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Development and Modeling of a Continuous Dispersion Copolymerization Process in the Presence of a Stabilizing Agent Elaborated *in situ*

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Summary: This work deals with the development of a process for the radical copolymerization of acrylonitrile and styrene in a dispersed medium. This process was carried out in a continuous stirred tank reactor, in the presence of a stabilizing agent produced *in situ* during the polymerization. The continuous phase is a polyol. Besides all elementary chemical mechanisms related to the copolymerization and to the synthesis and grafting of the stabilizing agent, this process involves several complex physical phenomena. A tendency model of the whole process was developed, using the corresponding mass balances and thermodynamics. Its unknown parameters were identified by use of an evolutionary algorithm and experimental data resulting from an adapted experimental strategy. This model was then validated and allowed to predict monomers and transfer agent conversions, amounts of solids and average molar masses, versus the operating conditions.

Keywords: copolymer polyol; dispersion polymerization; evolutionary algorithm; modeling

Introduction

Among all polymerization processes, dispersion polymerization is one of the most complex. It has been first developed by Osmond et al.[1] and can be considered as a particular case of precipitation polymerization.

The principle of this process can be summed up as follows: typically, polymer particles are formed in a homogeneous medium that contains the monomer dissolved in a solvent, an initiator and a stabilizer. The solvent must be a non-solvent of the polymer. Indeed, during the polymerization, the resulting macromolecules precipitate to form particles which flocculation is avoided due to the presence of the stabilizer.

The first dispersion polymerization, reviewed by Barret,[2] dealt essentially with aliphatic hydrocarbons as a medium and resulted in particles smaller than 2 μm. The studies which followed were focused on the ways to control particle size and to achieve narrow particle size distribution in the range of 1 to 2 μm. In the 1980s, these processes were extended to the use of more polar solvents as continuous phase. This allowed to widening the range of monomers that can be polymerized. Hydrophilic polymers such as hydroxypropylcellulose, poly(acrylic acid) and poly(N-vinylpyrrolidone) were used as precursor stabilizers that react *in situ* with radicals to provide amphiphilic graft polymers that stabilize sterically the polymer particles. Other studies were also developed to understand the mechanisms involved in these processes for various systems i.e.: the grafting mechanism[3] and its visualization over the particles surface,[4] the solvency control[5] and the influence of different reaction parameters.[6–20] From these experimental studies, different workers

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tried to provide some mathematical models for dispersion polymerization in polar media to forecast monomer partitioning, particle size and molecular weight distributions.[21–31]

This paper deals with the synthesis of copolymer polyols (CPPs) via radical dispersion copolymerization of styrene (St) and acrylonitrile (AN) in polyol medium. The objective is to obtain copolymer polyols with the lowest viscosity and optimum filterability but with the maximum amount of solids. In order to reach this goal and to control the influence of the process conditions on the properties of the final product, a tendency model able to forecast the main characteristics of the copolymer polyols, is proposed.

General Considerations

During dispersion polymerization, nucleation starts in an essentially homogeneous solution containing monomers, initiator, chain transfer agent and polyol. The first step involves the production of radicals resulting from the decomposition of the initiator, which in turn react with the monomers to form growing oligoradicals. Each oligoradical has an extended configuration, but then collapses into a condensed state when a certain threshold molecular weight is reached, depending on its solubility in the medium. Precipitation depends on (i) molecular weight, (ii) styrene to acrylonitrile ratio of these growing radicals, (iii) temperature and (iv) monomers concentration. Therefore, the condensed oligomer radicals constitute new primary particles. Due to Van der Waal's attractive forces, these particles attract either other primary particles or already existing larger particles, which are not completely covered with steric stabilizer. Thus, the mechanism by which poly(styrene-co-acrylonitrile) CPP particles grow is due to particle agglomeration and also to bulk polymerization inside particles, which are swollen by the monomers. Therefore, the partitioning of the monomers, initiator and chain transfer agent between the two phases is of major importance in this process, together with the nature and the structure of the stabilizer. Actually, the copolymer polyols developed in this work are produced by using both a stabilizer precursor containing Si–C=C bonds (SMAC) and a preformed stabilizer (PFS). SMAC results from the transesterification of a small amount of vinyltrimethoxysilane with a polyethertriol. Grafting of SMAC happens *in situ* through the copolymerization of its Si–C=C bonds with the styrene/acrylonitrile system, providing a polyol grafted poly(styrene-co-acrylonitrile) which serves as the final particle steric stabilizer. The reactivity of the steric stabilizer precursor with both styrene and acrylonitrile is very low while the reactivity of the precursor with itself is extremely low, which are the ideal conditions to be a good steric stabilizer. The PFS, provided by Dow Benelux N.V. was produced by reaction between a small amount of styrene and acrylonitrile and an excess of SMAC. Therefore, it contains both soluble and insoluble SAN polymeric material.

The different aspects of the process briefly described above show the complexity of this heterogeneous polymerization process where particularly occur, polymerization in both phases, precipitation, *in situ* formation of the stabilizer and particle stabilization in order to prevent renucleation and agglomeration. All these mechanisms depend on the experimental conditions and impact the quality of the final dispersion.

Elaboration of the Model

Main Assumptions

Even if the tendency needed for the present work is not a deterministic model its establishment requires the use of several assumptions to enhance the speed of convergence. Some of these assumptions will be made without providing justification, as they are readily accepted and validated in the classical literature. Others will be given with the necessary explanations. The major useful assumptions can be summarized as following:

- Acrylonitrile (A) and Styrene (B) undergo homo-termination almost exclusively by combination[32] while the reactivity of the propagating species depends only on the terminal monomer unit, which leads to use the terminal model.[33]
- Due to the temperatures used in this process, (between 120 °C and 140 °C), it is assumed that there is no glass effect.
- Cross-termination in the continuous phase (c) is expressed by the following relationship[32] between the homotermination rate coefficients k_{tcAA} and k_{tcBB}:

$$k^{c}_{tcAB} = \phi_c \sqrt{k^{c}_{tcAA} k^{c}_{tcBB}} \tag{1}$$

$\phi_c < 1$ means that cross-termination is not favored, while $\phi_c > 1$ means that it is favored. The tendency towards cross-termination is parallel to the tendency toward cross-propagation in that ϕ_c increases as the product of reactivity ratios approaches zero, which is the case for the styrene-acrylonitrile system. Mendizabal et al.[34] found values of ϕ_c in the range 10–70 at 60 °C for this system.

The decrease of k_{tcAA} and k_{tcBB}, due to the gel effect inside the particles, *p*, is accounted for by using the following empirical expressions[35,36]:

$$k^{p}_{tcAA} = k^{c}_{tcAA} \cdot g \tag{2}$$

$$k^{p}_{tcBB} = k^{c}_{tcBB} \cdot g \tag{3}$$

With,

$$g = Exp[-(gel_1 \cdot Y_B + gel_2 \cdot (1 - Y_B))x_p] \tag{4}$$

where the subscript *c* represents the continuous phase, Y_B is the weight fraction of styrene in the SAN copolymer, x_p the copolymer weight fraction in particles swollen by the monomers and gel_1 and gel_2 are adjustable parameters of the model.

The cross-termination inside the particles was expressed by the same kind of relationship as equation (1):

$$k^{p}_{tcAB} = \phi_p \sqrt{k^{p}_{tcAA} k^{p}_{tcBB}} \tag{5}$$

In order to simplify the model, and as cross-termination may happen in the same way in both phases, it is considered that:

$$\phi_p = \phi_c \tag{6}$$

- Transfer to chain transfer agent (CTA) is assumed to be developed with the same reactivity in both phases.
- Usually, modeling of copolymerization processes uses the notion of monomeric unit to simplify the average molecular weights calculation. Here, $M_A = 53\ g \cdot mol^{-1}$ and $M_B = 104\ g \cdot mol^{-1}$. Therefore, we consider that the weight of the monomer unit is between 52 $g \cdot mol^{-1}$ and 53 $g \cdot mol^{-1}$. Then, it is assumed 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.
- The grafting of the precursor stabilizer on SAN polymer chains is considered to result mainly from the reaction of growing oligoradicals with the vinyl bond of the silane group. Moreover, according to experimental data,[37] it is assumed that there is only one graft per SAN chain.
- The oligoradicals undergo termination almost exclusively by coupling. It is assumed that the quantity of grafted species is small compared to the quantity of ungrafted SAN chains and the probability for two grafted species to undergo termination is too small to be considered. For oligoradicals terminated by a graft G (SMAC), as further propagation with styrene or acrylonitrile are neglected, only disproportionation is taken into account.
- The concentrations of the monomers, initiator and chain transfer agent in the two phases are considered to be in thermodynamic equilibrium. The corresponding partitioning coefficients between the two phases will be considered. It is also assumed that there is no free polyol

or free SMAC inside particles, but only grafted onto their surfaces.

- The grafted SAN chains may be differently absorbed by the polymer particles depending on the way they are grafted (with polyol solvent or with SMAC). Desorption of radicals from the particles is neglected.
- Homogeneous nucleation could be, in a first attempt, the simplest way to model the precipitation phenomenon (transfer of chains from continuous to disperse phase). This implies that at a given critical number of monomeric units, i_{crit}, the oligoradicals precipitate. Nevertheless, in this case there are two important difficulties: firstly, it is necessary to evaluate this critical length, which depends on the solvency of the medium, the composition in styrene/acrylonitrile, and the temperature, and secondly, the combination terminations may induce precipitation if the degree of polymerization of the resulting dead polymer is greater than i_{crit}. Considering all the possible combinations that induce precipitation will provide too heavy computational calculations and this will not allow further parameter identification in acceptable times.

Aggregative nucleation (which may be closer to the reality than the homogeneous one) is therefore considered: the oligomer chains formed by solution polymerization associate with each other increasingly as their molecular weight and concentration rise.

If $\overline{J}_p$ is the precipitation rate of all the species of the continuous phase (c) : dead polymer (P) oligoradicals terminated by acrylonitrile (A), styrene (B) and SMAC (G) the following relationship is proposed :

average molecular weight in the continuous phase, V_c is the volume of the continuous phase in the reactor, M_u is the average molecular weight of the monomer unit. The subscripts $[_{T,0}]$, $[_{T,1}]$ and $[_{T,3}]$ mean total concentration of species units having 0 graft, 1 graft unit (polyol) and 1 graft unit (SMAC) respectively.

This means that in this model, the rate of precipitation of a given species depends on its quantity in the continuous phase and on the average size of the SAN chains that are in the medium, with which each oligoradical or dead polymer may precipitate.

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

Kinetic Scheme

Table 1 gives the elementary reactions considered to model copolymerization and grafting.

Setting up of the Model

From this kinetic scheme, the development of the model comprises the writing of:

- Balance on the total concentrations of the species in the reactor
- Balance on the concentrations of free species in the reactor (An, St, SMAC, solvent, CTA, initiator) using the partitioning coefficients
- Balance on radicals, dead polymer and moments of order one and two in the reactor
- Balance on particle volume and surface area assuming (i) that all the particles were covered by the grafts, which are firmly attached, and (i.i) that the particles are monodisperse. The average particle diameter is calculated from the total volume and the total surface of the particles.

$$\overline{J}_p = \overline{K}_p \left(\begin{array}{c} \left[A^*_{T,0}\right]_c + \left[A^*_{T,1}\right]_c + \left[A^*_{T,3}\right]_c + \left[B^*_{T,0}\right]_c + \left[B^*_{T,1}\right]_c \\ + \left[B^*_{T,3}\right]_c + \left[G^*_{T,3}\right]_c + \left[P_{T,0}\right]_c + \left[P_{T,1}\right]_c + \left[P_{T,3}\right]_c \end{array} \right) V_c \, \overline{M}_n^c \Big/ M_u \qquad (7)$$

Where, $\overline{K}_p$ (in s^{-1}) is a constant of precipitation, which is an adjustable parameter of the model, $\overline{M}_n^c$ is the number

- Calculation of data to be compared to the measurements (average molecular weights of oligoradicals, whole CPP and

Table 1.
Elementary reactions involved in the two phases of the medium.

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

SAN dissolved in the continuous phase, weight % of solids in stripped CPP and residual quantities of reactants, composition of the SAN copolymer, grafting quantification).

Programming of the Model

The steady state regime of this system is needed to be calculated. Nevertheless, as the system described previously is non-linear, it was decided to solve it by dynamic resolution. In order to avoid numerical instabilities during the system resolution, the quasi-steady state approximation was used in order to stabilize the integration. Only the differential equations concerning monomers, initiator, chain transfer agent, precursor stabilizer SMAC, polyol, none-functional polymer and their moments were considered. The system was resolved through a numerical integration of the differential equations with a Runge-Kutta method from $t = 0$ to $t = 10\,000$ s (almost 8 residence times) with a step of integration of $\Delta t = 0.1$ s. The choice of these two values is a compromise between the necessity to have the best accuracy and the smallest computing times as possible. It defines a kind of standard for the simulations that will have to be realized with these conditions to take into account the parameters identification. At a given time of integration, t, two systems are integrated successively: the global concentrations firstly, and secondly, the concentrations of the free species and of the dead polymer concentrations with their moments of order one and two.

Parameters Identification

An evolutionary algorithm[38,39] was used to identify the unknown parameters of the model. The purpose was to find the acceptable set of solutions such as theoretical and experimental data may be the closer as possible. The individuals, vectors X, contained the possible values of the parameters. Performance of each individual X was calculated by the method of maximum likelihood estimator[40]which allowed to minimize function F:

$$F(X) = \sum_{k=1}^{nm} n_{ek} Log[J(k,X)] \tag{8}$$

where nm is the number of different types of measurements used for the identification, and n_{ek} is the number of experiments taken into account for the measurement of data k.

J(k,X) is the sum of squared discrepancies (the most straightforward way to measure the fitness between the model, Z_{theo}, and the measurements, Z_{exp}) for each type, k, of data Z measured:

$$J(k,X) = \sum_{i=1}^{ne} k[Z_{theo}(i,k,X) - Z_{\exp}(i,k)]^2 \tag{9}$$

where i corresponds to the different experiments and ne is the total number of experiments taken into consideration.

Experimental Part

Materials

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 N.V. The initiator was a liquid peroxide: ter-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.

Polymerization Process

The experiments were realized using a primary continuous reactor at laboratory scale constructed by De Feyter Terneuzen B.V. The process control and the corresponding software were realized by Camile Products. 2.3. In most experiments, the monomers to solvent ratio used was 40/60 wt % (with a styrene/ acrylonitrile ratio of 70/30 wt %).

Analytical Methods

Before analyses, the 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 a rotavapor equipment. The samples were then characterized by use of: (i) a Headspace GC coupled with a flame ionization detector to quantify the residual monomers and CTA, (ii) a GPC coupled with an UV detector to determine (through a calibration with polystyrene standards) the molecular weight distribution of SAN in the whole CPP and to quantify the amount of SAN present in the serum, (iii) a Malvern MS100 and a Coulter LS230 equipments together with a Philips FEG-SEM XL 30 to determine the particle size distribution, (iv) Proton (^{1}H)-NMR and carbon (^{13}C)-NMR spectroscopy to establish the global composition in styrene and acrylonitrile of the SAN copolymer and to determine the overall polyol bonded to the total SAN solid.

Results and Discussion

Fixed Parameters of the Model

Some reliable parameters issued from a previous work[36] were used. They concerned first the partitioning coefficients of acrylonitrile (A) $H_A = 1$ and styrene (B) $H_B = 0.9$ in thermodynamic equilibrium. Concerning the initiator, 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 at $Q_{sm} = 25$ g/min), it is decomposed almost completely as soon as it enters in the reactor and therefore the quantity of free initiator inside the particles is negligible with a partitioning coefficient $H_I = 0$. That means that the polymerization in the particles only occurs after precipitation of active radicals, which terminate rather quickly.

The kinetic constant of initiator dissociation is:

$$k_d^c = 2,45 \cdot 10^{15} Exp\left(-\frac{134000}{8,314 \cdot T}\right) \ (\mathrm{s}^{-1}) \tag{10}$$

To simplify the system to solve, the coefficients of absorption of the different species were considered to be equal.

Identified Parameters of the Model

24 parameters were identified with data resulting from runs carried out using different monomers, initiator, chain transfer agent and stabilizer precursor concentrations at 140 °C and 120 °C respectively. This allowed then to validate the model on measurements done on standards recipes produced at 130 °C. Twelve different physical properties of the CPP samples were used:

- The average molecular weights in the whole CPP : $\overline{M}_n$ and $\overline{M}_w$ ($g \cdot mol^{-1}$),
- The weight percentage of solids in stripped CPP (wt-% solid),
- The residual acrylonitrile, styrene and CTA quantities (wt-%),
- The quantity of SAN copolymer present in the continuous phase (wt-%),
- The acrylonitrile composition of the SAN copolymer (wt-%),
- The percentage of grafted SAN chains in the serum phase, (%)
- The percentage of grafted high molecular weight SAN in the whole CPP, (%)
- The weight percentage of polyol in the solids, (wt-%)
- The surface area moment mean diameter (μm).

At 140 °C, 17 runs were carried out with 12 measurements per experiment. Therefore 204 data were used to identify the 24 parameters of the model. At 120 °C, 13 runs were carried out with 12 measurements per experiment (i.e.156 data). The values of the parameters corresponding to the lowest maximum likelihood estimator, F(X), for each temperature, are given in Table 2,

Table 2.
Results of parameter identification at 140 °C and 120 °C

Parameter	Meaning	T = 140 °C	T = 120 °C
k^c_{pAA} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for acrylonitrile homopropagation (continuous phase)	2380	2200
k^c_{pBB} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for styrene homopropagation (continuous phase)	48.1	48
k^c_{tcAA} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for homotermination by combination of oligoradicals terminated by acrylonitrile (continuous phase)	$1.27\ 10^8$	$1.67\ 10^8$
k^c_{tcBB} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for homotermination by combination of oligoradicals terminated by styrene (continuous phase)	$3.40\ 10^6$	$2.43\ 10^6$
R^c_{AB}	Reactivity ratio between oligoradicals terminated by acrylonitrile and styrene (continuous phase)	0.42	0.43
R^c_{BA}	Reactivity ratio between oligoradicals terminated by styrene and acrylonitrile (continuous phase)	0.30	0.29
$R^c_{t,A}$	Reactivity ratio between oligoradicals terminated by acrylonitrile and chain transfer agent (continuous phase)	3.9	2.7
$R^c_{t,B}$	Reactivity ratio between oligoradicals terminated by styrene and chain transfer agent (continuous phase)	8.1	9.0
ϕ	Cross-termination coefficient	27	28
k^p_{pAA} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for the homopropagation of acrylonitrile in the particles	9840	8800
k^p_{pBB} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for the homopropagation of styrene in the particles	490	265
Gel1	Gel effect coefficient (adjustable parameter of the model)	1.0	1.3
R^p_{AB}	Reactivity ratio between oligoradicals terminated by acrylonitrile and styrene in the particles	0.50	0.45
R^p_{BA}	Reactivity ratio between oligoradicals terminated by styrene and acrylonitrile in the particles	0.48	0.28
K_p (s^{-1})	Constant of precipitation	$5.9.10^{-5}$	$8.85\ 10^{-5}$
R^c_{AG}	Reactivity ratio between oligoradicals terminated by acrylonitrile and SMAC (continuous phase)	0.32	0.77
R^c_{BG}	Reactivity ratio between oligoradicals terminated by styrene and SMAC (continuous phase)	29.3	36.3
$k^c_{tr,G}$ ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant of the transfers of the oligoradicals to SMAC (continuous phase)	1900	1810
k^c_{tdAG} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for dismutation of oligoradicals terminated by SMAC and by acrylonitrile (continuous phase)	$1.72\ 10^8$	$1.57\ 10^8$
k^p_{tdBG} ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	Kinetic rate constant for dismutation of oligoradicals terminated by SMAC and by styrene in the particles	$1.01\ 10^7$	$1.57\ 10^7$
a $m \cdot (mol \cdot kg^{-1})^{1/3}$	Adjustable parameter of the model	$2.5\ 10^{-9}$	$3.65\ 10^{-9}$
Gel2	Gel effect coefficient (adjustable parameter of the model)	11.0	11.9
f_c	Initiator efficiency in the continuous phase	0.27	0.28
H_{CTA}	Partitioning coefficient of the chain transfer agent	0.64	0.55
F(x)	Maximum likelihood estimator	322.60	384.98

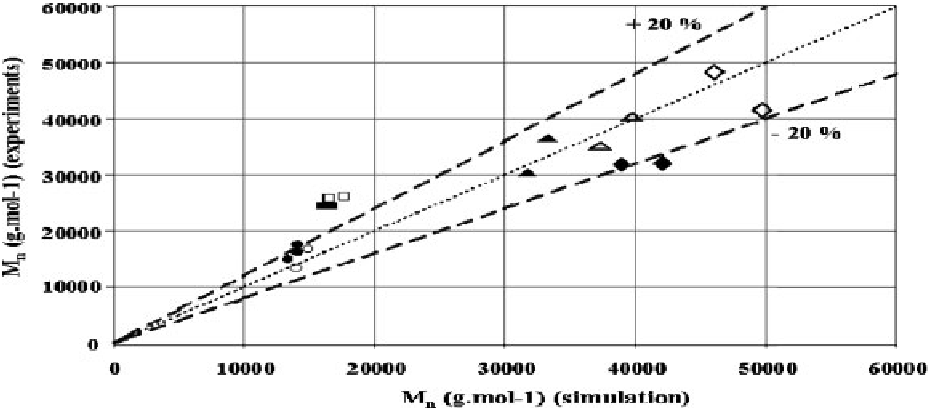

Figure 1.
Mn: experimental vs. simulated values (Identification at 140 °C). ◇: [I] = 0.1%, [CTA] = 0.15%; ◆: [I] = 0.2%, [CTA] = 0.15%; □: [I] = 0.1%, [CTA] = 0.45%; ■: [I] = 0.2%, [CTA] = 0.45%; △: [I] = 0.1%, [CTA] = 0.15%; ▲: [I] = 0.2%, [CTA] = 0.15%; ○: [I] = 0.1%, [CTA] = 0.45% ; ●: [I] = 0.2%, [CTA] = 0.45%. Squares and rhombs correspond to St/AN = 60/40 wt%. Circles and triangles correspond to St/AN = 80/20 wt%.

which shows that the values obtained at both temperatures are close.

The analysis and comparison of the results thus obtained with some corresponding values from the literature make it possible to attest coherence of these identified values.

Associated Results

Figure 1 to 6 compare, as examples, for some experiments, certain experimental and simulated results (e.g. Mn, Mw, total amount of solids, AN, St and CTA conversions) obtained for two temperatures, [I] and [CTA] concentrations and St/AN ratios.

Except for molecular weights (mainly Mw) which are underestimated, a good agreement between the model and the experiments is shown. Experimental errors of ±20% for Mn and Mw and ±5% for the other properties show the actual limits of the model. The underestimation of the average molecular weights will be discussed in next paragraph.

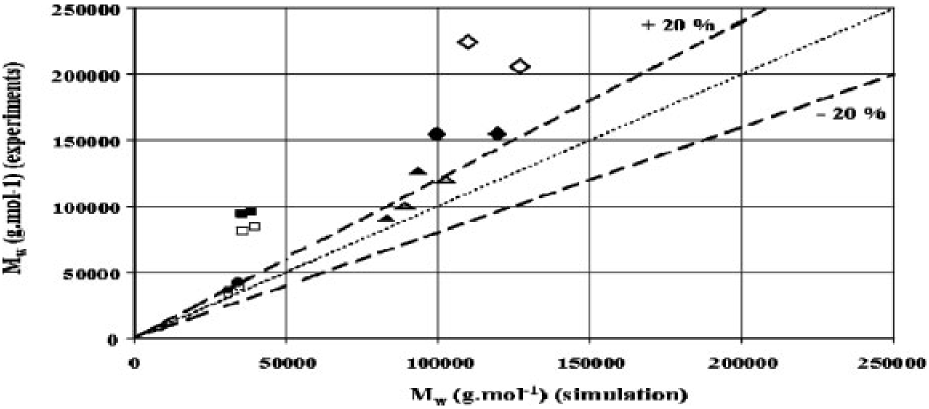

Figure 2.
Mw: experimental vs. simulated values (Identification at 140 °C)

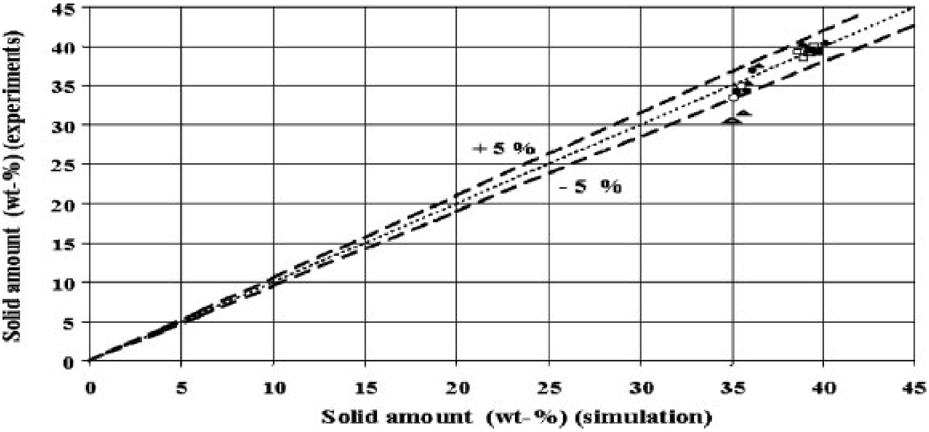

Figure 3.
Solid amount: experimental vs. simulated values (Identification at 140 °C).

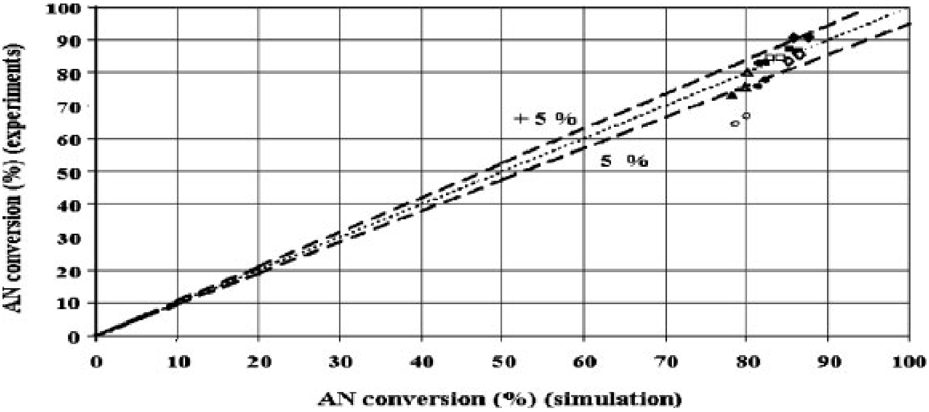

Figure 4.
Acrylonitrile conversion: experimental vs. simulated values (identification at 140 °C).

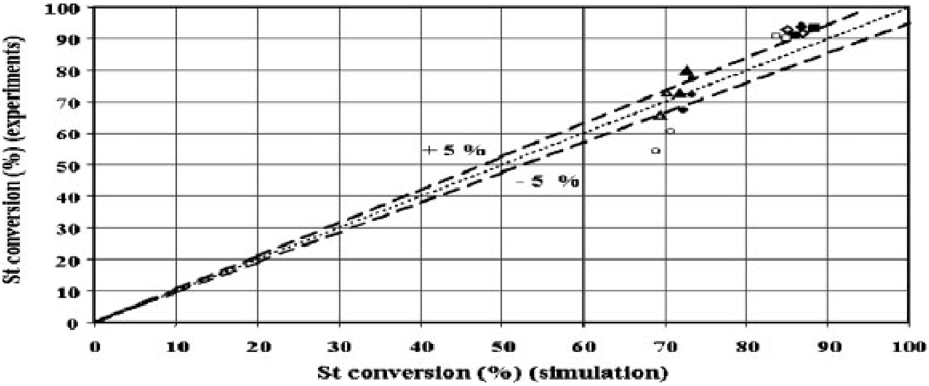

Figure 5.
Styrene conversion: experimental vs. simulated values (Identification at 120 °C).

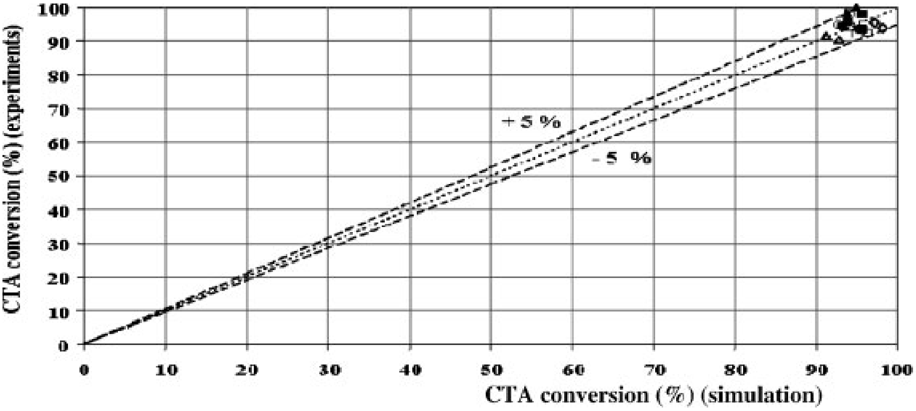

Figure 6.
CTA conversion: experimental vs. simulated values (Identification at 120 °C).

Validation of the Model and Discussion

The parameters of the model were determined at 130 °C from the parameters identified at 120 °C and 140 °C. Indeed, as these values are close to each other (Table 2) at these temperatures, the values of the parameters at 130 °C were considered to be the arithmetic mean values between 120 °C and 140 °C.

Table 3 shows the results of the simulation at 130 °C under standard industrial operating conditions and the experimental intervals established with the corresponding runs. For each data the number of measurements realized is indicated. Then, the experimental intervals take into account the estimated accuracy on each measurement.

As previously, Mn and Mw are also underestimated by the model, but the experimental confidence interval does not take into account the fact that the measured values are not the absolute ones which should indeed be around 0.8 times the values obtained using polystyrene standards as reference considering that the SAN copolymer composition of the standard premix (St/AN = 70/30) is close to the composition of the azeotropic point (St/AN = 75/25). The solid amount fore-

Table 3.
Data simulated with standard conditions at 130 °C.

Data	Theoretical values	Experimental Interval	Unit	Number of measurements
$\overline{M}_n$	25300	26000–37900	g mol^{-1}	5
$\overline{M}_w$	59800	64100–98200	g mol^{-1}	5
Solids	38.5	32.1–40.3	wt-%	2
Residual AN	1.85	1.58–2.17	wt-%	2
AN conversion	85.7	83.2–87.7	%	2
Residual St	5.42	3.61–4.57	wt-%	2
Sty conversion	82.0	84.8–88.0	%	2
Residual CTA	140	96.3–118	ppm	1
CTA conversion	95.3	96.1–96.8	%	1
SAN composition in AN	30.9	19.2–34.8	wt-%	2
SAN in serum	0.56	0.84–1.28	wt-%	2
SAN grafted in serum	24.2	42.1–93.2	%	2
SAN grafted in CPP	16.2	12.9–19.3	%	1
Polyol in solid	5.98	1.54–3.25	wt-%	2
D[3, 2]	0.346	0.71–1.06	μm	1

casted corresponds well to the measurements, together with that of acrylonitrile conversion.

Styrene and CTA conversions are slightly underestimated (82% and 95.3% respectively). Nevertheless, overall the order of magnitude of the conversions is rather well foreseen. SAN copolymer composition in AN (30.9 wt-%), is in the range observed experimentally.

Concerning the serum, the model underestimates the quantity of SAN copolymer in the medium and the percentage of SAN chains that are grafted. Concerning the grafting in the whole CPP and in the solid, the percentage of SAN grafted in CPP that is forecasted is in the range of the measurements. However, the amount of polyol in the solid is overestimated. This means that the relationship in the model between the percentage of grafted SAN chains and the amount of polyol in the solid is not correct. This relationship is indeed based on the fact that all the grafts are SMAC molecules.

The mean particle size forecasted [D3,2] is underestimated. Nevertheless, the order of magnitude remains acceptable because the experimental particle size distribution is actually bimodal that cannot be foreseen by the model.

Conclusion

The purpose of this work was to study the CPP process on the widest range of experimental conditions, even using the less stable experimental conditions. It allowed understanding better the process and establishing a tendency model which is based on analytical data and which describes the properties of the copolymer polyols. Due to the complexity of the system, many parameters were required to be identified. Several assumptions and simplifications were done to reduce as far as possible their number, to solve the system and to identify these parameters. It must be remembered anyway, that this model is a tendency model. The parameters defined here are not the actual kinetic constants, but were obtained through parameter reduction in order to simplify the model, but with the aim to forecast the same data with an acceptable accuracy. Considering the lack of accuracy and the instability of several samples, the identification method tried to forecast as well as possible the experimental data. The final model obtained gives acceptable orders of magnitude for the average molecular weights, the solid composition and the conversions.

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