A NEW APPROACH FOR THE KINETIC MODELLING OF NON-LINEAR FREE RADICAL POLYMERIZATIONS AND ITS APPLICATION TO POLY(VINYL ACETATE) BULK AND SOLUTION MANUFACTURING PROCESSES

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SUMMARY

A recently described kinetic method for modelling and simulation of non-linear irreversible polymerizations can be advantageously used with non-linear free radical polymerization, as it is easily extended to complex mechanisms and avoids approximations such as the pseudo-steady state hypothesis and neglecting of the concentrations of multiple radicals. A consistent set of kinetic parameters for free radical polymerization of vinyl acetate at 60 C in bulk and solution in *t*-butanol has been obtained fitting previously published experimental data of monomer conversion and average molecular weights in batch polymerization, as well as measurements for saponified and reacetylated polymer. Experimental results in CSTR agree with theoretical predictions if perfect micromixing is assumed.

Kinetic model

The kinetic approach the authors propose to call *stoichiometric method* [1, 2] defines a set of active groups $\mathbf{A}_j$, a set of reactive compounds $\mathbf{B}_j$ (monomers, initiators, transfer agents) and a set of product groups $\mathbf{X}_j$, unable to react any further, coming from the reactions among active groups, so that they fully describe the mechanism of the polymerization with the needed details. They are shown in table I for the case of free radical polymerization of vinyl acetate started by a symmetrical azo or peroxide initiator. In table II are presented the stoichiometric coefficients of the reactions involving them, as well as the kinetic constants which were computed in this work from the fitting of experimental data. Main assumptions are :

- Termination by primary radicals of initiator is considered, in order to explain the apparent decrease of average kinetic chain length at higher solvent concentration [3].
- Kinetic constants of termination and efficiency factor of initiation f change with polymer weight fraction. They were correlated to excess Van der Waals volume fraction v_e, as computed by Bondi's group contributions and overall density, which in terms of polymer, monomer and *t*-butanol volume fractions v_P, v_M, v_S is:
$$v_e = 0.381\ v_P + 0.466\ v_M + 0.442\ v_S$$
The consideration of the change in f is crucial in order to simultaneously fit conversion and molecular weight data in bulk at high polymer concentration found in [4].
- All other kinetic parameters were taken as invariant with solvent and polymer concentration. They are based on an absolute value of k_p obtained by pulsed laser initiation [5] equal to 11700 $dm^3\ mol^{-1}\ s^{-1}$.

Fitting was done using weighted least-squares assuming equal relative standard deviations in average molecular weights and monomer conversions. The observed $\overline{M}_n$ at zero conversion and very low amount of initiator yields the relative transfer constant to monomer. Experimental average molecular weights for a batch reactor before and after saponification + reacetylation [6] were used to estimate, with a fairly good accuracy, the relative rate constants of transfer to polymer and propagation on terminal double bonds (see fig. 1). Termination by combination is almost negligible, since gelation is not observed even at high conversion.

TABLE I: Chemical species in the free radical polymerization of vinyl acetate ($CH_3COOCH{=}CH_2$) polymerization initiated by a symmetrical compound (**R-R**).

Species	**Description**	**Formula**
A_1	Generic radical	
A_2	Non saponificable transfer site	$-C\underline{H}(OOCCH_3)-CH_2-$
A_3	Saponificable transfer site	$-CH(OOCC\underline{H}_3)-CH_2-$
A_4	Terminal double bond	$CH_2{=}CHOOCCH_2-$
B_1	Monomer	$CH_3COOCH{=}CH_2$
B_2	Primary radical	$R^{\cdot}$
B_3	Initiator	RR
B_4	Solvent	$(CH_3)_3COH$
X_1	Polymerised monomer	$-CH(OOCCH_3)-CH_2-$
X_2	Initiator fragment	R-
X_3	Saturated terminal group	$CH_3COOCH_2-CH_2-$
X_4	Non saponificable branch	$-\underset{\vert}{C}(OOCCH_3)CH_2-$
X_5	Saponificable branch	$-CH(OOCCH_2-)CH_2-$
X_6	Unreactive terminal double bond	$CH_3COOCH{=}CH-$

TABLE II: Mechanism of free radical polymerization of vinyl acetate

Reaction name	**Chemical equation**	**Rate parameter @ 60 C**
Initiator scission	$B_3 \xrightarrow{k^*_{B3}=k_d} 2fB_2$	9.0 10^{-6} (AIBN); 2.9 10^{-4} s^{-1}(DCP) $f = 0.5\exp[-0.9(1/v_e - 1/v_{e0})]$
Monomer initiation	$B_1 + B_2 \xrightarrow{k_{BB_{12}}=k'_{p1}} A_1 + A_3 + X_1 + X_2$	90 (AIBN); 11700 (DCP) $M^{-1}s^{-1}$
Terminal double bond initiation	$A_4 + B_2 \xrightarrow{k_{AB_{42}}=k'_{p2}} A_1 + X_2 + X_5$	64 (AIBN); 8300 (DCP) $M^{-1}s^{-1}$
Monomer propagation	$A_1 + B_1 \xrightarrow{k_{AB_{11}}=k_{p_1}} X_1 + A_1 + A_2 + A_3$	11700 M^{-1} s^{-1}
Terminal double bond propagation	$A_1 + A_4 \xrightarrow{k_{AA_{14}}=k^*_{p_2}} X_5 + A_1 + A_2$	8300 M^{-1} s^{-1}
Chain transfer to monomer	$A_1 + B_1 \xrightarrow{k^{**}_{AB_{11}}=k_M} X_1 + X_3 + A_1 + A_4$	2.84 M^{-1} s^{-1}
Chain transfer to solvent	$A_1 + B_4 \xrightarrow{k^{*}_{AB_{14}}=k_S} X_3 + B_2$	0.32 M^{-1} s^{-1}
Chain transfer to polymer in a non saponificable branch	$A_1 + A_2 \xrightarrow{k^*_{AA_{12}}=k_{Pns}} X_3 + X_4 + A_1$	1.11 M^{-1} s^{-1}
Chain transfer to polymer in a saponificable branch	$A_1 + A_3 \xrightarrow{k^*_{AA_{13}}=k_{Ps}} X_3 + X_5 + A_1$	1.13 M^{-1} s^{-1}
Termination by dismutation	$2A_1 \xrightarrow{k^*_{AA_{11}}=k_{td}} X_3 + X_6$	8.40 $10^{16}\exp(-8.3/v_e)$ M^{-1} s^{-1} (bulk) 2.64 $10^{16}\exp(-8.3/v_e)$ M^{-1} s^{-1} (solut.)
Mutual primary radical termination	$2B_2 \xrightarrow{k^*_{BB_{22}}=k_{ii}}$ Inert products	1.0 10^{10} M^{-1} s^{-1} (AIBN)
Primary radical termination	$A_1 + B_2 \xrightarrow{k_{AB_{12}}=k_{ii}} X_3$	1.5 $10^{8}\exp(-2.7/v_e+12.9w_S)M^{-1}$ s^{-1} (AIBN)

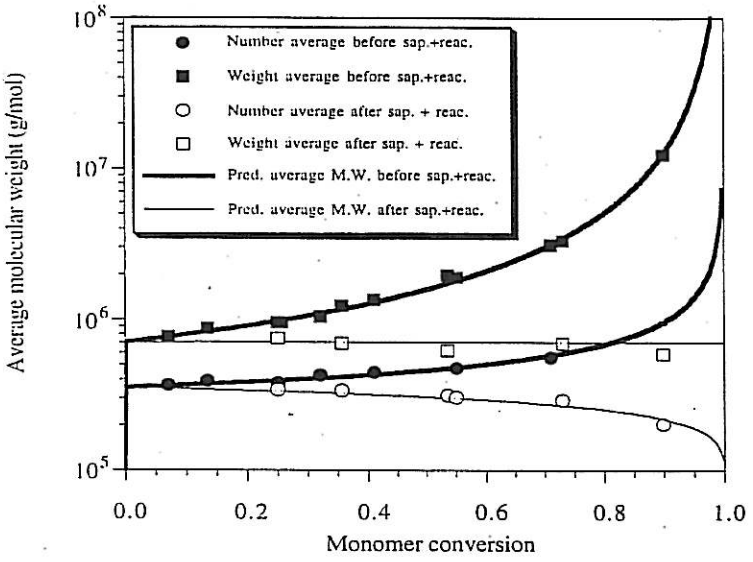

Figure 1: Comparison between experimental [6] and predicted (this work) $\overline{M}_n$ and $\overline{M}_w$ of PVAc made in a batch reactor before and after saponification + reacetylation.

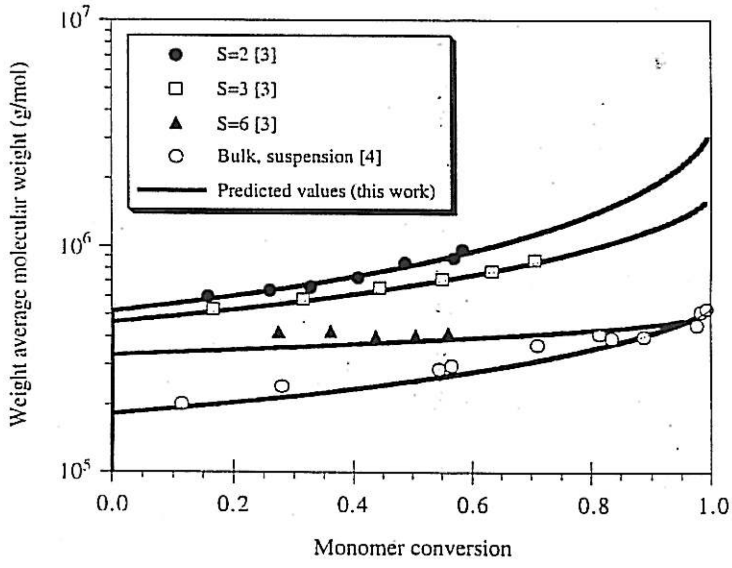

Figure 2: Comparison between experimental [3, 4] and predicted (this work) $\overline{M}_w$ for batch reactor, either in bulk or with different values of *t*-butanol / monomer initial mole ratio *S*.

In a later stage, experimental data in bulk and suspension [4] were used to refit the values of efficiency of initiator and of termination rate constant. Literature values were used for the rate constants of monomer initiation [8]. Results in solution yield finally information about the rate of primary radical termination.

Discussion and conclusions

In earlier works [3, 4], a satisfactory fit of experimental data was not possible owing to the approximate nature of the mathematical method used to predict the molecular weights. A surprising dependence on solvent concentration of the transfer constants to polymer had also been found. The more exact calculations of this work allow the postulate of this non-physical dependence to be avoided. The rate constant of primary radical termination with AIBN was nevertheless found to increase strongly with *t*-butanol concentration, and more experiments would be welcome so that a better understanding of this phenomenon could be grasped.

In the CSTR, the method of moments predicts a fast rise in $\overline{M}_w$ above a certain value of space-time, followed by gelation, but, once again, this is a mathematical artifact which does not occur when stoichiometric method is used (see figure 3).

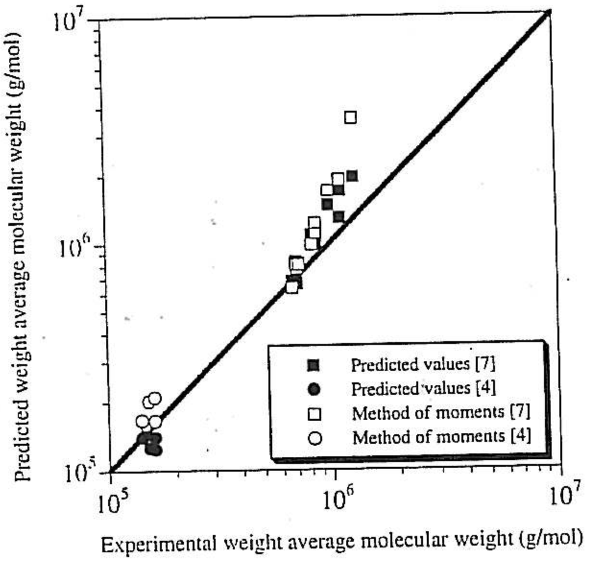

Figure 3: Comparison between experimental [4, 7] and predicted $\overline{M}_w$ in CSTR (stoichiometric method and method of moments [4], with same values of rate parameters).

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