

The reaction locus in supercritical carbon dioxide dispersion polymerization. The case of poly(methyl methacrylate)

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Abstract

The problem of determining the reaction locus in the supercritical carbon dioxide dispersion polymerization of methyl methacrylate is considered. For this, two limit models are comparatively evaluated using experimental data of polymerization kinetics and molecular weight distribution. The two models take opposite assumptions with respect to the relative rate of interphase radical transport with respect to the radical life time, which lead to different relative importance of the polymerization in the continuous or in the dispersed phase. The model parameters have been estimated using independent literature sources so as to ensure genuinely predictive modelling. The results clearly indicate that the interphase transport of the active chains is a key process in determining the reaction locus and it has to be carefully considered in order to reliably simulate any polymerization process of this type.

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1. Introduction

Dispersion polymerization in supercritical CO₂ appears to be a promising alternative to the solvent-intensive, heterogeneous polymerization processes largely in use in industry (Canelas and DeSimone, 1997; Ajzenber et al., 2000). Various monomers, ranging from conventional vinyl monomers to special fluorinated ones, can be polymerized this way (Canelas et al., 1996; Shiho and DeSimone, 2000, 2001; Wang et al., 2003). Moreover, effective stabilizers have been reported and cheaper and better ones are continuously investigated (DeSimone et al., 1994; Schaffer et al., 1996; Giles et al., 2000; Christian and Howdle, 2000; Li et al., 2000). Fundamental research work is still needed in order to better clarify the physico-chemical phenomena underlying this process before a reliable scale-up can be achieved, in particular when a close control of the product quality is required.

Mathematical modelling, combined with suitable experimental measurements, can provide a useful tool to elucidate the process mechanisms and their impact on product properties. Very few models have been proposed so far and the only comprehensive one has been recently developed by Chatzidoukas et al. (2003), where the reactions in both the continuous (supercritical) and the dispersed (polymer) phase are accounted for.

One aspect which is currently under debate refers to the polymerization loci. Since in general the initiator is soluble both in the dispersed polymer phase and in the continuous supercritical phase, the radicals are formed in both phases. In the case where the chain radical growth and termination process (i.e., the chain life) in the continuous phase is slower than its transport to the dispersed phase, most of the polymer is made in the polymer particles. This is the typical situation for water emulsion polymerization. On the other hand, we could have the opposite situation whereby a good fraction of the polymer is made in the continuous phase, and therefore exhibits different characteristics (e.g. molecular weight) than the polymer made in the dispersed phase. The latter is the

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situation considered by Saraf et al. (2002) for PVDF in order to explain the clear bimodality which is typically found for this polymer in the case of precipitation polymerization. The same assumption has been made in the model mentioned above (Chatzidoukas et al., 2003; Kiparissides et al., 1997) where the growing radicals are assumed to remain segregated in the phase where they have been originally formed through the initiator decomposition.

In this work, we investigate this issue by developing two different models, corresponding to two opposite limiting conditions in terms of interphase radical transport. The first one conforms to the previously mentioned segregation limit, thus assuming that interphase radical transport is much slower than the chain life. In the second model it is assumed that the interphase radical transport is extremely fast, so that equilibrium conditions are achieved for the active species. The two models are referred to in the following as “radical segregation” model (RS) and “radical partitioning” model (RP), respectively. It is worth noting that the RP model is different from the previously developed “one-locus” model (Rosell et al., 2001; Bonavoglia et al., 2002) since, even though in both cases the transport rate is infinite, in the latter the radicals were assumed to diffuse only from the continuous to the dispersed phase, coherently with the assumption of no solubility of the polymer chains in the continuous phase.

The comparative evaluation of the two models is carried out using our own experimental data for methyl methacrylate dispersion polymerization in supercritical CO₂ using AIBN as initiator and Krytox as stabilizer. It is to be noted that the values of all the kinetic parameters in the model have been either taken from independent and reliable literature sources or estimated through fundamental relationships. This allowed us producing truly predictive simulations and therefore achieving a reliable comparative evaluation of the two limiting models.

2. Experimental set-up and procedure

All experiments were carried out in the lab-scale unit described in (Rosell et al., 2004). This is a thermostated, stainless-steel reactor, equipped with a magnetically coupled mechanical stirrer and a mass flow meter used to accurately measure the injected amount of CO₂. Recipe and operating conditions for considered experimental runs are summarized in Table 1. Methyl methacrylate and 2,2'-azobis(isobutyronitrile) (AIBN) were obtained from Fluka (Switzerland) and used as received. Carbon dioxide was obtained from Pangas (Switzerland) with analytical grade 4.5 (purity = 99.995%) and used as received. The stabilizer, Krytox 157 FSL, was supplied by Dupont (Switzerland) and used as received. To monitor the time evolution of the reaction, repeated experiments under the same conditions were carried out and interrupted at different time values. The amount of polymer produced was evaluated by gravimetry,

Table 1
Recipe and operating conditions of the experimental runs

<i>Initial amounts</i>	
MMA	= 30 g
CO ₂	= 320 ± 2 g
AIBN	= 0.33 g
Krytox	= 0.33 g
<i>Operating conditions</i>	
Temperature	= 65 °C
Pressure	= 140 ± 3 bar (initial value)
V _{reactor}	= 0.58 L

the particle size by SEM and the complete distribution of molecular weight (MWD) by GPC. More details about these characterization procedures can be found elsewhere (Rosell et al., 2004).

3. Model development

Two models representing two opposite extreme conditions in terms of interphase transport of active polymer chains are considered:

The radical segregation model (RS): The active chains spend their whole life in the same phase where they have been initiated. This model corresponds to the situation where, in each phase, the characteristic time for radical termination is much shorter than that for interphase mass transport.

The radical partitioning model (RP): The rate of mass transport between polymer particles and continuous phase is assumed to be infinitely fast for all species, so that thermodynamic equilibrium is established at every time during reaction. In general, the interparticle driving forces are such that radicals are transported from the continuous to the dispersed phase. However, the opposite is also possible as in the case of very short radicals produced in polymer particles. A notable example is the desorption of radicals produced by chain transfer to monomer in water emulsion polymerization. This situation corresponds to the case where the characteristic time for radical termination is large compared to that for interphase transport.

3.1. Model assumptions, kinetic scheme and thermodynamic modelling

The main model assumptions are as follows:

- (1) Two reaction loci are considered: the polymer-rich dispersed phase and the CO₂-rich continuous phase.
- (2) Low molecular weight species (solvent, initiator and monomer) undergo very fast transport between the

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