Emulsion Polymerisation of MMA Employing a Chain Transfer Agent of Low Environmental Impact: iso-Octyl-3-Mercaptopropionate

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The unseeded batch-emulsion polymerisation of methyl methacrylate (MMA) was investigated using the chain transfer agent iso-octyl-3-mercaptopropionate (iOMP), which exhibits a low environmental impact. The commercial iOMP is a mixture of over 10 isomers that proved adequate to control the molecular weights of poly(methyl methacrylate) with a decreasing evolution of both the number- and weight-average molecular weights along the reactions. The iOMP also affects the polymerisation kinetics as a consequence of the lower reactivity of the iOMP radicals with respect to the MMA-ended radicals. Experimental results were interpreted with the help of a first principles mathematical model.

Keywords: poly(methyl methacrylate), emulsion polymerisation, molecular weight distribution, chain transfer agent, iso-octyl-3-mercaptopropionate

INTRODUCTION

The final properties of homopolymers are mainly determined by their molecular weight distributions (MWD). In emulsion polymerisations, chain transfer agents (CTA) are normally required for reducing the high molecular weights that would be otherwise produced, due to the 'compartmentalisation' of free-radicals in the polymer particles.[1,2]

The most common CTAs used in the emulsion industrial processes are mercaptans with long hydrocarbon-chain. In order to guarantee the molecular weight control during the whole polymerisation reaction, the final latex normally contains a remnant CTA concentration, which compromises the product harmlessness. On the other hand, physical separation of the residual CTA from the final latex is difficult and costly. Therefore, the use of less toxic CTA than the normally employed mercaptans could be an alternative for controlling the MWD in emulsion polymerisation, with a reduction of the latex environmental impact.

Some important characteristics of CTAs employed in emulsion polymerisations are their water solubility, their mass transfer resistance to diffusion between phases and their activity expressed as reactivity ratios $C_X = k_{fX}/k_p$ in the polymer phase, where k_{fX} is the rate constant of chain transfer to the CTA and k_p is the rate constant of propagation. When CTAs of long hydrocarbonated chains are used in emulsion polymerisations, the CTA concentration in the polymer phase is normally below equilibrium and therefore the transfer reaction results diffusion-controlled. In practice, however, the typically used èffective' C_X values assume equilibrium conditions between phases, for both the CTA and the monomer, and are determined from batch experiments.[3-7]

According to the Safety Data Sheets, iso-octyl-3-mercaptopropionate (iOMP) is less odorous and toxic (hazard code GHS02) than other more common CTA-mercaptans, such as dodecyl mercaptans (hazard codes GHS02, GHS07, GHS08, and GHS09). The iOMP is normally commercialised as a mixture of several isomers, and it has not been extensively studied for controlling the MWD of polymer latexes. The use of iOMP in emulsion polymerisations was previously reported by Minari et al.,[7] Vail et al.,[8] Segall et al.,[9] Bobsein and Lindstrom,[10]

Kalinina and Kumacheva[11] and Hong et al.[12] Minari et al.[7] investigated the emulsion polymerisation of styrene (St) with iOMP as CTA. The utilised iOMP (from Aldrich Chemical, Milwaukee) was a mixture of more than 10 isomers, with 5 of them constituting more than 95 % of the total mass and four out of such five exhibiting similar chain transfer characteristics with St. Therefore, for modelling purposes, they assumed that the iOMP behaves as a binary mixture with two different C_X values, which resulted higher than the unity. Also, the different (and high) reactivity of the CTA-isomers produced polystyrene (PSt) with broad and bimodal MWDs at the end of a batch process without significantly affecting the St polymerisation rate.

With respect to the employment of iOMP as CTA in polymerisations involving acrylic monomers, Vail et al.[8] investigated the emulsion homo- and copolymerisations of MMA and n-butyl methacrylate (nBMA). The iOMP was treated as a pure compound, and the global effective C_X values for MMA and nBMA determined at 5 % monomer conversion were 0.4 and 1.6, respectively. Segall et al.[9] employed iOMP for synthesising a core-shell latex with a poly(benzyl methacrylate-co-styrene) core and a poly(n-butyl acrylate) shell, observing that the CTA concentration affected the particles' morphology. Bobsein and Lindstrom[10] suggested the use of high CTA concentrations (about 4 mol/100 monomer mol) of 3-mercaptopropionate esters, including iOMP, for synthesising acrylic polymers with controlled molecular weights. Also, Kalinina and Kumacheva[11] used an iOMP isomer (2-ethylhexyl-3-mercaptopropionate) for producing polymer films based on MMA and butyl acrylate with liquid inclusions. Unfortunately, these last articles did not report kinetic or molecular weights data along the polymerisation. More recently, Hong et al.[12] used iOMP in the emulsion terpolymerisation of St,

n-butyl acrylate and methacrylic acid with a polymerisable amphiphilic macromonomer as stabiliser and observed that the increase in the *i*OMP concentration produced both a reduction in the average molecular weights and a slight increase in the particle size.

The present work was developed by researchers of the Polymer Reaction Engineering Group (PREG) at INTEC. The PREG was created about 30 years ago by Prof. Gregorio Meira, and the main research fields are: (1) modelling, optimisation and control of industrial polymer processes; (2) microstructure characterisation of polymers by size exclusion chromatography; (3) characterisation of particle size distributions of polymer latexes by light scattering techniques and (4) synthesis and characterisation of polymer colloids for biomedical applications. Concerning the mathematical modelling and control of variables related to molecular microstructure (such as molecular weights, copolymer composition and degree of branching) in emulsion polymerisation, the following problems have been considered: (i) modelling and MWD control in the styrene polymerisation employing different CTAs[4,7,13]; (ii) modelling, optimisation and control of a reactor train for the production of styrene-butadiene rubber[14−18]; (iii) modelling and control of the acrylonitrile-butadiene copolymerisation[19−26]; and (iv) modelling of the isoprene polymerisation.[27,28]

The emulsion polymerisation of acrylic polymers with controlled molecular weights has a high interest in industrial applications such as coatings and adhesives. Also, the use of less toxic CTAs than those normally employed is promoted by the increasing environmental regulation. This work investigates the inclusion of *i*OMP, as a more ecofriendly CTA, in the isothermal batch emulsion polymerisation of MMA. The effect of *i*OMP on both the polymerisation rate and the MWD of the produced poly(methyl methacrylate) PMMA is investigated. The experimental results are interpreted in the light of a representative mathematical model.

EXPERIMENTAL

Materials

Distilled and deionised water was used throughout the work. The following reagents were used as received: MMA monomer (Aldrich, St. Louis, purity >99%) containing ≤30 ppm monomethyl ether hydroquinone as inhibitor; sodium lauryl sulphate (SLS) emulsifier (Cicarelli, San Lorenzo, Santa Fe, Argentina, 95% purity); potassium persulphate (KPS) initiator (Mallinckrodt, Mallinckrodt, Hazelwood, MO, 99% purity); sodium bicarbonate buffer salt (Anedra, San Fernando, Buenos Aires, Argentina, purity 99.7%); *i*OMP (Aldrich, Milwaukee, isomers mixture >99%); and hydroquinone (HQ) as polymerisation inhibitor (Fluka AG, St. Louis, >99% purity). A set of nine narrow polystyrene (Shodex, New York) standards in the molar mass range 10^3–10^6 g/mol was used for calibration of the size exclusion chromatography (SEC) system. Tetrahydrofuran (Cicarelli) was used as eluent in the SEC runs.

Polymerisation Experiments

Polymerisations were carried out in a 1 L jacketed glass reactor equipped with a digital thermometer, a reflux condenser, a stirrer, a sampling device and a nitrogen inlet. The reaction temperature was controlled at 70°C by manipulating the temperature of the fluid in the reactor jacket through a thermostatic bath. The stirring rate was 200 rpm.

Table 1. General recipe for the batch emulsion polymerisations of MMA at 70°C

Reagent	pphm[a]
MMA	100
*i*OMP	0–0.3–0.67–1.03–1.38
KPS	0.2
SLS	0.2
NaHCO$_3$	0.2
Water	397

[a] Parts per 100 monomer.

The general recipe is summarised in Table 1. The reactions involved varying amounts of CTA while other reagents concentrations were maintained constant. The polymerisations were carried out as follows. First, the emulsifier and the buffer salt were dissolved in 500 g of water and loaded into the reactor. Then, the mixture of monomer and CTA was loaded, and the temperature was stabilised at 70°C. The polymerisation was started by adding the initiator dissolved in the remaining water (10 g). The reactions were carried out under continuous N$_2$ bubbling and were stopped after 75 min by adding 5 mL of a 0.1 wt% HQ aqueous solution.

Characterisation

Samples were withdrawn during the reactions, and the following were measured: (i) monomer conversion (x), by gravimetry; (ii) average particle diameter $\bar{d}_\mathrm{p}$, with a Brookhaven BI-9000 AT dynamic light scattering photometer at a detection angle of 90°; and (iii) MWD and their averages ($\bar{M}_n$ and $\bar{M}_\mathrm{w}$), with a Waters 1515 chromatograph fitted with a differential refractometer Waters 2414 and a set of 6μ-styragel Waters columns, of nominal fractionation range 10^2–10^7 g mol^{-1}. The PMMA molecular weights were determined on the basis of the universal calibration calculated from the chromatograms of the PSt standards. The required Mark-Houwink constants in tetrahydrofuran at 30°C were directly taken from Kurata and Tsunashima [29] and are $K = 1.1 \times 10^{-2}$ mL g^{-1} and $a = 0.725$ for PSt and $K = 7.5 \times 10^{-3}$ mL g^{-1} and $a = 0.720$ for PMMA.

RESULTS AND DISCUSSION

Experimental

Table 2 summarises the final experimental results of x, $\bar{d}_\mathrm{p}$, $\bar{M}_n$ and $\bar{M}_\mathrm{w}$ obtained in the batch emulsion polymerisation of MMA with different *i*OMP concentrations (experiments MMA$_1$–MMA$_5$). The estimated final number of particles per liter of latex (N_p) is also presented in Table 2. Figure 1 shows the experimental evolution of x, $\bar{d}_\mathrm{p}$, $\bar{M}_n$ and $\bar{M}_\mathrm{w}$ (in symbols).

Table 2. MMA emulsion polymerisations at 70°C with varied *i*OMP concentrations. Final results for the main reaction variables

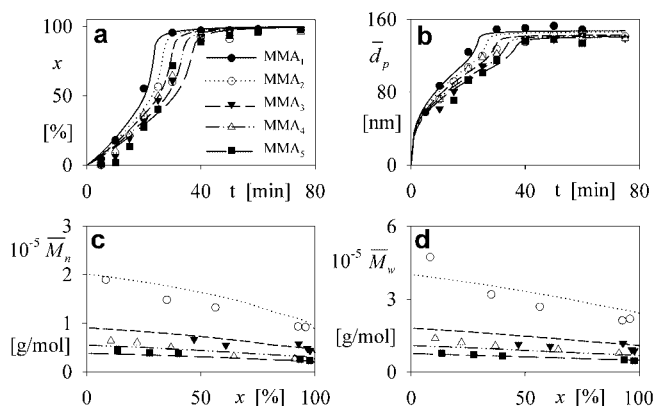|	MMA$_1$	MMA$_2$	MMA$_3$	MMA$_4$	MMA$_5$
*i*OMP (pphm)	0	0.30	0.67	1.03	1.38
x (%)	98.49	97.26	97.66	96.02	97.75
$\bar{d}_\mathrm{p}$ (nm)	150	142	139	140	136
$\bar{M}_n$ (g mol^{-1})	1 885 000	112 100	43 500	35 700	22 800
$\bar{M}_\mathrm{w}$ (g mol^{-1})	2 594 000	239 900	87 800	87 400	46 400
$10^{-16} N_\mathrm{p}$ (# L^{-1})	10.0	11.4	11.7	11.7	12.5

Figure 1. Evolution of x (a), $\bar{d}_p$ (b), $\bar{M}_n$ (c) and $\bar{M}_w$ (d) obtained in the batch emulsion polymerisations of MMA carried out at 70°C with varied *i*OMP concentrations.
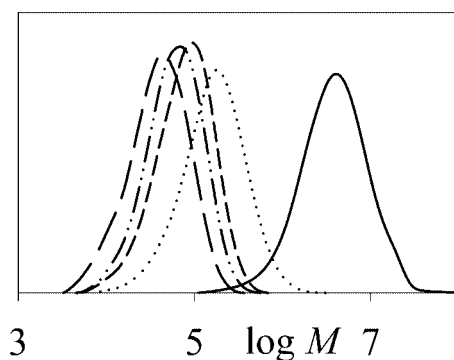

Figure 2. MWDs for the final PMMA obtained in the emulsion polymerisation of MMA with the presence of *i*OMP as CTA, compared with that of the PMMA produced without CTA (MMA$_1$). MMA$_1$ (——); MMA$_2$ (· · ·); MMA$_3$ (–· · –· · –); MMA$_4$ (– – –) and MMA$_5$ (— — —).

When final conversions are higher than 96%, the presence of *i*OMP reduces both the polymerisation rate (Figure 1a) and $\bar{d}_p$ (Figure 1b) but increases N_p (Table 2). The reduction of the polymerisation rate together with the increase in N_p could be due to (a) the desorption of *i*OMP radicals from the polymer particles and (b) the lower reactivity of the *i*OMP radicals with respect to the MMA-ended radicals. However, the water solubility of *i*OMP ($7.49 \times 10^{-3}\,\mathrm{g\,L^{-1}}$)[7] is too low to assume that the desorption of *i*OMP radicals from the polymer particles could affect N_p and the average number of radicals per particles ($\bar{n}$). Since the water solubility of MMA ($15\,\mathrm{g\,L^{-1}}$) is relatively high, one might specu- late that radicals produced by addition of MMA to *i*OMP radicals would exhibit an increased desorption ability. However, according to predictions from the Universal Functional Activity Coefficient (UNIFAC) method based on group contribution, water solubility of such species decreases with the successive incorporation of MMA units to the *i*OMP radical, and for this reason those radicals are also difficult to be desorbed. On the other hand, the lower reactiv- ity of the *i*OMP radicals with respect to the MMA-ended radicals also diminishes the propagation rate through a reduction in the global propagation rate constant. The reduction in the polymeri- sation rate due to the presence of *i*OMP affects the particle growth, thus prolonging the nucleation period and increasing the number of nucleated particles. (In the next section the reduced reactivity of the *i*OMP radical with respect to the MMA-ended radicals will be considered, and its effect will be evaluated on the basis of a mathematical model.)

Furthermore, final $\bar{M}_n$ and $\bar{M}_w$ are significantly reduced when increasing the *i*OMP initial concentration. Moreover, average molecular weights decrease along the reaction (Figure 1c and d), which is indicative of an *i*OMP accumulation (with respect to MMA) in the course of polymerisation (i.e. the CTA exhibits a rate transfer constant k_{fX} lower than the propagation rate constant k_p, thus resulting $C_X < 1$). This behaviour is opposite to that observed by Minari et al.[7] for the emulsion polymerisation of St, where $C_X \gg 1$, but consistent with the $C_X = 0.4$ reported by Vail et al.[8] for the polymerisation of MMA at 5% of conversion. These results are also more compatible with the lower reactivity reported when an electron accepting CTA (as the *i*OMP) reacts with a PMMA- radical than when it reacts with an electron donating PSt-radical, as a result of the polar effect on chain transfer.[30]

Figure 2 shows the final MWDs when the *i*OMP concentra- tion is increased from 0 to 1.38 pphm. For reactions employing *i*OMP, Figure 3 shows (in continuous traces) the evolution of the

measured MWDs along the reaction. Notice that as the reaction proceeds, the MWD is shifted toward lower molecular weight (M) as a consequence of the CTA accumulation with respect to the MMA.

Mathematical Model

Based on pioneer papers by Penlidis et al.,[31] Saldivar et al.,[32] Storti et al.,[33] Forcada and Asua,[34] and in particular Minari et al.[7] and Vega et al.,[19] a mathematical model was developed for the emulsion polymerisation of MMA in the presence of a CTA mixture to help interpret the experimental results. The mathe- matical model is presented in Appendix. The kinetic mechanism considers (i) initiation, propagation and termination in the aque- ous phase and (ii) propagation, chain transfer to the CTA and to the monomer and termination in the polymer phase.

The main model hypotheses are (a) the polymer particles are generated by both micellar and homogenous nucleation; (b) pseudo-steady state for the free-radicals in both the aqueous and
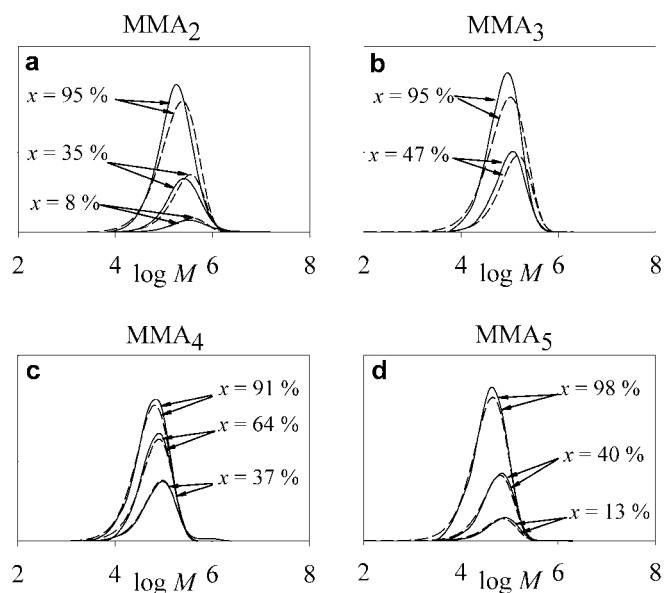

Figure 3. Measured (continuous traces) and predicted (dashed traces) MWDs along the MMA emulsion polymerisation for experiments MMA$_2$ (a), MMA$_3$ (b), MMA$_4$ (c) and MMA$_5$ (d).

the polymer phases; (c) the monomer is only consumed by propagation (long-chain hypothesis) in both the polymer and the aqueous phases; (d) the termination, propagation and transfer rate coefficients are diffusion-controlled; (e) monodisperse particle size distribution; (f) desorption from the polymer particles of monomeric radicals; (g) distribution of monomer and CTA between phases according to equilibrium with constant partition coefficients; (h) the CTA isomers exhibit different chain transfer constants; (i) all CTA isomers are equally distributed between the phases; (j) in presence of iOMP, the MWD is mainly determined by chain transfer to the CTA and is unaffected by the termination reactions; and (k) different reactivity of the primary CTA radicals ($X_i^\bullet$) with respect to the MMA-ended propagating radicals ($M_n^\bullet$).

While most of the model parameters were directly taken from literature, the homogeneous nucleation rate constant (k_{ho}), the rate constants for the radical absorption into the particles and the emulsifier micelles (k_a and k_m), the A_1 and A_2 coefficients of the diffusion-controlled termination rate constant (Equation A.23), the ratio between the mass transfer resistance in the water side and the overall mass transfer resistance for monomeric radicals (δ_M), the propagation rate constant of radicals $X_i^\bullet$ (k_{pX}), and

Table 3. Model parameters for the batch emulsion polymerisation of MMA with iOMP at 70°C

Parameter	Value	Refs.
A_1, A_2	−14.12, −0.98	Adjusted on the basis of Urretabizkaia et al.[39]
$A_s{}^a$	2.53×10^7 dm^2 mol^{-1}	Alhamad et al.[42]
$D_{Mw}{}^b$	1×10^{-5} dm^2 min^{-1}	Alhamad et al.[42]
δ_M	1.30×10^{-5}	Adjusted in this work
$[E]_{CMC}{}^c$	3×10^{-3} mol dm^{-3}	Alhamad et al.[42]
f^d	0.6	Salazar et al.[4]
$j_c{}^e$	10	Alhamad et al.[42]
$k_d{}^f$	1.30×10^{-3} min^{-1}	Salazar et al.[4]
$k_{po}{}^g$	6.24×10^4 dm^3 mol^{-1} min^{-1}	Beuermann and Buback[43]
k_{pX}	$0.0032\, k_{po}$	Adjusted in this work
$k_a = k_m$	2.24×10^{-2} dm min^{-1}	Adjusted in this work
k_{ho}	98.53 min^{-1}	Adjusted in this work
$k_{tw}{}^h$	2.10×10^9 dm^3 mol^{-1} min^{-1}	Nomura et al.[44]
$k_{tpo}{}^i$	2.10×10^9 dm^3 mol^{-1} min^{-1}	Nomura et al.[44]
k_{fXm1o}	6.45×10^3 dm^3 mol^{-1} min^{-1}	Adjusted in this work
k_{fXm2o}	2.75×10^4 dm^3 mol^{-1} min^{-1}	Adjusted in this work
$k_{fMo}{}^j$	4.93 dm^3 mol^{-1} min^{-1}	Clay and Gilbert[45]
K_{Mdw}^k	61.26	Alhamad et al.[42]
K_{Mwp}^l	2.54×10^{-2}	Alhamad et al.[42]
K_{Xdw}^m	7.67×10^4	Minari et al.[7]
K_{Xwp}^n	2.03×10^{-5}	Minari et al.[7]

a Emulsifier surface coverage capacity.
b Diffusion coefficient of monomer in the aqueous phase.
c Emulsifier critical micellar concentration.
d Initiator efficiency.
e Critical chain length of polymer radical formed in the aqueous phase.
f Initiator decomposition rate constant.
g Propagation rate constant at volume fraction of polymer in the particles <0.8.
h Termination rate constant of free-radicals in the aqueous phase.
i Termination rate constant in the polymer phase at low volume fraction of polymer in the particles.
j Rate constant for chain transfer to the monomer at volume fraction of polymer in the particles <0.8.
k,m Monomer and CTA partition coefficients between the monomer droplets phase and the aqueous phase.
l,n Monomer and CTA partition coefficients between the aqueous phase and the polymer phase.

Table 4. Mass fraction for the five components of iOMP and adjusted k_{fXio}

Component	Mass fraction (%)	$10^{-4}\, k_{fXio}$ (dm^3 mol^{-1} min^{-1})
X1	25.4	2.4
X2	7.8	2.8
X3	7.8	0.5
X4	50.1	0.8
X5	8.9	2.5

the chain transfer constants for the different CTA components at low x (k_{fXio}) were adjusted to the experimental data. The most important model parameters are summarised in Table 3. The adjusting parameters procedure was done with a genetic algorithm routine that minimised the average absolute errors between measurements and model predictions. The procedure is described in what follows.

The experimental information of x and $\bar{d}_p$ of four additional polymerisation experiments were used to adjust (i) the parameters k_{ho}, k_a and k_m, which are associated to the nucleation mechanism and (ii) the A_1 and A_2 coefficients and δ_M, which were all considered independent of the CTA concentration. These experiments were carried out under the same reaction conditions that the previously described, but in absence of CTA and with different SLS and KPS concentrations ([SLS] = 1.3–0.2 pphm and [KPS] = 0.2–0.1 pphm).

The k_{pX} and k_{fXio} parameters depend on the CTA and were simultaneously adjusted to the time evolutions of x, $\bar{d}_p$, $\bar{M}_n$ and $\bar{M}_w$ for experiments MMA$_2$–MMA$_5$. After adjustment, the reactivity of the iOMP radicals resulted about 300 times lower than the reactivity of $M_n^\bullet$, thus resulting in $k_{pX} = 1.98 \times 10^2$ dm^3 mol^{-1} min^{-1}. When the CTA was considered as a mixture of five components, the adjusted k_{fXio} for X_3 and X_4 isomers (with a mass fraction of 57.9%) resulted much lower than that for the other three isomers (Table 4). Then the iOMP was simplified to a binary mixture with two hypothetical components, X_{m1} and X_{m2} (with mass fractions of 57.9% and 42.1%, respectively). The adjusted k_{fXmio} values were 6.45×10^3 dm^3 mol^{-1} min^{-1} for X_{m1} and 2.75×10^4 dm^3 mol^{-1} min^{-1} for X_{m2}, yielding $C_{Xm1} = 0.103$ and $C_{Xm2} = 0.441$.

Notice that the employed mathematical model considered the monomer consumption in both polymer and aqueous phases. Since the MMA consumption in the aqueous phase was predicted to be too low (around 0.01%), the chain transfer reactions (to the monomer and to the CTA) occurring in the aqueous phase were neglected for the estimation of the MWD, which is determined by the PMMA produced in the polymer phase.

For the main set of polymerisations, model predictions for x, $\bar{d}_p$, $\bar{M}_n$ and $\bar{M}_w$ are represented by traces in Figure 1. A reasonable adjustment of x and $\bar{d}_p$ was achieved when considering a reduced reactivity of the iOMP radical with respect to the MMA-ended radicals (Figure 1a and b). Also, the model was able to adequately predict the experimental data evolution of $\bar{M}_n$ (Figure 1c), $\bar{M}_w$ (Figure 1d) and the whole MWDs (Figure 3) along the polymerisations.

For $x = 30\%$, Table 5 shows the reduction of the effective propagation constant ($\bar{k}_p$) due to the loss of radical reactivity in the presence of iOMP and the model prediction for $\bar{n}$, which resulted slightly decreased with the CTA concentration. At $x = 30\%$, it is observed that the increment in the iOMP concentration from 0 to 1.38 pphm produced a $\bar{k}_p$ reduction of 40% and a decrease in $\bar{n}$ of 10%. According to the model predictions, the reduction in the

Table 5. Influence of iOMP on effective k_p and $\bar{n}$ at $x = 30\%$, estimated from the model

Experiment	CTA (pphm)	$10^{-4}\bar{k}_p$ [a] (dm^3 mol^{-1} min^{-1})	$\bar{n}$
MMA$_1$	0	6.24	0.88
MMA$_2$	0.30	5.45	0.87
MMA$_3$	0.67	4.76	0.83
MMA$_4$	1.03	4.24	0.81
MMA$_5$	1.38	3.85	0.79

[a] Calculated with Equation (A.14).

polymerisation rate by the presence of iOMP decreases the particle growth. Therefore, as a consequence of the reduced total particle area (A_p) observed in the first part of reaction, the nucleation period is extended, which promotes the formation of more polymer particles by both micellar (Equation A.20) and homogenous nucleations (Equation A.21). This effect is observed in Table 2 as an increment in N_p with the CTA concentration. However, the increment in N_p is more than compensated by the reduction in both $\bar{k}_p$ and $\bar{n}$, thus producing a net reduction of the propagation rate.

CONCLUSIONS

The emulsion polymerisation of MMA in presence of iOMP (an isomers mixture) as CTA was experimentally investigated and interpreted with the help of a first principles mathematical model. The iOMP produces a significant effect on both the polymerisation rate and the MWDs. When the CTA concentration is increased, the polymerisation rate is reduced as a consequence of the lower reactivity of the iOMP radicals with respect to the MMA-ended radicals. The MWD of the PMMA was controlled by chain transfer to the CTA, with a reduction of the average molecular weights along the reaction and an accumulation of iOMP with respect to MMA (i.e. $C_{Xi} < 1$). By considering the iOMP as a binary mixture ($X_{m1} + X_{m2}$), the model was able to adequately predict the MWD, with $C_{Xm1} = 0.103$ and $C_{Xm2} = 0.441$.
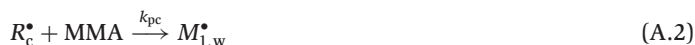
APPENDIX: MATHEMATICAL MODEL

Aqueous-Phase Reactions

Initiation

$$I_2 \xrightarrow{k_d} 2R_c^\bullet \tag{A.1}$$

$$R_c^\bullet + \text{MMA} \xrightarrow{k_{pc}} M_{1,w}^\bullet \tag{A.2}$$

where $M_{1,w}^\bullet$ is the monomeric primary radical.

Propagation and termination

$$M_{n,w}^\bullet + \text{MMA} \xrightarrow{k_{pw}} M_{n+1,w}^\bullet \tag{A.3}$$

$$M_{n,w}^\bullet + M_{m,w}^\bullet \xrightarrow{k_{tw}} P_{n,w} + P_{m,w} \text{ or } P_{n+m,w} \tag{A.4}$$

Polymer-Phase Reactions

Propagation

$$M_n^\bullet + \text{MMA} \xrightarrow{k_p} M_{n+1}^\bullet \tag{A.5}$$

$$X_i^\bullet + \text{MMA} \xrightarrow{k_{px}} M_1^\bullet \tag{A.6}$$

Termination

$$M_n^\bullet + M_m^\bullet \xrightarrow{k_{tp}} P_n + P_m \text{ or } P_{n+m} \tag{A.7}$$

Transfer to the CTA (X)

$$M_n^\bullet + X_i \xrightarrow{k_{fX_i}} P_n + X_i^\bullet \text{ with } (X_i = X_1, X_2, X_3, X_4, X_5 \text{ or } X_{m1}, X_{m2}) \tag{A.8}$$

Transfer to the monomer

$$M_n^\bullet + \text{MMA} \xrightarrow{k_{fM}} P_n + M_1^\bullet \tag{A.9}$$
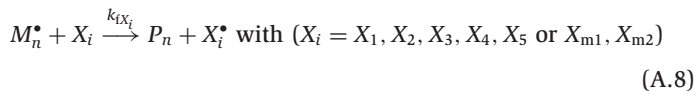
where X_i are the iOMP isomers (of molar mass 218.3 g mol^{-1}).

Model Equations

Based on Minari et al.[7] and Vega et al.,[19] the balances for the moles of MMA (N_M), initiator (N_I), iOMP (N_{Xi}) and the total number of polymer particles (N_p) are written as follows:

$$\frac{dN_M}{dt} = -\bar{k}_p[M]_p \frac{\bar{n}N_p}{N_A} - k_{po}[M]_w[R^\bullet]_w V_w \tag{A.10}$$

$$\frac{dN_I}{dt} = -k_d N_I \tag{A.11}$$

$$\frac{dN_{Xi}}{dt} = -k_{fX_i}[X_i]_p \frac{\bar{n}N_p}{N_A} \quad (i = 1, 2, \ldots, 5 \text{ or } m1, m2) \tag{A.12}$$

$$\frac{dN_p}{dt} = N_{gen} \tag{A.13}$$

where N_{gen} is the particle generation rate, as defined in Equation (A.19); $[j]_p$ and $[j]_w$ represent the concentration of reagent j ($= \text{MMA}, X_i$) in the polymer particles and in the aqueous phase, respectively; $[R^\bullet]_w$ is the concentration of free radicals in the aqueous phase; V_w is the volume of aqueous phase; and N_A is the Avogadro's constant.

The effective propagation rate constant ($\bar{k}_p$) that takes into account the different reactivity of radicals $X_i^\bullet$ and $M_n^\bullet$, was calculated through:

$$\bar{k}_p = k_p P_M + k_{pX} P_X \tag{A.14}$$

where k_p and k_{pX} are the propagation rate constants for radicals $M_n^\bullet$ and $X_i^\bullet$, respectively, and P_M, P_X are the probabilities of having a radical of type $M_n^\bullet$ and $X_i^\bullet$ in the polymer particles, which were calculated as follows:

$$P_M = \frac{k_{pX}[M]_p}{k_{pX}[M]_p + \sum_i k_{fX_i}[X_i]_p} \tag{A.15}$$

$$P_X = 1 - P_M \tag{A.16}$$

The average number of radicals per particle, $\bar{n}$, was calculated from the classical expression by Ugelstad and Hansen,[35] which

includes a rate constant of monomeric radical desorption from the polymer particles, given by Nomura et al.[36]:

$$k_{de} = K_M \left(\frac{k_{fM}[M]_p}{K_M \bar{n} + \bar{k}_p[M]_p} \right) \qquad (A.17)$$

with

$$K_M = \frac{12 D_{Mw} \delta_M K_{Mwp}}{d_p^2} \qquad (A.18)$$

The particle generation, N_{gen}, is calculated as in Vega et al.[19]:

$$N_{gen} = \left(k_m \frac{A_m}{V_T} + k_h \right) [R^\bullet]_w V_w N_A \qquad (A.19)$$

with:

$$A_m = (N_E^0 - [E]_{CMC} V_w) A_S - A_p \qquad (A.20)$$

where k_h is the rate coefficient for homogeneous nucleation; V_T is the total reaction volume; A_m is the surface area of micelles calculated through Equation (A.20); N_E^0 is the initial moles of emulsifier; and A_p represents the surface area of polymer particles.

To estimate k_h in Equation (A.19), Fitch and Tsai[37] proposed:

$$k_h = k_{ho} \left(1 - \frac{L A_p}{4 V_T} \right) \qquad (A.21)$$

where L is the average diffusion path length of the free radicals in the aqueous phase, given by Dubé et al.[38]:

$$L = \left(\frac{2 D_{Mw} j_{cr}}{k_{po}[M]_{w,sat}} \right)^{1/2} \qquad (A.22)$$

Calculation of Diffusion-Controlled Model Parameters

The termination coefficient is affected by gel effect and was calculated with the following empirical expression[39]:

$$k_{tp} = k_{tpo} \exp[A_1 \phi_p^p + A_2(\phi_p^p)^2] \qquad (A.23)$$

where ϕ_p^p is the volume fraction of polymer in the particles.

A diffusional control was also assumed for propagation. Then, at high monomer conversion, k_p was calculated through the following expression[40]:

$$k_p = k_{po} \exp[-23.88(\phi_p^p - 0.8)] \quad \phi_p^p \geq 0.8 \qquad (A.24)$$

By assuming that the iOMP has a similar diffusivity than the monomer in the polymer media at high monomer conversion,[41] then the rate constants for chain transfer to the monomer and to the CTA isomers can be calculated through Equation (A.24) as follows:

$$k_{fj} = k_{fjo} \exp[-23.88(\phi_p^p - 0.8)] \quad \phi_p^p \geq 0.8 \quad (\text{for } j = M, X_i) \qquad (A.25)$$

Model Outputs

The monomer conversion (x) was calculated from:

$$x = \frac{N_M^0 - N_M}{N_M^0} \qquad (A.26)$$

where N_M^0 represents the initial MMA moles.

The instantaneously produced MWD, $w(M)$, represents the mass fraction of PMMA for each molecular weight, M, and can be written as:

$$w(M) = \frac{M \tau^2}{M_{MMA}^2} \left(\frac{1}{\tau} \right)^{(M/M_{MMA})} \qquad (A.27)$$

where M_{MMA} is the MMA molecular weight and τ is a dimensionless parameter given by:

$$\tau = \frac{\sum_i k_{fX_i}[X_i]_p}{\bar{k}_p[M]_p} + \frac{k_{fM}}{\bar{k}_p} \qquad (A.28)$$

At any conversion, the cumulative MWD, $W(M)$, is calculated from:

$$W(M) = N_M^0 M_{MMA} \int_0^x w(M) \, dx \qquad (A.29)$$

Finally, the number- and weight-average molecular weights are obtained from:

$$\bar{M}_n = \frac{\int W(M) \, dM}{\int (W(M)/M) \, dM} \qquad (A.30)$$

$$\bar{M}_w = \frac{\int W(M) M \, dM}{\int W(M) \, dM} \qquad (A.31)$$

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