

Modeling the Bulk Polymerization of Methyl Methacrylate with Glycol Dimercapto Acetate as Chain Transfer Agent

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SYNOPSIS

This paper investigates the bulk polymerization of methyl methacrylate (MMA) when chain transfer to a low-molecular-weight agent is important. A transfer rate constant and a transfer efficiency are introduced into the equations. Calculations of the kinetics of polymerization and of the weight-average molecular weight distribution are in good agreement with experimental results.

INTRODUCTION

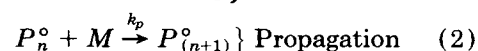
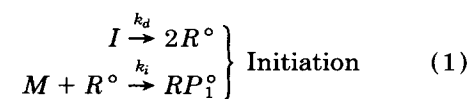
Poly(methyl methacrylate) (PMMA) possesses excellent optical properties. The good light transmittance is put to use in plastic optical fibers. The fiber can be obtained by drawing a "preform" that is made with a PMMA core clad with a fluorinated polymer. During the drawing process from a solid preform using infrared heating, the rheology of the neck-down region is greatly dependent on the weight-average molecular weight M_w of the polymer and on the heterogeneity index HI. A too large value of M_w can induce core diameter fluctuations and orientational birefringence, which increase loss of guided light due to scattering. On the opposite, a low M_w gives bad mechanical properties, like brittleness of the fiber. Experience shows that values $80,000 < M_w < 120,000$ provide a good compromise. Kinetic studies of PMMA polymerization¹ demonstrate that to obtain such a value in a bulk polymerization, the temperature should be raised high enough (depending on the initiator) to transform 90% of the monomers in less than 1 h. In such conditions, the exothermicity of the reaction, associated with the gel effect, with the low thermal conductivity and with the large size of the preform would result in a thermal runaway of the reaction.

Another way to control the molecular weight is to add a chain transfer agent (CTA) to the monomer. The role of the CTA is to transfer the free radical site from the end of a growing chain to a monomer. This leads to the "killing" of the "growing" macromolecule at a given length and to the initiation of a new chain. The concentration of CTA is the parameter which controls the weight-average molecular weight of the polymer. Others works have been published¹⁻¹⁰ that do not take into account the presence of a chain transfer agent. The work reported in this paper introduces a transfer rate constant k_{tr} and a transfer efficiency f_{tr} to modelize the free radical bulk polymerization of methyl methacrylate in the presence of glycol dimercapto acetate (GDMA) as chain transfer agent.

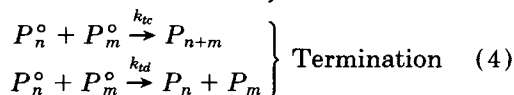
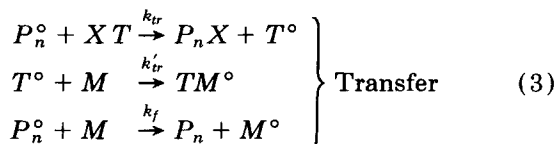
The model and the associated program allow to calculate the CTA concentration to be used to obtain the molecular weight M_w that is wanted.

KINETIC MODEL

A very general kinetic model for free radical polymerization is:



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where I is the initiator, M the monomer, R° the initiator generated free radical (primary radical), P_n° the growing polymer of chain length n , P_n the dead polymer of chain length n , XT the chain transfer agent that is decomposed in two parts X and T° .

To resolve the kinetic equations we use the following hypothesis:

1. All the processes are irreversible.
2. The monomer is only consumed in the propagation step.
3. The free radical concentration R° is constant: this is the quasi-steady state approximation (QSSA).
4. The reactivity of a radical at the end of the growing chain P_n° is unaffected by the chain length n .

Direct transfer from a growing chain to a monomer (rate constant k_f) can be neglected when compared to transfer via CTA. The transfer process is characterized by $k_{tr} \ll k'_{tr}$. The kinetics are controlled by the slower step, so that k'_{tr} is not taken into account in the calculation.

The equations giving the concentration of the different constituents can be written as:

$$\text{Initiator } [I]: d([I]V)/Vdt = -k_d[I] \quad (5)$$

$$\text{Monomer } [M]: d([M]V)/Vdt = -k_p[M][P^\circ] \quad (6)$$

$$\text{Free radical } [R^\circ]: d([R^\circ]V)/Vdt = 2fk_d[I] - k_i[R^\circ][M] \quad (7)$$

QSSA hypothesis allows the simplification:

$$[R^\circ] = 2fk_d[I]/k_i[M] \quad (8)$$

$$\begin{aligned} \text{Growing chain } [P_n^\circ]: d([P_n^\circ]V)/Vdt \\ = k_p[M]([P_{n-1}^\circ] - [P_n^\circ]) \\ - k_t[P_n^\circ][P^\circ] - k_{tr}[XT][P_n^\circ](1 - f_{tr}) \end{aligned} \quad (9)$$

$$\text{CTA } [XT]: d([XT]V)/Vdt = -k_{tr}[XT][P^\circ] \quad (10)$$

$$\begin{aligned} \text{Dead chain } [P_n]: d([P_n]V)/Vdt \\ = k_{td}[P_n^\circ][P^\circ] + 0.5k_{tc} \sum_{m=1}^{n-1} [P_{n-m}^\circ][P_n^\circ], \end{aligned} \quad (11)$$

where

$[P^\circ]$	is the growing chain concentration
V	is the total volume
k_d	is the initiator decomposition rate constant
k_p	is the propagation rate constant
f	is the initiator efficiency
k_i	is the chain initiator rate constant
$k_t = k_{tc} + k_{td}$	is the termination rate constant
k_{tr}	is the growing chain to CTA transfer rate constant
f_{tr}	is the CTA efficiency
k_{td}	is the termination by disproportionation rate constant
k_{tc}	is the termination by combination rate constant.

These equations are similar to those proposed by Louie et al.,¹ except that we take into account the effect of a chain transfer agent with an efficiency f_{tr} and a transfer rate constant k_{tr} .

The polymerization is characterized by a volume contraction that can be expressed by a contraction factor:

$$\epsilon = (\rho_p - \rho_m)/\rho, \quad (12)$$

ρ_p , ρ_m being the polymer and monomer densities, respectively.

The extent of polymerization can be expressed as:

$$x = ([M]_0V_0 - [M]V)/[M]_0V_0, \quad (13)$$

where $[M]_0$ is the concentration (mol/L) of pure monomer and $[M]$ is the concentration of monomer at a given time after the beginning of the polymerization.

Equations (9)–(13) can be recombined to give the differential equations used for calculation:

$$dx/dt = k_p(1 - x)[P^\circ] \quad (14)$$

$$\begin{aligned} d[I]/dt \\ = (-k_d - \epsilon[P^\circ](1 - x)k_p/(1 + \epsilon x))[I] \end{aligned} \quad (15)$$

$$\begin{aligned} d[P^\circ]/dt = & 2fk_d[I] - k_t[P^\circ]^2 \\ & + (f_{tr} - 1)k_{tr}[XT][P^\circ] \\ & - \epsilon(1-x)k_p[P^\circ]^2/(1+\epsilon x) \end{aligned} \quad (16)$$

$$\begin{aligned} d[XT]/dt = & -k_{tr}[XT][P^\circ] \\ & - \epsilon[P^\circ](1-x)k_p[XT]/(1+\epsilon x) \end{aligned} \quad (17)$$

Most of the physical constants can be found in the literature.^{1,11} For the calculation, we used the values listed below:

$$\begin{aligned} k_d &= 6.32 \cdot 10^{16} \exp(-30.66/kT) \quad \text{min}^{-1} \\ k_p &= k_p^\circ D / (D + \theta_p [P^\circ]) k_p^\circ \quad \text{L mol}^{-1} \text{min}^{-1} \\ k_t &= k_t^\circ D / (D + \theta_t [P^\circ]) k_t^\circ \quad \text{L mol}^{-1} \text{min}^{-1} \\ f &= 0.58 \\ \rho_p &= 1.2 \cdot 10^3 \quad \text{kg m}^{-3} \\ \rho_m &= 968 - 1.225(T - 273) \quad \text{kg m}^{-3} \\ k_p^\circ &= 2.95 \cdot 10^7 \exp(-4.35/kT) \quad \text{L mol}^{-1} \text{min}^{-1} \\ k_t^\circ &= 5.88 \cdot 10^9 \exp(-0.701/kT) \quad \text{L mol}^{-1} \text{min}^{-1} \end{aligned}$$

k_p° and k_t° represent the "true" propagation and termination constant rates. D is a term related to the diffusion of radicals in the CHIU model.⁹ It can be expressed by:

$$D = \exp(2.3\Phi_m/A + B\Phi_m)$$

Φ_m is the monomer volumic fraction given by:

$$\Phi_m = (1-x)/(1-\epsilon x)$$

A and B are determined by Louie et al.¹ as:

$$\begin{aligned} A &= 0.168 - 8.21 \cdot 10^{-6}(T - T_g)^2 \\ B &= 0.03 \end{aligned}$$

T_g is the glass transition temperature, which is taken as 387°K and is considered to be independent of the molecular weight M_w , at least as long as M_w is greater than a critical value $M_{wc} = 40,000$.

$$\begin{aligned} \theta_p &= 5.4814 \cdot 10^{-16} \exp(13982/T) \\ \theta_t &= 1.1353 \cdot 10^{-22} \exp(17420/T)/[I_0], \end{aligned}$$

where $[I]_0$ is the initial initiator concentration.

To solve the system of eq. (14)–(17), two constants are unknown:

f_{tr} the CTA efficiency

k_{tr} the CTA rate constant.

They were determined by the curve fitting method. For this purpose we carried out measurements of the polymerization extent vs. time at a constant temperature. When the end of the polymerization was reached, the weight-average molecular weight of the sample was measured by gel permeation chromatography. Experimental data were compared with theoretical curves drawn with different values of f_{tr} and k_{tr} . The best fit allowed the determination of the unknown values.

EXPERIMENTAL

Pure methyl methacrylate was obtained by vacuum distillation of the inhibited monomers obtained commercially (Norsolor). The initiator AIBN was used as received from Merck. The glycol dimeracetoacetate from Sigma was distilled under vacuum. The different distillates were mixed with the adequate concentrations:

$$[I]_0 = 0.00188 \text{ mol/L}$$

$$[\text{GDMA}] = 0.0159 \text{ mol/L}$$

The preparation was separated in nine ampoules that were degassed by several freeze-pump cycles. Then, they were sealed under vacuum and weighed. They were simultaneously immersed in an oil bath. The temperature was maintained constant at $60 \pm 0.1^\circ\text{C}$ during the polymerization. The ampoules were successively taken out of the oil bath after a polymerization period ranging from 4 h for the first sample to 12 h for the eighth. The polymerization was stopped by quenching the tubes in liquid nitrogen. They were broken and the syrup was dissolved in chloroform. The glass was weighed. The polymer was precipitated by addition of a large quantity of methanol. It was filtered and dried at room temperature for at least 5 h, and then to constant weight at 65°C . The degree of polymerization was calculated as the ratio:

$$\begin{aligned} & \text{Polymer weight /} \\ & (\text{Ampoule weight} - \text{Glass weight}). \end{aligned}$$

The results are reported in curve 3 of Figure 1 as a function of time. The ninth sample was maintained

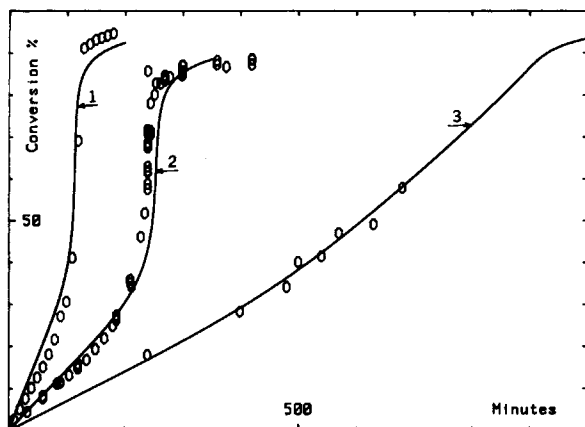


Figure 1 Conversion vs. time curves for PMMA. Curve 1, experimental data from Gulari et al.¹² $T = 60^{\circ}\text{C}$, $[I_0] = 0.0258 \text{ mol/L}$; curve 2, experimental data from Balke et al.⁴ $T = 50^{\circ}\text{C}$, $[I_0] = 0.0258 \text{ mol/L}$; curve 3, our experimental data $T = 60^{\circ}\text{C}$, $[I_0] = 0.00188 \text{ mol/L}$, $[\text{GDMA}]_0 = 0.0159 \text{ mol/L}$.

in the oil bath for a longer period to approach 100% polymerization. It was used to measure the molecular weight. GPC analysis was carried out with a solvent delivery system 590, a differential refractometer 410; and a data module 745 from Waters. Four Waters columns with different porosities (10^2 – 10^4 \AA) were mounted in series. The mobile phase was tetrahydrofuran (THF) purchased from Carlo Erba. The columns were calibrated with standard polymers from Touzart et Matignon. The weight-average molecular weight obtained with this method was:

$$M_w = 108,000 \text{ g}$$

RESULTS AND DISCUSSION

Calculations were carried out with a Hewlett Packard 9000/350. The program was tested using experimental results published by Gulari et al.¹² with $[I_0] = 0.0258 \text{ mol/L}$, $T = 60^{\circ}\text{C}$ (curve 1, Fig. 1) and Balke and Hamielec⁴ with $[I_0] = 0.0258 \text{ mol/L}$, $T = 50^{\circ}\text{C}$ (curve 2, Fig. 1) without chain transfer agent. Curve 3 shows our experimental (○) and calculated results (full line) obtained with $[I_0] = 0.00188 \text{ mol/L}$ and $[\text{CTA}] = 0.0159 \text{ mol/L}$. The value of $C_x = k_{tr}/k_p$, which determines the weight-average molecular weight M_w , was first determined to obtain a calculated M_w value close to the experimental one (i.e., 108,000). CTA efficiency was then adjusted to obtain the best fit of the conversion curve (Fig. 1, curve 3) with the experimental data.

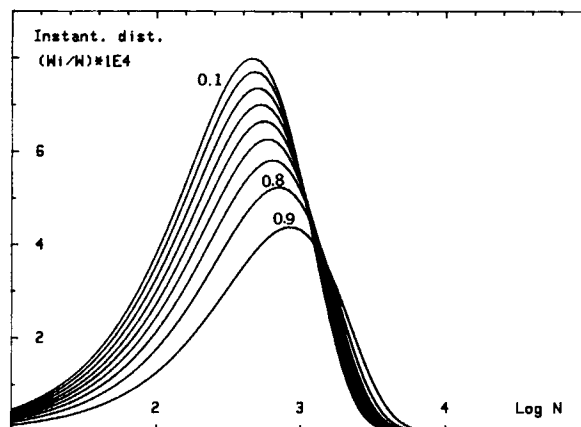


Figure 2 Predicted instantaneous molecular weight distribution for different steps of conversion for MMA polymerized at 60°C .

The theoretical curve was calculated with:

$$\text{a CTA efficiency } f_{tr} = 0.961$$

$$\text{a CTA constant } C_x = 1.26.$$

These results indicate that during the transfer process, 4% of the GDMA^o radicals do not participate to the polymerization. As a consequence, one can observe a decrease of the polymerization rate and the disappearance of the strong gel effect characteristic of PMMA polymerization.

The C_x value is much more important than those of $C_m = k_{tm}/k_p$ used by Cardenas and O'Driscoll¹³ ($0 < C_m < 10^{-3}$) because this author considers the transfer to the monomer. Unfortunately, they did not give any value for $C_s (=k_{ts}/k_p)$.

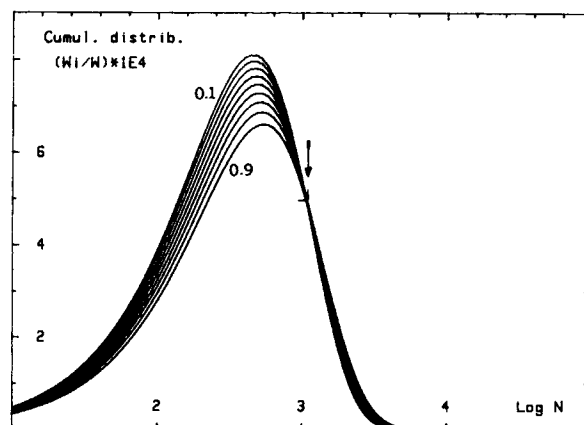


Figure 3 Predicted cumulative molecular weight distribution for different steps of conversion for MMA polymerized at 60°C .

The instantaneous and cumulative molecular weight distributions are plotted for different steps of the polymerization (10–90%) on Figures 2 and 3. One can observe a small shift of the maximum on the X axis. This is characteristic of a heterogeneity index that remains constant during the polymerization. In other words, the cumulative distribution does not appear very broad, even at a high degree of conversion and the high molecular weight tail, characteristic of polymers obtained without CTA, is no longer observed.

To summarize, the use of a CTA to produce an optical fiber preform has the advantage of facilitating the control of the polymerization process, and leads to a more homogeneous material. Values obtained for f_{tr} and C_x allow to run a program that predicts the polymerization kinetics and the molecular weight distribution in good agreement with experimental results.

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