CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124027

Design and Modeling of a Continuous Dispersion Copolymerisation Process in the Presence of a Stabilizing Agent Elaborated *in Situ*

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This work deals with the continuous copolymerization of acrylonitrile and styrene in a dispersed medium. Experiments were carried out in the presence of a stabilizing agent produced *in situ*. The continuous phase was a polyol. Considering the complex chemical and physical phenomena involved in the process, a tendency model of the whole system was developed, using mass balances and thermodynamics. Its unknown parameters were identified by use of an evolutionary algorithm and experimental data. This allowed predicting with acceptable order of magnitude the main characteristics of the resulting stabilized particles versus the operating conditions.

1. Introduction

Among all polymerization processes, dispersion polymerization is one of the most complex. Its principle can be summed up as follows: typically, the polymer is produced in a medium that initially contains the monomer, the initiator, and a stabilizer, dissolved in a solvent which must be a non-solvent of the polymer. The first step involves the production of radicals resulting from the thermal decomposition of the initiator, which in turn react with the monomer to form growing oligoradicals. Depending on its solubility in the medium, each oligoradical collapses into a condensed state when a certain threshold molecular weight is reached, giving rise to primary particles which, owing to Van der Waal's forces, attract either other primary particles or already existing larger ones. Flocculation of the particles is prevented by the stabilizer.
This paper deals with the synthesis of copolymers polyols (CPPs) via the continuous dispersion copolymerization of styrene (STY) and acrylonitrile (AN) in a polyol medium, in the presence of a chain transfer agent (CTA), a stabilizer precursor (SMAC) and a preformed stabilizer (PFS). The poly(styrene-co-acrylonitrile) particles growth is due (i) to their agglomeration and (ii) to bulk polymerization inside particles swollen by the monomers. Therefore, partitioning of monomers, initiator and CTA between the two phases, together with the nature and structure of the stabilizer are of major importance in this process. SMAC contains Si-C=C bonds which can provide a polyol grafted poly(styrene-co-acrylonitrile) acting as steric stabilizer. The final objective is to obtain CPPs with the lowest viscosity, optimum filterability but maximum amount of solids useful as raw materials for the manufacture of urethane elastomers and foams for the flexible polyurethane industry. In order to reach this goal, a model able to forecast the suitable CPPs properties will be proposed.

Please cite this article as: Pla F., Fonteix C., Van Der Wal H., Salvador B., 2011, Design and Modelling of a Continuous Dispersion Copolymerization Process in the Presence of a Stabilizing Agent Elaborated in Situ, Chemical Engineering Transactions, 24, 157-162, DOI: 10.3303/CET1124027

2. Modeling of the Process

2.1 Main assumptions

The establishment of the model requires the use of several assumptions. Some will be made without providing justification, as they are readily validated in the literature. Others, given with the necessary explanations, can be summarized as following:

a) Acrylonitrile (A) and Styrene (B) undergo homo-termination almost exclusively by combination (Odian, 1981) while the reactivity of the propagating species depends only on the terminal monomer unit. This leads to use the terminal model.

b) Due to the reaction temperatures used, there is no glass effect.

c) Cross-termination happens with the same probability in the two phases.

d) The decrease of termination rate constants, k_{tcAA} and $k_{tcBB,}$ due to the gel effect inside the particles, *p* is accounted for by using the following empirical expressions:

$$k_{tcAA}^{p} = k_{tcAA}^{c} \cdot g \quad ; \quad k_{tcBB}^{p} = k_{tcBB}^{c} \cdot g \tag{1}$$

$$g = Exp\left[-\left(gel_1 \cdot Y_B + gel_2 \cdot (1 - Y_B) \right) x_p \right] \tag{2}$$

where the *c* is the continuous phase, Y_B the weight fraction of STY in the copolymer, x_p the copolymer weight fraction in particles and gel_1 and gel_2 are adjustable parameters.

e) Transfer to CTA occurs with the same reactivity in both phases.

f) Usually, modelling of copolymerization processes uses the notion of "monomeric unit" to simplify the average molecular weights calculation. Here, M_A = 53 g/mol and M_B = 104 g/mol. Therefore, the weight of the monomer unit is considered to be between 52 g/mol and 53 g/mol, i.e., that when one unit A is added, a single "monomeric unit" is added to the growing chain and when one unit B is added, two "monomeric units" are added to the growing chain.

g) Grafting of the precursor stabilizer on SAN chains is considered to result from the reaction of growing oligoradicals with the vinyl bond of silane group. Moreover, previous experimental data (Salvador, 2004) showed that there is only one graft per SAN chain.

h) Oligoradicals undergo termination almost exclusively by coupling.

i) The quantity of grafted species is small compared to that of ungrafted chains and the probability for two grafted species to undergo termination is too small to be considered.

j) For oligoradicals terminated by a graft only disproportionation will be considered.

k) Monomers, initiator and CTA are considered to be in thermodynamic equilibrium.

l) Grafted SAN chains may be differently absorbed by the polymer particles depending on the way they are grafted (with polyol solvent or with SMAC).

m) Desorption of radicals from the particles is neglected.

n) The rate of precipitation of a given species depends on its concentration in the continuous phase and on the average size of the SAN chains that are in the medium.

o) The particles are monodisperse.

p) The reactor used (CSTR) is perfectly mixed and isothermal.

2.2 Kinetic scheme

Table 1 gives the elementary reactions involved in the process.

2.3 Setup of the model

Using this kinetic scheme and the previous assumptions, the state of the reactor is described through balance equations of the different species (Salvador, 2004). Then, theoretical data are calculated and compared to data resulting from runs carried out under different experimental conditions.

Table1. Elementary reactions involved in the two phases of the medium

Polymerization in the continuous phase	*Number of reactions*	*Polymerization in the particles*	*Number of reactions*
Initiator decomposition	1	Initiator	
Initiation	9	decomposition	1
Propagation	4	Initiation	2
Grafting	2	Propagation	4
Termination by combination	4	Termination	
Termination by disproportionation	2	by combination	4
Transfer to CTA	3	Transfer to CTA	2
Transfer to Polyol (solvent)	2		
Transfer to stabilizer precursor	2		

2.4 Parameter identification

To estimate the unknown parameters of the model, an evolutionary algorithm is used with the objective to find the optimal solution for which the values of experimental and simulated data are the closest possible. This solution is obtained using the maximum likelihood method (Walter and Pronzato, 1994; Pla et al., 2009). 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 are tested. The selected field is that which allows a correct integration of the parameters and the minimization of the criterion of the maximum likelihood.

3. Experimental

3.1 Materials and polymerization process

Styrene, containing 10 to 15 ppm of 4-*ter*t-butylcatechol inhibitor, and Acrylonitrile, containing 35 to 45 ppm of monomethyl ether hydroquinone inhibitor, were provided by Aldrich. The solvent used was a polyether provided by Dow Benelux. The initiator was tert-butyl peroxy-2-diethylacetate, provided by Akzo Nobel Chemicals. The chain transfer agent (CTA) was 1-Dodecanethiol, provided by Riedel-de-Haën. The stabilizer precursor (SMAC) was provided by Dow Benelux N.V. Polymerizations were realized using a continuous stirred tank reactor at laboratory scale constructed by De Feyter Terneuzen B.V. The process control was made using software from Camile Products.

3.2 Analytical methods

Before analyses, CPP samples were stripped in a film evaporator at 130°C under vacuum for half an hour. Then, in order to separate the solids from the serum, the polyol and other low molecular weight serum-soluble components were washed out of the solids by use of a 80/20 (v/v) hexane/ethyl acetate mixture. The final serum phase was obtained after removing the solvent by distillation in rotavapor equipment. 12 characterizations are performed on each sample by use of: (i) a Headspace GC coupled with a flame ionization detector to quantify residual STY, AN and CTA, (ii) a GPC coupled with an UV detector to determine (through calibration with polystyrene standards) number and weight average molecular weights of the copolymer (SAN) and to quantify its amount in the serum, (iii) a Malvern MS100 and a Coulter LS230 equipments together with a Philips FEG-SEM XL 30 to determine the average particle diameters, (iv) Proton (^{1}H)-NMR and carbon (^{13}C)-

NMR spectroscopy to establish the global composition in styrene and acrylonitrile of SAN and to determine the overall polyol bonded to the total SAN solid.

4. Results and Discussion

4.1 Fixed parameters of the model

Some reliable parameters issued from a preliminary study of the process (Salvador, 2004) were used. They concerned first the partitioning coefficients defined, for each reactant, as the ratio between its concentrations in the continuous phase and in the particles. For acrylonitrile (A) and styrene (B) these coefficients were *H*A = 1 and *H*B = 0.9. Concerning the initiator (I) it was supposed that, as its half-life time is very short (180 s at 120 °C and 25 s at 140 °C) compared to the residence time inside the reactor (20 min), it is decomposed almost completely as soon as it enters the reactor and, therefore, the quantity of free initiator inside the particles is negligible with a partitioning coefficient *H*I = 0. The kinetic constant of initiator dissociation is:

$$k_d^c = 2,45.10^{15} Exp\left(-\frac{134000}{8,314 \ . \ T}\right) \quad (3)$$

Moreover, to simplify the system to solve, the coefficients of diffusion of STY, AN, initiator, CTA and SMAC (small molecules whose molecular weights do not vary during the polymerization process) were considered to be equal.

4.2 Identified parameters of the model

Twenty-three parameters were identified at 140 and 120°C, with data resulting from runs carried out under operating conditions given in section 3.2 (17 runs at 140°C and 17 runs at 120°C, each with 12 characterizations). Table 2 shows that the values of these parameters obtained at both temperatures are close.

Table 2 – Optimal values of the parameters; Kinetic rate constants units: ($m^3.mol^{-1}.s^{-1}$)

Parameter	T=140°C	T=120°C	Meaning
k_{pAA}^c	2380	2200	Kinetic rate constant for AN homopropagation
k_{pBB}^c	48.1	48	Kinetic rate constant for STY homopropagation
k_{tcAA}^c	1.27 10^8	1.67 10^8	Kinetic rate constant for homotermination by combination of oligoradicals terminated by AN
R_{AB}^c	0.42	0.43	Reactivity ratio of oligoradicals terminated by AN and STY
R_{BA}^c	0.30	0.29	Reactivity ratio of oligoradicals terminated by STY and AN
$R_{t,A}^c$	3.9	2.7	Reactivity ratio of oligoradicals terminated by AN and STY
ϕ	27	28	Cross-termination coefficient
$R_{t,B}^c$	8.1	9	Reactivity ratio of oligoradicals terminated by STY

Table 2 – Optimal values of the parameters; Kinetic rate constants units: ($m^3.mol^{-1}.s^{-1}$)

Parameter	T=140°C	T=120°C	Meaning
			AN
k^p_{pBB}	490	265	Kinetic rate constant for homopropagation of STY
gel_1	1.0	1.3	Gel effect coefficient (adjustable parameter)
R^p_{AB}	0.50	0.45	Reactivity ratio of oligoradicals terminated by AN and STY
R^p_{BA}	0.48	0.28	Reactivity ratio of oligoradicals terminated by STY and AN
K_p (s^{-1})	$5.9.10^{-5}$	$8.85.10^{-5}$	Constant of precipitation
R^c_{AG}	0.32	0.77	Reactivity ratio of oligoradicals terminated by AN and SMAC
R^c_{BG}	29.3	36.3	Reactivity ratio of oligoradicals terminated by STY and SMAC
$k^c_{tr,G}$	1900	1810	Kinetic rate constant of transfer of oligoradicals to SMAC
k^c_{tdAG}	$1.72\ 10^8$	$1.57\ 10^8$	Kinetic rate constant for dismutation of oligoradicals terminated by SMAC and AN
k^p_{tdBG}	$1.01\ 10^7$	$1.57\ 10^7$	Kinetic rate constant for dismutation of oligoradicals terminated by SMAC and STY
a	$2.5\ 10^{-9}$	$3.65\ 10^{-9}$	Adjustable parameter [$m.(mol.\ kg^1)^{1/3}$]
gel_2	11.0	11.9	Gel effect coefficient (adjustable parameter)
f_c	0.27	0.28	Initiator efficiency
H_{CTA}	0.64	0.65	Partitioning coefficient of the chain transfer agent
F(x)	322.60	384.98	Maximum likelihood estimator

4.3 Associated results

Figures 1 to 4 show, as examples, the good agreement between experimental and simulated data resulting from runs carried out with 2 Sty/AN ratios and 2 initiator concentrations: I(-1) = 0.1 wt % and I(+1) = 0.2 wt %, and 2 CTA concentrations: CTA (–1) = 0.15 wt % and CTA (+1) = 0.45 wt %.

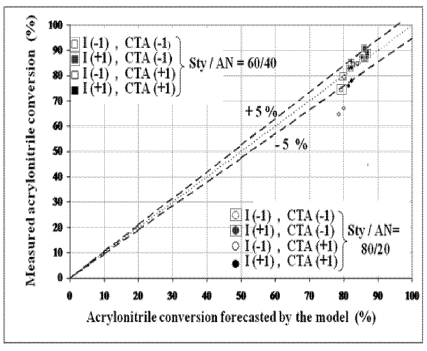

Figure 1. Acrylonitrile conversion

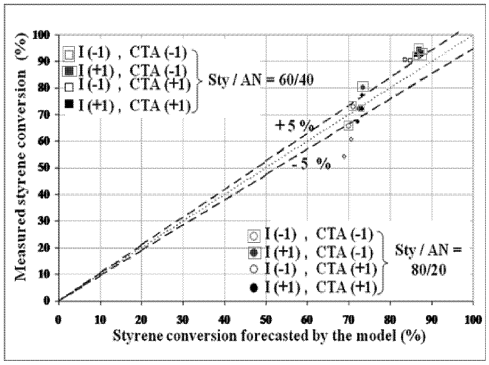

Figure 2. Styrene conversion

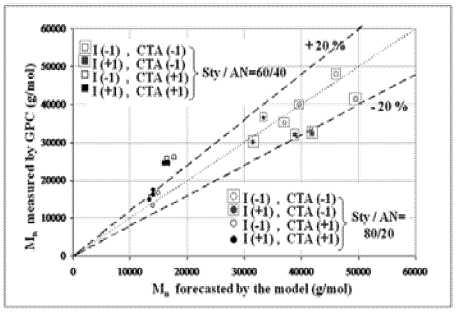

Figure 3.Number average molecular weight

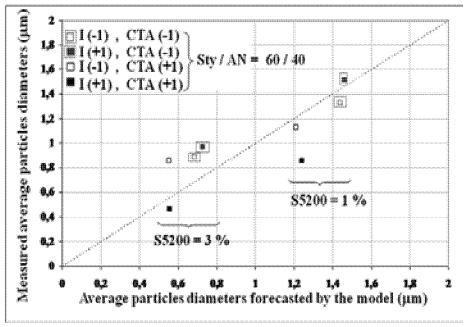

Figure 4. Average particles diameters

4.4 Validation of the model for runs carried out at 130°C

The model parameters were then deduced at 130°C through the arithmetic mean values identified at 120°C and 140°C.Table 3 shows the acceptable agreement between simulated and experimental data resulting from 5 standard industrial runs (Salvador, 2004).

Table 3. Comparison between simulated and experimental data obtained at 130°C

Data	Simulated values	Experimental interval	Unit	Measurements
$\bar{M}_n$	25300	26000 – 37900	g mol^{-1}	5
$\bar{M}_w$	59800	64100 – 98200	g mol^{-1}	5
Solids	38.5	32.1 – 40.3	wt-%	2
AN conversion	85.7	83.2 – 87.7	%	2
Sty conversion	82.0	84.8 – 88.0	%	2
CTA conversion	95.3	96.1 – 96.8	%	1
AN in SAN	30.9	19.2 – 34.8	wt-%	2
SAN grafted in CPP	16.2	12.9 – 19.3	%	1
Particles diameter	0.346	0.71 – 1.06	µm	1

5. Conclusion

This study allowed to understand better the CPP process and to establish a tendency model whose parameters were identified by use of an evolutionary algorithm. In spite of the lack of accuracy and the instability of several samples, this model allowed forecasting with acceptable agreement the main characteristics of the resulting materials.

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