Direct Measurement of Chain Transfer during Controlled Radical Polymerization

Michael F. Drenski,† Emmanuel Mignard,‡ and Wayne F. Reed*,†

Physics Department, Tulane University, New Orleans, Louisiana 70115, and UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, Bât. 24, 35042 Rennes Cedex, France

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Living polymerization reactions are used to produce polymers of well-defined molar mass and low polydispersity. Controlled radical polymerization (CRP) combines the robustness and economy of free radical polymerization with the benefits of anionic living polymerization, which has much more stringent limits on reaction conditions.[1−4] A prominent characteristic of living polymerization is the linear growth of number-average molar mass M_n with fractional monomer conversion f.

A disadvantage of CRP is that ideal living behavior can be lost due to chain transfer and termination reactions. This Communication demonstrates how automatic continuous online monitoring of polymerization reactions (ACOMP) can be used to measure chain transfer during CRP reactions, in this case nitroxide-mediated polymerization of butyl acrylate (BA) in butyl acetate (BAc). BAc is a chain transfer agent for BA, and the molar ratio of BAc to initiator, or the "chain transfer ratio" τ, determined the extent of the transfer reactions. The results were substantiated by multidetector gel permeation chromatography. ACOMP should be a broadly applicable tool for following deviations from ideal living polymerizations, including termination reactions.

The persistent radical, *N-tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, SG1 (89%), and the alkoxyamine initiator, methyl propionate-SG1 (MONAMS, 91%), were provided by Atofina Chemicals. The conditions for each experiment are given in Table 1, along with target M_n and τ. In all reactions the temperature was stable to within 0.5 °C.

Prior to polymerization the monomer/solvent mixture in the reactor, a three-neck round-bottom flask, was purged with nitrogen. MONAMS and excess SG1 were dissolved in BAc under nitrogen purge. After the reactor was heated to 118 °C this latter solution was injected into the reactor with a gastight syringe. The polymerization was then monitored for up to 13 h or to where radical transfer effects were clearly visible.

The ACOMP system, including the "front-end" for extraction, dilution, and conditioning, and the detector train, consisting of multiangle light scattering (MALS, Brookhaven Instruments Corp. BI-MwA), single capillary viscometer, a refractometer (RI, Waters 410), and a dual wavelength ultraviolet detector (UV, Shimadzu SPD10-AV), has been amply documented.[5,6] The solute concentration in the detector train was 0.010 g/cm^3, and the detectors were read at 1 Hz. The absolute value of weight-averaged molar mass M_w was obtained from the combined MALS and concentration data and the intrinsic viscosity $[\eta]_w$ from the viscometer and concentration data. The end products were analyzed with multidetector gel permeation chromatography (GPC), equipped with MALS and RI detection.

† Tulane University.
‡ Université de Rennes 1.
* Corresponding author. E-mail: wreed@tulane.edu.

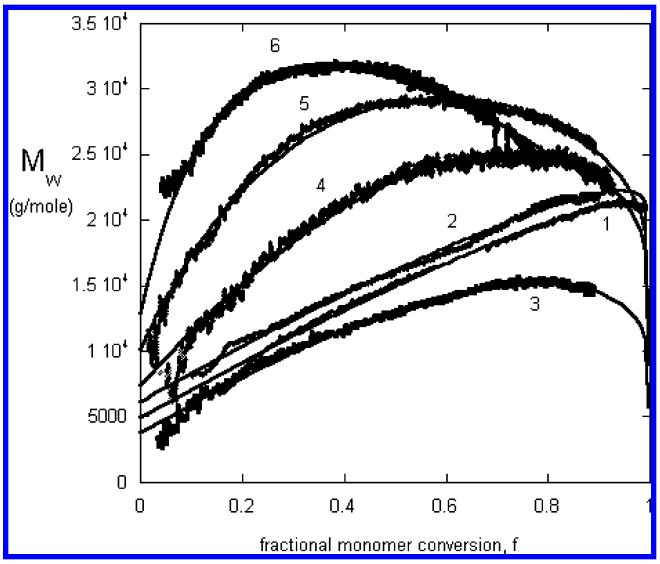

Figure 1. M_w vs f for the experiments in Table 1. The fits are according to eq 8.

The increasing deviation of M_w away from linearity vs conversion as τ is increased is illustrated strikingly in Figure 1. Experiments 1 and 2, with the lowest τ, are quite linear and come very close to their target mass. In contrast, in all other cases M_w has an initial negative second derivate, reaches a maximum value, and then decreases. In none of these cases does the final product ever reach its target mass, and in the case of highest τ, the deviation is extreme. Trends in the evolution of $[\eta]_w$ for these experiments were similar (data not shown).

To analyze the data, consider initial molar concentrations of MONAMS $[R_T]$, monomer $[m]_0$, and chain transfer agent $[T_T]$. Usually $[R_T]$ is close to the starting concentration of alkoxyamine, $[MONAMS]_0$.

In the case of CRP there is an average fraction σ of $[R_T]$ that is actively propagating at any instant. σ is dependent on the equilibrium constant K_{eq} between active and dormant species and, in excess, free SG1 that is added at the beginning of the reaction. When the initial mole ratio of free SG1 to MONAMS, ϵ, is on the order of 10^{-1}, a good approximation to σ is

$$\sigma \approx \frac{K_{eq}}{\epsilon} \tag{1}$$

For SG1 and BA at 120 °C $K_{eq} \sim 1.5 \times 10^{-10}$ mol/L. For $\epsilon = 0.04$, $\sigma \sim 3.8 \times 10^{-9}$ (experiments 1, 3−6) and $\sigma \sim 7.6 \times 10^{-9}$ (experiment 2). It is assumed here that termination reactions are insignificant compared to propagation and transfer reactions. Monomer is consumed according to

$$\frac{d[m]}{dt} = -(k_p + k_{um})\sigma[R_T][m] \tag{2}$$

where $k_p = 8.8 \times 10^4$ L mol^{-1} s^{-1} is the propagation rate constant and k_{um} is the rate constant for transfer to monomer.

The first-order monomer conversion f is

$$f(t) = 1 - e^{-bt} \tag{3}$$

where

$$b = \sigma[R_T](k_p + k_{um}) \tag{4}$$

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Table 1.

expt no.	τ	BA (g)	BAc (g)	MONAMS (g)[a]	target M_w (g/mol)	M_w final:f_{final}[b]	M_w/M_n (GPC)	M_z/M_w (GPC)	f at M_w max	f at M_η max
1	186	70	70	1.120	21 900	20700:1.00	1.05	1.06	0.92	0.92
2	186	70	70	1.120	21 900	22000:0.90	1.04	1.05	X	X
3	434	42	98	0.672	21 900	14700:0.89	1.15	1.15	0.79	0.80
4	868	42	98	0.336	43 800	22900:0.92	1.24	1.18	0.74	0.75
5	1732	42	98	0.168	85 300	25500:0.89	1.25	1.21	0.60	0.61
6	3964	42	98	0.084	175 100	25300:0.77	1.62	1.39	0.41	0.50

[a] $[MONAMS]_0/[SG1]_0 = 25$ was constant in each experiment, except in no. 2, where it was 50. [b] ACOMP final value at whatever final conversion obtained.

This gives the surprising, but previously reported, result[7,8] that the conversion rate depends only on ϵ and not on $[MONAMS]_0$. Figure 2 and its inset show to what extent this latter assertion is true, in that f vs t has roughly the same value of b, even though $[MONAMS]_0$ varies by over an order of magnitude among the experiments.

The expected degree of polymerization, N_0, at full conversion is

$$N_0 = \frac{[m]_0}{[R_T]} \tag{5}$$

The number-average degree of polymerization N_n at any time t during the polymerization reaction is, by definition

$$N_n(t) = \frac{[m]_0 - [m](t)}{[R_T] + [Q](t)} \tag{6}$$

where $[R_T] + [Q](t)$ is the total number of chains. $[Q](t)$ is the concentration of dead chains that have accumulated by time t due to transfer. Dead chains are produced at the rate

$$\frac{d[Q]}{dt} = \sigma[R_T](k_{um}[m] + k_u[T]) \tag{7}$$

where k_u is the chain transfer rate constant to the transfer agent.

For the case where the agent's initial concentration, $[T_T]$, changes negligibly due to transfer (i.e., $[T_T] \gg [R_T]$), eq 7 can be integrated and, with eqs 3 and 6, yields

$$N_n(f) = \frac{[m]_0 f}{[R_T] + \frac{k_{um} f [m]_0}{k_p k_{um}} - \frac{k_u [T_T]}{k_p + k_{um}} \ln(1 - f)} \tag{8}$$

The parameter controlling chain transfer can be defined as

$$\beta = \frac{a}{b} = \frac{k_u}{(k_p + k_{um})} \tau \tag{9}$$

where the chain transfer ratio τ is

$$\tau = \frac{[T_T]}{[R_T]} \tag{10}$$

and β is independent of σ and

$$a = k_u \sigma [T_T] \tag{11}$$

In the conversion domain the maximum value of N_n from eq 8 occurs for

$$\frac{1}{\beta} = \frac{1}{1 - f} - 1 + \ln(1 - f) \tag{12}$$

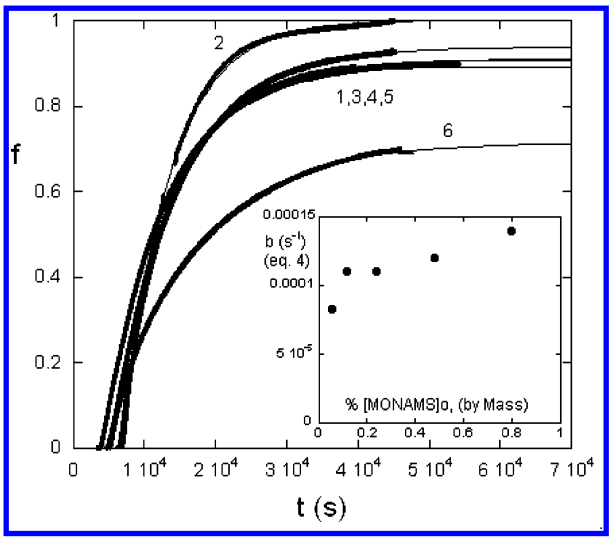

Figure 2. Monomer conversion f vs t. First-order fits are so close to data that they are not visible. Inset gives first-order rates b (eq 3) vs % mass of $[MONAMS]_0$.

if there is transfer to an agent. Transfer to monomer will not produce a maximum of $N_n(f)$. The computation of N_w is much more complex and is not pursued here. Rather, for low values of β the polydispersity will not be very high so that N_n and N_w will be roughly equal but should increase quickly as β increases.

The solid lines in Figure 1 are two parameter fits (k_u/k_p, k_{um}/k_p) to the experimental M_w using eq 8. They are remarkably good over the entire range of β, considering the comments in the last paragraph. k_{um} is negligible in the fits, indicating that virtually all the chain transfer is to solvent. From the fits $k_u/k_p = 0.00083 \pm 0.0003$.

Another estimate of k_u/k_p can be made from Figure 1, taking f where the maximum of M_w occurs for each experiment (again, assuming M_w is close to M_n) according to eq 12. These values are in Table 1, and the corresponding values of β are plotted vs τ in Figure 3. The relation between β and the maximum value of f for N_n is plotted in the inset to Figure 3. From this $k_u/k_p \sim 0.00098$, in good agreement with the above fits.

The molar mass relationship to $[\eta]$ can be used[9] to determine the viscosity-averaged mass M_η, which is closer to M_n than M_w and hence furnishes a better approximation for k_u/k_p.

$$M_\eta \text{ (g/M)} = \left(\frac{[\eta] \text{ (cm}^3\text{/g)}}{0.00927}\right)^{1.357} \tag{13}$$

The corresponding β vs $[BA]/[R_T]$ are also shown in Figure 3. This gives $k_u/k_p \sim 0.00084$. From this ratios $k_u \sim 74$ L mol^{-1} s^{-1}.

GPC polydispersity analysis on reaction endproducts confirms the trend expected; increasing τ increases the polydispersity (Table 1).

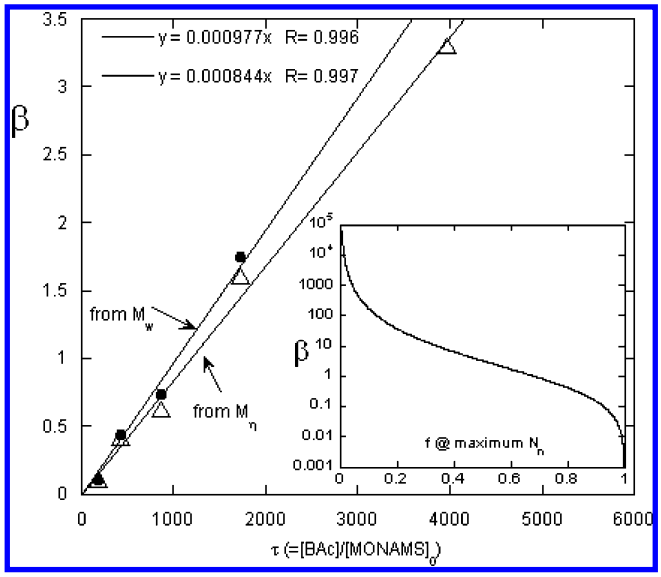

Figure 3. β vs τ from both ACOMP M_w and $[\eta]_w$ data.

ACOMP promises to be of decisive value in assessing deviations from ideal "livingness" in CRP and other living-type polymerization reactions. It can provide the quantitative difference between what is ideally thought to occur and what really occurs in such reactions.

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References and Notes

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