

BULK POLYMERIZATION OF METHYL METHACRYLATE IN A KNEADER REACTOR

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Abstract

The bulk free radical polymerization of methyl methacrylate (MMA) or the bulk free radical copolymerization of MMA based monomer recipes face a gel effect (Trommsdorff's effect) and exothermicity. The kneader reactor offers a perfect combination of surface renewal and evaporative cooling to control temperature at high conversion (85 to 95%).

This type of reactor can be tested batch-wise to optimize the recipe, such as concentrations of initiator and of chain transfer agent. A simulation program was correlated to experimental batch data to determine the optimum concentrations of initiator and of chain transfer agent to target a given molecular weight.

Introduction

The aim of this study is to correlate the molecular weight produced in a kneader reactor with a computer program. The kinetics code refers to differential scanning calorimetry (DSC) measurements carried out between 135 and 165°C (1). Reaction system is the bulk free radical polymerization of methyl methacrylate. The auto-acceleration of the reaction rate is a major parameter to be considered for scaling up a reactor especially in the case of absence of any solvent. This phenomenon, well known as Trommsdorff's or gel effect, may also influence the molecular weight at high conversion. The reaction has been studied in a large range of temperatures, below and above the glass point ($T_g = 110^\circ\text{C}$).

High volume kneaders are used for thermal processing of a broad range of viscous and crust-forming materials since 30 years. Self-cleaning and surface renewal are particularly appreciated for the conduction of bulk (co-)polymerizations. The self-cleaning assures that product will not stay in dead zones to avoid any thermal time dependant degradation. The surface renewal allows the monomer to evaporate homogeneously from the viscous phase to cool down the exothermic reaction and the kneading dissipation energy. The evaporated monomer is condensed in a dome positioned just above

the kneader reactor. The monomer reflux goes back to the reactor and is mixed again into the reaction mass. This so called "evaporative cooling" is a powerful technique to scale-up reactors with the guarantee of a controlled product temperature. But it is clear that the evaporative cooling can only be efficient if the chance is given to the monomer to get out from any local portion of polymeric mass. This is the technical advantage of the kneader reactor to assure a constant and homogeneous surface renewal even at high conversion and especially when the Trommsdorff's effect occurs.

The same principal can be realized for copolymerization. One monomer evaporates to maintain the product temperature constant and is condensed back (reflux) to the reaction mass after the cooling effect.

The kneader reactor exists in batch and continuous versions. The batch configuration is optimal to conduct experimental studies for developing recipes and to get time dependant profiles such as temperature, torque, conversion and molecular weight. The continuous mode has two major configurations: plug flow and back mixed behaviors. The new concept for bulk free radical (co-) polymerizations is the use of the continuous back mixed kneader reactor. During evaporative cooling, it permits to mix the refluxed monomer homogeneously into the polymeric mass avoiding any shifting of recipe in the copolymer composition.

Kneader reactors are able to process high viscous polymeric masses below and above the glass point of the product. Below the glass point, the kneader can cut the high viscous phase into small free-flowing particles at conversion of approximately 60 %. This cutting or granulating effect avoids the reactor to face high torque due to the free-flowing property of the cut / granulated particles. The granulation in the kneader reactor is strongly dependant on the molecular weight. High molecular weights tend to granulate easier. This point is discussed later. A disadvantage of this technique is that the particles have to be molten again for the devolatilization step following the reaction. A further disadvantage is the vacuum mode to establish a low product temperature. Vacuum creates oxygen leaks into the reactor and contaminates the reaction.

The alternative is the (co-) polymerization above the glass point giving the possibility to devolatilize the discharged melt by flashing into a devolatilizer directly after the

reactor. In order to avoid too high torque the reaction temperature shall be minimum 20°C above the glass point. Pressurized reactors permit to establish a targeted temperature by adjusting nitrogen pressure. In continuous mode the discharge twin screw is designed or combined with a gear pump to seal the reactor at the outlet. Oxygen contamination is eliminated due to overpressure in the reactor.

Experimental

The experiments were conducted in batch kneader reactors with total volume comprised between 3 and 12 liters. The reactor has a double jacket on the casing and actively heated shaft(s). A cooled dome is put on the reactor and condensate the evaporated monomer back to the reactor chamber (reflux). Since an increasing vapor load in the dome needs more cooling surface for condensing the monomer, there is a height limit to which the dome surface is used for cooling. Thus it is possible to optically monitor the vapor load. When the Trommsdorff's effect occurs, the level of monomer vapor reaches a maximal value, which can be estimated. Based on these observations the reaction rate can be estimated at any time during the reaction (figure 1).

Table 1 summarizes the reaction conditions tested in this study. Experiments 1 to 5 were carried out at a temperature above the glass point and were initiated with di - tertio-butyl peroxide (DtBP). Experiments 6 to 8 were carried out below the glass point and were initiated with Perkadox 16. All experiments conducted with a chain transfer agent were made with lauryl mercaptane (n - do - decanethiol, n - DDT). The concentrations of initiator (CI) and of chain transfer agent (CT), the wall temperature of jacket and shaft (T_w), the absolute pressure in the reactor (p) and the product range temperature during the evaporative cooling up to the end of reaction (T) are given. Two different external laboratories executed the molecular weight analysis (M_w values exp1 and exp2). The calculated molecular weight in weight (M_w calc) is the result of the computer simulation by integrating the molecular weight curve as a function of conversion. The kinetics code (1) was completed with a transfer constant on the chain transfer agent k_{tT} by using following equation:

$$k_{tT} = 0.78 k_p(X, T) \quad (1)$$

$k_p(X, T)$ is the propagation constant as a function of conversion X and temperature T .

Results and discussion

In general all batch experiments delivered high conversions in the region 85 - 90 % at temperatures below the glass point and in the region 90 to 95 % above the glass point. Below the glass point, the well-known glass effect limits the conversion at approximately 90 %. Schulz and Harborth (2) measured a final conversion of 88 % for the bulk polymerization of MMA at 50°C. Above the glass point, the depolymerization rate limits the final conversion. Referring to (1) the theoretical conversion at equilibrium is 95 % at 180 °C. We can say that the conversions at equilibrium in the kneader reactor seem to correlate with the theoretical values of reference (1). This result is in contradiction with what was stated in reference (1) showing that DSC measurements were characterized by equilibrium conversions much lower than the theory.

The first experiment of table 1 is carried out in absence of chain transfer agent and at high temperature (above T_g); as a result high molecular weight is obtained.

In the experiments 2 to 5 (again above T_g) the concentration of chain transfer agent n - DDT was gradually increased giving a corresponding decrease of molecular weights.

Experiments 6 to 8 were conducted at temperatures below the glass point. Experiment 8 (figure 4) with $M_w = 350$ kg/mol was the easier test for granulating or cutting the polymeric mass into small free-flowing particles. The specific granulation energy was in that case 0.35 MJ/kg PMMA and the maximum specific torque 33 Nm/liter machine. Experiments 6 and 7 showed very difficult granulation due to low molecular weights. These results show that it is not possible to produce PMMA below the glass point for a targeted molecular weight of 70 kg/mol. For that purpose the only possibility is to process at temperatures above the glass point.

The calculated molecular weights are between the experimental values M_w exp1 and M_w exp2 (see table 1). Index of polydispersity IP was for all experiments in the region 2.0 to 2.3.

Figure 2 shows different calculated profiles upon the time for the first batch experiment listed in table 1. The total reaction time is 25 minutes at $Z = 1$. Monomer conversion X , initiator conversion X_I , reaction rate $-dH/dt$ and molecular weight M_w profiles show a strong calculated gel effect. The integration of the calculated molecular weight curve as a function of conversion gives M_w calc = 194 kg/mol. The experimental values M_w exp1 and M_w exp2 are 175 and 265 kg/mol. During the auto-acceleration of the reaction rate, the vapor level in dome increased and is presented in figure 1. The

experimental points are vapor levels visualized and estimated into the condensation dome. $Y = 1$ represents the total height of the condensation dome. The line on figure 1 represents the calculated vapor level in the condensation dome considering exothermicity and dissipation kneading energy.

Figure 3 shows temperature and torque profiles of the first batch experiment listed in table 1. The total reaction time is 25 minutes at $Z = 1$. Torque is expressed in bar, which is the pressure difference on the hydraulic drive. The hydraulic drive has a specific torque of 11.13 Nm/bar. That value permits to calculate the torque in Nm. This figure 3 shows good correlations between experimental points and calculated curves. The calculated temperature curve begins at 22 °C and the experimental temperature points begin at 120 °C. The explanation to this is that the kneader reactor was fed at hot and the thermal inertia of the massive machine disturb the temperature measurement. The calculation of the torque is based on following equation (here units are Nm):

$$\text{Torque} = \frac{1.14 v_s \phi n D^2 (D - d) \eta L}{\delta} \quad (2)$$

The number of shaft(s) v_s , the fill level in the kneader reactor ϕ , the rotation speed of the shaft(s) n , the casing inside diameter of the reactor D , the outside shaft diameter d , the viscosity η , the length of process room L and the clearance δ permit to calculate the torque profile during the polymerization. The viscosity model taking into account the shear rate, the conversion, the temperature and the molecular weight refers to (1). The shear rate is estimated with (units s^{-1}):

$$\dot{\gamma} = \frac{\pi D n}{\delta} \quad (3)$$

Figure 4 shows different calculated profiles upon the time for the last batch experiment listed in table 1. The total reaction time is 160 minutes at $Z = 1$. Monomer conversion X , initiator conversion XI , reaction rate $-dH/dt$ and molecular weight Mw profiles show a very strong calculated gel effect. The calculated molecular weight Mw is 350 kg/mol before the gel effect and corresponds to the experimental value. The simulation curve Mw shows a strong increase just after the gel effect going above 2000 kg/mol. This calculated molecular weight increase could not be confirmed with that experiment. The granulation or the cutting of the polymeric mass occurred at conversion 60%.

From table 1 we can say in general that the computer program predicts the molecular weight with a pretty good correlation. A third laboratory was consulted at the end of this study to determine the molecular weight of some samples. Those experimental values are not listed in this

paper, but they tend to confirm the values Mw_{exp2} of table 1. Based on that information, we suggest in the future to lower a little bit the proportional factor in equation 1.

Summary

This study proposes a new technique for the bulk polymerization of methyl methacrylate (MMA) or for the bulk copolymerization of MMA based monomer recipes. The kinetics code proposed in reference (1) and completed with this study is a good tool to predict targeted molecular weights.

Nomenclature

CI	concentration of Initiator, mol/m ³
CT	concentration of Chain transfer agent
D	casing inside diameter of reactor, m
d	shaft outside diameter of reactor, m
n	rotation speed of reactor, rps
k_{tT}	kinetic transfer constant, m ³ mol ⁻¹ s ⁻¹
k_p	kinetic propagation constant, m ³ mol ⁻¹ s ⁻¹
Mw	molecular weight in weight, kg/mol
p	absolute pressure in reactor, mbar abs
T _g	glass point, °C
T	temperature, °C
T _w	wall temperature of reactor
X	monomer conversion, -
XI	initiator conversion, -
Y	height of vapor level, -
v_s	number of shaft(s), 1 or 2, -
ϕ	fill, -
η	viscosity, Pas
δ	clearance in reactor, m
$\dot{\gamma}$	shear rate

References

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Key words

Bulk, free, radical, polymerization, copolymerization, methyl methacrylate, MMA, PMMA, kneader reactor, back-mixing

n°	[mol/m ³]	[mol/m ³]	[°C]	[mbar abs]	[°C]	Mw [kg/mol]		
	CI	CT	Tw	p	T	exp1	exp2	calc
1	25	0	180	3500	142-162	175	265	194
2	12.5	17.5	155	3500	130-160	-	78	66
3	34	50	145	4700	170-181	22	28	25
4	34	100	145	3700	162-177	15	19	17
5	34	116	151	4500	161-171	-	19	13
6	50	17.5	50	320	53	-	94	78
7	50	70	45	165	45	-	31	26
8	12.4	0	50	300	47	-	350	350

Table 1: List of batch experiments, IP are 2.0 – 2.3, Initiator for experiments 1-5 : DtBP, Initiator for experiments 6 - 8: Perkadox 16, Chain transfer agent : n-DDT.

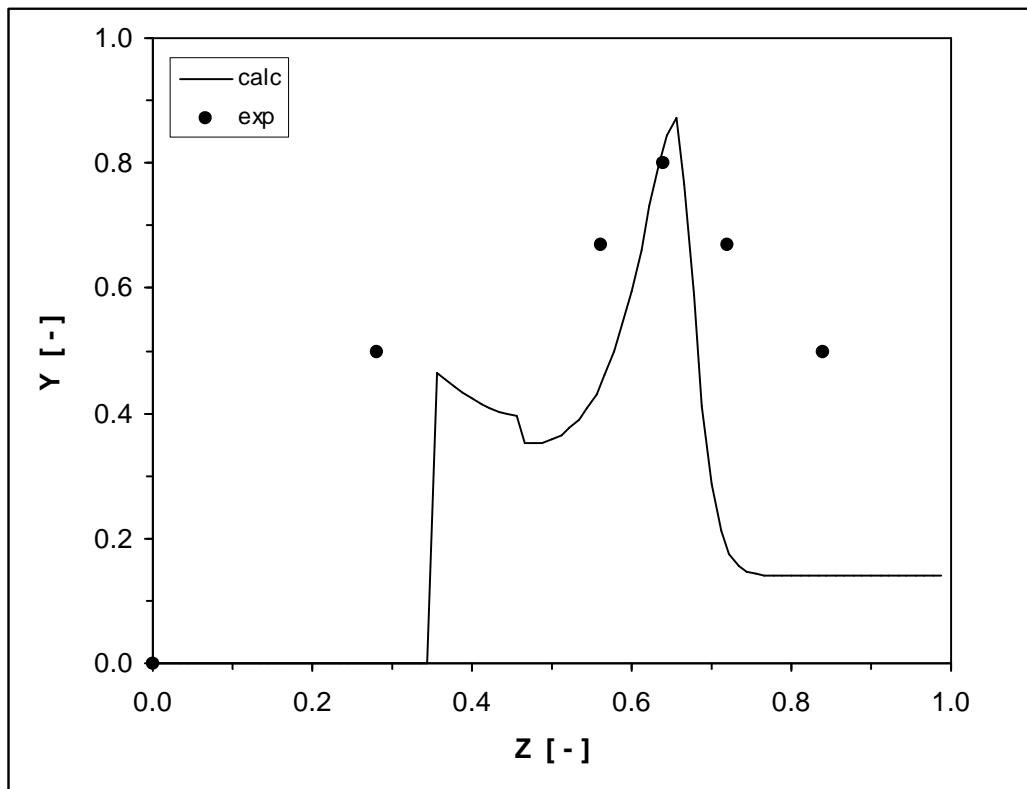


Figure 1: Experiment n°1 of table 1, total reaction time = 25 min at $Z = 1$. Y represents the height of the vapor level inside the condensation dome (without dimension).

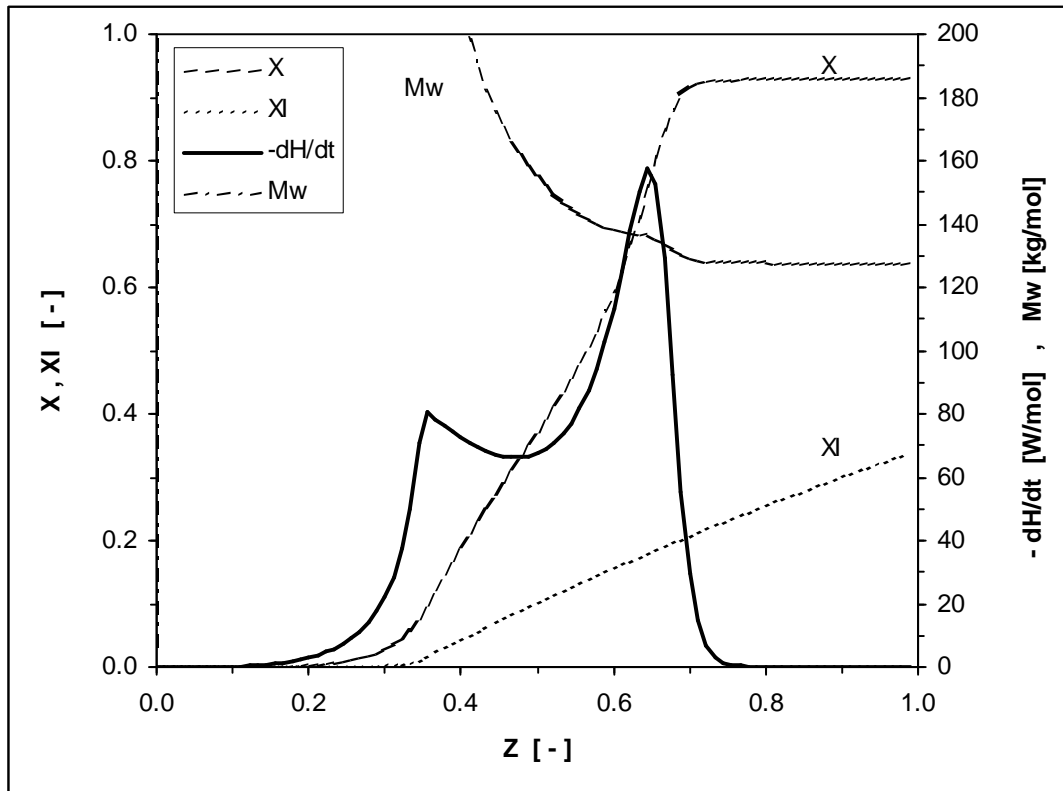


Figure 2: Experiment n°1 of table 1, total reaction time = 25 min at Z = 1. Different calculated profiles upon time.

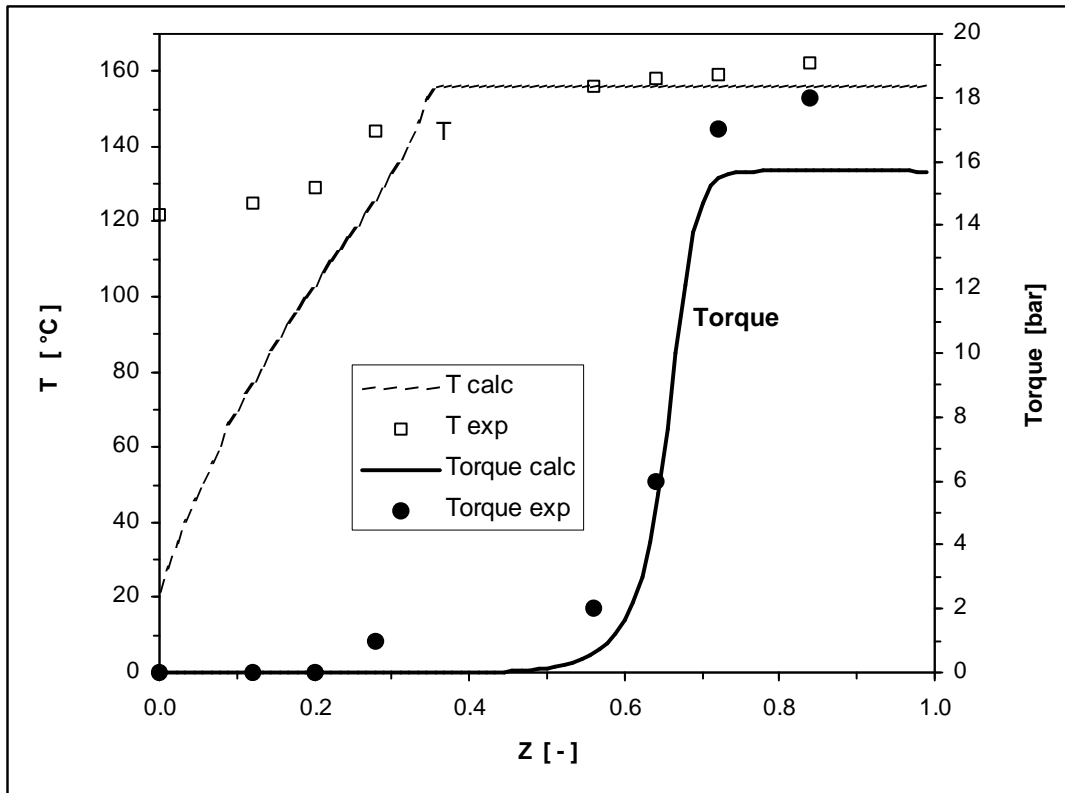


Figure 3: Experiment n°1 of table 1, total reaction time = 25 min at $Z = 1$. Temperature and Torque profiles upon time, calculated and experimental values.

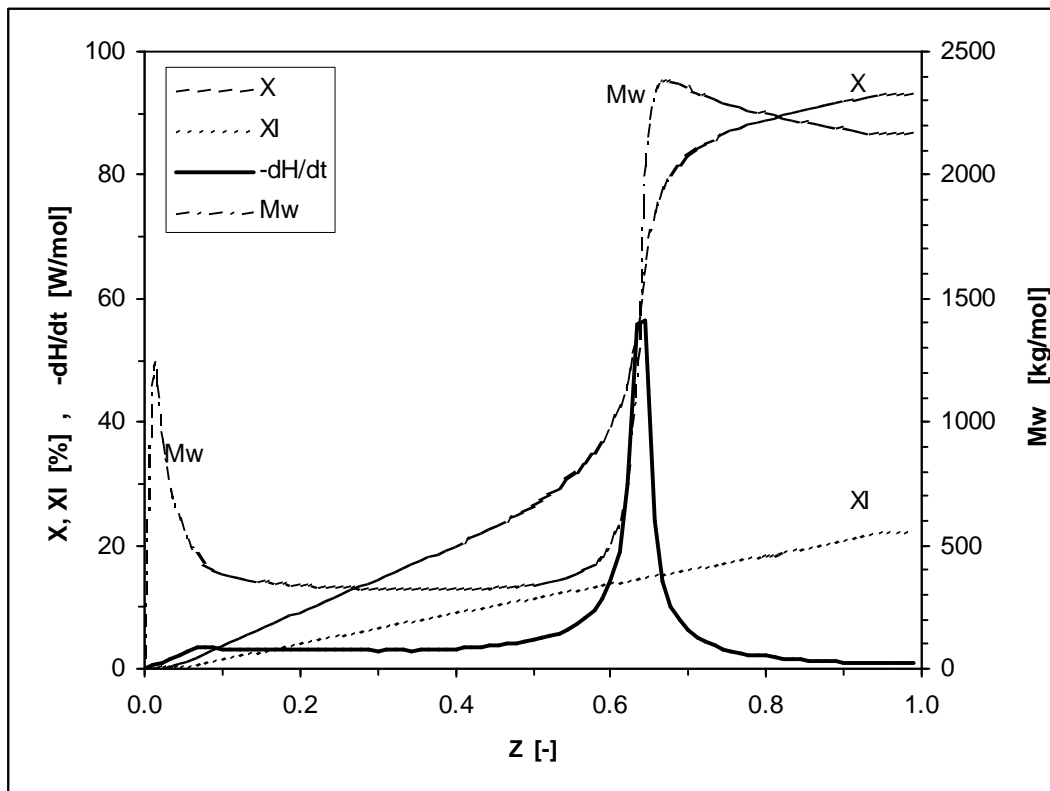


Figure 4: Experiment n°8 of table 1, total reaction time = 160 min at $Z = 1$. Different calculated profiles upon time.