Figure 3. ADMET mechanism at work in the amorphous region of a semicrystalline solid. Pathway A shows the diffusion of a ruthenium carbene by interchange reactions without a net change in molecular weight. Pathway B illustrates an increase in molecular weight by formation of ethylene. Pathway C illustrates how ethylene can migrate through a solid to the surface of the material via the same mechanism.

second generation Grubbs at 70 °C for 10 min and then quickly crystallized by cooling to room temperature. The resulting low molecular weight semicrystalline polymer (M_n = 1300 g/mol by NMR) was ground into a fine powder with a chilled mortar and pestle. This finely divided solid was brought to 45 °C and sampled over time as before, showing that M_n steadily increases over the course of a week, reaching 22 500 g/mol by NMR. This represents an approximate 20-fold increase in molecular weight, all while in the solid state.

Other monomers also are amenable to solid-state metathesis polymerization. The ketone-functionalized dienes, tricosa-1,22-dien-12-one (**6**) and heneicosa-1,20-dien-11-one (**7**),[19] as well as an alcohol-functionalized diene, tricosa-1,22-dien-12-ol (**10**),[20] react in a manner similar to 1,9-decadiene. For example, second generation Grubbs was mixed with the ketone-functionalized monomer **7** at 115 °C for 10 min and then allowed to cool to the solid state. The resulting polymer (4100 g/mol by GPC) was ground into a fine powder and then placed in a reaction flask at 80 °C. After 24 h, the molecular weight had approximately doubled with an M_n of 8300 g/mol.

Other polymer architectures operate in the solid state in a similar manner. For example, macromonomer **12** (M_n = 6700 g/mol) was synthesized via atom transfer radical polymerization (ATRP)[21] to create an amorphous "graft" of polystyrene at the center of a long-chain diene monomer. This macromonomer undergoes ADMET solid-state polymerization at 90 °C when combined with an appropriate metathesis catalyst, achieving an M_n of 12 700 g/mol over 24 h. This reaction occurs despite the large polystyrene branch attached to the diene. With only two olefins per macromonomer, it is significant that sufficient molecular mobility exists in the solid state to allow polycondensation metathesis chemistry to occur. In fact, even small changes in temperature have a large effect on this molecular mobility. At 75 °C, an almost negligible amount of solid-state polymerization occurs with macromonomer **12** over a 2 week period, whereas at 90 °C the number-average molecular weight doubles in 24 h.

Semicrystalline condensation polymers are thought to undergo solid-state polymerization due to this enhanced mobility, which exists within the amorphous region when above the glass transition temperature. While physical diffusion of ethylene within the solid is undoubtedly occurring, the situation is more complex than just that. The increase in molecular weight cannot be rationalized by diffusion of ethylene alone since the motions of amorphous chain segments in semicrystalline polymers are restrained by being anchored in the crystalline regions.[22] A more recent model suggests that migration of functionality can be explained by interchange reactions, a phenomenon termed "functional group diffusion" which has been described by Abhiraman et al.[22] and Lenz and Schuler.[23] We believe functional group diffusion complements the physical diffusion of ethylene.

Figure 3 illustrates how solid-state functional group diffusion operates in the case of metathesis polycondensation chemistry. Pathway A shows how the ruthenium carbene migrates within the polymer sample simply as a result of metathesis interchange reactions, which are congruent with the proposed mechanism for ADMET.[24] Reactions of this type do not lead to an increase in molecular weight, but rather to chain length redistribution that results in a most probable molecular weight distribution (M_w/M_n = 2.0). Nevertheless, functional groups are "diffusing" through the solid, which assists end group encounters. Pathway B shows how ethylene is generated, thereby increasing molecular weight. Transport of ethylene to the surface of the solid is also aided by the same mechanism, as illustrated in pathway C.

The opportunities afforded by solid-state metathesis polycondensation are evident, for it could offer a synthetic pathway to a variety of intractable polymer structures. Many such polymers either have not been made or are synthesized via indirect routes, usually via a soluble precursor macromolecule. A direct solid-state synthesis of such polymers has the potential of generating very pure materials. For example, the synthesis of pure poly(phenylenevinylene) may be possible; other intractable, and therefore inaccessible, conjugated polymers may become feasible as well. In addition, solid-state polycondensation may also be useful in ring-closing metathesis and/or cross metathesis. These opportunities are now under investigation.

Acknowledgment. We thank the National Science Foundation for financial support, the Army Research Office for catalyst preparations, and Mr. Wendell Bobb for his assistance with the 1,9-decadiene experiments. We also thank Professor Dr. Gerhard Wegner, Max Planck Institute Fur Polymerforschung, and Professor A. S. Abhiraman, Georgia Institute of Technology, for their helpful comments. We also thank Mr. Pat O'Donnell for providing macromonomer **12**.

References and Notes

(1) (a) Mrinal, T. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1989; Vol. 15, pp 362−380. (b) Wegner, G. *Faraday Discuss. R. Chem. Soc.* **1979**, *68*, 494−508.

(2) (a) Pilati, F. *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. 5, pp 201−216. (b) Herzberg, O.; Epple, M. *Eur. J. Inorg. Chem.* **2001**, 1395−1406.

(3) Bloor, D. *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. 5, pp 233−249.

(4) (a) Hasegawa, M. *Chem. Rev.* **1983**, *83*, 507−518. (b) Hasegawa, M. *Comprehensive Polymer Science*; Pergamon: New York, 1989; Vol. 5, pp 217−232.

(5) (a) Morosoff, N.; Lim, D.; Morawetz, H. *J. Am. Chem. Soc.* **1964**, *86*, 3167. (b) Macchi, E. M.; Morosoff, N.; Morawetz, H. *J. Polym. Sci., Part A-1* **1968**, *6*, 2033−2049. (c) Chen, F. C.; Griskey, R. G.; Beyer, G. H. *AIChE J.* **1969**, *15*, 680−685. (d) Chang, T. M. *Polym. Eng. Sci.* **1970**, *10*, 364−368.

(6) A recent exception has been reported by DeSimone and Kiserow, who used supercritical CO_2 as a plasicizer and sweep fluid for synthesis of polycarbonate, thereby promoting SSP as low as 90 °C. (a) Gross, S. M.; Roberts, G. W.; Kiserow, D. J.; DeSimone, J. M. *Macromolecules* **2001**, *34*, 3916−3920. (b) Shi, C.; DeSimone, J. M.; Kiserow, D. J.; Roberts, G. W. *Macromolecules* **2001**, *34*, 7744−7750.

(7) (a) *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Topics in Organometallic Chemistry; Springer: Berlin, 1998. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerizations*; Academic Press: New York, 1997. (c) *Metathesis Polymerization of Olefins and Polymerizations of Alkynes*; Imamoglu, Y., Ed.; NATA ASI Series; Kluwer Academic Publishers: Boston, 1998. (d) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037−2056. (e) Mol, J. C. Olefin Metathesis. In *Fine Chemicals through Heterogeneous Catalysis*; Wiley: Weinheim, 2001. (f) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043.

(8) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158−165. (b) Schrock, R. R. Ring Opening Metathesis Polymerization. In *Ring Opening Polymerization*; Bruneile, D. J., Ed.; Hanser: Munich, 1993; pp 129−156. (c) Grubbs, R. H.; Khosravi, E. Ring Opening Metathesis Polymerization (ROMP) and Related Processess. In *Synthesis of Polymers*; Schluter, A. D., Ed.; Materials Science and Technology Series; Wiley: Weinheim, 1999; pp 65−104.

(9) (a) Tindall, D.; Pawlow, J. H.; Wagener, K. B. Recent Advances in ADMET Chemistry. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Topics in Organometallic Chemistry Series; Springer: Berlin, 1998; pp 183−198. (b) Davidson, T. A.; Wagener, K. B. Acyclic Diene Metathesis (ADMET) Polymerization. In *Synthesis of Polymers*; Schluter, A. D., Ed.; Materials Science and Technology Series; Wiley: Weinheim, 1999; pp 105−122.

(10) (a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−452. (b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450. (c) Hoveyda, A. H. Catalytic Ring-Closing Metathesis and the Development of Enantioselective Processes. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Topics in Organometallic Chemistry Series; Springer: Berlin, 1998; pp 103−132.

(11) (a) Randall, M. L.; Snapper, M. L. *J. Mol. Catal. A: Chem.* **1998**, *133*, 29−44. (b) Gibson, S. E.; Keen, S. P. Cross-Metathesis. In *Alkene Metathesis in Organic Synthesis*; Fürstner, A., Ed.; Topics in Organometallic Chemistry Series; Springer: Berlin, 1998; pp 155−181.

(12) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041.

(13) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

(14) (a) Schaveria, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373−1374.

(15) (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897. (b) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749−750. (c) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153−2164.

(16) Ravindranath, K.; Mashelkar, R. A. *Chem. Eng. Sci.* **1986**, *41*, 2197−2214.

(17) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* 1**999**, *64*, 7202.

(18) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

(19) Zantour, H.; Pousse, A.; Mathilde, B. *Bull. Soc. Chim. Fr.* **1972**, *12*, 4715.

(20) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 5411−5417.

(21) O'Donnell, P. M.; Brzezinska, K.; Powell, D.; Wagener, K. B. *Macromolecules* **2001**, *34*, 6845−6849.

(22) Srinivasan, R.; Almonacil, C.; Narayan, S.; Desai, P.; Abhiraman, A. S. *Macromolecules* **1998**, *31*, 6813.

(23) Fitzgerald, J. A.; Irwin, R. S.; Memeger, W. *Macromolecules* **1991**, *24*, 3291.

(24) (a) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649−2657. (b) Lehman, S. E., Jr.; Wagener, K. B. *Macromolecules* **2002**, *35*, 48−53.

MA0215924