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Synthesis and modelling of bulk and solution terpolymerization of styrene, α-methylstyrene and acrylic acid in a tubular reactor

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This work deals with the development of continuous bulk and solution processes for the manufacture of hard acrylic resins, through the terpolymerization of styrene, α-methylstyrene and acrylic acid, carried out in a tubular reactor, at high temperature (200 °C-260 °C) and 20 bar, with residence times smaller than 5 minutes.
A model of the whole process was developed, using the corresponding mass and heat transfer balances. Its unknown parameters were identified by use of an evolutionary algorithm and experimental data resulting from an adapted experimental strategy. This allowed predicting the evolution of each monomer conversion and properties of the resulting terpolymers *(Mn, Mw and Tg)* versus the operating conditions.

1. Introduction

This study concerns the radical polymerization of styrene (STY or M_1) α-methylstyrene (AMS or M_2) and acrylic acid (AA or M_3). The resulting hard acrylic resins are used in the formulation of aqueous inks where they support the dispersion of pigments. Two processes are currently used for these syntheses: the first uses a continuous stirred reactor while the second uses a tubular reactor. In spite of its simplicity and its low cost, the second one is seldom used industrially, particularly for bulk polymerizations, because of the high viscosity of the medium which strongly limits heat and mass transfers. Mixing and temperature of the fluid then become very difficult to control, which induces fatal consequences on the properties of the products. The objective of this work aims to reduce these disadvantages. For that a tubular lab-scale pilot plant was designed to study and model the process in order to better understand and improve operation of an existing industrial manufacturing unit.

2. Elaboration of the model

2.1 Kinetic scheme

Main assumptions

Due to the chemical complexity of the process, the following assumptions will be made:
* The kinetic constants are independent of the degree of polymerization,
* The penultimate effect is neglected, i.e. the radical reactivity depends only on the nature of the terminal unit.

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* Transfer to polymer reactions are neglected,
* At temperatures higher than 200°C, M_2 depropagation rate is very high. This allows to neglect (i) its propagation on ^2R_k (macroradicals containing k monomer units and ending by M_2) and (ii) termination by combination of ^2R_k,
* Thermal initiation will be considered for each monomer. However, due to a lack of data concerning this reaction for each of them, the same kinetic constant and reaction order will be attributed to their thermal initiation. As for thermal initiation of styrene this reaction order, β, will be comprised between 2 and 3,
* Average molar masses of the terpolymers will be expressed in polystyrene equivalents as they will be determined by Size exclusion chromatography after calibration using polystyrene standards.

Elementary chemical reactions

The model will be based on chemical and thermal radical initiations (4 reactions), chain initiations (3 reactions), propagation (8 reactions), termination by disproportionation and combination (6 and 5 reactions respectively), chain transfer to monomers and solvent (9 and 3 reactions respectively).

2.2 Kinetic model

Using this scheme the development of the kinetic model will comprise the writing of reactions rates, mass balance of the various species (initiator, monomers, solvent, macroradicals and macromolecules), balance of the moments of order 0, 1 and 2 of the degree of polymerization distribution (DPD) of both macroradicals and macromolecules (Villermaux and Blavier, 1984), influence of temperature on kinetic constants, glass transition temperature, *Tg*, (Fox and Flory, 1950; Fox, 1956).

2.3 Hydrodynamic model

In addition to the kinetic model, the use of the tubular reactor implies developing a hydrodynamic model in order to write correctly the corresponding mass and enthalpy balances. The knowledge of residence time distribution is therefore necessary to determine the average concentrations at the outlet of the reactor.

Writing of mass and enthalpy balances will be simplified assuming (Chen, 1994) that: (1) the reaction medium is Newtonian, (2) the flow regime is permanent, laminar and symmetrical around the central axis of the reactor, (3) the radial speed component is equal to zero, (4) the speed profile is parabolic, (5) heat capacities and reactions heat are constant, (6) the momentum is preserved along a thread of current.

The global model thus defined is a model coupling the kinetics of the reactions and the hydrodynamics of the tubular reactor in an established laminar mode. It constitutes a non-linear differential-algebraic system of equations containing 9 differential equations and 6 algebraic equations.

2.4 Estimation of the model parameters

To estimate the unknown parameters of this model, an evolutionary algorithm will be used with the objective to find the optimal solution for which the values of experimental and simulated data are the closest possible. This solution will be obtained using the maximum likelihood method (Walter and Pronzato, 1994). The use of the evolutionary algorithm requires the definition of a field of research for each parameter. Parameters for which no order of magnitude is found in the literature, several fields of research will be tested. The selected field will be that which allows a correct integration of the parameters and the minimization of the criterion of the maximum likelihood.

3. Material and methods

3.1 Materials

The 3 monomers, provided by Cray Valley, are stabilized by 200 ppm of inhibitor (hydroquinone monomethyl ether). The initiator: tert-butyl peroxide (DTBP) and the solvent: carbitol (Carb), were provided by Arkema and Brenntag respectively.

3.2 Equipment for polymerizations

The experimental set-up is composed of 3 parts:
Part 1, formed of 7 tanks used to store and/or to mix monomers, solvent and initiator,
Part 2, comprising a stainless steel tubular reactor connected to 2 pumps and equipped with a system to recover samples, a pressure regulation valve and six temperatures sensors. Its internal diameter is 6 mm for a length of 1 m. Monomers, solvent and initiator are premixed before the entry in the tube through 6 elements of Sulzer SMX.
Part 3, used for devolatilization and recovery of the final and residual products.

3.3 Characterization of the polymers

Residual monomers content, Mn and Mw and Tg were determined by: GC using a Delsi Nermag DN 200 chromatograph equipped with a capillary column, SEC using a Waters Millipore equipment calibrated with polystyrene standards, DSC using a Pyris 1 Perkin Elmer apparatus.

4. Results and discussion

4.1 Experimental strategy

The study relates to six resins whose initial mass compositions are given in table 1:

Table 1 – Initial mass compositions of the resins

Resins #	1	50	53	60	65a	65b
STY (wt %)	30.83	40.26	16.95	14.55	14.12	14.80
AMS (wt %)	24.59	20.40	16.67	14.75	18.54	19.44
AA (wt %)	20.98	27.40	15.82	20.45	15.04	15.76
Carb (wt %)	22.77	11.50	50.00	50.00	50.00	50.00
DTBP (wt %)	0.83	0.44	0.56	0.25	2.30	0

A complete factorial design (6,3,3) based on 6 resin levels, 3 coolant temperature levels (between 200 and 260°C) and 3 residence time levels (between 60 and 360 s)] was used. In each case, the pressure in the reactor was maintained at 20 bars.

4.2 Parameters estimation

36 syntheses were carried out for this identification. Among the kinetic data resulting from the literature for this copolymerization, at T>200°C, only the kinetic coefficient of the initiator decomposition reported (Mark et al. (1989) will be considered ($k_{d\text{-}200}$ = 1.925 10^{-2} s^{-1}; activation energy, E_{ad} = 146.4 $kJ.mol^{-1}$). The model is then composed of 67 unknown parameters: 66 kinetic coefficients (initiator efficiency, thermal initiation reaction order, (β), activation energy and reaction rate constants at 200°C of thermal initiation, propagation, combination and disproportionation terminations, transfer to

monomers and to solvent reactions rates coefficients). h is the apparent heat flux coefficient . The resulting optimal values of all these parameters are given in table 2.

Table 2 – Optimal values of the 67 parameters

Parameter	Value	Units	Parameter	value	Units
f	0.94	-	Ea_{at}	$1.396\ 10^{5}$	$J.mol^{-1}$
β	2.69	-	Ea_{p11}	$4.030\ 10^{4}$	$J.mol^{-1}$
$k_{at\text{-}200}$	$3.588\ 10^{-6}$	$l^{\beta-1}.mol^{1-\beta}.s^{-1}$	Ea_{p12}	$2.263\ 10^{4}$	$J.mol^{-1}$
$k_{p11\text{-}200}$	$1.775\ 10^{4}$	$L.mol^{-1}.s^{-1}$	Ea_{p13}	$4.952\ 10^{4}$	$J.mol^{-1}$
$k_{p12\text{-}200}$	$1.091\ 10^{4}$	$L.mol^{-1}.s^{-1}$	Ea_{p21}	$3.874\ 10^{4}$	$J.mol^{-1}$
$k_{p13\text{-}200}$	$1.793\ 10^{4}$	$L.mol^{-1}.s^{-1}$	Ea_{p23}	$6.996\ 10^{4}$	$J.mol^{-1}$
$k_{p21\text{-}200}$	$6.933\ 10^{3}$	$L.mol^{-1}.s^{-1}$	Ea_{p31}	$4.092\ 10^{4}$	$J.mol^{-1}$
$k_{p23\text{-}200}$	$6.161\ 10^{3}$	$L.mol^{-1}.s^{-1}$	Ea_{p32}	$3.120\ 10^{4}$	$J.mol^{-1}$
$k_{p31\text{-}200}$	$6.349\ 10^{3}$	$L.mol^{-1}.s^{-1}$	Ea_{p33}	$2.614\ 10^{4}$	$J.mol^{-1}$
k_{p32200}	$9.763\ 10^{3}$	$L.mol^{-1}.s^{-1}$	Ea_{td11}	$3.465\ 10^{4}$	$J.mol^{-1}$
k_{p33200}	$4.966\ 10^{3}$	$L.mol^{-1}.s^{-1}$	Ea_{td22}	$1.143\ 10^{5}$	$J.mol^{-1}$
$k_{td11\text{-}200}$	$1.177\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{td33}	$2.190\ 10^{4}$	$J.mol^{-1}$
$k_{td22\text{-}200}$	$2.096\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{td12}	$3.327\ 10^{3}$	$J.mol^{-1}$
$k_{td33\text{-}200}$	$4.042\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{td13}	$5.367\ 10^{3}$	$J.mol^{-1}$
$k_{td12\text{-}200}$	$8.776\ 10^{6}$	$L.mol^{-1}.s^{-1}$	Ea_{td23}	$5.439\ 10^{3}$	$J.mol^{-1}$
$k_{td13\text{-}200}$	$5.536\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{tc11}	$1.744\ 10^{4}$	$J.mol^{-1}$
$k_{td23\text{-}200}$	$7.954\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{tc33}	$6.354\ 10^{4}$	$J.mol^{-1}$
$k_{tc11\text{-}200}$	$8.490\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{tc12}	$2.568\ 10^{3}$	$J.mol^{-1}$
$k_{tc33\text{-}200}$	$1.256\ 10^{8}$	$L.mol^{-1}.s^{-1}$	Ea_{tc13}	$4.375\ 10^{3}$	$J.mol^{-1}$
$k_{tc12\text{-}200}$	$2.100\ 10^{8}$	$L.mol^{-1}.s^{-1}$	Ea_{tc23}	$4.910\ 10^{3}$	$J.mol^{-1}$
$k_{tc13\text{-}200}$	$8.722\ 10^{7}$	$L.mol^{-1}.s^{-1}$	Ea_{tm11}	$7.531\ 10^{4}$	$J.mol^{-1}$
$k_{tc23\text{-}200}$	$1.809\ 10^{8}$	$L.mol^{-1}.s^{-1}$	Ea_{tm12}	$4.569\ 10^{4}$	$J.mol^{-1}$
$k_{tm11\text{-}200}$	70.02	$L.mol^{-1}.s^{-1}$	Ea_{tm13}	$1.275\ 10^{5}$	$J.mol^{-1}$
$k_{tm12\text{-}200}$	347.4	$L.mol^{-1}.s^{-1}$	Ea_{tm21}	$5.946\ 10^{4}$	$J.mol^{-1}$
$k_{tm13\text{-}200}$	55.27	$L.mol^{-1}.s^{-1}$	Ea_{tm22}	$4.911\ 10^{4}$	$J.mol^{-1}$
$k_{tm21200}$	60.64	$L.mol^{-1}.s^{-1}$	Ea_{tm23}	$6.537\ 10^{4}$	$J.mol^{-1}$
$k_{tm22\text{-}200}$	43.85	$L.mol^{-1}.s^{-1}$	Ea_{tm31}	$7.947\ 10^{4}$	$J.mol^{-1}$
$k_{tm23\text{-}200}$	32.63	$L.mol^{-1}.s^{-1}$	Ea_{tm32}	$4.443\ 10^{4}$	$J.mol^{-1}$
$k_{tm31\text{-}200}$	90.53	$L.mol^{-1}.s^{-1}$	Ea_{tm33}	$6.735\ 10^{4}$	$J.mol^{-1}$
$k_{tm32\text{-}200}$	90.37	$L.mol^{-1}.s^{-1}$	Ea_{ts1}	$7.105\ 10^{4}$	$J.mol^{-1}$
$k_{tm33\text{-}200}$	66.06	$L.mol^{-1}.s^{-1}$	Ea_{ts2}	$7.996\ 10^{4}$	$J.mol^{-1}$
$k_{ts1\text{-}200}$	3.12	$L.mol^{-1}.s^{-1}$	Ea_{ts3}	$8.112\ 10^{4}$	$J.mol^{-1}$
$k_{ts2\text{-}200}$	7.95	$L.mol^{-1}.s^{-1}$	h	$6.527\ 10^{5}$	$W.m^{-3}.\ K\text{-}1$
$k_{ts3\text{-}200}$	21.40	$L.mol^{-1}.s^{-1}$			

Comparison of these results with others from the literature (Hui and Hamielec, 1972), makes it possible to attest the coherence of the orders of magnitude of the identified values.

4.3 Associated results

Figures 1 to 6 compare some experimental and simulated results and clearly show the good agreement between the model and the experiments.

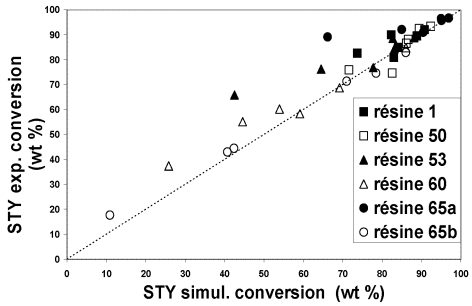

Figure 1. Styrene conversion

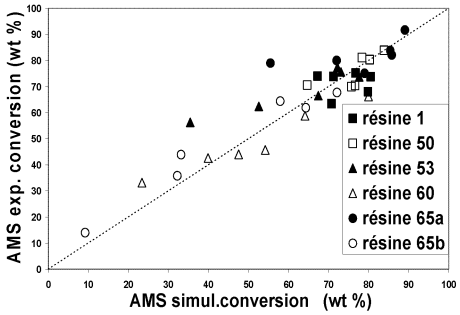

Figure 2. α–methylstyrene conversion

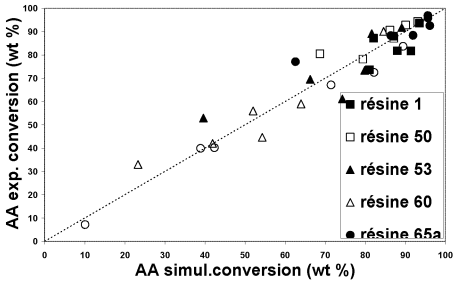

Figure 3. Acrylic acid conversion

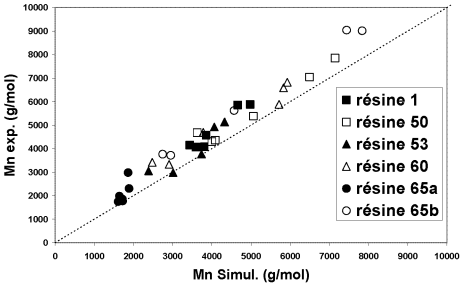

Figure 4. Number average molar masses

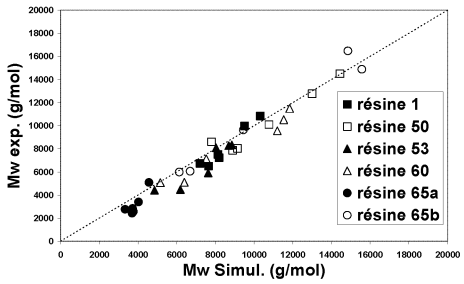

Figure 5. Weight average molar masses

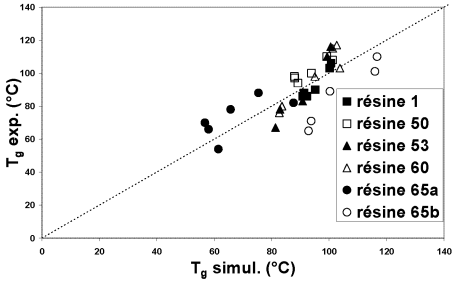

Figure 6. Glass transition temperatures

4.4 Model validation

18 experiments not having been used for the parametric identification were used for this validation. Figures 7, 8 and 9 make it possible to compare experimental and simulated results related to mass conversions of each monomer, number and weight average molar masses and glass transition temperatures respectively. For each of these characteristics, a good agreement is still found.

5. Conclusion

In this work, a model was elaborated for the synthesis in a tubular reactor of hard resins composed of styrene, α–methylstyrene and acrylic acid. This model results from the coupling of the kinetics and hydrodynamics of the process. It is able to correctly predict

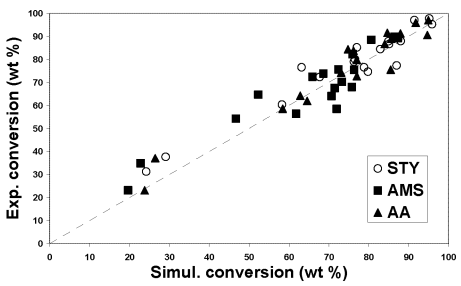

Figure 7. Monomers conversions

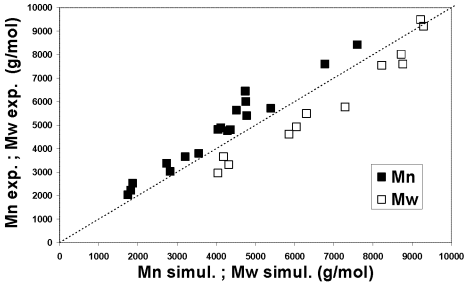

Figure 8. Average molar masses

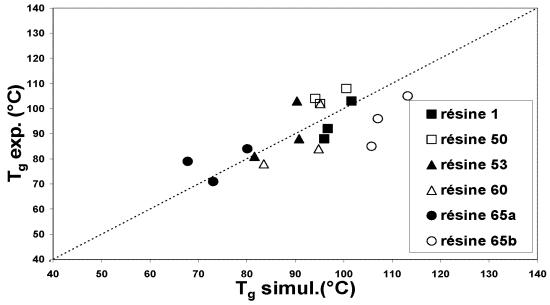

Figure 9. Glass transition temperatures

the conversion of the 3 monomers, the average molar masses and the glass transition temperature of the resulting products. It is now used to better understand the functioning of an existing industrial manufacturing unit.

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