Polymer Communication

High-pressure atom transfer radical polymerization of methyl methacrylate for well-defined ultrahigh molecular-weight polymers

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ABSTRACT

The feasibility of high-pressure atom transfer radical polymerization (ATRP) for synthesizing well-defined polymers of extraordinarily high molecular weights was demonstrated. ATRP of methyl methacrylate (MMA) under pressures up to 500 MPa was investigated at 60 °C. The addition of a small amount of a Cu(II)Cl$_2$/ligand complex along with the general benefits of high pressure of enhancing propagation and suppressing termination brought about an excellent control of polymerization even with an extremely low concentration of ATRP initiator. For example, there was produced PMMA with a number-average molecular weight M_n of 3.6×10^6 and a polydispersity index of 1.24, which had never been achieved by conventional ATRP.

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1. Introduction

Living (or controlled/living) radical polymerizations (LRPs) have attracted much attention as a powerful method to synthesize well-defined polymers with e.g., designed molecular weight, low polydispersity, and defined end group [1]. Mechanistically, LRP is distinguished from conventional free-radical polymerization (FRP) by the existence of a reversible activation process [1–3]. By thermal, photochemical, and/or chemical stimuli, the dormant chain P–X is activated to the polymer radical P˙, which undergoes propagation in the presence of monomer M until it is deactivated back to P–X, where P and X denote the polymer moiety and end-capping group, respectively. A sufficiently large number of activation–deactivation cycles is a requisite for low-polydispersity products. Like FRP, LRP also involves termination and chain transfer reactions producing dead chains. The number of dead chains increases with increasing polymerization time and hence with increasing number-average degree of polymerization, DP$_n$. To achieve low polydispersity, the total number of dead chains should be sufficiently smaller than that of living chains (dormant plus active chains). In other words, the target DP$_n$ in LRP should be sufficiently small compared to that in the FRP carried out under equivalent conditions (the same radical and monomer concentrations and the same temperature and pressure), which limits the DP$_n$ in LRP. If the target molecular weight is set equal to this upper limit, all chains will be dead at the end of polymerization with the controllability of LRP totally lost. Hence, unlike termination-free polymerizations such as living

anionic polymerization, it is difficult to access very high molecular weights by LRP (and FRP) under usual experimental conditions. We have firstly to seek for special experimental conditions that will give high molecular-weight polymers in FRP.

If we consider only propagation (rate constant k_p), termination (rate constant k_t) and chain transfer reactions as main elementary reactions in FRP, the kinetic chain length DP$_{kin}$, which is equal to DP$_n$ in the complete absence of recombination in termination, is given by

$$DP_{kin} = \frac{k_p[M]}{k_t[P^\bullet] + S_{tr}} \quad (1)$$

In Eq. (1), S_{tr} is the proportionality coefficient defined by

$$R_{tr} = S_{tr}[P^\bullet] \quad (2)$$

where R_{tr} is the sum of the rates of chain transfer reactions (hence S_{tr} depends on the concentrations of all chain-transferable species). Clearly, a method to increase DP$_{kin}$ is to carry out experiments at lower [P˙], as is well known and practically used. Other possibilities will be to enhance propagation (larger k_p) and/or suppress termination (smaller k_t) by some means or other. In this regard, high pressures are known to bring about a remarkable increase in polymerization rate R_p in FRP [5], as a result of increased k_p and decreased k_t [4]. For example, the activation volumes $\Delta V^\#$ of propagation and termination of poly(methyl methacrylate) (PMMA) radical were reported to be $-16.7\ \text{cm}^3\ \text{mol}^{-1}$ [6] and $15\ \text{cm}^3\ \text{mol}^{-1}$ [4], respectively, calculating the enhancement in k_p by a factor of about 20 and suppression in k_t by a factor of about 15 at 500 MPa, relative to the values at the ambient pressure of about 0.1 MPa. Under the premise that the coefficient S_{tr} in Eq. (2) does

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not heavily depend on pressure, which is likely because chain transfer reactions would not accompany a large change in volume, high pressures are expected to give extraordinarily high molecular-weight polymers in FRP, hence in LRP. Recently, reversible addition–fragmentation chain transfer (RAFT) polymerizations under high pressures were reported [7–10]. Rzayev and Penelle demonstrated the mentioned benefits of high pressure for improved R_p, DP_n and polydispersity, by successfully synthesizing PMMA with $M_n = 1.2 \times 10^6$ and polydispersity index (PDI) $M_w/M_n = 1.03$ (as determined by GPC-MALLS) at 500 MPa by dithiobenzoate-mediated RAFT polymerization [10], where M_n and M_w are number- and weight-average molecular weights, respectively.

In an attempt to explore the feasibility or possibility of LRP in synthesizing well-defined ultrahigh molecular-weight polymers, we in this communication give a report on the copper-catalyzed atom transfer radical polymerization [11] of methyl methacrylate (MMA) under pressures up to 500 MPa [12,13]. The reversible activation–deactivation in this system is mediated by the Cu(I)X/L and Cu(II)X$_2$/L complexes as shown in Scheme 1, where X and L represent a halogen and a ligand, respectively.

2. Experimental

2.1. Materials

MMA was obtained from Nacalai Tesque Inc., Japan and purified by passing through a column filled with activated basic alumina to remove inhibitor. Ethyl 2-bromoisobutyrate (EBIB) was used as received from Tokyo Chemical Industry Co., Ltd., Japan. 4,4′-Dinonyl-2,2′-bipyridine (dNbipy) was purchased from Aldrich and used without further purification. Copper(I) chloride (Cu(I)Cl) and copper(II) dichloride (Cu(II)Cl$_2$) were purchased from Wako Pure Chemicals, Japan.

2.2. Polymerization

All sample preparations were carried out in a glove box purged with argon, and all chemicals were deoxygenated by argon before the use in the glove box. The reaction mixture (ca. 1 mL) of MMA, EBIB, Cu(I)Cl, Cu(II)Cl$_2$ (if needed), and dNbipy was put into a sample bag made of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film and the bag was sealed by a heat sealer. The sample was further packed in a polyethylene-coated aluminum sheet to prevent oxygen contamination and put into the chamber, thermostated at 60 °C, of the high-pressure reaction system (HPS-700, Syn Corporation, Kyoto, Japan) and pressurized up to a prescribed pressure. After a prescribed time, the system was depressurized and an aliquot of the reaction mixture was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molecular weight and its distribution.

2.3. Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 40 °C on a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit $= 2 \times 10^7$), and a differential refractometer (Shodex RI-101).
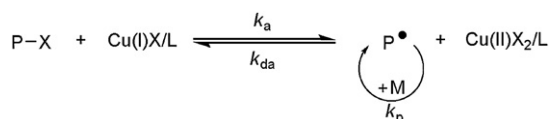
Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. The GPC system was basically calibrated by PMMA standards (Polymer Laboratories, $M_p = 2.00 \times 10^3$–1.64×10^6). The calibration was complemented by polystyrene standards (Polymer Laboratories, $M_p = 1.65 \times 10^3$–1.54×10^7) using the idea of universal calibration [14]. The M_n and PDI values were estimated by this calibration method, unless otherwise noted. Sample detection was also made with a multiangle laser light-scattering (MALLS) detector (Wyatt Technology DAWN EOS). ^{1}H (300 MHz) NMR spectra were obtained on a JEOL/AL300 spectrometer.

3. Results and discussion

The ATRP runs of MMA in the presence of the activator Cu(I)Cl/L$_2$ complex ([Cu(I)Cl/L$_2$]$_0 = 14$ mM) were performed at 60 °C in a pressure range from 0.1 to 500 MPa. The concentration of ATRP initiator [EBIB]$_0$ was adjusted to 0.32 mM, corresponding to the target M_n of 3.0×10^6 (at full conversion). Thermal initiation of MMA was negligibly small under all studied conditions. Figs. 1 and 2 show the conversion index ln([M]$_0$/[M]) vs. polymerization time t and the M_n and PDI of products vs. conversion c, respectively. As expected, the polymerization rate (estimated form the slope of the lines in Fig. 1) increased with increasing pressure. The figures also indicate that at the ambient pressure, the polymerization was not well controlled because of the extremely low initiator concentration, but elevated pressures resulted in better control with PDI effectively lowered even at high conversions. At 500 MPa, the polymerization was about 20 times faster than that at the ambient pressure, giving a polymer with $M_n = 5 \times 10^5$ and PDI $= 1.25$ at conversion 20%. However, the system gradually lost the control over M_n and PDI at higher conversions.

For improvement of the control, we added 0.31 mM of Cu(II)Cl$_2$/L$_2$ complex in the original feed as a deactivator and carried out the polymerization at 500 MPa. The closed symbols in Figs. 1 and 2 show the result. Clearly, the addition of the deactivator somewhat decreased the polymerization rate and lowered the PDI, giving a polymer with $M_n = 1.5 \times 10^6$ and PDI $= 1.25$ at conversion 60%. We then carried out a run in which the initiator concentration was lowered to 0.047 mM (target molecular weight $= 2.0 \times 10^7$) with other conditions almost unchanged. The first-order plot of the monomer concentration [M] (ln([M]$_0$/[M]) vs. t) was confirmed to
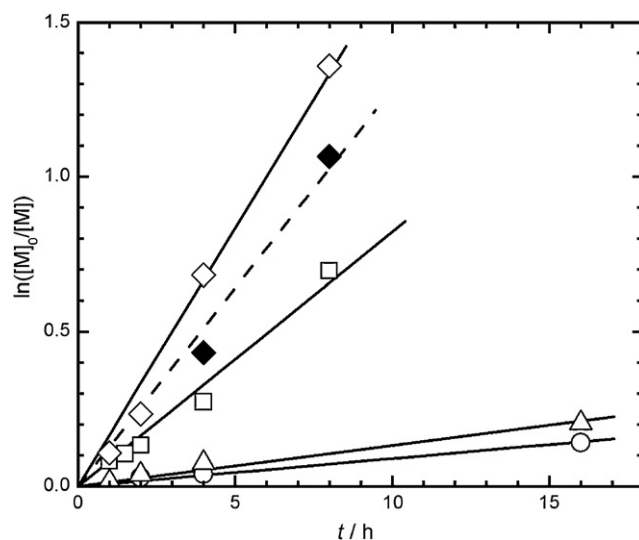

Fig. 1. Plot of ln([M]$_0$/[M]) vs. t for the ATRP of MMA at a temperature of 60 °C and pressures of 0.1 (○), 30 (△), 300 (□), and 500 MPa (◇ and ◆); [EBIB]$_0 = 0.32$ mM, [Cu(I)Cl/L$_2$]$_0 = 14$ mM, [Cu(II)Cl$_2$/L$_2$]$_0 = 0$ (open symbols) and 0.31 mM (◆).

Scheme 1. The mechanism of reversible activation in Cu-mediated ATRP.