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# Isothermal and non-isothermal polymerization of methyl methacrylate in presence of multiple initiators

Marco Biondi[1], Assunta Borzacchiello[2], Paolo Antonio Netti*,[1]

*Department of Materials and Production Engineering, University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy*

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ABSTRACT

Methyl methacrylate (MMA) polymerization is a diffusion-controlled reaction, characterized by a strong gel effect, which may cause uncontrolled heat generation and the thermal runaway of the process. For applications to industrial polymerization, kinetic control is particularly important and difficult to achieve due to the interplay between heat development and diffusional control occurring during polymerization. Sustaining the polymerization reaction (i.e. enhancing heat exchange) is a promising strategy to control MMA polymerization kinetics. In particular, different initiators triggering polymerization at different times can be used, thus reducing the possibility of thermal runaway by engineering temperature history and initiator nature/concentrations. There are few models accounting for the presence of multiple initiators and non-isothermal conditions. Therefore, a new, simple semi-empirical model, relating degree of conversion and polymerization rate to time and temperature, was developed. To validate the model, DSC tests were performed in isothermal and non-isothermal conditions, thus deriving the heat developed during polymerization. Model parameters were calculated from isothermal DSC experiments, and the model was predictive of monomer conversion in non-isothermal conditions in presence of single initiators and the mixture of them. Results indicate that, by varying formulation parameters (temperature history and initiator concentrations), polymerization kinetics may be optimized.

## 1. Introduction

Bulk free radical polymerization is a versatile process, which can be carried out on many monomers and in a wide range of temperatures. Free radical polymerization occurs in three steps, namely initiation (formation of free radicals because of initiator fragmentation), propagation (shifting of the reacting site on the chain end during monomer conversion) and termination, and is characterized by a strong increase of the system viscosity while the monomer is converted. In these conditions significant changes of mass and heat transfer occur. The reaction is characterized, especially at high monomer conversions, by conversion-related diffusional hindrances of the different reacting species, namely gel (or Trommsdorff), glass and cage effects [1–6]. Gel effect is related to the selective reduction of termination over propagation rate as termination step occurs when two growing (macro)radicals collide, and is therefore more sensitive to the mobility of macromolecules, while no appreciable effect on monomer mobility takes place. The net effect is a sharp increase in polymerization rate/heat generation, due to incipient macromolecular entanglement. Gel effect is particularly apparent in the bulk polymerization of methyl methacrylate (MMA), and is highly undesired in industrial applications as may lead to the thermal runaway of the process, thus causing depolymerization and plugging of equipment [1,7,8]. Glass effect occurs because glass transition temperature of the reacting mixture ($T_g$) increases with increasing monomer conversion. When $T_g$ equals polymerization temperature, also monomer mobility is reduced thus hindering also propagation events. In these conditions, occurring at later conversion stages, monomer diffusion is hindered, and the reacting solution anneals before 100% monomer conversion due to an extreme increase of the medium viscosity [2,9–11]. Finally, cage effect occurs when even the mobility of initiator radicals is hindered, thus preventing initiation events. This is detrimental to initiator efficiency, and affects monomer conversion and polymer molecular weight [11–14]. Glass and cage effects take place when polymerization is carried out at temperatures lower than the $T_g$ of the polymer, which makes the diffusional control predominant.

In the case of MMA polymerization for industrial applications, the kinetic control is particularly important since chemical reac-

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* Corresponding author. Current address: Interdisciplinary Research Centre on Biomaterials (CRIB), University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy/Italian Institute of Technology (IIT), via Morego 30, 16163 Genoa, Italy. Tel.: +39 0817682408; fax: +39 0817682404.

*E-mail address:* nettipa@unina.it (P.A. Netti).

[1] Current address: Interdisciplinary Research Centre on Biomaterials (CRIB) University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy/Italian Institute of Technology (IIT), via Morego 30, 16163 Genoa, Italy.

[2] Current address: Institute of Composite and Biomedical Materials, CNR and CRIB, University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy.

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tion and shaping occur simultaneously. The kinetic control is very difficult to achieve due to the highly exothermic nature of the reaction and to the aforementioned diffusional obstacles occurring during polymerization. This leads to uncontrolled temperature growth, process instabilities, monomer loss/boiling and uneven molecular weight distribution, and induces residual stresses and voids resulting in worsening of product quality/process efficiency. In addition, these problems are more significant with increasing product dimension/decreasing surface:volume ratios.

The optimization of MMA polymerization relies on many engineering variables such as temperature history, feed concentrations, product size, process times and may improve commercial potential/product quality, also reducing waste generation and production costs [15–19]. The kinetic control of MMA polymerization may be achieved by sustaining the polymerization process, thus enhancing heat exchange. To this end, a possible strategy is the contemporary use of different initiators triggering initiator scission at different times with the aim of distributing heat generation, thus reducing the possibility of thermal runaway under an optimized temperature history [20–26]. In addition to this, nature and concentration of initiators, and thermal history of the reacting system, are crucial parameters for the optimization of MMA polymerization.

There is vast literature, based on fundamental and empirical approaches, dealing with gel and glass effects [27–30], together with reviews focused on process improvement by mathematical modeling [31–33]. Some models attempt to correlate kinetic constants [8,34,35], or transport properties of polymer and monomer [36–38] with conversion, temperature, free volume/chain end mobility [6,37–41], or to view chain growth as a statistical phenomenon leading to different states based on some relevant kinetic parameters, or on diffusion/reptation theories [42–48]. More recently, attention was paid to non-isothermal and semi-batch conditions, which are extremely important in the industrial practice [49–54]. Some models consider the presence of different initiators or mixture of initiators, and other models take into account non-isothermal conditions [25,45,55–60]. To our knowledge, however, results on the contemporary presence of multiple initiators and the presence of dynamic conditions are still few. It must also be underlined that empirical approaches are more successful compared to molecular modeling as reviewed by Tefera et al. [61,62].

In this context, the aims of this work were the quantification and the prediction of heat generation/conversion history during MMA polymerization in presence of multiple initiators and in both isothermal and dynamic conditions. A simple semi-empirical model relating two state variables (degree of conversion and polymerization rate) to time and temperature was developed. In particular, in this work both the simultaneous presence of different initiators, used in the industrial practice, and non-isothermal temperature profiles were contemporarily taken into account in a simple, semi-empirical model. To validate the model, DSC tests were performed in both isothermal and non-isothermal conditions and used to calculate the heat generation associated to monomer conversion. Model parameters were estimated after isothermal DSC experiments, while dynamic conditions were predicted by the model, without any fitting, in presence of single initiators and the mixture of them.

## 2. Experimental

### 2.1. Materials

MMA containing 0.1% terpinolene (Sigma–Aldrich, Italy) as a polymerization inhibitor, and poly(methyl methacrylate) (PMMA) were provided by Clax Italia (Italy). Three non peroxide initiators, ADVN 2,2′-azobis (2,4-dimethylvaleronitrile), AIBN 2,2′-azobis (isobutyronitrile), ACHN 1,1′-azobis (cyclohexanecarbonitrile), namely Vazo®52, Vazo®64 and Vazo®88, were purchased from DuPont (Canada). Vazo® initiators decompose with first-order kinetics and produce less energetic radicals compared to peroxides, so they induce less branching and cross-linking [63]. Grade numbers of Vazo® initiators represent the temperature, expressed in Celsius degrees at which initiator half-life (the time necessary for initiator concentration to decay to half of its initial value) in solution is 10 h. Vazo® initiators thermally decompose forming two primary radicals triggering MMA polymerization. The initiator concentrations employed for Vazo®52, Vazo®64, Vazo®88 were $5.25 \times 10^{-5}$ mol/L MMA, $6.24 \times 10^{-5}$ mol/L MMA, $1.14 \times 10^{-4}$ mol/L MMA, respectively. These concentrations were chosen as they are used in the industrial practice and, to simulate the actual conditions, the same initiator concentrations were used for the experimental plan. In particular, it must be underlined that prolonged induction times are helpful for the system to reach thermal equilibrium before polymerization onset. The reactants were used as received.

### 2.2. Methods

To study the polymerization kinetics of MMA and determine the $T_g$ of PMMA, differential scanning calorimetry (DSC) experiments were performed (2910 DSC, TA Instruments, Wilmington, DE, USA) under a constant 50 cm$^3$/min nitrogen flow. Samples were prepared at room temperature and inserted in hermetically sealed aluminum pans. Isothermal measurements were carried out for 3–20 h, depending on the temperature and the initiator used, between 60 and 90 °C (step: 5 °C).

To determine the unreacted monomer fraction and the $T_g$ of the partially and completely cured polymer, two dynamic scans were performed after each isothermal test (temperature range: 40–180 °C; heating rates: 1 °C/min for the first scan; 10 °C/min for the second scan). In particular, $T_g$ of the partially cured polymer was calculated as the point of the thermogram immediately preceding the onset of polymerization after the first scan. Indeed, in the case of diffusion-controlled reactions, the residual monomer can polymerize only when the system temperature exceeds the $T_g$ of the reacting mixture. The $T_g$ of the fully cured system was the temperature corresponding to the inflection point of the DSC thermogram obtained by the second dynamic scan.

To minimize monomer evaporation during experiments, kinetic tests were performed on a 30% (w/v) solution of PMMA in MMA. Dynamic experiments were carried out, in presence of one initiator, and with the mixture of the three Vazo®s, added with halved initial concentrations. Heating rate was 0.5 °C/min. The conversion and rate resulting from dynamic experiments were compared, without any fitting, to the predictions of the model obtained by using the parameters as derived from isothermal experiments after fitting to the experimental results. To assess mass conservation during DSC experiments, samples were weighed before and after each experiment, and the mass loss evaluated.

## 3. Kinetic modeling

MMA polymerization is a free radical chain reaction, which can be schematized in three steps: initiation, propagation and termination. The rate of monomer disappearance is considered to be coincident with the rate of polymerization, i.e. with the rate of propagation. If the quasi stationary state approximation (QSSA) holds, the concentration of radicals initially increases, but almost instantaneously reaches a steady value. Another basic assumption needed to build the model is the long chain hypothesis (LCH), which assumes that the radical chain is composed by a high num-