Living Polymerization

HP-RAFT: A Free-Radical Polymerization Technique for Obtaining Living Polymers of Ultrahigh Molecular Weights**

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Synthetic methods based on living polymerizations have become indispensable tools for modern polymer chemists. By minimizing the influence of termination and chain transfer over the final outcome of the polymerization, they provide the only reasonable route to polymers with narrow molecular weight distributions and controlled end groups, and to most of the nonlinear polymer architectures such as block, star, cyclic, and other macromolecules with controlled branching patterns.[1–5] By making possible the design of polymers with tailored properties, these methods have contributed significantly to the development of nanostructured polymeric materials whose dimensions are controlled by the size of the macromolecules involved in the structuration process.[5,6]

The many fundamental accomplishments and myriad of papers published every year on the synthesis, properties, and use of polymers prepared by living polymerization techniques contrast heavily with the industrial impact, which thus far has been quite modest, largely due to the high costs associated with the required reaction conditions. Living polymerizations demand that a propagation proceeds hundred of times in sequence without the interference of any side reaction leading to termination or chain transfer. Such a selectivity is hardly a hallmark of organic chemistry, and only a handful of polymerizations have been successfully optimized to the required level.[1,5]

Living/controlled free-radical polymerization techniques were supposed to overcome this technical limitation by allowing experimental conditions to be used that are less stringent and costly than those based on organometallic or ionic species, a goal that has largely been achieved by now.[7] Free-radical polymerizations have their own limitations, though; being very slow, they do not provide a good route to polymers of high degrees of polymerization, the polymerizations in this case requiring theoretical reaction times of several weeks to several years depending on the targeted degree of polymerization.[8]

Herein, we report a simple, practical methodology to overcome the above limitation. We demonstrate, using

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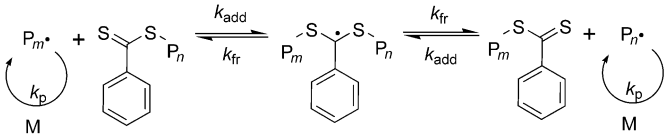
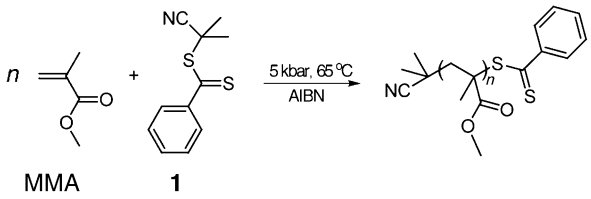
methyl methacrylate (MMA) polymerization as an example, that polymers with very high molecular weights can be obtained under simple experimental conditions that are fully compatible with current industrial polymerization processes. The methodology uses known living/controlled free-radical-polymerization procedures, and overcomes their inherent limitations under normal conditions by using very high hydrostatic pressures, in the 1–10 kbar range (1 kbar = 987 atm = 14 504 psi). The main purpose of using high pressures is to increase the propagation rate coefficient of the polymerization k_p by several orders of magnitude and to benefit from the overall activation volumes of −16 to −21 $cm^3 mol^{-1}$ reported in the literature.[9] Under these experimental conditions, polymerizations can become reasonably fast, with reaction times of less than a few hours even when the amount of propagating free-radicals has to be maintained very low to maintain the living/controlled character of the reaction. Although theoretically expandable to most living/controlled free-radical-polymerization techniques described in the literature, the present study uses RAFT conditions to control the livingness. A mechanistic scheme summarizing the key steps in a RAFT polymerization is provided in Scheme 1. Further information on the scope, limitations, and mechanism of RAFT-type reactions is available in the literature.[10–13]



Scheme 1. Mechanism of RAFT polymerization.

In experiments 1–8 (Table 1), MMA was polymerized in a high-pressure reactor at 5 or 9 kbar at 65 °C in the presence of cyanoisopropyl dithiobenzoate (**1**) as the RAFT agent and 2,2′-azobis(isobutyronitrile) (AIBN, **2**) as the free-radical initiator (Scheme 2). The results of a control experiment at ambient pressure (10^{-3} kbar) is also summarized in Table 1 (expt 9). Although bulk polymerization is possible, solvents such as toluene and methyl ethyl ketone (MEK) were used to avert very high viscosities and prevent the mixture reaching the gel point at low conversions. Polymers were characterized



Scheme 2. Living polymerization of MMA.

by gel-permeation chromatography (GPC) coupled to a multi-angle laser light-scattering (MALLS) detection unit to prevent problems associated with instrumental broadening.

The NMR spectra of the synthesized PMMA indicated that the polymers have 72 % syndiotactic dyads, close to the tacticity obtained by free-radical polymerization at ambient pressure. This observation is consistent with previous reports that had indicated a very small dependence of PMMA tacticity on polymerization pressures.[14]

As shown in Table 1, polymers of very high molecular weights (up to 1.25 million) and very low polydispersities ($\bar{M}_w/\bar{M}_n < 1.2$, see also Figure 1; $\bar{M}_w$ is the weight-average molar mass, $\bar{M}_n$ is the number-average molar mass) can be obtained under high pressure after reasonably short reaction times (< 9 h). The highest molecular weight of 1.25 million does not correspond to an upper limit, but to our inability to reliably measure the molecular weight distributions of PMMA samples of higher molecular weight based on the equipment currently available to us. In contrast, results obtained at ambient pressure (expt 9) indicate a dramatic loss of control in the polymerization in addition to a much lower reactivity.

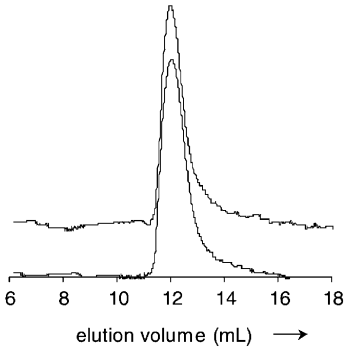


Figure 1. GPC chromatograms of a commercial PMMA standard (top curve, $\bar{M}_n = 1.3 \times 10^6$, PDI = 1.03) and a PMMA sample synthesized in this study by HP-RAFT polymerization (bottom curve, $\bar{M}_n = 1.25 \times 10^6$, PDI = 1.03). The sharper slope observed on the left side of each peak was independently demonstrated not to result from the exclusion limit of the system.

The degrees of polymerization reported in this communication are the highest ever obtained for a living/controlled free-radical polymerization, leading to a linear polymer.

Table 1: RAFT polymerization of MMA under high-pressure conditions.[a]

Expt	Solvent	$[M]_o:[\mathbf{1}]_o:[\mathbf{2}]_o$	T [h]	Conv. [%]	$\bar{M}_{n,th}[\times 10^{-3}]$[b]	$\bar{M}_{n,GPC}[\times 10^{-3}]$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	MEK	2000:1:0.1	2	61	122	114[d]	1.15[d]
2	MEK	2000:1:0.1	5	> 99	200	202	1.04
						197[d]	1.15[d]
3[e]	MEK	2000:1:0.1	2	> 99	200	150[d]	1.61[d]
4	MEK	5000:1:0.1	9	> 99	500	485	1.03
5	toluene	12 000:1:0.2	1	9	108	164	1.20
6	toluene	12 000:1:0.2	2	30	360	367	1.03
7	toluene	12 000:1:0.2	4	72	864	838	1.05
8	toluene	12 000:1:0.2	7	> 99	1200	1250	1.03
9[f]	toluene	12 000:1:0.2	51	40	480	284	1.38

[a] $P = 5$ kbar (except for expts 3 and 9), $T = 65$ °C, [MMA] = 4.67 M. [b] Calculated from the monomer-to-**1** ratio. [c] Measured by GPC-MALLS. [d] Measured by GPC relative to PMMA standards. [e] $P = 9$ kbar. [f] $P = 1$ atm = 10^{-3} kbar.

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Results for living/controlled free-radical polymerizations published in the literature have consistently led to a practical upper limit of about 2×10^3 for the degree of polymerization.[7,15,16] From a preparative viewpoint, it is interesting to note that the polymerization can be driven to completion without loss of control over the molecular weights.

The observed linear increase in molecular weight and decrease in polydispersities with conversion (Figure 2) are

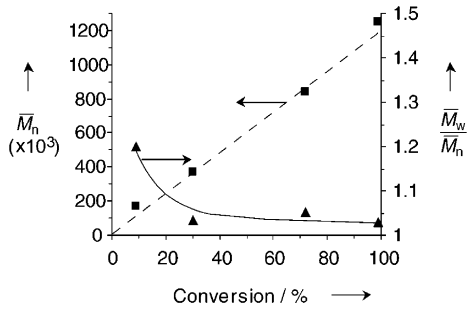

Figure 2. Dependence of molecular weights (■ $\bar{M}_{n,GPC}$; ----- theoretical curve) and polydispersities (▲) on conversion for RAFT polymerization of MMA at 5 kbar ($T=65\,^\circ$C, [MMA] = 4.67 mol L^{-1} in toluene, [MMA]:[**1**]:[**2**] = 12000:1:0.2).

consistent with a living/controlled mechanism. An analysis of the kinetic data reveals that the polymerization does not follow the expected first-order kinetics with respect to monomer concentration over the entire conversion range. The rate of polymerization increases significantly with increasing conversion (Figure 3), a behavior probably related

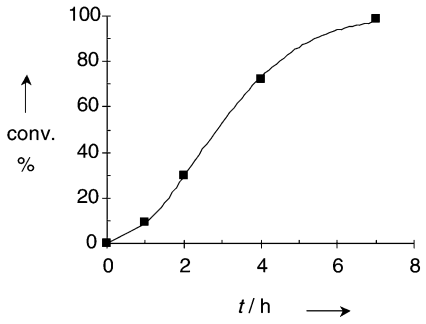

Figure 3. Evolution of monomer conversion (conv.) with time (t) for RAFT polymerization of MMA at 5 kbar ($T=65\,^\circ$C, [MMA] = 4.67 mol L^{-1} in toluene, [MMA]:[**1**]:[**2**] = 12000:1:0.2).

to a progressive viscosity buildup in the reactor. This behavior, although unusual, is nevertheless highly beneficial from a preparative standpoint as polymers with high molecular weights can be obtained in much shorter times than expected based on strict first-order kinetics. Extrapolation of the initial kinetic features to higher conversions shows that 49 h would have been necessary to reach 99% conversion while the polymerization was actually complete in only 7 h.

The polymerizations were carried out in the presence of inert diluents (50 vol%) to provide enough mobility to the reactive polymer chains up to high conversions. Excellent results were obtained with either MEK and toluene when medium-high molecular weights were targeted ($<0.5\times10^6$). When higher molecular weights were needed and very low amounts of the RAFT agent and initiator had to be used, toluene provided far better results (entries 5–8 in Table 1). This is probably due to some impurities present in MEK at low concentrations, such as peroxides, since MMA was found to polymerize in regularly purified MEK even in the absence of any added AIBN, while no such polymerization could be observed when MEK was passed through an alumina column to remove peroxidic impurities.

The exact influence of several parameters on HP-RAFT polymerizations is currently under investigation, but it is already clear that the use of higher pressure is not always helpful. As an example, polymerization at 9 instead of 5 kbar (expt 3 in Table 1) resulted in a higher polydispersity index. The origin of this effect is unclear and might result from a decreased chain-transfer constant to the RAFT agent or from the fact the gel point is reached, but these and other findings[17,18] clearly suggest that experimental conditions have to be carefully optimized and that simple extrapolation based on conditions reported for ambient pressure polymerization is not feasible.

The reactors needed to obtain the high pressures reported in this study are rarely found in research laboratories, but are easily accessible in industry. In addition, recent progress in food science in which multiliter high-pressure reactors of the type used in this study are currently used to eliminate bacteria from food according to the high-pressure equivalent of pasteurization, should increasingly make the purchase of such pieces of equipment attractive to synthetic chemists.[19,20]

In summary, we have demonstrated that PMMA polymers of extremely high molecular weights and narrow molecular-weight distributions can be easily obtained by using living/controlled free-radical polymerization techniques at high pressures. Although extrapolation to other monomers that have already been reported to undergo living polymerizations under free-radical conditions at ambient pressure will require additional work, the present HP-RAFT and associated techniques should ultimately allow a much larger range of molecular weights to become accessible for monodisperse vinyl polymers, and provide an easy route to advanced polymeric materials whose ultimate properties (e.g., optical, mechanical, nanoporosity) critically depend upon the molecular weight of at least one component.[21–23]

Experimental Section

Polymerizations were carried out in 2 mL teflon ampoules in a high-pressure microreactor purchased from the High Pressure Research Center of the Polish Academy of Sciences. The reactor includes a hydraulic press model LCP20 and a pressure reaction vessel equipped with a temperature controller. The RAFT agent **1** was synthesized according to a procedure reported in the literature.[11] All other chemicals were purchased from Aldrich. MMA was distilled before use and AIBN recrystallized in methanol; all other reagents were used as received. The initial solution was deoxygenated by bubbling with nitrogen for 20–30 minutes prior to polymerization. Polymers were precipitated in methanol. Yields were determined gravimetrically.

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Molecular weights of the polymers were determined by Polymer Laboratories PL-220 high temperature GPC system equipped with two PL MIXED-A columns, Wyatt MiniDawn (620 nm diode laser) light scattering detector and refractive index detector. Measurements were performed at 135 °C in 1,2,4-trichlorobenzene with a flow rate of 1.0 mL min^{-1}. PMMA standards of very high molecular weights were used to estimate the influence of the second virial coefficient on the scattering signal, and recalibrate the light-scattering detectors accordingly. Polymers with medium-high molecular weights (<300000) were characterized by GPC in THF using 13 monodisperse PMMA commercial standards as calibrants (2× MIXED-D and 1× 50 Å columns, 25 °C, 1.0 mL min^{-1}). ^{1}H NMR spectra were recorded on a 300 MHz Bruker DPX 300 spectrometer.

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