In-Situ NMR Spectroscopy for Probing the Efficiency of RAFT/MADIX Agents

Gwenaelle Pound,[†] James B. McLeary,[†] Jean M. McKenzie,[‡] Ronald F. M. Lange,[§] and Bert Klumperman*[,†,⊥]

Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa; Central Analytical Facility, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa; BASF Research, GKT/U−B1, D-67056 Ludwigshafen, Germany; and Lab of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received August 11, 2006
Revised Manuscript Received September 26, 2006

This Communication shows the first experimental evidence of selective initialization of poorly stabilized monomers in reversible addition fragmentation chain transfer (RAFT)[1] mediated living radical polymerization. Xanthate chain transfer agents[2] (CTAs) of the general formula EtO−C(═S)−SR were used to mediate the polymerization of *N*-vinylpyrrolidone (NVP) and vinyl acetate (VAc). In-situ ^{1}H NMR spectroscopy was performed to follow the concentrations of xanthate and monomer and to identify the nonradical species involved in the RAFT mechanism. Various xanthates were screened (Figure 1), and a direct relationship between a xanthate−monomer system which gives fast and selective initialization and a high degree of control over the molar mass distribution of the polymer was found.

From the concentration profiles of the xanthate, monomer (NVP), and the single monomer adduct of the xanthate shown in Figure 2, we observe that during the first 275 min the reaction is highly selective. There is no significant further polymerization until the xanthate is completely converted into the single monomer adduct. At the end of the initialization process, a slight but sudden change in the rate of monomer consumption occurs.

A selection of four ^{1}H NMR spectra at different reaction times is shown in Figure 3. This figure qualitatively confirms the selectivity during the first monomer addition. Similar behavior was earlier observed for dithiobenzoate-mediated polymerization of styrene.[3] However, for a poorly stabilized monomer such as NVP or VAc, it is quite unexpected to see such high selectivity.

The nature of the leaving group radical (R•) was identified as the determining factor in the initialization process. Until it was directly observed via in-situ ^{1}H NMR spectroscopy monitored polymerizations, slow selective initialization due to a low rate of addition of the leaving group radical to the monomer (slow reinitiation) was often mistaken for inhibition.[4] The slow formation of the single monomer adduct and the abnormally high concentration of the cyanoisopropyl recombination product (R_1R_1) gave evidence of the slow rate of addition of cyanoisopropyl radicals to VAc[5] (VAc-X1) and its effect on the rate of CTA conversion.

The experiment illustrated in Figure 2 was repeated with R = 2-carboxyethyl (X2) and with R = *tert*-butyl (X3). The use of xanthate X3 led to the simultaneous formation of oligomeric adducts (n = 1, 2, and 3). This was attributed to the monomer derived radicals having better leaving group ability than the *tert*-butyl R group. More than 1 mol equiv of monomer units was consumed before complete conversion of the initial CTA, indicating that propagation had already occurred to a significant extent. In such a so-called "hybrid" system,[6] higher molar mass material is obtained from the beginning of the reaction, and new xanthate end-capped chains are formed late in the polymerization, leading to broad molar mass distribution of the resulting polymer. It needs to be stressed that the possible causes

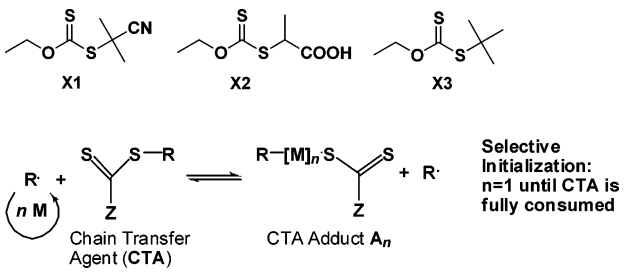

Figure 1. Xanthate chain transfer agents and mechanism of fragmentation of the initial chain-transfer agent.

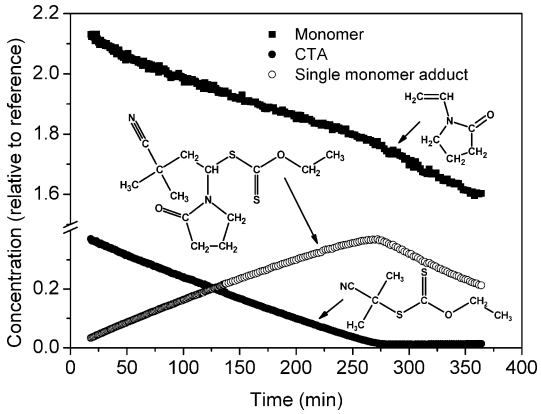

Figure 2. Concentration profiles of the species involved in initialization in the xanthate-mediated polymerization of NVP at 70 °C in C_6D_6, $[monomer]_0/[xanthate]_0 = 5$, probed by in-situ ^{1}H NMR spectroscopy (R = cyanoisopropyl).

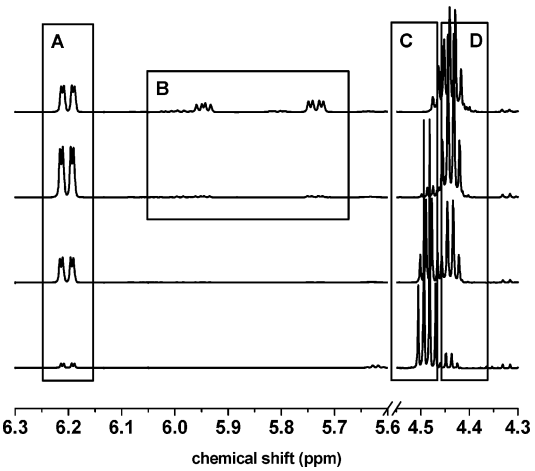

Figure 3. Four ^{1}H NMR spectra at different reaction times. From bottom to top: t (min) = 17, 137, 257, and 377. A, single monomer adduct; B, oligomer adducts; C, initial xanthate; D, single monomer adduct and oligomer adducts.

[†] Department of Chemistry and Polymer Science, University of Stellenbosch.
[‡] Central Analytical Facility, University of Stellenbosch.
[§] BASF Research.
[⊥] Eindhoven University of Technology.
* Corresponding author. E-mail: L.Klumperman@tue.nl.

10.1021/ma061843z CCC: $33.50
Published on Web 10/12/2006

Table 1. Relationship between Initialization and Molecular Weight Distribution

monomer	CTA	conv (%)	M_n[a] (g mol^{-1})	PDI[a]	selective initialization (time, min)[b]
VAc	X1	<1			yes (1320)
	X2	28	9 700	1.26	yes (25)
	X3	54	21 500	1.43	no
VP	X1	27	14 400	1.32	yes (270)
	X2	26	15 500	1.34	no[c]
	X3	48	31 900	1.74	no

[a] Experimental molar masses obtained by size exclusion chromatography (using RI detection) in THF with PS calibration for poly(vinyl acetate) (PVAc) and in HFIP with PMMA calibration for poly(*N*-vinylpyrrolidone) (PVP) prepared via RAFT polymerizations mediated by X1 or X2 or X3 in bulk at 60 °C for 3.5 h (PVAc) or 6 h (PVP); $[monomer]_0/[xanthate]_0 = 450$; $[xanthate]_0/[AIBN]_0 = 10$. [b] Initialization refers to selective formation of the single monomer adduct investigated by in-situ ^{1}H NMR spectroscopy polymerizations in C_6D_6 at 70 °C; $[monomer]_0/[xanthate]_0 = 5$. [c] See Supporting Information.

of hybrid behavior can be (1) choice of the Z group,[7] (2) ability of the R group to fragment from the intermediate radical (relative to the oligomer/polymer chain), and (3) ability of the R group radical to react with the monomer. The variation of R and Z groups of RAFT agents and their study via in-situ ^{1}H NMR spectroscopy will quickly pinpoint the origin of poor selectivity in initialization. The system VAc-X2 showed fast and selective initialization whereas NVP with X2 underwent a hybrid behavior regarding initialization as well as significant side reactions, which are still under investigation. It is likely that 2-carboxyethyl and NVP derived radicals have similar reactivities. Consequently, fragmentation occurs statistically on either side of CTA adduct radicals. The number of propagation steps prior to release of the R group will affect the polydispersity. This number remains low in the system VP-X2, and therefore PDI is probably not going to be much higher than in VP-X3 where initialization is completely selective.

Bulk polymerizations of NVP and VAc with low concentrations of CTA were performed in order to correlate the characteristics of initialization with the molar mass distribution of the polymers (Table 1). It was confirmed that selective initialization leads to more narrowly distributed molar masses, whereas the absence of initialization results in higher polydispersities, while still producing polymer chains end-capped with the xanthate mediating moiety.

In conclusion, in-situ ^{1}H NMR spectroscopy can quantitatively probe the mechanism of initialization involved in the transformation of a CTA into a dormant oligomeric chain. Conversely, kinetic studies combined with molar mass distribution characterization are not sufficient to pinpoint the origin of either inhibition or high polydispersities in RAFT/MADIX-mediated polymerization.[8] The results presented here show that NMR spectroscopy allows a defined distinction to be made between a "hybrid" RAFT mediated polymerization and an ideal RAFT-mediated polymerization for the first time. Moreover, it allows the investigation of the origin of the hybrid behavior. In this specific investigation the leaving and reinitiating abilities of the CTA R group were correlated to the occurrence of selective initialization, which in turn was correlated to well-defined molar mass distribution. This technique can thus be used to directly probe the efficiency of a CTA in controlling the polymerization of a given monomer.

Acknowledgment. The authors thank the Central Analytical Facility of the University of Stellenbosch for generous time on the NMR spectrometers, Mr. Wieb Kingma at the Eindhoven University of Technology for SEC analyses, and the BASF AG for research funds.

Supporting Information Available: ^{1}H NMR peak assignments, in-situ NMR spectroscopy polymerization conditions, and concentration profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Chiefari, J.; Chong, Y. K. B.; 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.
(2) Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, B. G. *Macromol. Symp.* **2000**, *150*, 23−32.
(3) McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383−2394.
(4) McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Chem. Commun.* **2004**, 1950−1951.
(5) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340−1371.
(6) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849−7857.
(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*, 2273−2282.
(8) Barner-Kowollik, C.; Buback, M.; Charleux, B.; Coote, M. L.; Drache, M.; Fukuda, T.; Goto, A.; Klumperman, B.; Lowe, A. B.; McLeary, J. B.; Moad, G.; Monteiro, M. J.; Sanderson, R. D.; Tonge, M. P.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5809−5831.

MA061843Z