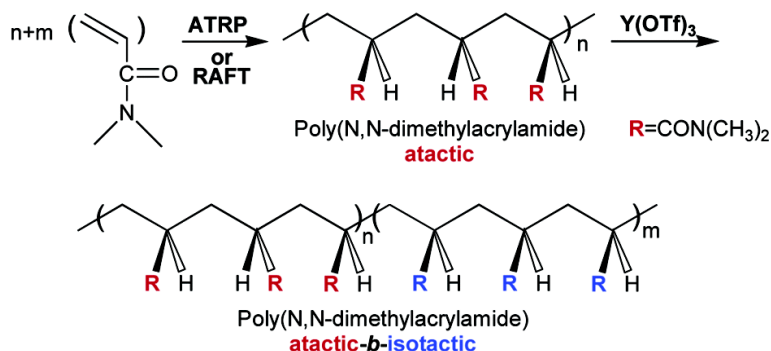


## Stereoblock Copolymers and Tacticity Control in Controlled/Living Radical Polymerization

Jean-Francois Lutz, Dorota Neugebauer, and Krzysztof Matyjaszewski

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### Stereoblock Copolymers and Tacticity Control in Controlled/Living Radical Polymerization

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**Abstract:** Three controlled/living radical polymerization processes, atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP), were investigated for the polymerization of *N,N*-dimethylacrylamide in the presence of Lewis acids known to enhance isotacticity, such as yttrium trifluoromethanesulfonate (Y(OTf)<sub>3</sub>) and ytterbium trifluoromethanesulfonate (Yb(OTf)<sub>3</sub>). Poly(*N,N*-dimethylacrylamide) with controlled molecular weight, low polydispersity ( $M_w/M_n < 1.2$ ), and a high proportion of meso dyads (~85%) was prepared by ATRP (with initiating system methyl 2-chloropropionate/CuCl/Me<sub>6</sub>TREN) and RAFT (with cumyl dithiobenzoate transfer agent) in the presence of Y(OTf)<sub>3</sub>. The combination of NMP (using *N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, SG1) and a Lewis acid complexation technique led to less precise control over chain architecture and microstructure (~65% meso dyads), as compared to RAFT/Y(OTf)<sub>3</sub> or ATRP/Y(OTf)<sub>3</sub>. The latter two systems were used for the first one-pot synthesis of stereoblock copolymers by radical polymerization. Well-defined stereoblock copolymers, atactic-*b*-isotactic poly(*N,N*-dimethylacrylamides), were obtained by adding Y(OTf)<sub>3</sub> at a given time to either RAFT or ATRP polymerizations, initially started without the presence of the Lewis acid.

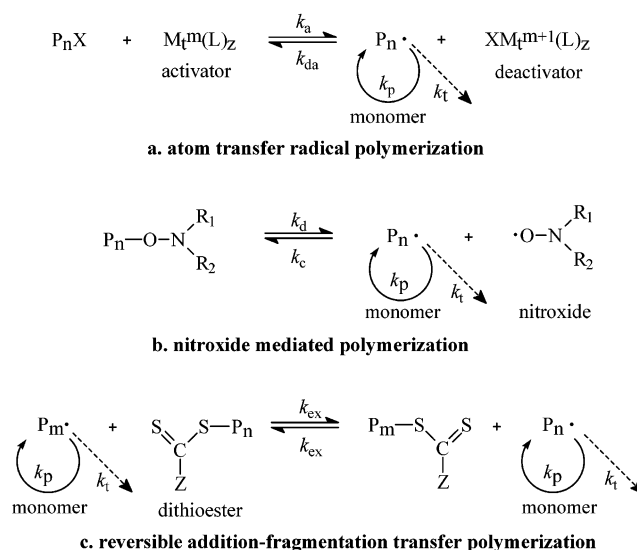
#### Introduction

Atom transfer radical polymerization (ATRP),<sup>1–4</sup> nitroxide-mediated polymerization (NMP),<sup>5</sup> and degenerative transfer with dithioesters via reversible addition-fragmentation transfer polymerization (RAFT)<sup>6,7</sup> are among the most studied and promising controlled/living radical polymerization systems (CRP).<sup>8–11</sup> These three CRP methods are based on the same concept, formation of a dynamic equilibrium between a low concentration of active propagating chains and a large amount of dormant chains, which are unable to propagate or self-terminate, although they employ different chemistries to reach this goal (Scheme 1).

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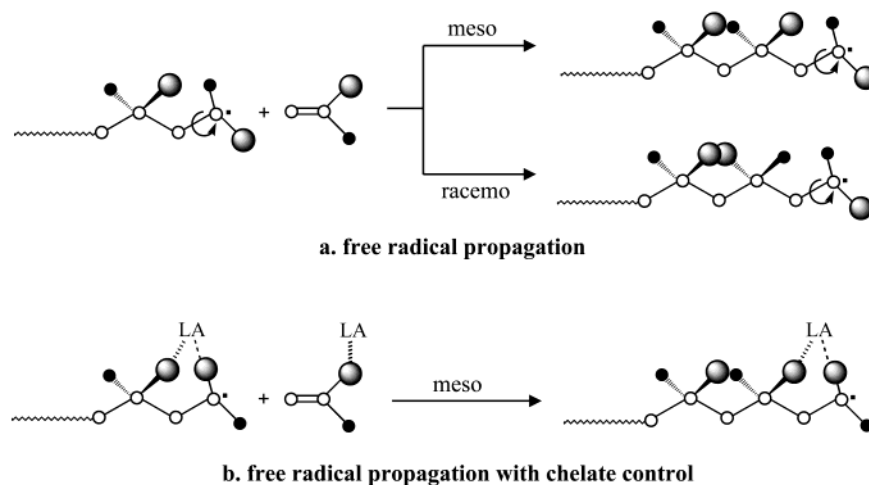
- (1) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
- (2) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866–868.
- (3) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
- (4) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.
- (5) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
- (6) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.
- (7) Chiefari, J.; Rizzardo, E. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, 2002; pp 621–690.
- (8) Matyjaszewski, K., Ed. *Controlled Radical Polymerization. ACS Symp. Ser.*; American Chemical Society: Washington, DC, 1998; Vol. 685.
- (9) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT. ACS Symp. Ser.*; American Chemical Society: Washington, DC, 2000; Vol. 768.
- (10) Matyjaszewski, K.; Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, 2002.
- (11) Matyjaszewski, K., Ed. *Advances in Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2003; Vol. 854.

**Scheme 1.** Mechanisms of Controlled/Living Radical Polymerizations



Thus, the probability of bimolecular termination reactions is decreased, and the radical polymerization behaves as a living system.<sup>12</sup> Therefore, CRP offers the opportunity of synthesizing various homopolymers and copolymers with molecular weight predetermined by the ratio of consumed monomer to the introduced initiator, low polydispersities, controlled composi-

- (12) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638–644.

**Scheme 2.** Free Radical Propagation in the Presence and Absence of Lewis Acid

tions, functionalities, and chain topologies.<sup>10,13–15</sup> However, until now, CRP has been much less successful at attaining control over chain microstructure in terms of sequence distribution and tacticity, because chemoselectivities (reactivity ratios), regioselectivities (proportions of head-to-head units), and stereoselectivities (tacticities) are similar to those in conventional radical polymerization, due to the radical nature of the propagation step.<sup>10</sup> In free radical polymerization, the  $sp^2$  hybridized carbon radical has a nearly planar configuration, which offers similar probability of meso and racemo addition and therefore leads to atactic polymers (Scheme 2a).<sup>16</sup>

This situation could not be improved through the use of either chiral initiators or chiral CRP control agents, because these species are not chemically involved in the propagation step.<sup>17,18</sup> On the other hand, a significant control over tacticity was reported using specific monomers, monomers with either extremely bulky substituents<sup>19</sup> or a chiral auxiliary.<sup>20</sup> However, the range of polymers that can be obtained in this way is quite limited. A simpler approach would be the use of a Lewis acid as a chelating agent. Both chemoselectivity and stereoselectivity in a radical polymerization can be altered in the presence of Lewis acids. For example, aluminum alkyl halides can form complexes with alkenes containing electron-withdrawing groups such as (meth)acrylates and dramatically increase the rate of the cross-propagation step in copolymerization with styrene.<sup>21</sup> This results in the formation of alternating copolymers poly(styrene-*alt*-(meth)acrylate).<sup>21</sup> In a similar way, bulky Lewis acids such as lanthanide triflates that interact simultaneously with several coordination sites (Scheme 2b) can increase the isotacticity of polyacrylamides,<sup>22</sup> poly(methacrylamides),<sup>23,24</sup> and

poly(methacrylates).<sup>25</sup> Coordination of the Lewis acid with the last two segments of a growing polymer chain forces them into the meso configuration during the monomer addition and leads to isotactic poly(meth)acrylamides, even in the presence of catalytic amounts of lanthanide triflates.<sup>26</sup>

Although Lewis acids in conventional free radical polymerizations can affect both sequence distribution and tacticity, they still provide ill-defined polymers with uncontrolled molecular weight and high polydispersity. The combination of controlled microstructures (both tacticity and sequences) with control of macromolecular architecture through CRP is a very tempting target because it would enrich the macromolecular engineering tools and enable formation of new stereoblock copolymers. We have previously reported the first well-defined alternating copolymers of styrene and (meth)acrylates prepared by using Lewis acids in CRP. The addition of  $AlClEt_2$  and  $AlCl_{1.5}Et_{1.5}$  to a RAFT copolymerization of styrene and methyl methacrylate resulted in the preparation of a poly(styrene-*alt*-methyl methacrylate) with precisely controlled molecular weight and molecular weight distribution ( $M_w/M_n < 1.3$ ).<sup>27</sup> We subsequently extended this system to butyl methacrylate, methyl acrylate, and also prepared the corresponding block copolymers.<sup>28</sup> In this article, we describe tacticity control in ATRP, RAFT, and NMP of *N,N*-dimethylacrylamide (DMAA) in the presence of yttrium trifluoromethanesulfonate ( $Y(OTf)_3$ ) and ytterbium trifluoromethanesulfonate ( $Yb(OTf)_3$ ). In addition, the first one-pot synthesis of stereoblock copolymers by radical polymerization is reported. It is interesting to note that after submission of the present Article, the stereocontrolled RAFT polymerization of *N*-isopropylacrylamide (NIPAM) was reported by Okamoto et al.<sup>29</sup>

## Experimental Section

**Chemicals.** *N,N*-Dimethylacrylamide (Aldrich, 99%) was distilled over  $CaH_2$  and stored over molecular sieves. Methanol (Pharmco, ACS grade) distilled over magnesium methoxide and stored over molecular

- (13) Davis, K.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 1–157.  
 (14) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337–377.  
 (15) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901–915.  
 (16) Matsumoto, A. In *Handbook of Radical Polymerization*; Matyjaszewski, K. D., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, 2002; pp 691–773.  
 (17) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323–3325.  
 (18) Ananchenko, G.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 8323–8329.  
 (19) Nakano, T.; Mori, M.; Okamoto, Y. *Macromolecules* **1993**, *26*, 867–868.  
 (20) Porter, N. A.; Allen, T. R.; Breyer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 7676.  
 (21) Hirai, H. *J. Polym. Sci., Macromol. Rev.* **1976**, *11*, 47–91.  
 (22) Isobe, Y.; Fujioka, D.; Habaue, S.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 7180–7181.  
 (23) Okamoto, Y.; Habaue, S.; Isobe, Y.; Nakano, T. *Macromol. Symp.* **2002**, *183*, 83–88.  
 (24) Habaue, S.; Isobe, Y.; Okamoto, Y. *Tetrahedron* **2002**, *58*, 8205–8209.

- (25) Isobe, Y.; Nakano, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1463–1471.  
 (26) Okamoto, Y.; Habaue, S.; Isobe, Y. *ACS Symp. Ser.* **2003**, *854*, 59.  
 (27) Kirci, B.; Lutz, J.-F.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 2448–2451.  
 (28) Lutz, J.-F.; Kirci, B.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 3136–3145.  
 (29) Ray, B.; Isobe, Y.; Morioka, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2003**, *36*, 543–545.

sieves. Toluene (Fisher Scientific, 99.9%) was distilled over sodium and stored over molecular sieves. Ethanol (Aaper, 200 proof) and *n*-butanol (Fisher Scientific, 99.8%) were distilled and stored over molecular sieves. Yttrium trifluoromethanesulfonate (98%), ytterbium trifluoromethanesulfonate (98%), and methyl 2-chloropropionate (MeClPr) (98%) were purchased from Aldrich and used as received. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol, filtered, and dried. Copper(I) chloride (Acros, 95%) was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed with ethanol, and dried. Tris(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>TREN)<sup>30</sup> and cumyl dithiobenzoate (CDB)<sup>31</sup> were synthesized according to published procedures. *N*-tert-Butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) (92%) was kindly provided by ATOFINA (CRRA, France).

**General Procedure for RAFT Polymerization (Example).** 2,2'-Azobisisobutyronitrile (1.35 mg; 0.008 mmol), cumyl dithiobenzoate (22 mg; 0.08 mmol), and yttrium trifluoromethanesulfonate (0.25 g; 0.46 mmol) were added to a dry Schlenk flask. The flask was thoroughly purged by flushing with nitrogen, and then degassed *N,N*-dimethylacrylamide (1 mL; 0.96 g; 9.7 mmol) and degassed methanol (1 mL) were added via degassed syringes. The mixture was stirred for 5 min at room temperature to obtain complete solubilization of all components. The mixture was then heated at 60 °C in an oil bath and stirred for several hours. Samples were withdrawn through a degassed syringe at timed intervals to follow the progress of the reaction.

**General Procedure for Nitroxide-Mediated Polymerization (Example).** 2,2'-Azobisisobutyronitrile (7.95 mg; 0.048 mmol), SG1 (28.5 mg; 0.097 mmol), and yttrium trifluoromethanesulfonate (0.26 g; 0.485 mmol) were added to a dry Schlenk flask. The flask was thoroughly purged by flushing with nitrogen, and then degassed *N,N*-dimethylacrylamide (1 mL; 0.96 g; 9.7 mmol) and degassed *n*-butanol (1 mL) were added via degassed syringes. The mixture was stirred 5 min at room temperature to obtain complete solubilization of all components. The mixture was then heated at 110 °C in an oil bath and stirred for several hours. Samples were withdrawn through a degassed syringe at timed intervals.

**General Procedure for Atom Transfer Radical Polymerization (Example).** *N,N*-Dimethylacrylamide (2 mL; 1.92 g; 19.41 mmol), methanol (2 mL), and yttrium trifluoromethanesulfonate (0.52 g; 0.97 mmol) were added to a Schlenk flask, stirred for 0.5 h, and then degassed by three freeze–pump–thaw cycles. After the mixture was stirred at room temperature, copper(I) chloride (0.019 g; 0.19 mmol) and Me<sub>6</sub>TREN (0.045 g; 0.19 mmol) were added and stirred for 10 min. Finally, the initiator methyl 2-chloropropionate (0.024 g; 0.19 mmol) was added, and the flask was heated to 30 °C. The polymerization was stopped by opening the flask and exposing the catalyst to air. Prior to size exclusion chromatography analysis, the reaction mixture was diluted in DMF and passed through a neutral alumina column to remove the copper complex.

**General Procedure for the Synthesis of Poly(*N,N*-dimethylacrylamide) Stereoblock Copolymer: Atactic-*b*-isotactic (Example).** 2,2'-Azobisisobutyronitrile (1.35 mg; 0.008 mmol) and cumyl dithiobenzoate (22 mg; 0.08 mmol) were added to a dry Schlenk flask. The flask was thoroughly purged by flushing with nitrogen, and then degassed *N,N*-dimethylacrylamide (1 mL; 0.96 g; 9.7 mmol) and degassed methanol (1 mL) were added via a degassed syringe. The mixture was stirred 5 min at room temperature to obtain complete solubilization of all components. The mixture was then heated at 60 °C in an oil bath. After 22 h, a solution of yttrium trifluoromethanesulfonate (0.25 g; 0.46 mmol) in methanol (0.5 mL) was added in the flask via a degassed syringe. The reaction was then allowed to stir at 60 °C for several additional hours and was stopped by cooling to ambient temperature.

**Measurements and Analysis.** Monomer conversion (conv) was calculated from the 300 MHz <sup>1</sup>H NMR spectra (Bruker WM300

spectrometer) of the raw experimental samples in DMSO-*d*<sub>6</sub> by comparing the integration of the 3 ethylenic protons of remaining *N,N*-dimethylacrylamide at 6.8, 6.1, and 5.6 ppm to the integration of the 2 methylene protons of poly(*N,N*-dimethylacrylamide) at 1.7–0.9 ppm. Molecular weight and polydispersity were determined by size exclusion chromatography (SEC) equipped with a Waters 515 pump and Waters 410 differential refractometer. SEC was performed using PSS columns (Styrogel 10<sup>5</sup>, 10<sup>3</sup>, 10<sup>2</sup> Å) in DMF as an eluent at the flow rate of 1 mL/min. Linear poly(methyl methacrylate) standards were used for calibration. Theoretical molecular weights were calculated for RAFT and ATRP, respectively, with eqs 1 and 2. For both conventional radical polymerization and NMP, eq 3 was used. *M*<sub>DMAA</sub> is the molar mass of DMAA.

$$M_{n\text{ th}} = M_{\text{DMAA}}[\text{DMAA}]_0\text{conv}/(2[\text{AIBN}]_0 + [\text{CDB}]_0) \quad (1)$$

$$M_{n\text{ th}} = M_{\text{DMAA}}[\text{DMAA}]_0\text{conv}/([\text{MeClPr}]_0) \quad (2)$$

$$M_{n\text{ th}} = M_{\text{DMAA}}[\text{DMAA}]_0\text{conv}/(2[\text{AIBN}]_0) \quad (3)$$

Poly(*N,N*-dimethylacrylamide) samples were purified by dialysis (Spectra/Por molecular porous membrane) in water and dried by rotary evaporation under vacuum. The microstructure of the purified polymers was analyzed by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> using either a 300 MHz (Bruker WM300) or a 600 MHz (Bruker Avance DRX 600) spectrometer. The spectroscopic measurements were performed on a UV/vis/NIR spectrometer (Lambda 900, Perkin-Elmer), using a quartz UV cell joined to a Schlenk flask.

## Results and Discussion

*N,N*-Dimethylacrylamide, DMAA, was successfully polymerized in a controlled/living manner by all three CRP methods: RAFT,<sup>32,33</sup> NMP,<sup>34,35</sup> and ATRP.<sup>36–40</sup> The RAFT transfer agent cumyl dithiobenzoate (CDB),<sup>32</sup> the stable nitroxyl radical *N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1),<sup>35</sup> and the ATRP initiating system methyl 2-chloropropionate/copper(I) chloride/Me<sub>6</sub>TREN<sup>37</sup> have been reported to be efficient systems for controlling the homopolymerization of DMAA. Poly(*N,N*-dimethylacrylamide) (PDMAA) prepared by ATRP or NMP retains chain-end functionality and has been successfully used for the preparation of well-defined block copolymers.<sup>35,38</sup> In the present study, the aforementioned RAFT, NMP, and ATRP systems for the polymerization of DMAA were studied in the presence of Lewis acid added as a stereocontrol chelating agent. We first applied the reaction conditions reported earlier for the optimized conventional radical stereoregular polymerization of DMAA.<sup>22,24</sup> Y(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub> were chosen as the Lewis acids, and methanol was chosen as the solvent. In the case of NMP, because this technique requires a higher reaction temperature than RAFT or ATRP, an alcohol with a higher boiling point (*n*-butanol, bp = 116–118 °C) was chosen instead of methanol (bp = 64 °C).

(32) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *ACS Symp. Ser.* **2000**, *768*, 278–296.

(33) Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570–4572.

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

(35) Diaz, T.; Fischer, A.; Jonquieres, A.; Brembilla, A.; Lochon, P. *Macromolecules* **2003**, *36*, 2235–2241.

(36) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826–4831.

(37) Teodorescu, M.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2000**, *21*, 190–194.

(38) Neugebauer, D.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 2598–2603.

(39) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 8005–8009.

(40) Kamigaito, M.; Onishi, I.; Kimura, S.; Kotani, Y.; Sawamoto, M. *Chem. Commun.* **2002**, 2694–2695.

(30) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958–5959.

(31) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. Wo 9801478 Chem. Abstr.* **1998**, *128*, 115390.

**Table 1.** Experimental Conditions and Properties of Poly(*N,N*-dimethylacrylamide) Prepared by RAFT<sup>a</sup> and RP<sup>b</sup>

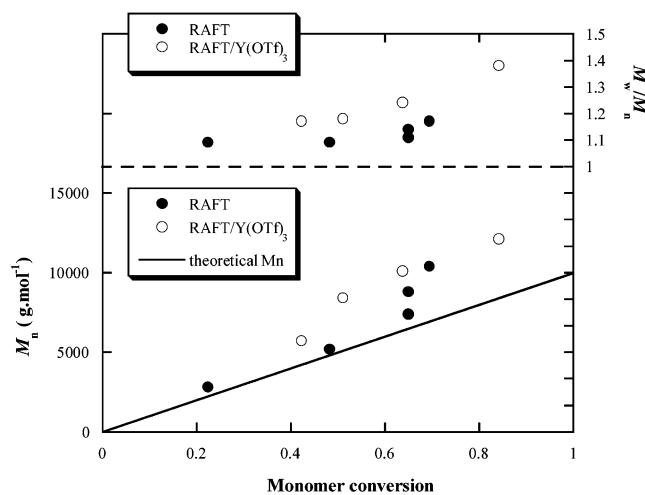
		[Y(OTf) <sub>3</sub> ]/ [DMAA] <sub>0</sub>	[Yb(OTf) <sub>3</sub> ]/ [DMAA] <sub>0</sub>	<i>t</i> (h)	conv	<i>M</i> <sub>n</sub> (g mol <sup>-1</sup> )	<i>M</i> <sub>n</sub> (g mol <sup>-1</sup> )	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	<i>m</i> <sup>c</sup>	<i>mm</i> <sup>d</sup>
1	RP	0.1	0	1	0.97	102 300	9700	3.13	0.83 ± 0.03	0.69 ± 0.03
2	RAFT	0	0	120	0.69	10 400	6900	1.17	0.53 ± 0.03	0.24 ± 0.03
3	RAFT	0.05	0	14	0.64	10 100	6400	1.24	0.83 ± 0.03	0.64 ± 0.03
4	RAFT	0.1	0	22	0.93	18 300	9300	1.41	0.85 ± 0.03	
5	RAFT	0	0.1	22	0.78	26 700	7800	2.10	0.85 ± 0.03	

<sup>a</sup> RAFT in MeOH at 60 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [CDB]<sub>0</sub> = 4 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 4 × 10<sup>-3</sup> mol L<sup>-1</sup>. <sup>b</sup> RP in MeOH at 60 °C: [DMAA]<sub>0</sub> = 0.97 mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 4.85 × 10<sup>-3</sup> mol L<sup>-1</sup>. <sup>c</sup> Measured by 300 or 600 MHz <sup>1</sup>H NMR. <sup>d</sup> Measured by 600 MHz <sup>1</sup>H NMR.

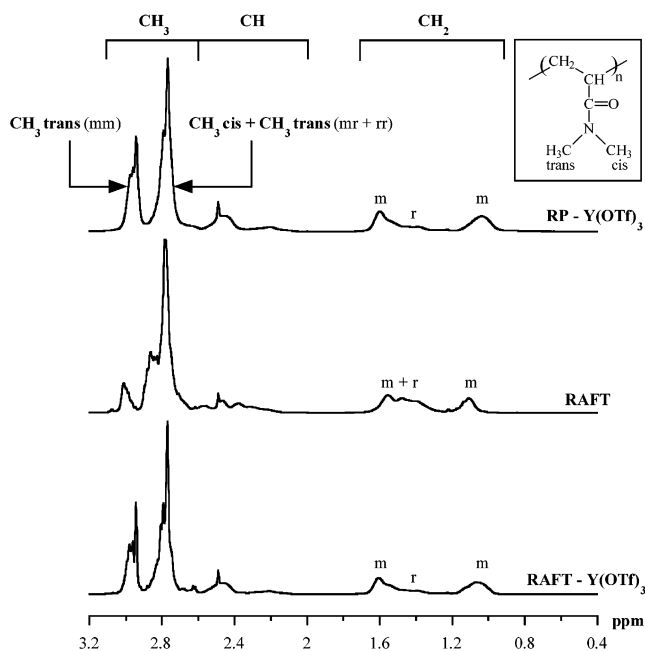
### RAFT Polymerization in the Presence of Lewis Acids.

Table 1 presents reaction conditions and compares polymer properties obtained for DMAA polymerization under conventional radical polymerization conditions (RP), with added Lewis acid, and under RAFT conditions with and without added Lewis acid. Okamoto et al.<sup>22</sup> reported that a ratio of Lewis acid/monomer equal to 0.1 is sufficient to achieve successful stereocontrol of the polymerization. However, in the presence of such an amount of either Yb(OTf)<sub>3</sub> or Y(OTf)<sub>3</sub>, a RAFT polymerization of DMAA exhibited experimental molecular weights higher than was targeted and a relatively broad molecular weight distribution (Table 1, entries 4 and 5). This could be plausibly attributed to some side reactions induced by Lewis acids. It is also possible that Lewis acids increase the rate of propagation by monomer/radical complexation<sup>41–43</sup> and also reduce the rate of exchange by coordination to the dithioester moiety. Similar observations were reported earlier,<sup>22,24,41–43</sup> and these interactions could result in higher polydispersities of the resulting polymers.<sup>44,45</sup> Because the molecular weight distribution of the polymer synthesized in the presence of 0.1 equiv of Y(OTf)<sub>3</sub> (Table 1, entry 4) was found to be narrower than that for the polymer prepared using 0.1 equiv of Yb(OTf)<sub>3</sub> (Table 1, entry 5), Y(OTf)<sub>3</sub> was selected for further investigation. The RAFT polymerization was therefore investigated in the presence of a lower amount of Y(OTf)<sub>3</sub> (Lewis acid/monomer = 0.05) (Table 1, entry 3).

Figure 1 compares the evolution of molecular weight and polydispersity with conversion for RAFT polymerization with and without Lewis acid. A linear increase of molecular weight with conversion indicates a constant number of propagating chains throughout each polymerization. Because of the difference in hydrodynamic volume between PDMAA and the linear PMMA standards used for GPC calibration, experimental molecular weights are slightly higher than calculated, as was observed earlier.<sup>36–39</sup> For the reasons discussed above, the polydispersity index of polymers prepared in the presence of Y(OTf)<sub>3</sub> was slightly higher than that in its absence. Despite these differences, RAFT remained well controlled in the presence of 0.05 equiv of Y(OTf)<sub>3</sub>. On the other hand, there was no control of molecular weights in RP with Y(OTf)<sub>3</sub> in the absence of any RAFT reagent, leading to polymers with high *M*<sub>w</sub>/*M*<sub>n</sub> and uncontrolled molecular weight (Table 1, entry 1).



**Figure 1.** Number-average molecular weight *M*<sub>n</sub> and polydispersity index *M*<sub>w</sub>/*M*<sub>n</sub> as a function of monomer conversion for the RAFT polymerization of DMAA in MeOH solution at 60 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [CDB]<sub>0</sub> = 4 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 4 × 10<sup>-3</sup> mol L<sup>-1</sup>; [Y(OTf)<sub>3</sub>]<sub>0</sub> = 0 mol L<sup>-1</sup> (●), 2.42 × 10<sup>-1</sup> mol L<sup>-1</sup> (○).



**Figure 2.** 600 MHz <sup>1</sup>H NMR of poly(*N,N*-dimethylacrylamide) in DMSO-*d*<sub>6</sub> at 28 °C prepared by RP/Y(OTf)<sub>3</sub>, RAFT, and RAFT/Y(OTf)<sub>3</sub>.

Figure 2 compares 600 MHz <sup>1</sup>H NMR spectra obtained from PDMAA samples prepared by RP/Y(OTf)<sub>3</sub>, RAFT, and RAFT/Y(OTf)<sub>3</sub>. For all polymers, the spectrum can be analyzed in three main regions: 3.1–2.6 ppm (6H) representative of the methyl protons of the amide function, 2.6–2.0 ppm (1H) representative of the backbone methine protons, and 1.7–0.9

- (41) Bamford, C. H.; Brumby, S.; Wayne, R. P. *Nature* **1966**, *209*, 292–294.  
 (42) Zubov, V. P.; Lachinov, M. B.; Golubev, V. B.; Kulikova, V. F.; Kabanov, V. A.; Polak, L. S.; Kargin, V. A. *J. Polym. Sci., Polym. Symp.* **1968**, *No. 23*, 147–155.  
 (43) Kabanov, V. A. *J. Polym. Sci., Polym. Symp.* **1980**, *67*, 17–41.  
 (44) Mueller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326–4333.  
 (45) Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402–408.

**Table 2.** Influence of the Solvent on the Properties of Poly(*N,N*-dimethylacrylamide) Prepared by RAFT<sup>a</sup> and RP<sup>b</sup>

		solvent/ DMAA (v/v)		<i>t</i> (h)	conv	<i>M<sub>n</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>n,th</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>w</sub>/M<sub>n</sub></i>	<i>m<sup>c</sup></i>
1	RAFT	MeOH	1:1	16	0.70	10 100	7000	1.10	0.86 ± 0.03
2	RAFT	EtOH	1:1	16	0.60	7200	6000	1.10	0.84 ± 0.03
3	RAFT	<i>n</i> -BuOH	1:1	16	0.80	10 100	8000	1.13	0.81 ± 0.03
4	RAFT	MeOH/toluene 1:1	1:1	16	0.83	9800	8300	1.18	0.84 ± 0.03
5	RAFT	MeOH/toluene 1:4	1:1	16	0.78	10 100	7800	1.17	0.82 ± 0.03
6	RAFT	toluene	1:1	16	0.68	8900	6800	1.22	0.80 ± 0.03
7	RP	toluene	9:1	3	0.96	23 600	2300	3.01	0.55 ± 0.03

<sup>a</sup> RAFT at 60 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [Y(OTf)<sub>3</sub>]<sub>0</sub> = 2.42 × 10<sup>-1</sup> mol L<sup>-1</sup>; [CDB]<sub>0</sub> = 4 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 4 × 10<sup>-3</sup> mol L<sup>-1</sup>. <sup>b</sup> RP at 60 °C: [DMAA]<sub>0</sub> = 0.97 mol L<sup>-1</sup>; [Y(OTf)<sub>3</sub>]<sub>0</sub> = 9.7 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 1.94 × 10<sup>-2</sup> mol L<sup>-1</sup>. <sup>c</sup> Measured by 300 MHz <sup>1</sup>H NMR.

ppm (2H) representative of the backbone methylene protons.<sup>46</sup> An examination of the region of the methylene protons enables one to calculate the proportion of meso and racemic dyads and estimate the degree of isotacticity in the polymer.<sup>24,47–49</sup> In the signal from the meso dyads, the two methylene protons are not equivalent and lead to two broad peaks of equal intensity centered at 1.60 and 1.05 ppm. On the other hand, the methylene protons of racemo dyads are equivalent and resonate as a single broad peak at 1.40 ppm. This latter peak overlaps with the meso peak at 1.60 ppm. However, the meso peak at 1.05 ppm is cleanly separated; therefore, the fraction of meso dyads is equal to twice its integral divided by the integration of the whole region 1.7–0.9 ppm. In the absence of any added Lewis acid, RAFT polymerization yields a polymer with a similar proportion of meso and racemic dyads (Table 1, entry 2), that is, an atactic PDMAA (*m* = 53 ± 3%). On the other hand, in polymerization conducted in the presence of Y(OTf)<sub>3</sub>, both RP and RAFT yield polymers with nearly identical high isotacticity (*m* = 83 ± 3%) (Table 1, entries 1 and 3). Tacticity can be also assessed by the analysis of the NMR signal of the amido methyl protons. The methyl protons *cis* and *trans* to the carbonyl group are not equivalent. The signals of both methyl groups are sensitive to chain configuration, splitting into three peaks due to triad sequences. According to San Roman et al.,<sup>49</sup> the broad region 2.9–2.6 ppm contains three *cis* triads, *mm* + *mr* + *rr*, and two *trans* triads, *mr* + *rr*. The separate region 3.1–2.9 ppm is representative only of the *trans mm* triad. Therefore, the fraction of isotactic triads in the polymer is equal to twice the integration of the region 3.1–2.9 ppm divided by the integration of the whole region 3.1–2.6 ppm. A significant increase of isotactic *mm* triads was observed for the PDMAA polymers prepared in the presence of Y(OTf)<sub>3</sub> (Table 1, entries 1 and 3) as compared to the polymer prepared in the presence of the RAFT agent, without Lewis acid (Table 1, entry 2). For all polymers, the calculated fractions of meso dyads *m* and of isotactic triads *mm* obey Bernoullian statistics, that is, (*mm*) = *m*<sup>2</sup>. The NMR studies indicate that the use of a reduced amount of Lewis acid (0.05 equiv of Y(OTf)<sub>3</sub> as compared to monomer) still allows efficient stereocontrol of DMAA in a RAFT polymerization. It seems that the RAFT dithioester does not reduce the Lewis acids' control over the stereoselectivity of the propagation step. Also, the control of the RAFT process is retained in the presence of small amount of Lewis acid. Therefore, the combination of RAFT and Lewis acid complexation allows the synthesis of

**Table 3.** Experimental Conditions and Properties of Poly(*N,N*-dimethylacrylamide) Prepared by NMP<sup>a</sup>

		[Y(OTf) <sub>3</sub> ] <sub>0</sub> / [DMAA] <sub>0</sub>	<i>t</i> (h)	conv	<i>M<sub>n</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>n,th</sub></i> (g mol <sup>-1</sup> )	<i>M<sub>w</sub>/M<sub>n</sub></i>	<i>m<sup>b</sup></i>
1		0	28	0.94	14 000	9400	1.18	0.55 ± 0.03
2		0.05	28	0.96	16 400	9600	3.20	0.66 ± 0.03

<sup>a</sup> NMP in *n*-butanol at 110 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [SG1]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 2.42 × 10<sup>-2</sup> mol L<sup>-1</sup>. <sup>b</sup> Measured by 300 MHz <sup>1</sup>H NMR.

well-defined isotactic PDMAA with controlled molecular weight, narrow molecular weight distribution, and controlled tacticity (Table 1, entry 3).

It was reported earlier that stereocontrol in RP of DMAA requires not only a complexing Lewis acid but also the presence of relatively polar solvents. The highest level of stereocontrol was obtained in methanol (84% *m*), with progressively lower degrees of control, in ethanol (80% *m*), 2-propanol (70% *m*), THF (65% *m*), and toluene (55% *m*).<sup>26</sup> In the case of RAFT polymerization, this solvent effect was found to be less explicit. Table 2 compares the properties of PDMAA synthesized with the system RAFT/Y(OTf)<sub>3</sub> in various pure solvents (methanol, ethanol, *n*-butanol, toluene) and solvent mixtures (methanol/toluene). Surprisingly, good control over molecular weight, polydispersity (*M<sub>w</sub>/M<sub>n</sub>* < 1.2), and tacticity (*m* > 80%) was obtained in all solvents. Even in toluene, RAFT/Y(OTf)<sub>3</sub> allowed the synthesis of well-defined isotactic PDMAA (Table 2, entry 6), whereas RP/Y(OTf)<sub>3</sub> led to atactic polymers (Table 2, entry 7). This result is a consequence of the differences in dilution used for each polymerization technique. In the case of RP, high dilution was used (toluene/DMAA = 9/1) following original reports.<sup>22,24,26</sup> Under these conditions, Y(OTf)<sub>3</sub>, which is poorly soluble in toluene, precipitated out in the form of large insoluble agglomerates and was therefore less available for chelate control. In the case of RAFT, a smaller volume of solvent was used (toluene/DMAA = 1/1), and the optimized amount of Y(OTf)<sub>3</sub> (0.05 equiv as compared to monomer) was nearly completely soluble at 60 °C in this reaction mixture.

**Nitroxide-Mediated Polymerization in the Presence of Lewis Acids.** Figure 3 compares the evolution of molecular weight and polydispersity with conversion for the SG1-mediated polymerization of DMAA at 110 °C in the presence and in the absence of Lewis acid. Table 3 shows the final properties of the PDMAA prepared in these experiments. In the presence of Y(OTf)<sub>3</sub> (ratio Lewis acid/monomer = 0.05, as optimized earlier for RAFT), the radical polymerization of DMAA was not very well controlled by SG1. Although molecular weight increased with conversion (insignificant transfer), a strong broadening of molecular weight distribution was observed with increasing

(46) Huynh Ba, G.; McGrath, J. E. *Polym. Bull.* **1980**, *2*, 837–840.

(47) Yoshino, T.; Kikuchi, Y.; Komiyama, J. *J. Phys. Chem.* **1966**, *70*, 1059–1063.

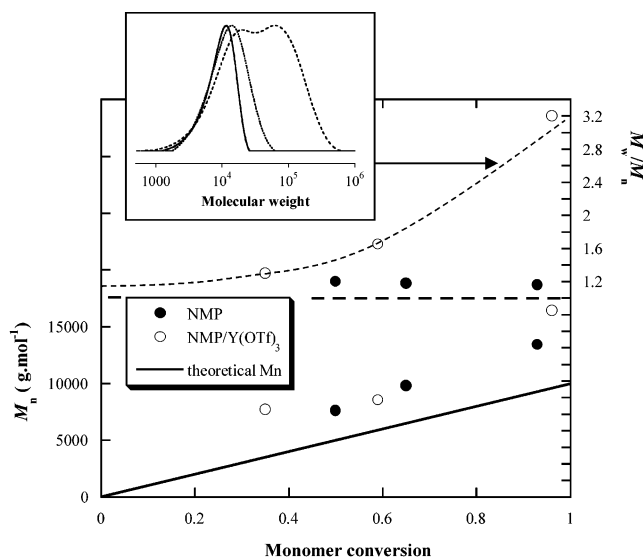
(48) Heatley, F.; Bovey, F. A. *Macromolecules* **1968**, *1*, 303–304.

(49) Bulai, A.; Jimeno, M. L.; Alencar de Queiroz, A.-A.; Gallardo, A.; San Roman, J. *Macromolecules* **1996**, *29*, 3240–3246.

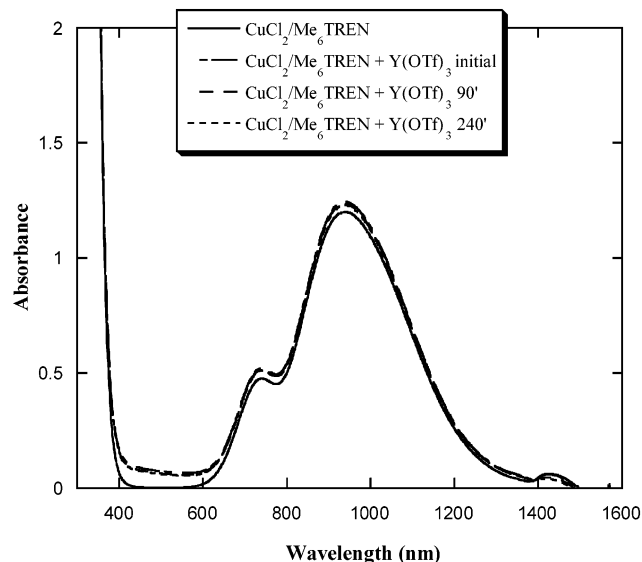
**Table 4.** Experimental Conditions and Properties of Poly(*N,N*-dimethylacrylamide) Prepared by ATRP<sup>a</sup>

	[Y(OTf) <sub>3</sub> ] <sub>0</sub> / [DMAA] <sub>0</sub>	[Yb(OTf) <sub>3</sub> ] <sub>0</sub> / [DMAA] <sub>0</sub>	solvent	<i>t</i> (h)	conv	<i>M</i> <sub>n</sub> (g mol <sup>-1</sup> )	<i>M</i> <sub>n</sub> (g mol <sup>-1</sup> )	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	<i>m</i> <sup>b</sup>
1	0	0	MeOH	2	0.56	11 900	5600	1.10	0.50 ± 0.03
2	0.05	0	MeOH	3	0.40	5600	4000	1.13	0.86 ± 0.03
3	0	0.05	MeOH	1	0.30	4700	3000	1.13	0.86 ± 0.03
4	0.05	0	MeOH/toluene 1:1	4	0.45	6000	4500	1.09	0.82 ± 0.03
5	0.05	0	<i>n</i> -BuOH	2	0.55	10 800	5500	1.10	0.80 ± 0.03
6	0.05	0	toluene	4	0.32	5200	3200	1.13	0.82 ± 0.03

<sup>a</sup> ATRP at 30 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [CuCl/Me<sub>6</sub>TREN]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>; [MeClPr]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>. <sup>b</sup> Measured by 300 MHz <sup>1</sup>H NMR.

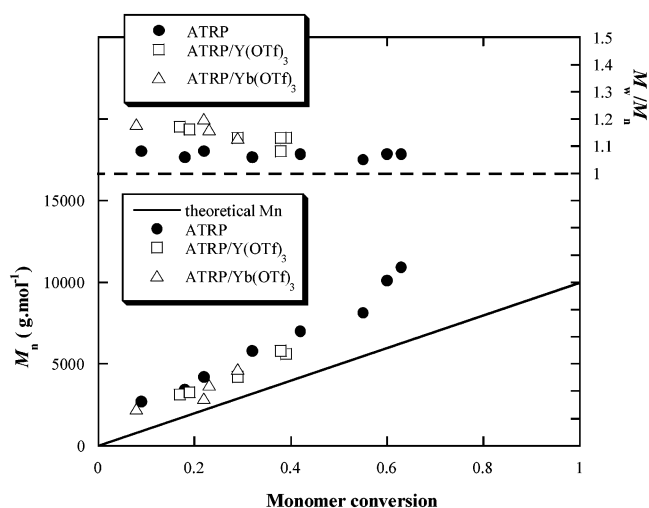


**Figure 3.** Number-average molecular weight *M*<sub>n</sub> and polydispersity index *M*<sub>w</sub>/*M*<sub>n</sub> as a function of monomer conversion for the NMP of DMAA in *n*-butanol solution at 110 °C: [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [SG1]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>; [AIBN]<sub>0</sub> = 2.42 × 10<sup>-2</sup> mol L<sup>-1</sup>; [Y(OTf)<sub>3</sub>]<sub>0</sub> = 0 mol L<sup>-1</sup> (●), 2.42 × 10<sup>-1</sup> mol L<sup>-1</sup> (○). Inset shows evolution of the SEC traces obtained for the polymerization in the presence of Y(OTf)<sub>3</sub>.



**Figure 4.** Absorption spectra UV/vis/NIR of Cu(II)Cl<sub>2</sub>/Me<sub>6</sub>TREN in methanol at 25 °C with or without Lewis acid. [CuCl/Me<sub>6</sub>TREN]<sub>0</sub> = 2.7 × 10<sup>-3</sup> mol L<sup>-1</sup>; [Y(OTf)<sub>3</sub>]<sub>0</sub> = 1.35 × 10<sup>-2</sup> mol L<sup>-1</sup>.

conversion. At high conversion, the majority of chains terminated, but a small fraction grew to relatively high molecular weight, leading to a bimodal molecular weight distribution (Figure 3, inset) and high final polydispersity index (Table 3,

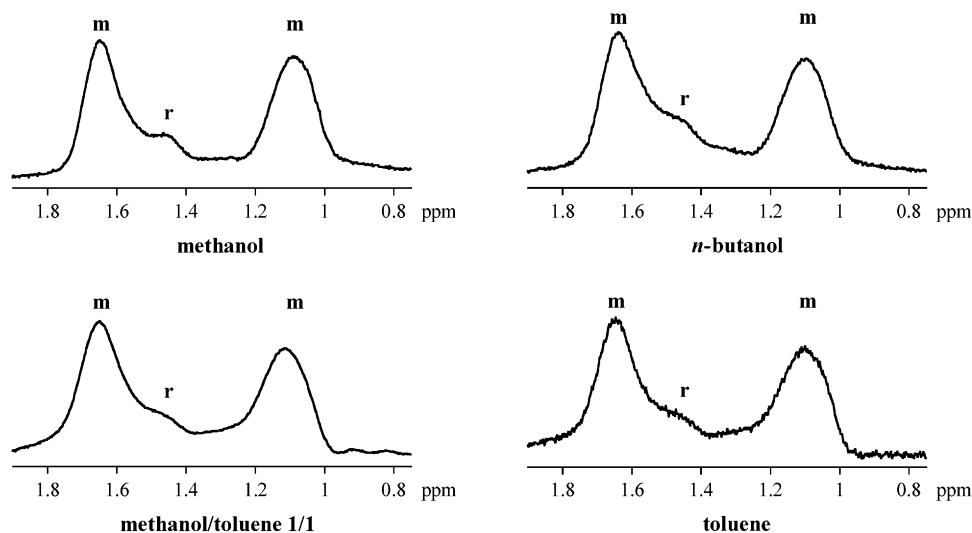


**Figure 5.** Number-average molecular weight *M*<sub>n</sub> and polydispersity index *M*<sub>w</sub>/*M*<sub>n</sub> as a function of monomer conversion for the ATRP of DMAA in MeOH solution at 30 °C in the presence of no Lewis acid (●) or [Y(OTf)<sub>3</sub>]<sub>0</sub> = 2.42 × 10<sup>-1</sup> mol L<sup>-1</sup> (□) or [Yb(OTf)<sub>3</sub>]<sub>0</sub> = 2.42 × 10<sup>-1</sup> mol L<sup>-1</sup> (△). [DMAA]<sub>0</sub> = 4.85 mol L<sup>-1</sup>; [CuCl/Me<sub>6</sub>TREN]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>; [MeClPr]<sub>0</sub> = 4.85 × 10<sup>-2</sup> mol L<sup>-1</sup>.

entry 2). This limited control of the radical polymerization is plausibly due to side reactions between the nitroxide/alcoxyamine and the Lewis acid. A strong interaction between electrophiles and the mediator in a NMP had been reported earlier.<sup>50</sup> Indeed, we failed to control alternating copolymerization of styrene and methyl methacrylate using Lewis acids in a NMP.<sup>28</sup> In addition, the degree of stereocontrol was significantly lower with the NMP/Y(OTf)<sub>3</sub> system than that with RAFT/Y(OTf)<sub>3</sub> or RP/Y(OTf)<sub>3</sub>. The final PDMAA obtained in the NMP reaction conducted in the presence of Y(OTf)<sub>3</sub> had only 66% of meso dyads. This behavior is not a consequence of the solvent used in this experiment, because isotactic PDMAA was prepared in *n*-BuOH by RAFT and ATRP. This result could be due to higher temperature and also due to the reaction of Lewis acid with the nitroxide/alcoxyamine. In conclusion, the NMP/Y(OTf)<sub>3</sub> system provided only limited control over molecular weight, polydispersity, and tacticity of PDMAA.

**ATRP in the Presence of Lewis Acids.** Atom transfer radical polymerization of DMAA was studied at 30 °C in methanol in the presence of Y(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub> (ratio Lewis acid/monomer = 0.05, was optimized earlier for RAFT). ATRP in the presence of Lewis acids is more challenging than RAFT because the ligand that forms a complex with the transition metal ATRP catalysts could be transferred to the Lewis acid. This side reaction prevented use of ATRP for efficient synthesis of

(50) Malmstrom, E.; Miller, R. D.; Hawker, C. J. *Tetrahedron* **1997**, *53*, 15225–15236.

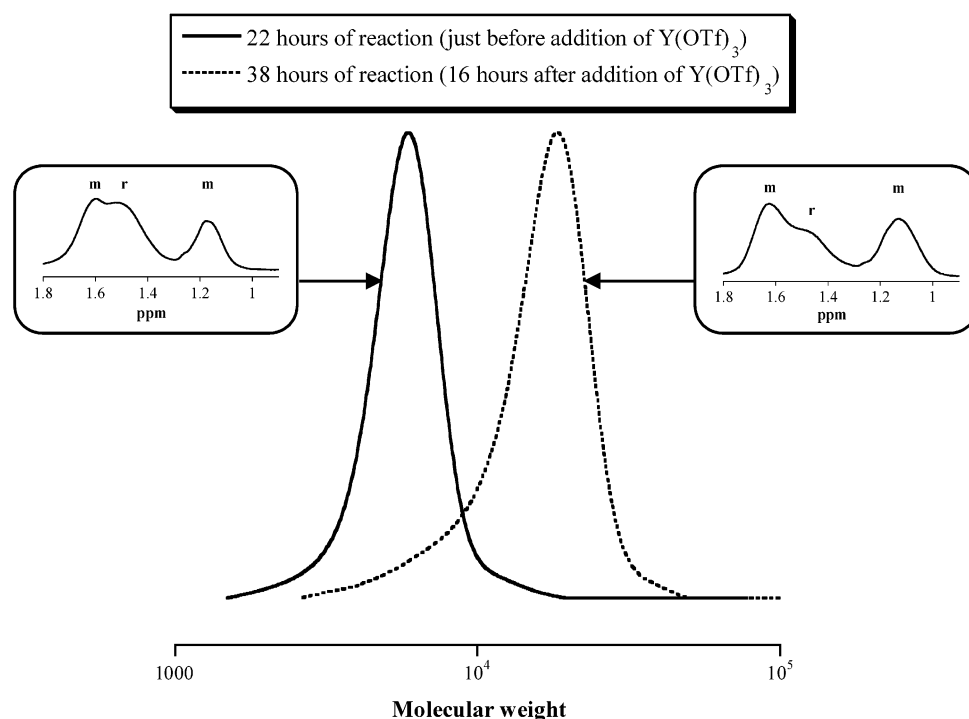


**Figure 6.** Expansion of the methylene region of the 300 MHz  $^1\text{H}$  NMR spectra of PDMAA prepared at 30 °C by ATRP with  $\text{Y}(\text{OTf})_3$  in various solvents (DMAA/solvent = 1:1 (v/v)).

**Table 5.** RAFT Synthesis of Stereoblocks Atactic-*b*-isotactic

		$t$ (h)	conv	$M_n$ ( $\text{g mol}^{-1}$ )	$M_{n,\text{th}}$ ( $\text{g mol}^{-1}$ )	$M_w/M_n$	DP	$m^e$	$m_2$
1	RAFT atactic block <sup>a</sup>	22	0.43	5300	4300	1.1	DP <sub>1</sub> = 43	$0.55 \pm 0.03$ ( $m_1$ )	
2	RAFT isotactic block <sup>b</sup>	38	0.88	13 800	8800	1.21	DP <sub>2</sub> = 45	$0.71 \pm 0.03$ ( $m$ )	$0.86 \pm 0.10$
3	ATRP atactic block <sup>c</sup>	1	0.49	12 400	12 250	1.09	DP <sub>1</sub> = 49	$0.55 \pm 0.03$ ( $m_1$ )	
4	ATRP isotactic block <sup>d</sup>	15	0.62	17 000	15 500	1.16	DP <sub>2</sub> = 13	$0.61 \pm 0.03$ ( $m$ )	$0.84 \pm 0.10$

<sup>a</sup> Initial conditions:  $[\text{DMAA}]/[\text{MeOH}]/[\text{CDB}]/[\text{AIBN}] = 100/250/0.83/0.083$ , 60 °C. <sup>b</sup> 22 h: addition of  $[\text{Y}(\text{OTf})_3]/[\text{MeOH}] = 5/125$ . <sup>c</sup> Initial conditions:  $[\text{DMAA}]/[\text{toluene}]/[\text{CuCl}/\text{Me}_6\text{TREN}]/[\text{MeClPr}] = 250/120/1/1$ , 30 °C. <sup>d</sup> 1 h: addition of  $[\text{Y}(\text{OTf})_3]/[\text{CuCl}/\text{Me}_6\text{TREN}]/[\text{MeOH}] = 5/2/625$ . <sup>e</sup> Measured by 300 MHz  $^1\text{H}$  NMR.



**Figure 7.** SEC traces for the PDMAA atactic segment and stereoblock copolymer. Insets show the methylene region of the 300 MHz  $^1\text{H}$  NMR spectrum of PDMAA recorded before and after addition of  $\text{Y}(\text{OTf})_3$ .

alternating copolymers.<sup>28</sup> However, absorption spectra of  $\text{Cu}(\text{II})\text{Cl}_2/\text{Me}_6\text{TREN}$  in the presence of excess of Lewis acids remained unchanged with time (Figure 4).

Figure 5 shows the evolution of molecular weight and polydispersity with conversion for ATRP experiments. In the

presence or in the absence of Lewis acids, the ATRP polymerizations behaved similarly (Figure 5), leading to polymers with controlled molecular weights and low polydispersities, which indicates efficient ATRP activation/deactivation cycles in all cases. PDMAA with a high degree of isotacticity was obtained



( $m = 86 \pm 3\%$ ) (Table 4), with both Lewis acids suggesting efficient stereocontrol by the chelating Lewis acid during the polymerization.

Conversion of DMAA in ATRP is often limited due to a slow loss of activity with the ATRP catalyst.<sup>36–38</sup> Higher conversion can be reached using alkyl chlorides rather than bromides as initiators in conjunction with strongly reducing and strongly complexing ligands (such as Me<sub>6</sub>TREN) and by addition of a new amount of catalyst at the later stage of the polymerization.<sup>37</sup> It was also shown that the nature of the solvent may influence the polymer yield.<sup>36,37</sup> Therefore, the ATRP of DMAA in the presence of Y(OTf)<sub>3</sub> was investigated in several solvents (methanol, *n*-butanol, toluene, methanol/toluene) at 30 °C. In all solvent mixtures, well-defined isotactic PDMAA polymers (Figure 6 and Table 4, entries 2, 4–6) were obtained. However, the polymer yield remained relatively low in all cases (<50%).

**Synthesis of Stereoblock Copolymers.** The combination of CRP and Lewis acid complexation techniques allows control over both chain architecture and microstructure. This extended level of control has been applied to the first one-pot synthesis of stereoblock copolymers by a radical polymerization technique. First, the CRP (RAFT or ATRP) was started in the absence of Lewis acid, leading to a well-defined atactic block, and, after the polymerization reached a certain degree of conversion (typically around 50%), a solution of Y(OTf)<sub>3</sub> in methanol was added to impose stereocontrol on the polymerization from this stage until the end of the reaction. The result of this simple procedure is a well-defined stereoblock (atactic-*b*-isotactic) copolymer. This concept was studied with both RAFT and ATRP, because these two systems were more efficient for preparing isotactic PDMAA in the presence of Lewis acid than was NMP. For RAFT, both the atactic block and the isotactic block were prepared in methanol. In the case of ATRP, the first atactic block was synthesized in toluene, because this solvent favored higher polymer yield in the absence of Lewis acid,<sup>38</sup> and then the second isotactic block was prepared in a methanol/toluene mixture (methanol is needed in this stage to enhance solubility of the Lewis acid). Table 5 shows the properties of PDMAA prepared under these conditions. For the RAFT polymerization, the Lewis acid solution was added after 22 h of reaction. At that stage, the experimental molecular weight was close to theoretical, polydispersity was low, and (as expected) NMR indicated an atactic microstructure. After addition of the Lewis acid, the reaction was kept at 60 °C for an additional 16 h. The final polymer had a controlled molecular weight and low polydispersity, suggesting an efficient control of the radical polymerization by the RAFT agent in the presence of Y(OTf)<sub>3</sub>.

SEC traces show a shift of the distribution toward a higher molecular weight region, demonstrating efficient block formation (Figure 7). The overall content of meso dyads  $m$  in the polymer increased to ~70%. The content of the meso dyads in

the second block  $m_2$  may be estimated from  $m$  and  $m_1$  through eq 4:

$$m_2 = (mDP - m_1DP_1)/DP_2 \quad (4)$$

where  $m$ ,  $m_1$ , and  $m_2$  are the fraction of meso dyads in the copolymer, first, and second block, and  $DP_1$ ,  $DP_2$ ,  $DP$  are the degrees of polymerization for the first block, second block, and the final DP, respectively. The former can be estimated from NMR, and the DP values can be estimated from SEC and/or monomer conversion. The precision of measurements of  $m_2$  was lower than that for  $m_1$  because it required subtraction of  $m_1$  from  $m$  and also some errors in estimates of  $DP_2$  ( $DP_2 = DP - DP_1$ ). Nevertheless, it seems that conducting a sequential block copolymerization does not sacrifice any stereocontrol during the synthesis of the second block (Table 5).

## Conclusion

Three CRP techniques, RAFT, NMP, and ATRP, were examined for the preparation of poly(*N,N*-dimethylacrylamide) in the presence of Lewis acids to prepare polymers with controlled tacticity. RAFT and ATRP of *N,N*-dimethylacrylamide conducted in the presence of Y(OTf)<sub>3</sub> allowed for the synthesis of well-defined polymers with controlled molecular weight, low polydispersities, and controlled tacticity (proportion of meso dyads was typically ~85%). In the case of RAFT, the polymerization reactions were conducted in methanol, whereas for ATRP, a mixture of methanol/toluene was used to increase the polymer yield. In NMP, control over both polydispersity and tacticity was lower, and a significant broadening of molecular weight distribution was observed with increasing conversion. The combination of either ATRP or RAFT with Lewis acid complexation techniques was used for the preparation of well-defined stereoblock atactic-*b*-isotactic copolymers. These copolymers were obtained via a simple one-pot process for both RAFT and ATRP by adding the chelating Lewis acid at the desired partial monomer conversion. Thus, techniques that permit modification of chemo-, regio-, and stereoselectivity in conventional radical processes were successfully applied to controlled radical polymerization techniques, opening a new avenue for the synthesis of well-defined polymers with tailored microstructures.

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**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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