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# High Molecular Weight Polymethacrylates by AGET ATRP under High Pressure

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Controlled/living radical polymerization is always accompanied by irreversible radical termination.[1−4] The fraction of terminated chains increases with polymerization rate (d ln[M]/d$t$), i.e., with concentration of propagating radicals. This fraction also increases with conversion (Δln[M]) and is higher for higher targeted molecular weight (∼1/$[RX]_0$). The fraction (or percent) of terminated chains also depends on the ratio $k_t/k_p^2$, according to the equation:[5]

$$\%_t = 100(\mathrm{dln[M]/d}t)\Delta\mathrm{ln[M]/[RX]_0}(k_t/k_p^{\,2})$$

Thus, in order to decrease proportion of terminated chains, one can reduce concentration of radicals (i.e., slow down polymerization), limit conversion, and target lower molecular weight. Also, under comparable conditions (rate, molecular weight, conversion), the fraction of terminated chains is smaller for monomers with higher propagation rate constants (e.g., acrylates, $k_p > 10^4$ M$^{-1}$ s$^{-1}$) than for those with lower propagation rate constants (styrenes or methacrylates, $k_p < 10^3$ M$^{-1}$ s$^{-1}$ at room temperature).[6] The rate constants of radical termination are usually diffusion-controlled, and they are strongly conversion and chain length dependent.[7] Also, for monomers with smaller substituents they are larger than for those with larger substituents.

It is challenging to identify conditions under which fast polymerization could occur without an increase of the fraction of terminated chains and without sacrificing molecular weight or conversion. Thus, the ultimate target is to increase the $k_p/k_t$ ratio. There are several possible pathways to reach this goal.[1] One can manipulate the medium to increase this ratio (more viscous systems will reduce $k_t$ values due to diffusion control). It is possible to increase reaction temperature, since the energy of activation of propagation is always larger than that of termination. Unfortunately, at higher temperatures, transfer reactions, proceeding with even higher activation energy, become more dominant. This will reduce polymerization control, as clearly observed in the radical polymerization of ethylene but also of acrylates or vinyl acetate.[8] Another possibility is to increase pressure. It is well-known that radical propagation has a negative volume of activation ($\Delta V_p^‡ \sim -20$ cm$^3$ mol$^{-1}$), whereas termination has a positive volume of activation ($\Delta V_t^‡ \sim +20$ cm$^3$ mol$^{-1}$).[6,9−11] Thus, by increasing pressure, it is possible to both enhance the propagation rate constant and reduce the termination rate constant.

High-pressure chemical synthesis has been applied, but rarely, to controlled/living radical polymerization.[12−15] The effect of pressure has been first reported for reversible addition−fragmentation (chain) transfer polymerization (RAFT), resulting in higher polymerization rates and in polymers with higher molecular weights and lower polydispersity.[16−19] Herein, we report the synthesis of high molecular weight polymethacrylates using high-pressure AGET (activators generated by electron transfer) ATRP (atom transfer radical polymerization) with low concentration of Cu catalyst.[20−31] The choice of AGET ATRP with low concentration of copper was dictated by plausible reduced solubility of a catalyst under high pressure and also by a simple manipulation of the reaction mixture, enabling use of air-stable $CuBr_2$ complexes with tris(2-pyridylmethyl)amine (TPMA) ligand in the presence of a reducing agent, ascorbic acid (AsAc). Ascorbic acid reduces Cu$^{II}$ to Cu$^{I}$ species and can also compensate for a small loss of Cu$^{I}$ through the termination process, resembling the ARGET (activators regenerated by electron transfer) ATRP process.[25,28,32]

Figure 1 presents the kinetic plot together with the evolution of molecular weight and polydispersity (PDI) with conversion for AGET ATRP of *n*-butyl methacrylate (BMA). Polymerization was carried out at 6 kbar pressure using the following reaction conditions: $[BMA]_0/[EtBrIB]_0/[CuBr_2]_0/[TPMA]_0/[AsAc]_0 = 10000/1/2/25/25$ in anisole (55 vol %) and DMF (7 vol %) at 22 °C, where EtBrIB is ethyl 2-bromoisobutyrate and DMF is dimethylformamide. The reaction rate was first-order with respect to time, and molecular weights of the formed polymer were close to theoretical values and had a narrow molecular weight distribution (PDI < 1.3). In Figure 2, the entire molecular weight distribution moved smoothly toward higher molecular weight, demonstrating good control over polymerization.

Several series of experiments were performed in order to determine the effect of pressure, solvent, target degree of polymerization ($DP_{target}$), and type of monomer on the polymerization of methacrylates via AGET ATRP. Results from these experiments are summarized in Table 1. Entries 1−4 illustrate how pressure affects polymerization of methyl methacrylate (MMA). Using otherwise identical conditions, it was observed that at 3 kbar pressure only a small increase of polymerization rate is observed in comparison with ambient pressure conditions. On the other hand, 10 kbar pressure resulted in initially very fast polymerization, accompanied by limited conversion (polymerization stopped after 20 min at ∼46% of monomer conversion) and higher polydispersity. High pressure can solidify the reaction mixture and trap growing radicals in a glassy matrix. This leads to an uncontrolled polymerization process due to increasing radical concentrations.[33] High pressure can also limit the fast deactivation rate constant and reduce the relative rate of the exchange between active and dormant species, as compared to propagation.

Entries 4−6 present results with various values of $DP_{target}$ at 6 kbar. Under these conditions, each polymerization of MMA provided good control over molecular weight. As expected, polymerization rates decreased with increasing $DP_{target}$. Entries 7−9 describe experiments with variable amounts of solvent at 6 kbar with $DP_{target}$ = 10 000. In general, the polymerizations

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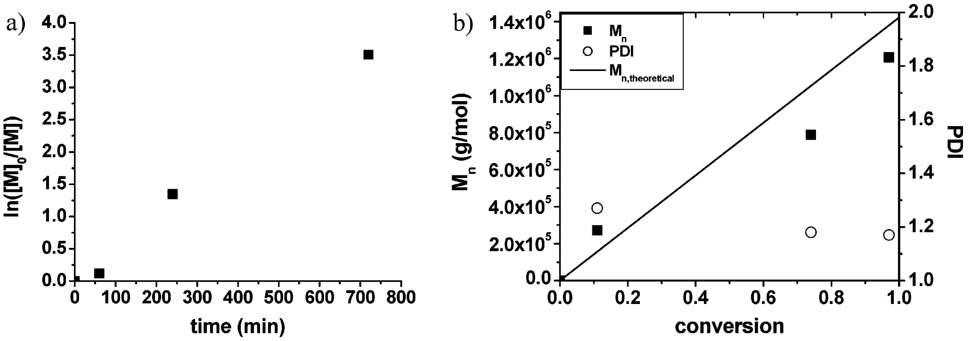

**Figure 1.** (a) Kinetic plot and (b) molecular weight and polydispersity as a function of conversion for AGET ATRP of *n*-butyl methacrylate under high pressure. Experimental conditions: BMA/EtBrIB/CuBr$_2$/TPMA/AsAc = 10000/1/2/25/25; [BMA]$_0$ = 4.9 M, $T$ = 22 °C, in anisole (55 vol %) with DMF (7 vol %), $P$ = 6 kbar.

**Table 1. Experimental Conditions and Properties of Polymers Prepared by AGET ATRP under High Pressure at Ambient Temperature**[a]

| entry | monomer | DP$_{target}$ | DMF (vol %) | press. (kbar) | time (min) | conv (%) | $M_{n,theor}$[b] | $M_{n,GPC}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | MMA | 10 000 | 1 | $10^{-3}$ | 2400 | 16 | 160 000 | 215 000 | 2.02 |
| 2 | MMA | 10 000 | 1 | 3 | 1800 | 18 | 180 000 | 192 000 | 1.48 |
| 3 | MMA | 10 000 | 1 | 10 | 20 | 46 | 460 000 | 593 000 | 1.96 |
| 4 | MMA | 10 000 | 1 | 6 | 900 | 90 | 900 000 | 1 007 000 | 1.16 |
| 5 | MMA | 33 000 | 1 | 6 | 900 | 57 | 1 881 000 | 1 934 000 | 1.25 |
| 6 | MMA | 100 000 | 1 | 6 | 900 | 15 | 1 500 000 | 1 900 000 | 1.32 |
| 7 | MMA | 10 000 | 2 | 6 | 60 | 24 | 240 000 | 170 000 | 1.39 |
| 8 | MMA | 10 000 | 5 | 6 | 60 | 66 | 660 000 | 605 000 | 1.12 |
| 9 | MMA | 10 000 | 10 | 6 | 60 | 85 | 850 000 | 834 000 | 1.11 |
| 10 | HEMA−TMS | 10 000 | 10 | 6 | 60 | 33 | 667 000 | 639 000 | 1.27 |
| 11 | HEMA−TMS | 10 000 | 5 | 6 | 240 | 77 | 1 560 000 | 1 372 000 | 1.72 |

[a] M/EtBrIB/CuBr$_2$/TPMA/AsAc = DP$_{target}$/1/2/25/25; [M]$_0$ = 4.9 M; $T$ = 22 °C, in anisole (50 vol %) and DMF. [b] $M_{n,\ theo}$ = ([M]$_0$/[EtBrIB]$_0$) × conversion.

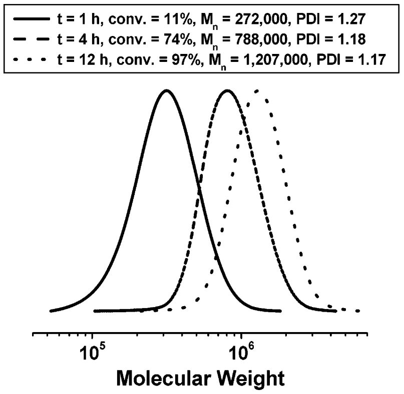

**Figure 2.** Evolution of molecular weight distribution during AGET ATRP of *n*-butyl methacrylate under high pressure. Experimental conditions: BMA/EtBrIB/CuBr$_2$/TPMA/AsAc = 10000/1/2/25/25; [BMA]$_0$ = 4.9 M, $T$ = 22 °C, in anisole (55 vol %) with DMF (7 vol %), $P$ = 6 kbar.

were faster when greater amounts of DMF were used. This is attributed to the enhanced solubility of the reducing agent, AsAc, in DMF. Cu$^{II}$ is reduced to Cu$^{I}$ activator faster when more reducing agent is available in the polymerization system, resulting in the increase of polymerization rate.

Entries 10 and 11 include results of the polymerization of 2-(trimethylsilyloxy)ethyl methacrylate (HEMA−TMS). It was observed that control over the polymerization of HEMA−TMS was good up to a certain limit. At 33% conversion (DP = 3300), a polymer with monomodal GPC trace and low polydispersity was obtained. However, at a higher conversion (77%, DP = 7700), a high molecular weight shoulder was detected increasing polydispersity to PDI = 1.72. This can be ascribed to branching, most likely due to the presence of a very small amount of a dimethacrylate impurity (<0.1%) or transesterification.

In conclusion, high pressure enables relatively fast synthesis of well-defined high molecular weight polymethacrylates even at room temperature.[34] Further studies on the effect of pressure on activation and deactivation rate constants as well as on the ATRP of other monomers are currently being investigated.

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**Supporting Information Available:** Experimental part including description of all chemicals used, polymerization procedures, and polymer sample analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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