 DOI: 10.1002/masy.200751312

Estimation of Kinetic Parameters for the Polar-Modified Anionic Solution Copolymerization of 1,3-Butadiene and Styrene

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Summary: The application of the terminal copolymerization model to polar modified anionic initiated 1,3-butadiene/styrene systems in hydrocarbon solvent requires the determination of twelve kinetic model parameters. These include frequency factors ($k_{xY,\infty}$), activation energies (E_{xY}) and live chain end association numbers (n_{xY}) for all four possible combinations of live chain end termini and free monomer. The individual determination of all twelve parameters requires an enormous numerical effort and a large number of experiments. A method for estimating parameters with a minimum number of kinetic batch experiments in an industrial environment will be demonstrated.

Keywords: anionic; copolymerization; gPROMS; kinetics; S-SBR

Introduction

At the Dow Olefinverbund GmbH site in Schkopau, Germany, a wide variety of advanced Solution-Styrene-Butadiene-Rubber (S-SBR) recipes are manufactured in world scale 100 m^3 batch reactors by anionic solution copolymerization. When the market demands increased volume, opportunities to increase capacity of installed plants are investigated. A systematic methodology is essential for the optimization of the world scale batch reactors for the various S-SBR recipes. Maximized reactor output can be achieved in two ways:

1. Increasing polymer mass per batch
2. Reducing batch cycle time

Due to limitations of reactor and agitator geometry as well as process safety, the maximum polymer mass per batch is well defined and quickly achieved.

A batch cycle time reduction requires accurate knowledge of the fundamental kinetics of the reaction. The anionic solution copolymerization of 1,3-butadiene and styrene is a well studied reaction.[1–6] The choice of solvent or solvent-mixtures, initiator system, and microstructure modification system has a large influence on the kinetics of the reaction. It is therefore not always possible to find the required kinetic data from the literature for the recipe of interest. In some cases fundamental batch kinetic experiments are necessary to obtain the information needed to optimize the reactors for a particular S-SBR recipe.

Running batch kinetic experiments including materials preparation, operating the process control system, sampling, and clean up is very time consuming. In addition, expensive analyses of the samples have to be financed.

The aim of this paper is to present a practical method for the quick and reliable estimation of kinetic parameters for a single S-SBR recipe out of 10 l batch kinetic experiments.

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Initiator Model

An initiator molecule in a living anionic polymerization initiates a single polymer chain. This chain remains active until it is terminated by an intentional reaction. This has the consequence, that the initiator concentration is pre-determined by the molecular weight of the polymer needed. Chain transfer and thermal termination are not included in the model.[4–6] Despite conflicting reports in the literature, initiation is assumed to be instantaneous[7,8] and full conversion of initiator (I) to active initiator (I^*) is achieved:

$$I_0 \rightarrow I^*$$

It is well known that the activated initiator (I^*) and therefore the active chain ends associate in hydrocarbon solvents. The degree of association (α) is dependant on type of solvent and presence and concentration of polar modifier. The following species are assumed to be in equilibrium:

$$I^*_\alpha \leftrightarrow \alpha \cdot I*$$

$$K_{eq} = \frac{(c_{I*})^\alpha}{c_{I^*_\alpha}}$$

where only the disassociated form of I^* participates in the reaction. The equilibrium is strongly dominated by the associated form ($I_\alpha{}^*$), which leads to:

$$c_{I_0} \approx \alpha \cdot c_{I^*_\alpha}$$

$$c_{I^*} = \left(\frac{1}{\alpha} \cdot K_{eq} \cdot c_{I_0}\right)^{\frac{1}{\alpha}}$$

This behavior applies to the active chains as well. This implies that the total molar concentration of active chain ends is equal to the initial concentration of initiator:

$$\begin{aligned} c_{I_0} &= c_{\tilde{x}^*} \\ &= c_{\tilde{s}^*} + c_{\tilde{b}*} = const. \end{aligned}$$

Copolymerization Model

The terminal copolymerization model is well defined and has often been used for the S-SBR system.[1,9] Here it is assumed that only the species of the terminal unit on the living polymer chain influences the propagation reaction:

1. Butadiene Homopolymerization (xY = bB)
$$\tilde{b}^*_i + B \rightarrow \tilde{b}^*_{i+1}$$
2. Cross Polymerization (xY = bS)
$$\tilde{b}^*_i + S \rightarrow \tilde{s}^*_{i+1}$$
3. Cross Polymerization (xY = sB)
$$\tilde{s}^*_i + B \rightarrow \tilde{b}^*_{i+1}$$
4. Styrene Homopolymerization (xY = sS)
$$\tilde{s}^*_i + S \rightarrow \tilde{s}^*_{i+1}$$

The reaction is 1st order with respect to monomer and a fractional order ''n'' with respect to chain ends due to the characteristic living chain end association in a hydrocarbon solvent.[10–13] The association number ''n'' is the reciprocal of the degree of association:

$$n = \frac{1}{\alpha}$$

The resulting general rate law with intrinsic kinetic rate constants $k_{xY,kin}$ is:

$$r_{xY} = k_{xY,kin} \cdot (n_{xY} \cdot K_{eq,xY} \cdot c_{\tilde{x}*})^{n_{xY}} \cdot c_Y$$

which is further lumped to the general rate equation for the terminal model:

$$r_{xY} = k_{xY} \cdot c^{n_{xY}}_{\tilde{x}*} \cdot c_Y$$

Implementing an Arrhenius-Type temperature dependency, the final rate equation is:

$$r_{xY} = k_{xY,\infty} \cdot e^{-\frac{E_{xY}}{R \cdot T}} \cdot c^{n_{xY}}_{\tilde{x}*} \cdot c_Y$$

1. Butadiene Homopolymerization (xY = bB)
$$r_{bB} = k_{bB,\infty} \cdot e^{-\frac{E_{bB}}{R \cdot T}} \cdot c^{n_{bB}}_{\tilde{b}*} \cdot c_B$$
2. Cross Polymerization (xY = bS)
$$r_{bS} = k_{bS,\infty} \cdot e^{-\frac{E_{bS}}{R \cdot T}} \cdot c^{n_{bS}}_{\tilde{b}*} \cdot c_S$$
3. Cross Polymerization (xY = sB)
$$r_{sB} = k_{sB,\infty} \cdot e^{-\frac{E_{sB}}{R \cdot T}} \cdot c^{n_{sB}}_{\tilde{s}*} \cdot c_B$$
4. Styrene Homopolymerization (xY = sS)
$$r_{sS} = k_{sS,\infty} \cdot e^{-\frac{E_{sS}}{R \cdot T}} \cdot c^{n_{sS}}_{\tilde{s}*} \cdot c_S$$

Frequency factors ($k_{xY,\infty}$), activation energies (E_{xY}) and live chain association

Table 1.
Twelve model parameters to be estimated

Parameter	$k_{xY,\infty}$	E_{xY}	n_{xY}
xY = bB	1	2	3
xY = bS	4	5	6
xY = sB	7	8	9
xY = sS	10	11	12

numbers (n_{xY}) are needed for each of the four possible chain propagation reaction equations. It is clear from the reaction equations that the terminal model requires twelve parameters for the S-SBR system. This poses a challenge for parameter estimation.

Depending on the details of the system considered, certain simplifying assumptions can be made. According to investigations on the associated species, there are no significant mixed association complexes,[13] so:

$$n_{bB} = n_{bS}$$

$$n_{sS} = n_{sB}$$

Under certain circumstances, i.e. fully polar modified systems,[5] the equality of the association numbers for all reactions may be assumed.

$$n_{bB} = n_{bS} = n_{sB} = n_{sS}$$

Parameter Estimation Strategy

The estimation of all parameters as a single high-dimensional optimization task is principally possible with the gPROMS software.[14,15] This poses an enormous effort to properly parameterize the numerical problem for convergence and always leads to mathematical instability. The key to dealing with the large number of parameters to be estimated is to break the complex optimization task down to a series of single and double dimensional optimization tasks. This is achieved under the assumption that the homopolymerization kinetics are totally independent of the other monomer species present, which is implied in the reaction rate equations.

The following method is proposed:

Uncoupling the homopolymerizations from the copolymerization allows kinetic parameters for the homopolymerizations to be determined by running simple single species homopolymerization batch experiments. Analysis of samples is therefore limited to simple gravimetric determination of polymer content. This is the key to obtain the most information with the least effort. The frequency factors and activation energies can then be regressed using the classical Arrhenius diagram for experiments run at a wide range of temperatures.

The more challenging task is the estimation of the parameters for the cross polymerizations. Experiments run with both monomer species are necessary. The most effective method for evaluation is to:

1. Run experiments at constant temperature
   → Independence from activation energy
2. Run all experiments at the same typical initiator concentration
   → Independence from degree association
3. Fix the estimated homopolymerization parameters during evaluation
   → Reduction to 2-dimensional optimization task

It is, however, mathematically no longer possible to estimate the two remaining parameters (k_{sB} and k_{bS}) with simple gravimetric determination of polymer content. The composition of the polymer samples or the concentration of residual monomer for one species is necessary. This makes the analysis more time consuming and expensive, so these experiments especially need to be minimized.

Further experiments at a wide range of initiator concentration are required to estimate the degrees of association (n_{xY}).

Preliminary Experimental Plan

Based on the parameter estimation strategy, a preliminary experimental plan can be

developed with a minimum number of experiments required. Due to unavoidable variation in the experimental results caused by the characteristic dependence of the anionic polymerization rate on slight variations in the trace impurities level,[16] it is practical to run 4 experiments at a wide temperature range for each series. In addition, if one experiment in the series is not successful, there are still 3 other points available for Arrhenius parameter estimation. This reduces the need to go back and repeat experiments after obtaining analysis results. This also allows for the identification of non-Arrhenius temperature effects (i.e. thermal termination or initiation effects).

As seen in Table 2, the practical minimum is 15 experiments for the preliminary estimation of all parameters for a single S-SBR recipe.

The temperatures chosen should include the minimum and maximum temperatures practically applied in production. The two temperatures in-between should be evenly spaced with respect to the reciprocal temperature to increase leverage.

The additional experiments for determination of the association number should be run at the most representative temperature in-between. The practical limits for the initiator concentration are:

Minimum: The smallest concentration possible to finish the experiment in a single work day with reasonable over-time

Maximum: The largest concentration where the cooling capacity and dynamics still achieve a constant temperature throughout the experiment.

The preliminary experimental plan for an imaginary S-SBR recipe is presented in Table 3:

Table 3.
Practically optimal experimental plan for imaginary S-SBR recipe

No.	Styrene [wt%]	T [°C]	c_I [mmol/l]
1	0	30	1,0
2	0	45	1,0
3	0	60	1,0
4	0	70	1,0
5	100	30	1,0
6	100	45	1,0
7	100	60	1,0
8	100	70	1,0
9	25	30	1,0
10	25	45	1,0
11	25	60	1,0
12	25	70	1,0
13	25	60	0,1
14	25	60	0,5
15	25	60	2,0

Imaginary S – SBR Recipe :

Styrene = 25%

cI = 1 mmol/l

$T_{min} = 30°C$

$T_{max} = 70°C$

Solvent, modifier and total monomer concentrations are constant

After numerical evaluation of the analyses from the preliminary experimental plan, the Experiment Design tools in gPROMS may be applied to identify optimum conditions and sampling times for one or more additional kinetic batch experiments if needed.[17]

Demonstration of Method

The presented method was applied to an S-SBR recipe with a high concentration of

Table 2.
Practical optimum number of experiments required

	Analyses required	Experiment Plan
1,3-Butadiene Homopolymerization	Gravimetric polymer content	4
Styrene Homopolymerization		4
Copolymerization at S-SBR recipe conditions	Gravimetric polymer content & composition	4
Additional copolymerizations for association numbers		3
Total number of experiments		15

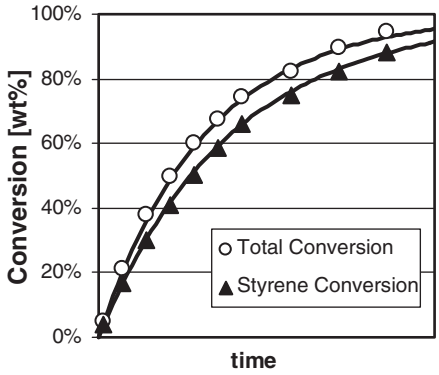

Figure 1.
Copolymerization example batch.

polar modifier. The results of the parameter estimation task and the statistical evaluation for the kinetic batch experiments of the highly modified system using gPROMS are shown in the following figures. Although the individual results are statistically accurate as indicated by the t-values, there is a relatively high level of correlation between the copolymerization rate constants. In addition, the rate constants for the ''sB'' reaction are much less accurate than the rate constants for the ''bS'' reaction.

The next step is to estimate Arrhenius parameters (and) with gPROMS:

According to the t-values at 95% confidence level, there is too little data to estimate the frequency factors precisely. This is due to their logarithmic nature. More disturbing is the high level of weighted residuals, especially for the ''sB'' parameters. The actual reaction system is indeed quite insensitive to the value of the rate constant k_{sB} (Table 6) because it is always an order of magnitude larger than the competing reaction with the rate constant k_{sS}. This explains the difficulty in estimating accurate parameters.

Table 4.
Estimated rate constants and statistical evaluation with gPROMS

T [°C]	k_{bB}	k_{bS}	k_{sB}	k_{sS}
	Estimated Parameter $\times 10^3$ [l/mol/s]			
30	483	480	220	116
45	1020	1080	1790	257
60	2410	1920	3220	513
70	4030	3150	10100	949
	95% Confidence Interval $\times 10^3$ [l/mol/s]			
30	10	25	22	5
45	20	70	430	12
60	60	30	380	21
70	120	130	3600	69
	95% t-value			
30	46,6	19,4	10,2	24,1
45	45,7	16,2	4,2	46,5
60	39,6	59,4	8,5	24,6
70	33,3	24,4	2,8	26,6
	Reference t-value:	1,7		

The insensitivity of conversion to k_{sS} is due to the randomization effect of the polar modifier. The styrene homopolymerization is practically non-existent. This avoids block styrene for this S-SBR recipe, which would have a strong influence on product quality.[18]

Finally, the association numbers were regressed using the experiments at a wide range of initiator concentrations at the copolymerization conditions (60°C):

As previously mentioned, the parameters regressed for the ''sB'' reaction are not very accurate and the parameter estimation is significantly lacking fit. However, both values agree with the assumption for highly modified systems that chain end association practically does not occur. For this case, the result is:

$$n_{bB} = n_{bS} = n_{sB} = n_{sS} = 1$$

Table 5.
Arrhenius parameter estimates and statistical evaluation with gPROMS ($\chi^2 = 6$)

$k_{xY,\infty}$ E_{xY}/R	Parameter		95% Conf. Interval		95% t-value		weighted residual
	[l/mol/s]	[K]	[l/mol/s]	[K]	Ref. t-value = 2,9		
xY = bB	9,7E + 07	5831	7,7E + 07	272	1,2	21,5	11
xY = bS	5,5E + 06	4939	4,8E + 06	294	1,2	16,8	46
xY = sB	2,4E + 12	8998	1,3E + 12	191	1,8	47,0	4738
xY = sS	2,3E + 07	5854	3,6E + 07	558	0,6	10,5	3

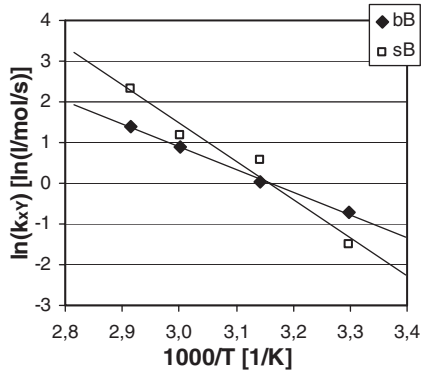

Figure 2.
Arrhenius diagram for 1,3-butadiene monomer polymerizations.

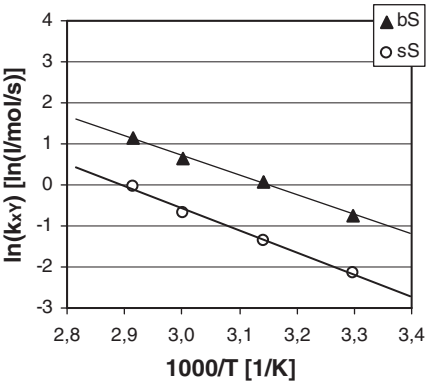

Figure 3.
Arrhenius diagram for styrene monomer polymerizations.

Validation of Scale-Up Results with Plant Data

The kinetic parameters estimated from the 10 l kinetic batch experiments were used in process simulations of the 100 m^3 production reactors. The cooling duty profile of a typical recipe was simulated using a measured temperature profile and compared to measured cooling duty data from the production reactors. With the exception of the batch start-up, where deviations caused by strong technical system dynamics occur (control system dynamics, cooling water system heat transfer dynamics, temperature measurement heat transfer dynamics), there is an acceptable level of agreement.

Table 6.
Sensitivity analysis: Sensitivity of conversion half-times to ±10% changes of the individual rate constants at 60 °C

Function	Total Conversion		Styrene Conversion	
Parameter Change	−10%	+10%	−10%	+10%
k_{bB}	7,3%	−6,3%	−0,2%	0,2%
k_{bS}	2,6%	−2,3%	10,4%	−8,5%
k_{sB}	0,8%	−0,7%	0,7%	−0,5%
k_{sS}	0,1%	−0,1%	0,2%	−0,2%

Refinement of Process Simulation

There may be value created by minimizing the error of the kinetic parameter estimation in gPROMS. We have shown that the parameters for the reaction

$$\tilde{s}_i^* + B \rightarrow \tilde{b}_{i+1}^*$$

are not statistically significant. The Experiment Design functions in gPROMS[17] may be applied to design further experiments that account for the sensitivity of these parameters.

Considering the industrial nature of this investigation, however, model improve-

Table 7.
Estimations and statistical evaluations for the parameters $k_{xy}{}^* c^n{}_{I,o}$

$c_{I,o}$	Parameter × 10^5		95% Conf. Interval × 10^5		95% t-value	
[mmol/l]	$k_{bS}{}^* c^n{}_{I,o}$	$k_{sB}{}^* c^n{}_{I,o}$	$k_{bS}{}^* c^n{}_{I,o}$	$k_{sB}{}^* c^n{}_{I,o}$	$k_{bS}{}^* c^n{}_{I,o}$	$k_{sB}{}^* c^n{}_{I,o}$
	[1/s]	[1/s]	[1/s]	[1/s]	ref. t-val: 1,7	
0,86	173	214	17	155	10,1	1,4
0,61	119	105	11	50	11,3	2,1
0,35	66,1	111	1,1	13	24,4	2,8
0,11	20,3	16,1	1,3	5	15,6	3,2

Table 8.
Estimations and statistical evaluations for the association numbers n_{xY} ($\chi^2 = 8$)

	n_{xY}	95% Conf.	95% t-value	ref. t-value	Weighted Residual
xY = bS	0,98	0,06	16,6	2,4	13
xY = sB	1,01	0,10	10,1	2,4	647

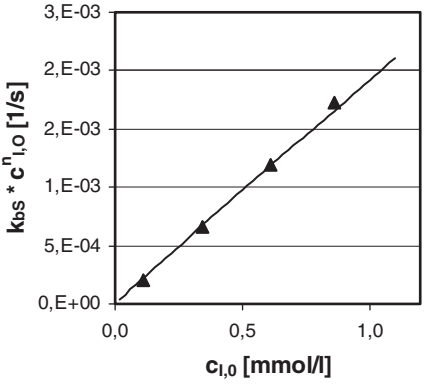

Figure 4.
Association number regression "bS".

ment efforts will be concentrated on refining the process model rather than the kinetic model parameters. Accounting for control dynamics and dynamic heat transfer to temperature measurements will most likely increase the accuracy of the process simulation.

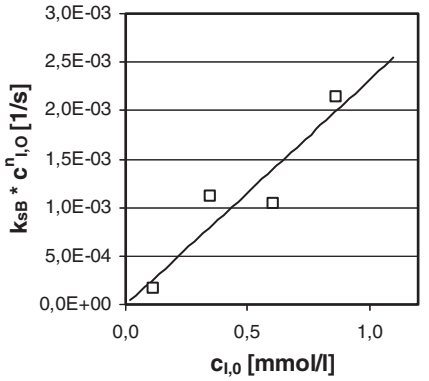

Figure 5.
Association number regression "sB".

Conclusion

A method was presented for the minimization of the number of kinetic batch experiments to obtain reliable kinetic parameters for industrial process simulation. A kinetic model with 12 parameters was parameterized using 15 kinetic batch experiments, of which only 7 involve expensive analysis, for an example S-SBR recipe. Together with the demonstrated parameter estimation strategy, scale-up results were obtained that agree reasonably with production plant data. Process simulations can therefore be used for a better insight of the world-scale copolymerization for optimization purposes.

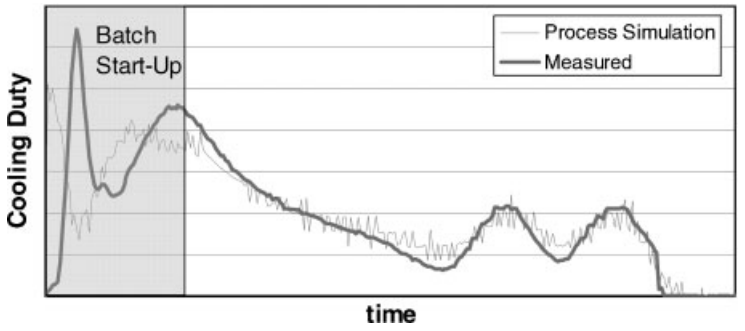

Figure 6.
Cooling-duty in 100 m^3 reactors: measured data & process simulation.

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