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Controlled/Living Free-Radical Polymerization under Very High Pressure

Javid Rzayev and Jacques Penelle*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003-4530

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Recent progress in “living” free-radical polymerization (LRP) techniques, such as iniferter polymerization, atom-transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization, and reversible addition−fragmentation chain-transfer (RAFT) polymerization, opens new routes for the synthesis of polymers with predefined molecular weights, well-defined end groups, and narrow polydispersities.[1] These “living” polymerization techniques, based on free-radical intermediates, are not sensitive to moisture and facilitate the synthesis of more complex architectures such as block copolymers. Controlled/living polymerization techniques are based on a delicate balance between dormant and active species that effectively reduces the concentration of free radicals in the system and minimizes the extent of termination. So far, LRP techniques have been applied mostly to conventional monomers, such as styrene and (meth)acrylate derivatives, and the polymerizations have usually been conducted under classical free-radical polymerization conditions. Controlled polymerization of monomers that require the use of nontraditional conditions, such as very high pressure (>1 kbar), to polymerize has not been attempted yet, and optimum experimental conditions cannot be easily extrapolated from results at ambient pressure due to the sensitivity of LRP techniques to reaction conditions.

In this communication, we report the first example of a controlled free-radical polymerization under very high pressure.[2] The RAFT technique was specifically investigated due to its known lower sensitivity to reaction conditions. Methyl ethacrylate (MEA) was selected for this study as a model “nonpolymerizable” monomer since its oligo/polymerization kinetics at both ambient and high pressure have been previously investigated. Because of the steric hindrance of its α-ethyl substituent, MEA has a low ceiling temperature (82 °C at ambient pressure) and is reluctant to polymerize under traditional free-radical conditions.[3] However, recent studies in our group have shown that this and other α-substituted acrylates can be easily polymerized under high-pressure conditions.[4]

Polymerizations were carried out in a high-pressure apparatus at 5 kbar and 65 °C using 2,2′-azobis(isobutyronitrile) (AIBN) as the free-radical initiator and cyanoisopropyl dithiobenzoate (DTB)[1f] as the RAFT agent (Scheme 1).[5] First-order kinetics with respect to monomer concentration was observed, as shown in Figure 1a. A linear relationship was observed throughout the studied region (15−75% conversion), although the intercept of the regression line did not reach the origin. A value of 2.64×10^{-4} $L^{1/2}$ $mol^{-1/2}$ s^{-1} for the $R_p[M]^{-1}[I]^{-1/2}$ ratio can be calculated from the straight line, which is close to the number observed under traditional free-radical conditions at 5 kbar (2.80×10^{-4} $L^{1/2}$ $mol^{-1/2}$ s^{-1}),[4] and indicates that even at high pressures the RAFT reagent DTB behaves as an ideal chain-transfer agent with addition as the rate-determining step. An inhibition period similar to the one observed here has previously been observed in the case of a styrene polymerization with cumyl dithiobenzoate as the RAFT agent and was attributed to a slow initiation by the cumyl radical.[1f] This clearly cannot be the origin of the initial retardation observed in the present system: the cyanoisopropyl radical, generated from both the RAFT agent and the initiator, is known to act as an efficient initiating species. It seems more reasonable to attribute the slow initial kinetics to a slower fragmentation of the initial adduct (**1** in Scheme 2) compared to the fragmentation of adduct **2** that dominates the RAFT process at higher conversion. This difference in reactivity most probably arises from the steric crowding and the resulting difference in stability between **1** and **2**.

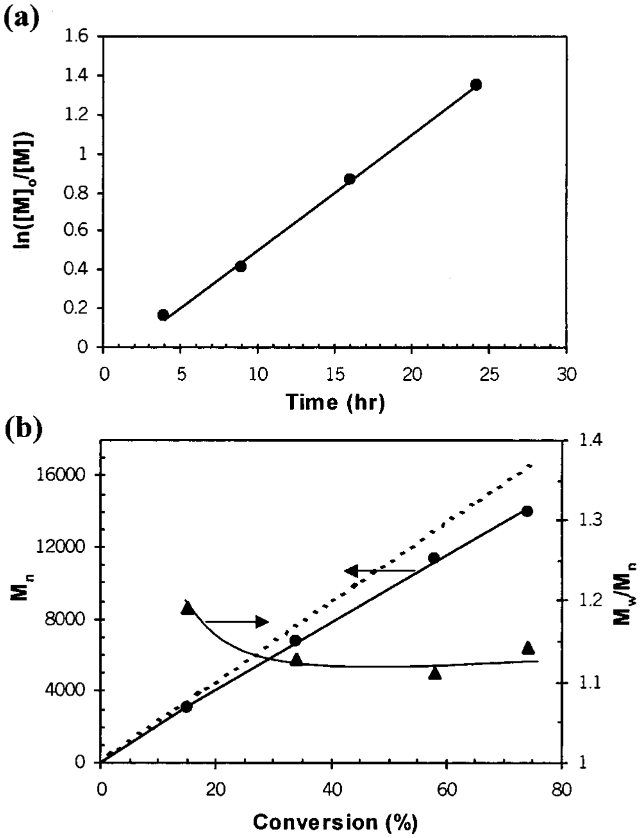

Figure 1. Results for the RAFT polymerization of MEA at 5 kbar ($T = 65$ °C, [MEA]:[DTB]:[AIBN] = 2000:10:1): (a) first-order kinetic plot, (b) dependence of molecular weights (●, $M_{n,exp}$; - - -, $M_{n,th}$) and polydispersities (▲) on conversion.

The controlled character of the polymerization is consistent with the observed linear increase in molecular weight with conversion (Figure 1b). Relative molecular weights determined by GPC calibrated with poly(methyl methacrylate) standards were close but consistently lower than the theoretical values calculated from the monomer-to-RAFT-agent molar ratio. Polydispersities remained low (<1.2) throughout the polymerization, decreasing up to 40% conversion and then leveling off (Figure 1b). This last experimental observation indicates the absence of major chain termination events.

One of the key advantages of controlled polymerizations is the ability to reactivate chain ends and synthesize complex polymer architectures. In a RAFT polym-

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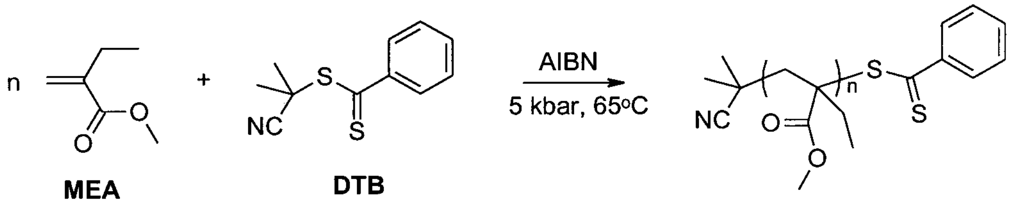
Scheme 1



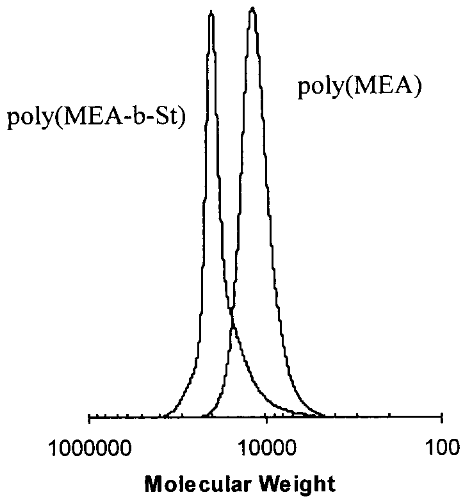
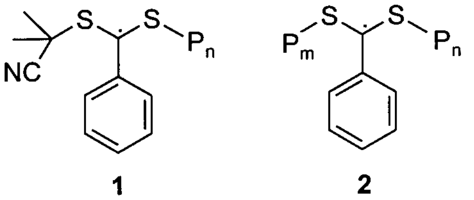


Figure 2. GPC traces obtained for poly(MEA) homopolymer precursor and poly(MEA-*b*-styrene) copolymer. Molecular weights were measured relative to polystyrene standards.

Scheme 2



erization, the active chain end is a dithioester group that can be reactivated by utilizing a free-radical initiator. The presence of dithioester end groups was confirmed by ^{1}H NMR, with the aromatic protons clearly identified in the 7.3−8.0 ppm region. Additional evidence arises from a GPC experiment conducted with a UV detector set at 320 nm, a region where only the end groups absorb. Experimentally, the GPC curves obtained from both RI and UV detectors are almost identical, confirming that the dithiobenzoate groups are indeed attached to the polymer chains.

A poly(MEA-*b*-styrene) diblock copolymer can be obtained from a poly(MEA) precursor (M_n = 14 000) by polymerizing styrene at ambient pressure and 60 °C using AIBN as the initiator.[6] The polymerization proceeded smoothly and resulted in a copolymer with M_n = 33 100 and M_w/M_n = 1.22 as measured by GPC calibrated with PS standards. Figure 2 includes the GPC traces for both the starting homopolymers and final copolymers. High reinitiation efficiency can be inferred from the comparison between the two traces. The final copolymer peak has small shoulders in both the high and low molecular weight regions. The former results from the recombination of polystyrene radicals and has been observed previously during the RAFT homopolymerizations of styrene.[1f] The shoulder in the lower molecular weight region can possibly arise from either some homopolystyrene, dead poly(MEA) chains, or both. It can be effectively removed by selective solvent extractions with cyclohexane and acetonitrile.

To investigate whether some unzipping of the poly(MEA) chain had occurred before the addition of the first styrene unit, a ^{1}H NMR of the crude reaction mixture was obtained before full conversion was reached. No peaks corresponding to the MEA monomer could be observed, indicating that the depropagation of poly(MEA) radical is slow enough compared to the addition on styrene, and clean reinitiation had indeed occurred. The structure of the block copolymer was also confirmed by ^{1}H NMR, with peaks similar to those observed in polystyrene and poly(MEA) spectra.

In conclusion, the RAFT polymerization of a sterically hindered “nonpolymerizable” monomer, MEA, has been achieved under high-pressure conditions, extending the pool of monomers available for living free-radical polymerization techniques. Well-controlled polymers with narrow polydispersities have been obtained. The efficient reinitiation with styrene resulted in a poly(MEA-*b*-styrene) diblock copolymer.

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Supporting Information Available: ^{1}H NMR spectra and GPC traces of poly(MEA) and the diblock copolymer. This material is available free of charge via the Internet at http://pubs.acs.org

References and Notes

(1) For recent reviews, see: (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745. (c) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688. (d) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581−3610. (e) Otsu, T.; Matsumoto, A. *Adv. Polym. Sci.* **1998**, *136*, 75−137. (f) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.

(2) Polymerizations under medium-high pressures (up to 0.33 kbar) in supercritical carbon dioxide have already been reported: (a) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802. (b) Odell, P. G.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1996**, *74*, 404. It should be noted, however, that the highest pressure reported in those studies (4900 psi = 0.33 kbar vs 5 kbar used in this study) is not high enough to significantly affect the ceiling temperature of vinyl monomers.

(3) Penelle, J.; Collot, J.; Rufflard, G. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2407.

(4) Rzayev, J.; Penelle, J. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

(5) Experimental procedure: Polymerization mixtures ([MEA] = 7.56 M in benzene, [DTB] = 0.51 mol %, [AIBN] = 0.05 mol %) were degassed by three freeze−pump−thaw cycles and transferred into Teflon ampules under nitrogen. Polymerizations were carried out in a high-pressure apparatus purchased from the High-Pressure Research Center of the Polish Academy of Sciences. The polymers were precipitated in hexane. Conversions were determined by ^{1}H NMR.

(6) Experimental conditions: poly(MEA) = 0.2 g, AIBN = 0.35 mg, St = 1.45 mL; T = 60 °C, time = 32 h, conversion = 33%.

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