Free Radical and Ionic Polymerizations: PS and SBS Rubber

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Abstract

This chapter explores the modeling of manufacturing processes for polystyrene (PS) and poly(styrene-butadiene-styrene) (SBS) rubber, emphasizing their industrial relevance and production challenges. Unlike traditional polyolefin-focused literature, which often excludes PS, we incorporate it due to its significant production volume and valuable properties such as high dimensional stability and rigidity. PS, primarily produced through free radical polymerization, presents unique modeling challenges, notably the formation of oligomers, a complex aspect rarely addressed in depth in existing literature.

Additionally, the chapter examines the production of SBS rubber, a significant styrene-butadiene copolymer produced through ionic polymerization with living initiators, paralleling the precision of metallocene catalysts in polyolefins. Our approach combines free radical and ionic polymerization modeling, offering insights into process kinetics, component characterization, and polymer property prediction. This integrated modeling methodology enhances understanding of these commercially important polymers, contributing novel approaches for process optimization and production scalability.

This is a preprint version of a chapter from our book - *Integrated Process Modeling, Advanced Control and Data Analytics for Optimizing Polyolefin Manufacturing [25,31]. Please cite the original work if referenced*

Introduction

This chapter covers the modeling of manufacturing processes for polystyrene (PS) using free radical polymerization, and for poly(styrene-butadiene-styrene) rubber or SBS rubber using ionic polymerization.

Although some polyolefin textbooks (e.g. [1]) exclude PS in their discussion, we include PS in this book for the following reasons.

According to the classic polymerization book by Odian [2]: "Low- and high-density polyethylene, propylene and polymers of other alkene (olefin) monomers constitute the polyolefin family of polymers". One could argue for the inclusion of polystyrene based on its useful properties and its huge annual production. Odian states that "Although completely amorphous (glass transition temperature T_g = 85°C), its bulky rigid chains (due to phenyl-phenyl interactions) impart good strength with high-dimensional stability (only 1-3% elongation); polystyrene is a typical rigid plastic. About 2 billion pounds of styrene homopolymer are produced annually in the United States".

Schaller [3] states that: "Resonance delocalization in its reactive intermediates makes styrene amenable to almost any method of polymerization, including anionic, cationic, radical, and Ziegler-Natta methods". Likewise, Lohse [4] writes: "In general, polyolefins are defined as polymers made from olefins, which are principally ethylene and propylene, but also 1-butene, 1-hexene, 1-octene, isobutylene, and other monomers. (By this definition, one could also include polymers made from styrene as polyolefins)."

From a chemistry perspective, styrene polymerization to form polystyrene is always covered as a polyolefin, but in a context that may not be obvious from looking at a table of contents of textbooks. Usually, the context is chain polymerization, olefin polymerization, or specific methods such as radical polymerization [2, 4 to 7]. In fact, Odian has included styrene polymerization to form polystyrene in a table of chain polymerization by various unsaturated monomers in Table 3-1, p. 200 of his textbook [2].

For an engineering perspective, common polyolefins, such as HDPE, PP, LLDPE, and their copolymers (e.g., EVA copolymer), represent approximately 50% to 55% of commercial polymer production, and step-growth polymers (e.g., PET, Nylon, PLA) represent approximately 20% of the commercial polymer production [8]. By contrast, PS and its related copolymers such as styrene-butadiene block copolymer (SBC) represent approximately 10% of commercial polymer production, which is indeed a significant fraction. Secondly, PS is typically made by free radical polymerization in bulk, solution or suspension processes [2].

Modeling of commercial PS processes to match production targets and polymer properties, however, is a challenging task, mostly because of the presence of significant oligomer formation [9-11]. We are not aware of any published studies that demonstrate how to quantitatively incorporate oligomer formation in the modeling of PS.

A significant commercial copolymer of styrene is the poly(styrene-butadiene-styrene) rubber or SBS rubber using ionic polymerization. In particular, SBS rubber is the only example of large-volume styrene anionic polymerization with living organolithium initiators. It is similar to the use of metallocene catalysts for polyolefins which exhibit living polymerization characteristics; and the tacticity element of PS would also relate to the importance of tacticity for PP.

Therefore, this chapter covers both free radical and ionic polymerizations for producing PS and SBS rubber. Section 6.1 presents a hands-on workshop on the simulation of polystyrene with gel effect and oligomer formation. We explain the representation and characterization of components, oligomers and polymers; the selection of appropriate thermodynamic methods; estimation of essential property parameters; the kinetics of free radical polymerization, oligomer formation, and copolymerization for PS; and the simulation of commercial stirred autoclave reactors with multiple feed ports and of polymer product separation and monomer recycle. Section 6.2 covers a hands-on workshop on the production of poly(styrene-butadiene-styrene) or SBS rubber by ionic polymerization. We discuss the kinetics of anionic polymerization for SBS rubber, and the simulation of batch and semi-batch reactors for anionic copolymerization of styrene and butadiene to produce SBS rubber. We use the simulation software Aspen Polymers for this study. Section 6.3 gives the bibliography.

6.1 Workshop 6.1 - Simulation of Polystyrene Reactors with Gel Effect and Oligomer Formation

6.1.1 Objective

This workshop expands the fundamentals and practice of free radical polymerization presented in Chapter 4. In particular, we demonstrate how to deal with gel effect (Section 4.2.6) and oligomer formation in the polymerization kinetics.

Aspen Polymers has an example of polystyrene (PS) bulk polymerization by thermal initiation [12], which includes the gel effect. However, when applying this model to simulate a commercial PS process, we find that the calculated mass balance and polymer properties do *not* match the plant data. This follows because the Aspen Polymers PS model *has ignored the significant oligomer formation in commercial PS production*. An objective of this workshop is to demonstrate the details of simulating oligomer formation based on the published reaction information in references [9-11]. We illustrate how to draw the molecular structure of oligomers, how to generate functional groups to characterize the oligomers and estimate their property parameters, and how to define the relevant oligomer formation reactions. We also demonstrate how to use data fit tool to estimate relevant kinetic parameters to match plant data of PS production rate, MWN and MWW. This detailed illustration of how to include the oligomer formation distinguishes our work from all previous studies of PS simulation in the literature.

6.1.2 Process Flowsheet

Figure 6.1 shows a simplified schematic diagram of the three-reactor system of a commercial process for producing *general-purpose polystyrene (GPPS) homopolymer*.

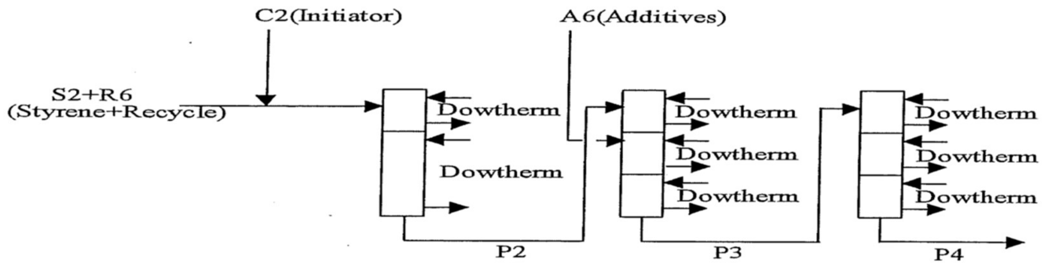


Figure 6.1 A schematic diagram of the three-reactor system of a polystyrene process.

In the system, we see two, three and three reaction zones within the three reactors in series. We use continuous stirred-tank reactor (CSTR) model to represent each reaction zone. Figure 6.2 shows an Aspen Polymers simulation flowsheet for the reactor system, with each CSTR representing a reaction zone within the three reactors in series. We save the simulation file as ***WS7.1_With Oligomers.bkp***. In doing this workshop, please make sure to save the simulation file as soon as we have completed the input for a given folder.

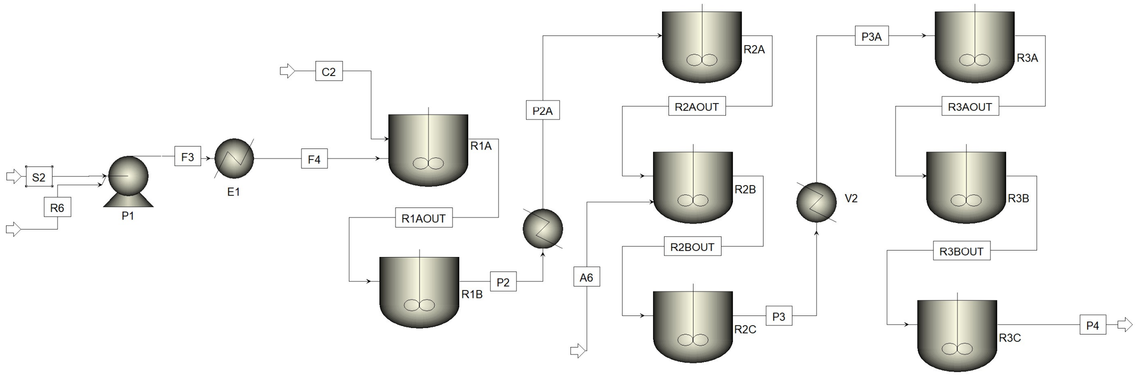
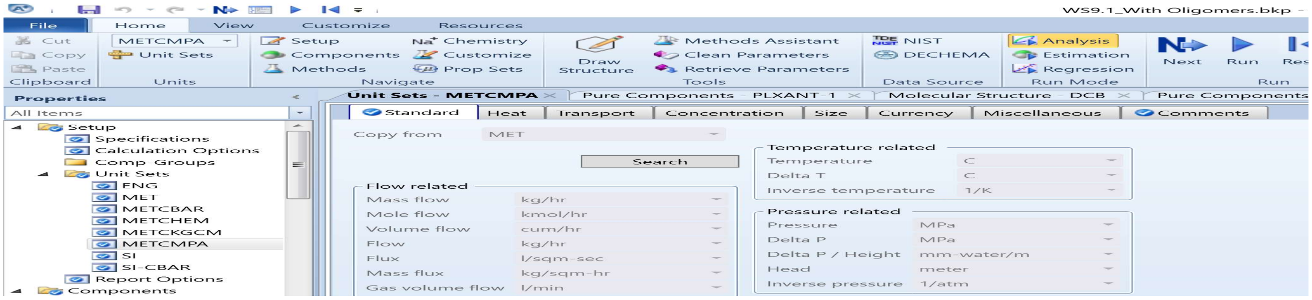


Figure 6.2 A simulation flowsheet of the three-reactor system for producing GPSS homopolymer.

6.1.3 Unit System, Components and Characterization of Polymer

We define a unit system METCMPA by copying most units from MET system, except to replace temperature unit by °C and pressure unit by MPa. See Figure 6.3.



Copy from: MET

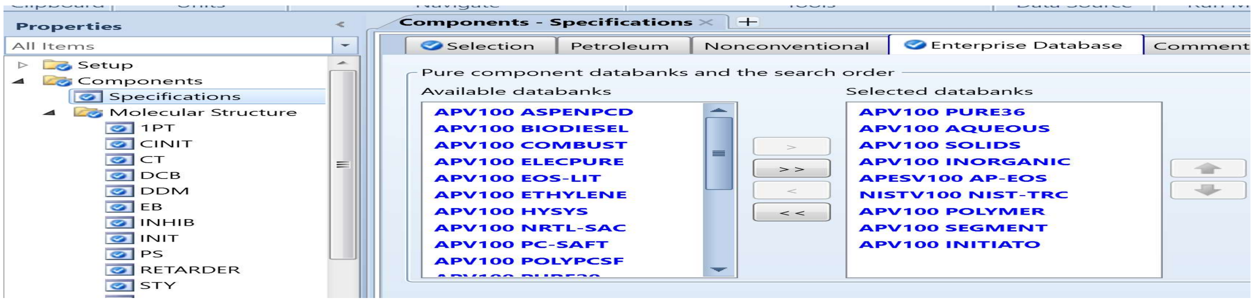
Flow related
Mass flow: kg/hr
Mole flow: kmol/hr
Volume flow: cum/hr
Flow: kg/hr
Flux: l/sqm-sec
Mass flux: kg/sqm-hr
Gas volume flow: l/min

Temperature related
Temperature: C
Delta T: C
Inverse temperature: 1/K

Pressure related
Pressure: MPa
Delta P: MPa
Delta P / Height: mm-water/m
Head: meter
Inverse pressure: 1/atm

Figure 6.3 Defining a unit system METCMPA by copying most units from MET system.

Figure 6.4 and 7.5 show the enterprise databanks and components used in the simulation of the GPPS and other free radical polymerization processes.

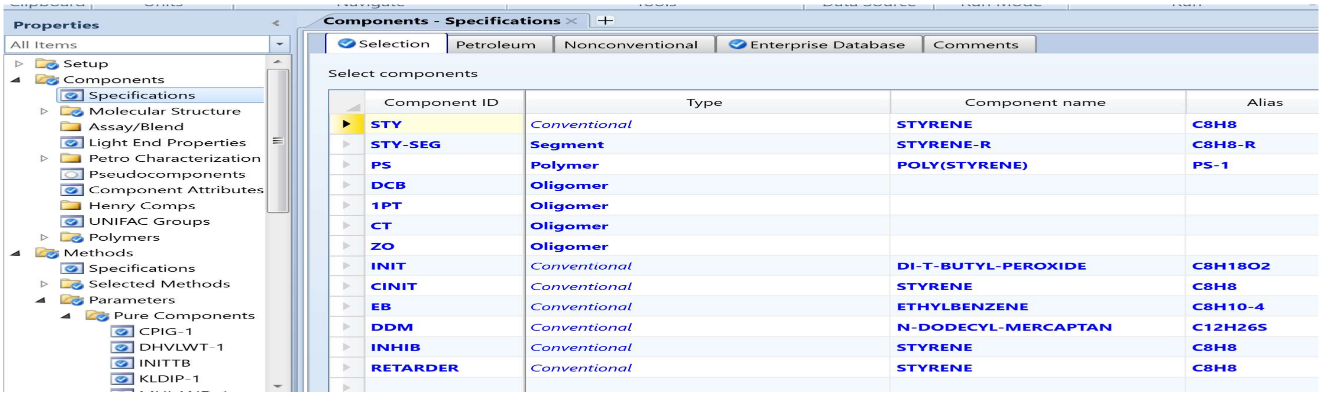


Pure component databanks and the search order

Available databanks
APV100 ASPENPCD
APV100 BIODIESEL
APV100 COMBUST
APV100 ELECPURE
APV100 EOS-LIT
APV100 ETHYLENE
APV100 HYSYS
APV100 NRTL-SAC
APV100 PC-SAFT
APV100 POLYPCSF

Selected databanks
APV100 PURE36
APV100 AQUEOUS
APV100 SOLIDS
APV100 INORGANIC
APESV100 AP-EOS
NISTV100 NIST-TRC
APV100 POLYMER
APV100 SEGMENT
APV100 INITIATO

Figure 6.4 Selected databanks used in the simulation.



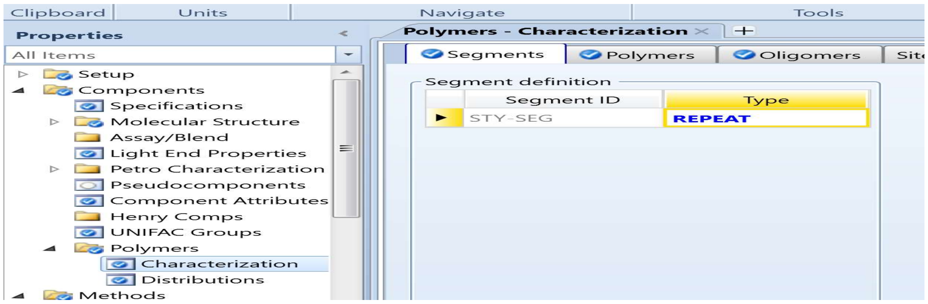
Select components

Component ID	Type	Component name	Alias
STY	Conventional	STYRENE	C8H8
STY-SEG	Segment	STYRENE-R	C8H8-R
PS	Polymer	POLY(STYRENE)	PS-1
DCB	Oligomer		
1PT	Oligomer		
CT	Oligomer		
ZO	Oligomer		
INIT	Conventional	DI-T-BUTYL-PEROXIDE	C8H18O2
CINIT	Conventional	STYRENE	C8H8
EB	Conventional	ETHYLBENZENE	C8H10-4
DDM	Conventional	N-DODECYL-MERCAPTAN	C12H26S
INHIB	Conventional	STYRENE	C8H8
RETARDER	Conventional	STYRENE	C8H8

Figure 6.5 Component specifications.

STY and STY-SEG are styrene monomer and styrene segment (repeat type). PS is the polystyrene product. INIT is the chain initiator, di-t-butyl-peroxide (DTBP), which is available within the Aspen Polymers initiator database. CINIT is the co-initiator, which is a *hypothetical* component required to activate the thermal initiation reaction in the model [12]. We use STY to represent CINIT, and set its mass flow rate in the feed to be zero. EB (ethyl benzene) and DDM (n-dodecyl mercaptain) are chain transfer agents. INHIB and RETARDER are inhibitor and retarder, which are presented by STY.

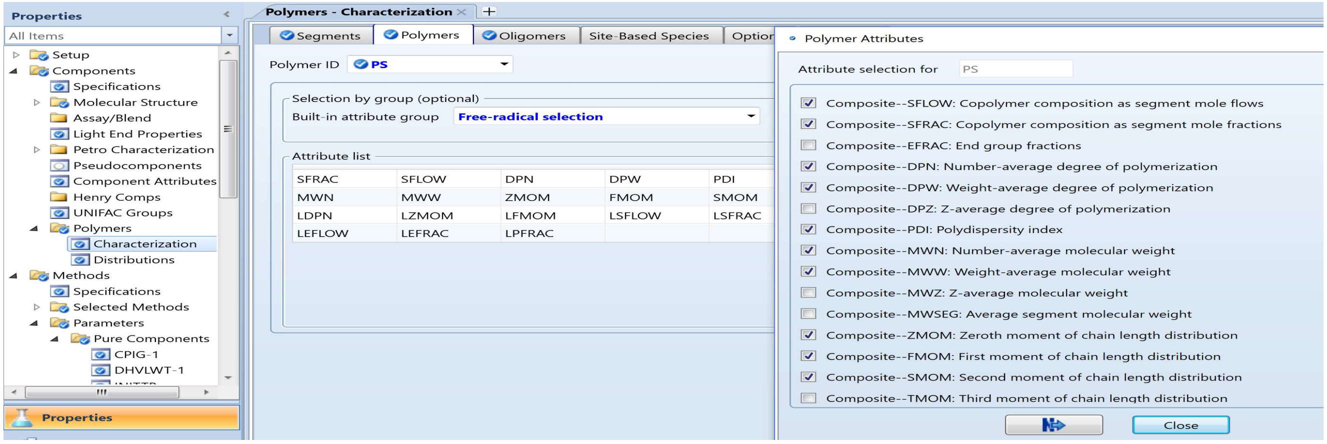
Figure 6.6 shows the definition of styrene segment, STY-SEG, and Figure 6.7 displays polymer attributes in the free radical polymerization and the attribute selection.



Segment definition

Segment ID	Type
STY-SEG	REPEAT

Figure 6.6 Definition of STY-SEG.



Polymer ID: PS

Selection by group (optional)

Built-in attribute group: Free-radical selection

Attribute list

SFRAC	SFLOW	DPN	DPW	PDI
MWN	MWW	ZMOM	FMOM	SMOM
LDPN	LZMOM	LFMOM	LSFLOW	LSFRAC
LEFLOW	LEFRAC	LPFRAC		

Attribute selection for: PS

- ☑ Composite--SFLOW: Copolymer composition as segment mole flows
- ☑ Composite--SFRAC: Copolymer composition as segment mole fractions
- ☐ Composite--EFRAC: End group fractions
- ☑ Composite--DPN: Number-average degree of polymerization
- ☑ Composite--DPW: Weight-average degree of polymerization
- ☐ Composite--DPZ: Z-average degree of polymerization
- ☑ Composite--PDI: Polydispersity index
- ☑ Composite--MWN: Number-average molecular weight
- ☑ Composite--MWW: Weight-average molecular weight
- ☐ Composite--MWZ: Z-average molecular weight
- ☐ Composite--MWSEG: Average segment molecular weight
- ☑ Composite--ZMOM: Zeroth moment of chain length distribution
- ☑ Composite--FMOM: First moment of chain length distribution
- ☑ Composite--SMOM: Second moment of chain length distribution
- ☐ Composite--TMOM: Third moment of chain length distribution

Figure 6.7 Free radical polymer attribute selection.

We characterize the oligomers DCB, 1PT, CT and ZO in the following section.

6.1.4 Characterization of Oligomers

Figure 6.8 illustrates the formation of four oligomers and intermediates identified by references [9-11]. These components are not available in the Aspen Polymers databanks. In the following, we demonstrate how to draw the molecular structure, characterize the structure by atoms and by functional groups, and estimate the required property parameters for the simulation. Figures 7.9a to 7.9d show the steps to use the drawing tools within Aspen Polymers to draw the DCB molecular structure.

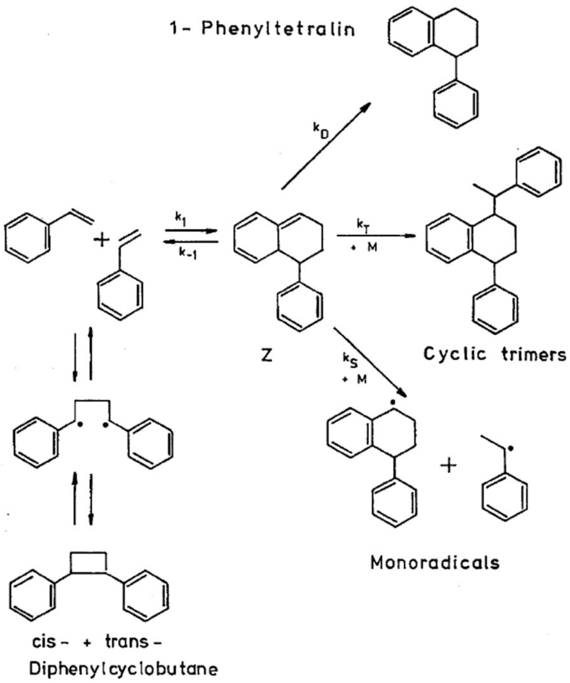


Figure 6.8 Formation of oligomers and intermediates in styrene polymerization [9,10]. We use DCB to represent 1,2-diphenylcyclobutane, 1PT to represent 1-phenyltetralin, ZO (instead of Z in the figure) to represent dimer (intermediate), and CT to represent cyclic trimer.

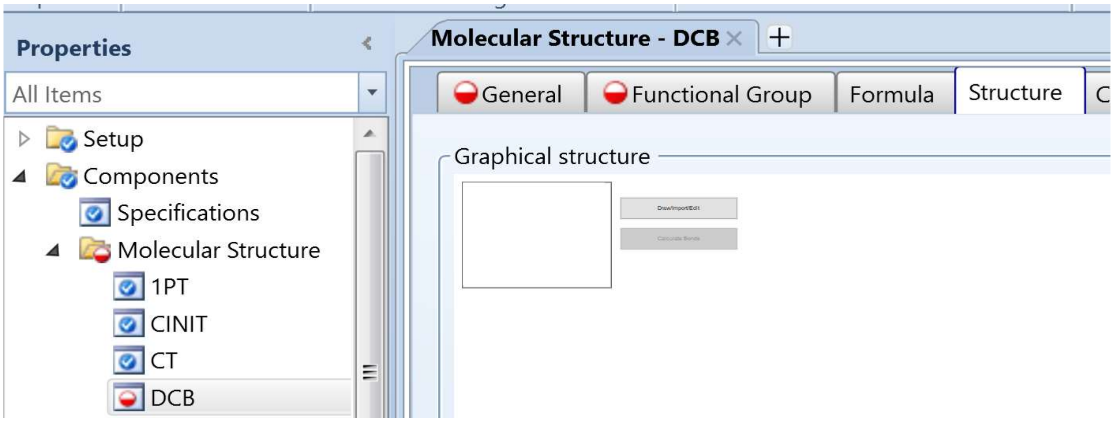


Figure 6.9a. Click on the Draw/Import/Edit button within the DCB molecular structure window to draw the structure.

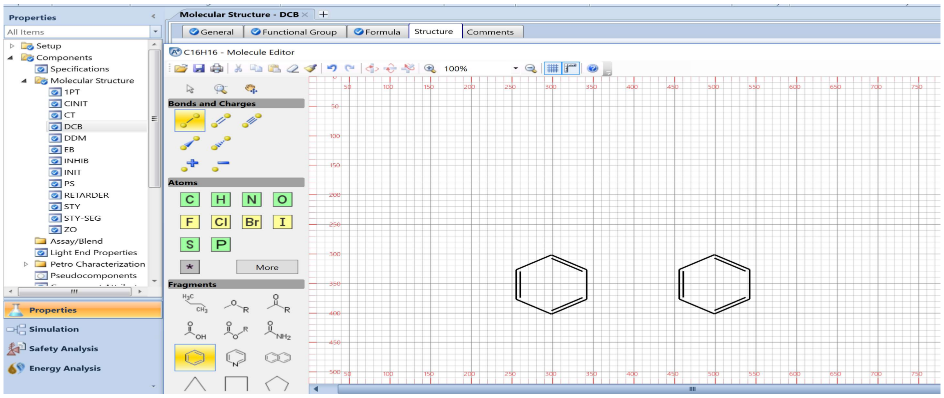


Figure 6.9b**.** Drawing the DCB structure –Step 1. Click on the benzene ring within Fragments, and paste it twice into the drawing plane, and then cancel the benzene ring within Fragments.

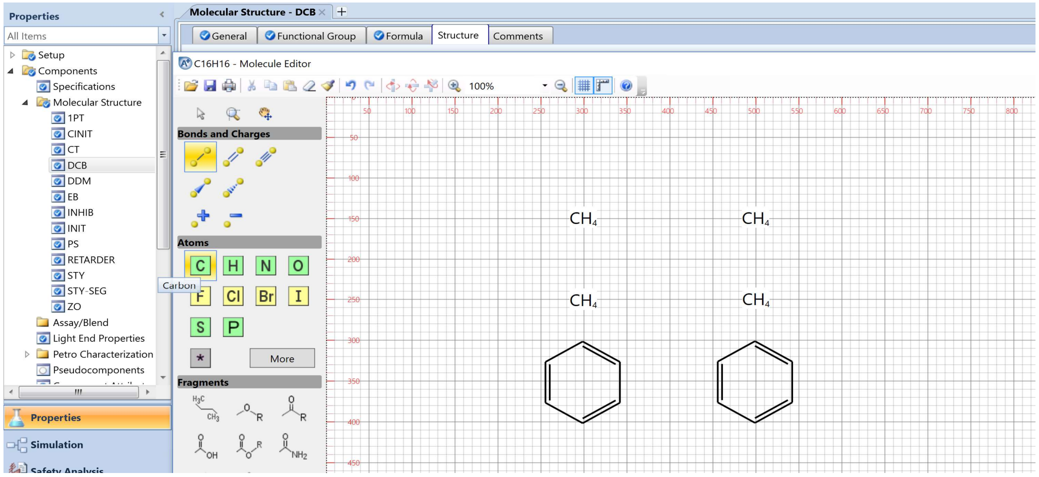


Figure 6.9c**.** Drawing the DCB structure –Step 2. Click on the carbon atom “C” within Atoms, and paste it four times into the drawing plane, and then cancel the carbon atom.

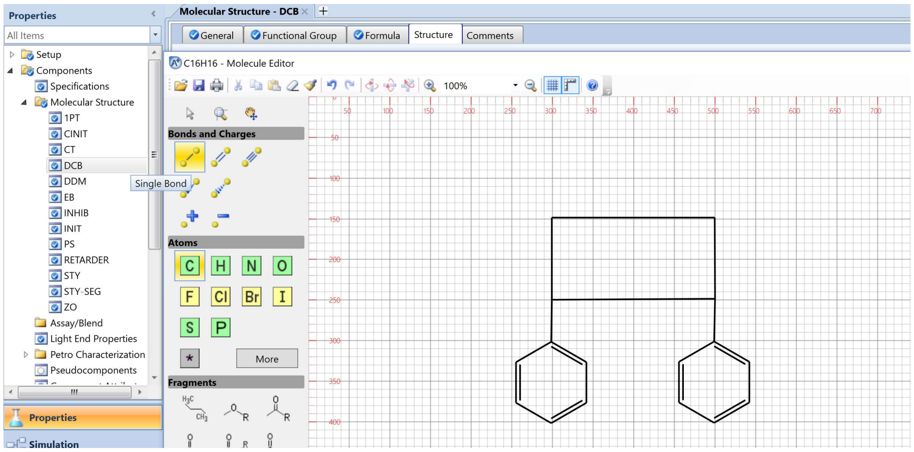


Figure 6.9d**.** Drawing the DCB structure –Step 3. Click on the single bond within Bonds and Charges, and connect carbon atoms with straight lines six times into the drawing plane, and then cancel the single bond.

We save the molecular structure drawn in Figure 6.9d as a molecular file, ***DCB.mol***, and close the drawing window. (*Note*: In Section 4.4.3, Figures 4.18, 4.19a and 4.19b, we demonstrate how to search for the molecular file, ****.mol***, of our component molecule that is not available within Aspen Polymers databank, but may be available in the Internet. If it is available, we can download the ****.mol*** and import it directly into Aspen Polymers. This will save us time by not going through the steps illustrated in Figures 7.9a to 7.9d). Next, we see the "Calculate Bonds" button, as displayed in Figure 6.9e.

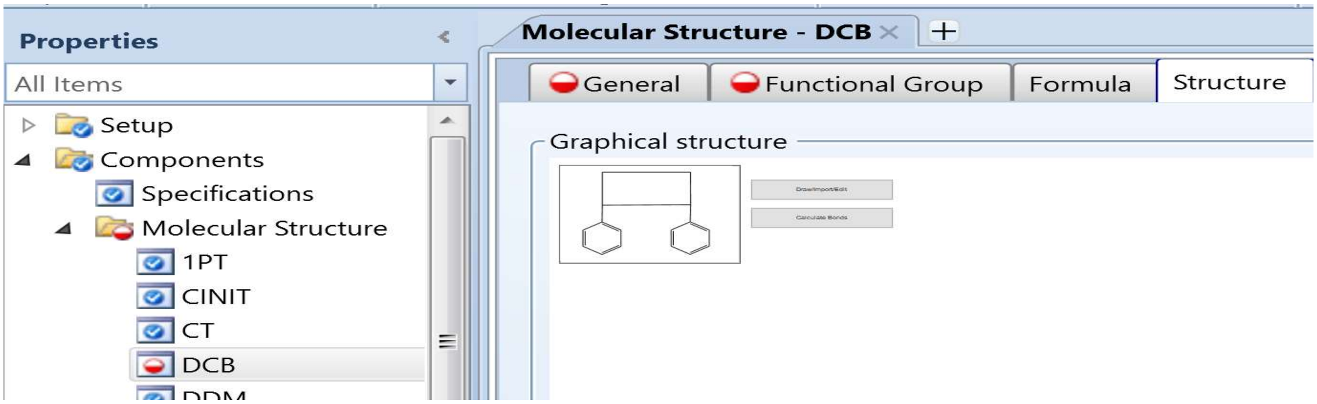
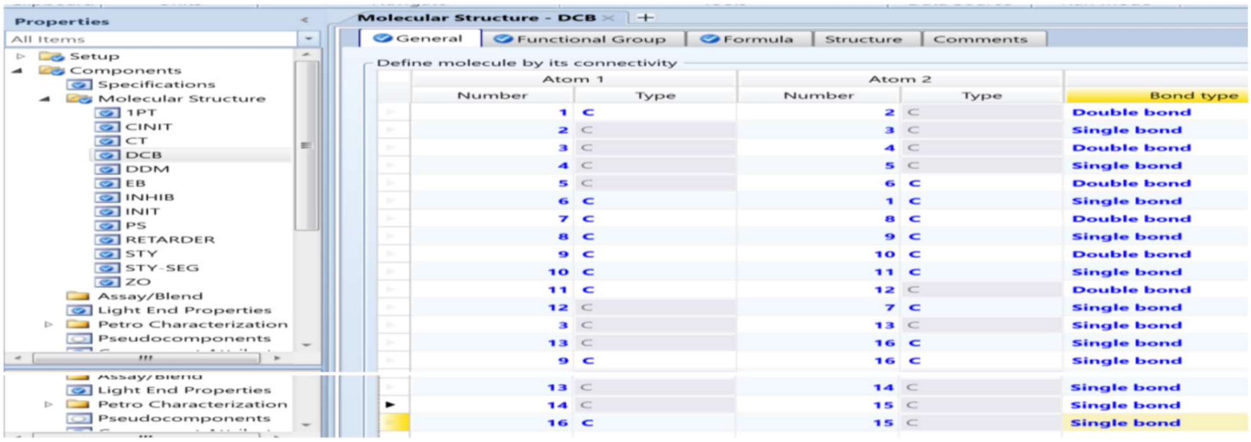


Figure 6.9e The DCB molecular structure and the "Calculate Bonds" button.

After clicking on the "Calculate Bonds" button, Aspen Polymers automatically completes the "General" structure folder, and the "Functional Group" folder. Figure 6.9f shows the general structure.



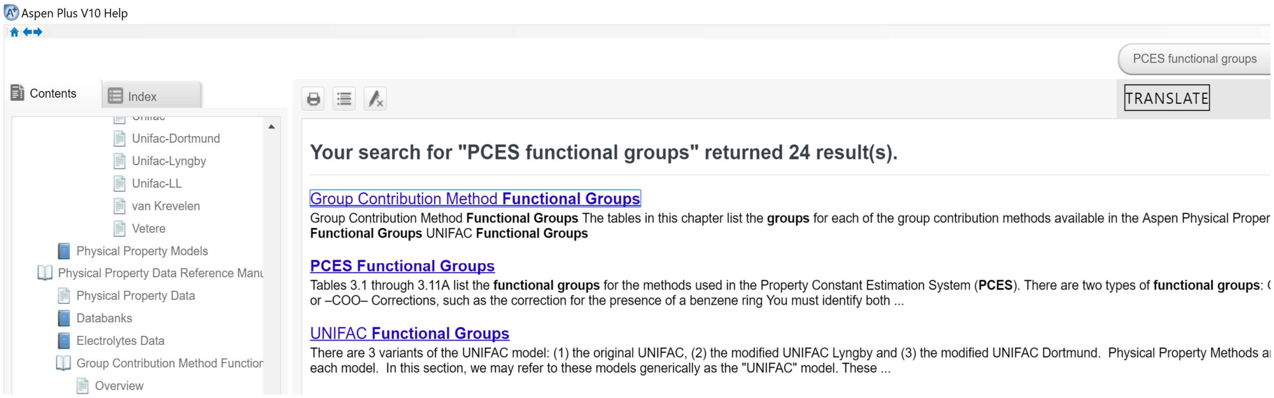
Define molecule by its connectivity

Atom 1		Atom 2		
Number	Type	Number	Type	Bond type
1	C	2	C	Double bond
2	C	3	C	Single bond
3	C	4	C	Double bond
4	C	5	C	Single bond
5	C	6	C	Double bond
6	C	1	C	Single bond
7	C	8	C	Double bond
8	C	9	C	Single bond
9	C	10	C	Double bond
10	C	11	C	Single bond
11	C	12	C	Double bond
12	C	7	C	Single bond
3	C	13	C	Single bond
13	C	16	C	Single bond
9	C	16	C	Single bond
13	C	14	C	Single bond
14	C	15	C	Single bond
16	C	15	C	Single bond

Figure 6.9f. The molecular structure automatically defined by Aspen Polymers based on the chemical structure of Figure 6.9d.

To understand the atom number and the connectivity in Figure 6.9f, we note that from atom 1 to atom 6, and from atom 7 to atom 12, each connectivity represents a benzene structure. Aspen Polymers specifies a *clockwise* 360-degree benzene structure, with the upper top carbon atom and lower bottom carbon atom occupying the 0° and 180° locations, respectively. For two connected benzene rings, the first atom is at 240° location.

Based on the molecular structure displayed in Figure 6.9d, Aspen Polymers also automatically specifies the numbers of UNIFAC and JOBACK functional groups for the structure in order for the PCES (Physical Constant Estimation System) to estimate the required property parameters for the structure. To understand the details of the UNIFAC and JOBACK functional groups, we search for the functional group numbers: Aspen Polymers ->Help -> Search for “PCES functional groups” -> Results: PCES functional groups and UNIFAC functional groups, as seen in Figure 6.9g. Table 3.5 within “PCES functional groups” of Aspen Polymers online help specifies the JOBACK functional group numbers, and Table 3.12 within “UNIFAC functional groups” of Aspen Polymers online help specifies the UNIFAC functional group numbers.



Your search for "PCES functional groups" returned 24 result(s).

Group Contribution Method **Functional Groups**

Group Contribution Method **Functional Groups** The tables in this chapter list the **groups** for each of the group contribution methods available in the Aspen Physical Proper **Functional Groups** UNIFAC **Functional Groups**

PCES Functional Groups

Tables 3.1 through 3.11A list the **functional groups** for the methods used in the Property Constant Estimation System (**PCES**). There are two types of **functional groups**: or –COO– Corrections, such as the correction for the presence of a benzene ring You must identify both ...

UNIFAC **Functional Groups**

There are 3 variants of the UNIFAC model: (1) the original UNIFAC, (2) the modified UNIFAC Lyngby and (3) the modified UNIFAC Dortmund. Physical Property Methods a each model. In this section, we may refer to these models generically as the "UNIFAC" model. These ...

Figure 6.9g. Search results for “PCES functional groups”.

We summarize the resulting numbers of UNIFAC and JOBACK functional groups for our four oligomers in Table 6.1. We also show the molecular structures of 1PT (1-phenyltetralin), ZO (dimer), and CT (cyclic trimer) in Figure 6.10a to 6.10c. Because of the largest numbers of UNIFAC functional groups available within the Aspen Polymers databank, two different combinations of UNIFAC group numbers may represent the same molecular structure. For example, Aspen Polymers uses UNIFAC functional group 1050 (C=C), instead of functional groups 1005 (>CH-) and 1100 (>CH2) as in Table 6.1, to represent ZO (dimer). In other words, the correct listing of functional group numbers is not unique. As long as we have drawn the correct molecular structure, we can simply let Aspen Polymers define the functional group combination for a given molecule.

Table 6.1 Numbers of UNIFAC and JOBACK functional groups within the molecular structures of oligomers.

Functional groups	>CH-	=C<	-CH3	>CH2	=CH-
UNIFAC group number	1005	1010	1015	1100	1105
JOBACK group number	111	114	100	110	113
Number of functional groups in the molecular structure					
DDB	2	2		2	10
1PT	1	3		3	9
ZO	1	2		2	10
CT	3	2	1	4	14

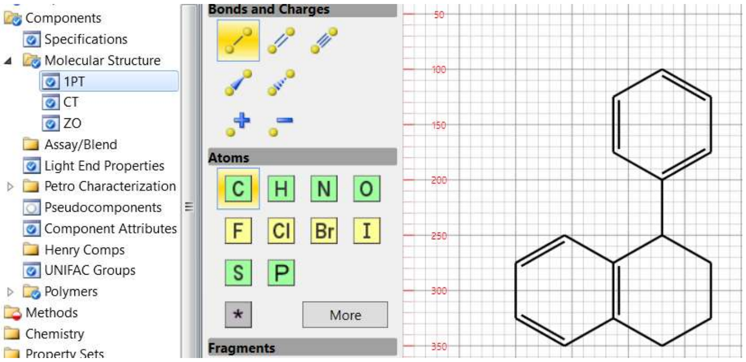


Figure 6.10a. Molecular structure of 1PT (1-phenyltetralin)

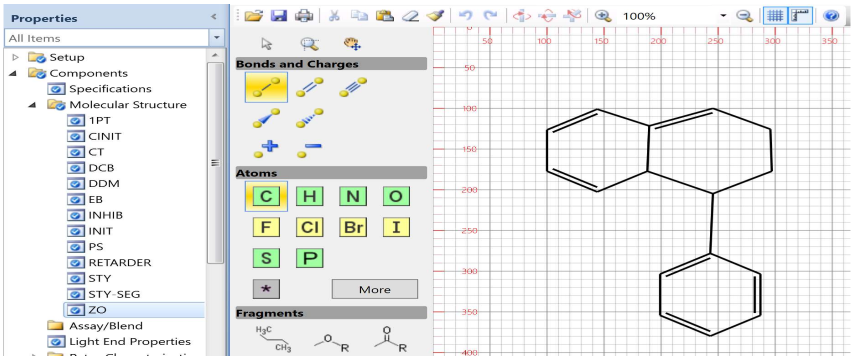


Figure 6.10b. Molecular structure of ZO (dimer)

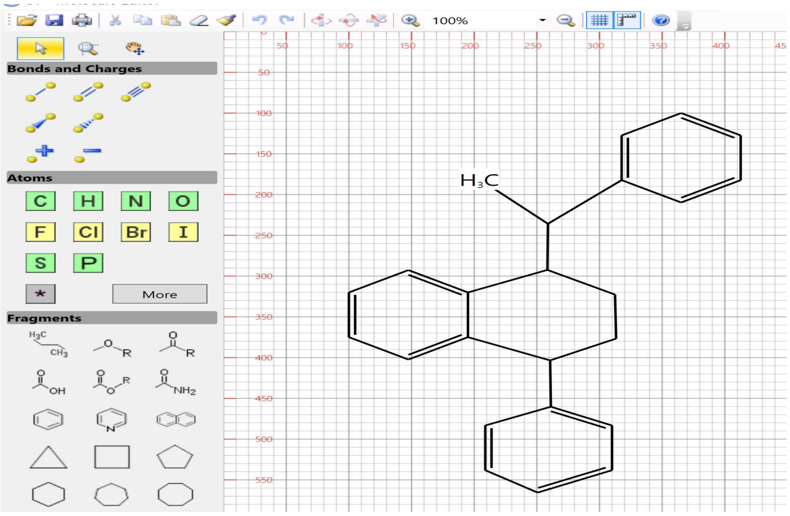
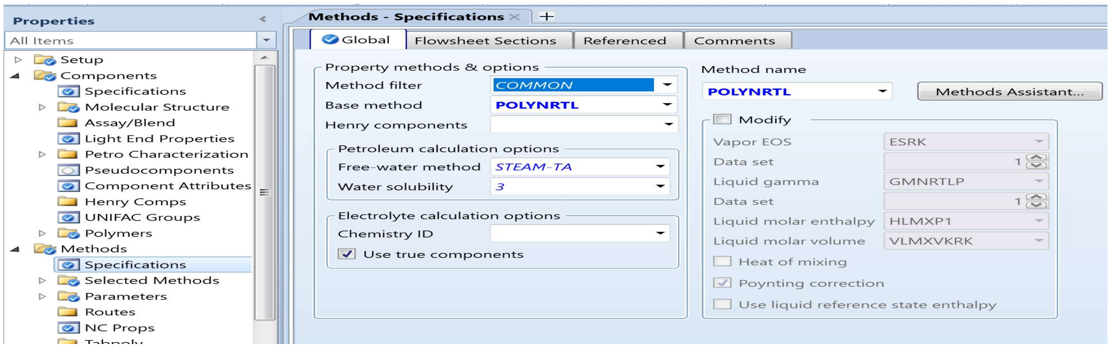


Figure 6.10c. Molecular structure of CT (cyclic trimer).

6.1.5 Thermodynamic Method and Property Parameters for Components and Oligomers

We choose POLYNRTL thermodynamic method (see Section 2.1 and Table 4.3) for the PS simulation. See Figure 6.11.



Property methods & options
Method filter: COMMON
Base method: POLYNRTL
Henry components:

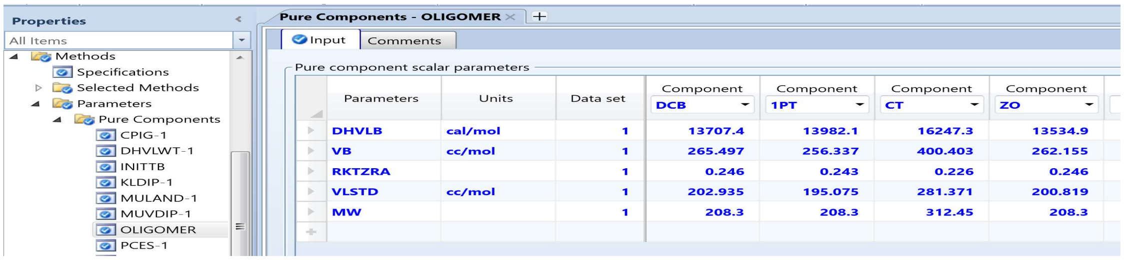
Petroleum calculation options
Free-water method: STEAM-TA
Water solubility: 3

Electrolyte calculation options
Chemistry ID:
☑ Use true components

Method name: POLYNRTL
☐ Modify
Vapor EOS: ESRK
Data set: 1
Liquid gamma: GMNRTLP
Data set: 1
Liquid molar enthalpy: HLMXP1
Liquid molar volume: VLMXVKRK
☐ Heat of mixing
☑ Poynting correction
☐ Use liquid reference state enthalpy

Figure 6.11 Selection of POLYNRTL thermodynamic method for PS simulation.

Based on references [10,11], we enter the following pure component parameters for oligomers: Properties-> Methods -> Parameters -> Pure Components -> New -> Scalar -> Change Name from Pure-1 to Oligomer->Enter values as in Figure 6.12.

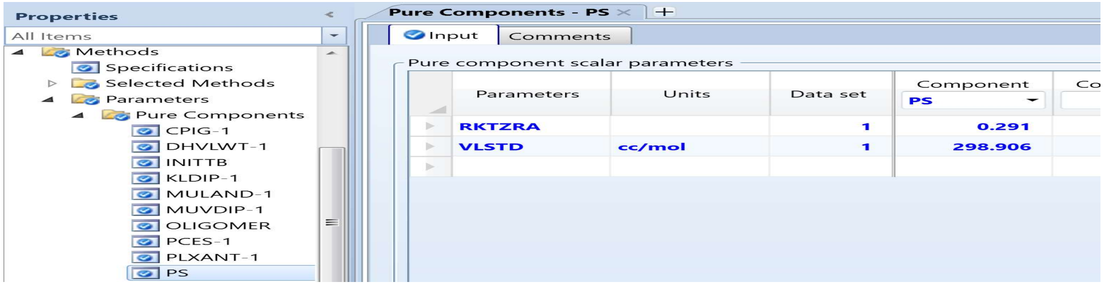


Pure component scalar parameters

Parameters	Units	Data set	Component DCB	Component 1PT	Component CT	Component ZO
DHVLB	cal/mol	1	13707.4	13982.1	16247.3	13534.9
VB	cc/mol	1	265.497	256.337	400.403	262.155
RKTZRA		1	0.246	0.243	0.226	0.246
VLSTD	cc/mol	1	202.935	195.075	281.371	200.819
MW		1	208.3	208.3	312.45	208.3

Figure 6.12. Enter pure component parameters for oligomers: DHVLB (enthalpy of vaporization at boiling point), VB (liquid molar volume at boiling point), RKTZRA (parameter for Rackett liquid molar volume model), VLSTD (standard liquid molar volume at 60°F), and MW (molecular weight).

Following the same procedure as for Figure 6.12, we enter the pure component parameters for PS as in Figure 6.13.

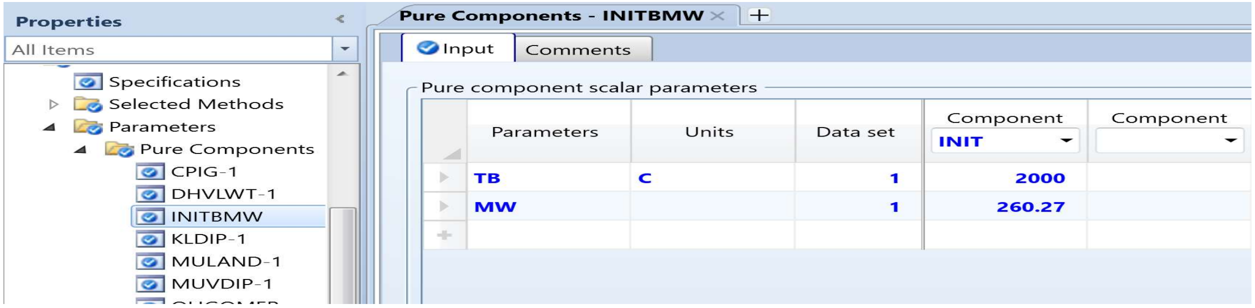


Pure component scalar parameters

Parameters	Units	Data set	Component PS
RKTZRA		1	0.291
VLSTD	cc/mol	1	298.906

Figure 6.13. Enter pure component parameters for PS.

Next, we assume a high boiling point for our initiator, INIT. Aspen Polymers databank does not have our initiator, 1,1-(di-tert-butylperoxy) cyclohexane (CAS no. 3006-86-8, molecular weight = 260.37). We approximate INIT with a known initiator, DTBP (di-t-butyl peroxide), but must enter the correct molecular weight of 260.27 for INIT. See Figure 6.14.

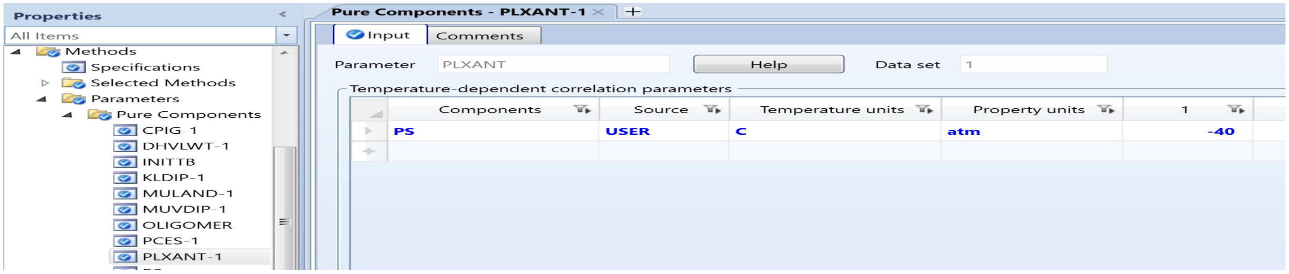


Pure component scalar parameters

Parameters	Units	Data set	Component INIT	Component
TB	C	1	2000	
MW		1	260.27	

Figure 6.14 Enter the assumed boiling point and the correct molecular weight of INIT.

To ensure that PS does not vaporize and stay in the liquid phase, we specify the first parameter in the T-dependent liquid vapor pressure correlation PLXANT-1 for PS to a large negative number like -40. This makes the vapor pressure of PS extremely small (4.24 E-23 Bar) [14]. To do so, we follow the path: Properties-> Methods -> Parameters -> Pure Components -> New -> T-dependent correlation -> liquid vapor pressure -> PLXANT-1 -> Use default name: PLXANT-1 ->Enter values as in Figure 6.15.



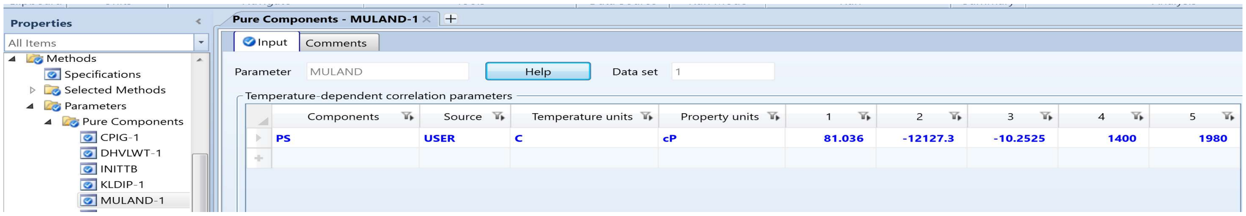
Parameter: PLXANT
Data set: 1

Temperature-dependent correlation parameters

Components	Source	Temperature units	Property units	1
PS	USER	C	atm	-40

Figure 6.15. Enter the first parameter of the liquid vapor pressure correlation for PS to a large negative number of -40 to ensure that PS does not vaporize. Clicking on “Help” will show the detail of the extended Antoine equation for the liquid vapor pressure with parameters.

We enter the parameters for the Andrade liquid viscosity correlation for PS by following the path: Properties-> Methods -> Parameters -> Pure Components -> New -> T-dependent correlation -> liquid viscosity -> MULAND-1 -> Use default name: MULAND-1 ->Enter values [12] as in Figure 6.16.



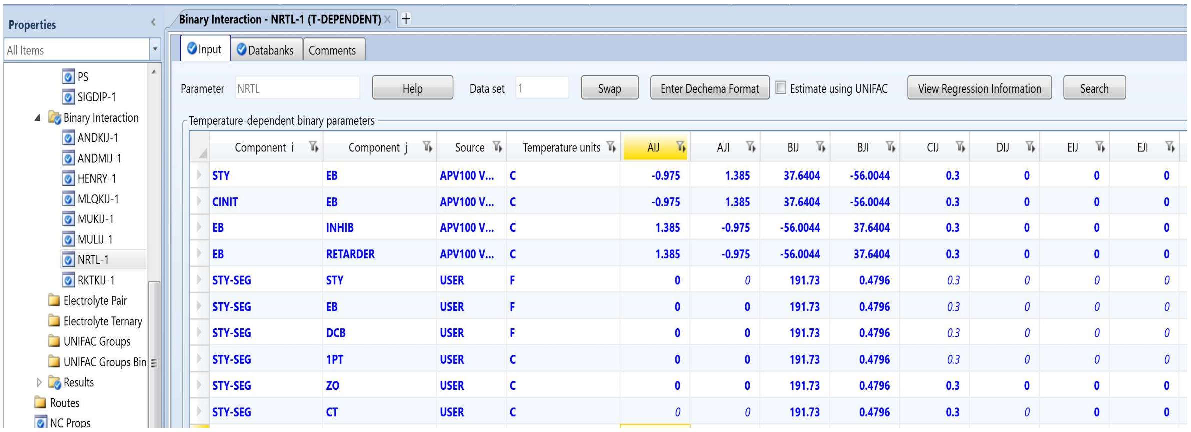
Parameter: MULAND
Data set: 1

Temperature-dependent correlation parameters

Components	Source	Temperature units	Property units	1	2	3	4	5
PS	USER	C	cP	81.036	-12127.3	-10.2525	1400	1980

Figure 6.16. Enter the parameters of the Andrade liquid viscosity correlation for PS [12].

Next, we enter the NRTL binary interaction parameters for oligomers by using the value for the SEG-STY and STY component pair. See Figure 6.17.



Parameter NRTL

Data set 1

☐ Estimate using UNIFAC

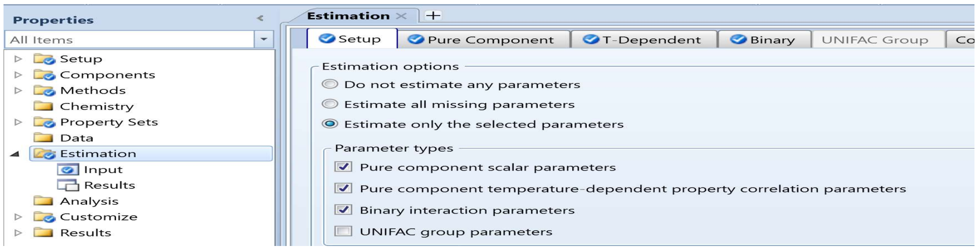
Temperature-dependent binary parameters

Component i	Component j	Source	Temperature units	AIJ	AJI	BIJ	BJI	CIJ	DIJ	EIJ	EJI
STY	EB	APV100 V...	C	-0.975	1.385	37.6404	-56.0044	0.3	0	0	0
CINIT	EB	APV100 V...	C	-0.975	1.385	37.6404	-56.0044	0.3	0	0	0
EB	INHIB	APV100 V...	C	1.385	-0.975	-56.0044	37.6404	0.3	0	0	0
EB	RETARDER	APV100 V...	C	1.385	-0.975	-56.0044	37.6404	0.3	0	0	0
STY-SEG	STY	USER	F	0	0	191.73	0.4796	0.3	0	0	0
STY-SEG	EB	USER	F	0	0	191.73	0.4796	0.3	0	0	0
STY-SEG	DCB	USER	F	0	0	191.73	0.4796	0.3	0	0	0
STY-SEG	1PT	USER	C	0	0	191.73	0.4796	0.3	0	0	0
STY-SEG	ZO	USER	C	0	0	191.73	0.4796	0.3	0	0	0
STY-SEG	CT	USER	C	0	0	191.73	0.4796	0.3	0	0	0

Figure 6.17. Enter the NRTL binary interaction parameters for oligomers.

6.1.6 PCES (Physical Constant Estimation System) for Estimating Property Parameters for Oligomers

Based on the molecular structures of oligomers defined in Section 6.1.4, we estimate the missing property parameters using the PCES system. See Figure 6.18.



Estimation options

○ Do not estimate any parameters

○ Estimate all missing parameters

● Estimate only the selected parameters

Parameter types

☑ Pure component scalar parameters

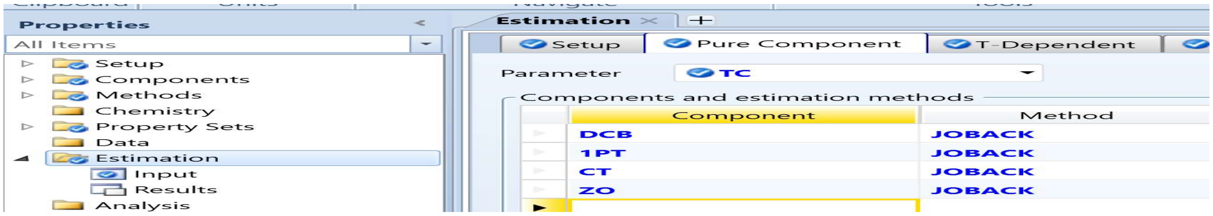
☑ Pure component temperature-dependent property correlation parameters

☑ Binary interaction parameters

☐ UNIFAC group parameters

Figure 6.18 Specification of property estimation for selected missing parameters.

Figure 6.19 specifies the estimation of scalar parameter TC (critical temperature) for oligomers using the Joback method. We do the same to estimate PC (critical pressure), VC (critical volume), DHFORM (standard enthalpy of formation for ideal gas at 25°C), DGFORM (standard Gibbs free energy of formation for ideal gas at 25°C), and TB (normal boiling point). We also estimate scalar parameters Omega (acentric factor) and ZC (critical compressibility factor) by choosing the definition for the parameter, DEFINITI. See Figure 6.20.

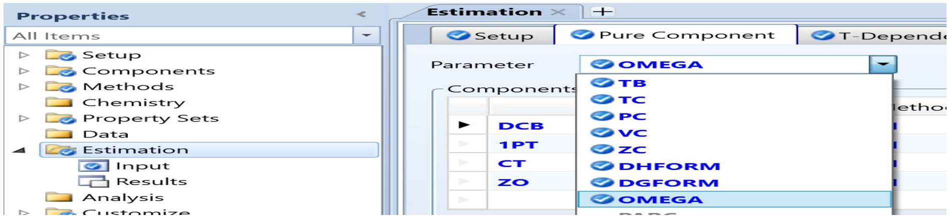


Parameter TC

Components and estimation methods

Component	Method
DCB	JOBACK
1PT	JOBACK
CT	JOBACK
ZO	JOBACK

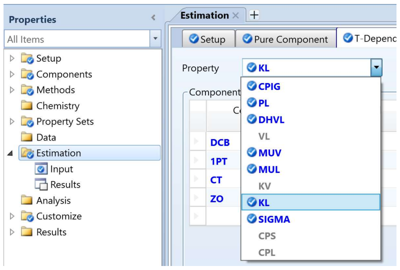
Figure 6.19 Specification of estimation of TC (critical temperature) for oligomers.



Parameter OMEGA

Figure 6.20 Estimation of pure component property parameters for oligomers.

We estimate the parameters of temperature-dependent correlations of CPIG (ideal gas heat capacity; Joback method), PL (liquid vapor pressure; Riedel method), DHVL (enthalpy of vaporization; definition method), MUV (vapor viscosity; Reichenberg method), MUL (liquid viscosity; Orrick-Erbar method), KL (liquid thermal conductivity; Sato-Riedel method), and Sigma (surface tension; Brook-Bird method). See Figure 6.21.

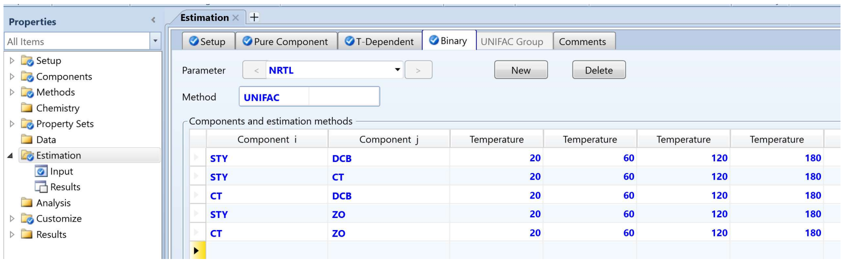


Property: KL

DCB
1PT
CT
ZO

Figure 6.21 Estimation of temperature-dependent property parameters for oligomers.

Lastly, we estimate the unknown binary interaction parameters using UNIFAC method. See Figure 6.22.



Parameter: NRTL

Method: UNIFAC

Components and estimation methods

Component i	Component j	Temperature	Temperature	Temperature	Temperature
STY	DCB	20	60	120	180
STY	CT	20	60	120	180
CT	DCB	20	60	120	180
STY	ZO	20	60	120	180
CT	ZO	20	60	120	180

Figure 6.22 Estimation of NRTL binary interaction parameters using UNIFAC method.

6.1.7 Defining Free Radical Reactions and Oligomer Reactions

Figure 6.23 shows the molecular structure of INIT or DTBP (di-t-butyl peroxide). The initiator decomposition reaction will break the bond between two oxygen atoms, producing two free radicals.

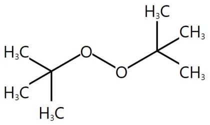


Figure 6.23. Initiator decomposition breaks the bond between two oxygen atoms to produce two free radicals.

Following Table 4.4, we summarize in Table 6.2 the relevant free radical polymerization reactions for our PS simulation. For our process without adding an inhibitor, we can set the pre-exponential factor of the inhibition reaction rate constant to zero.

Table 6.2 Free Radical Polymerization Reactions for the PS Workshop.

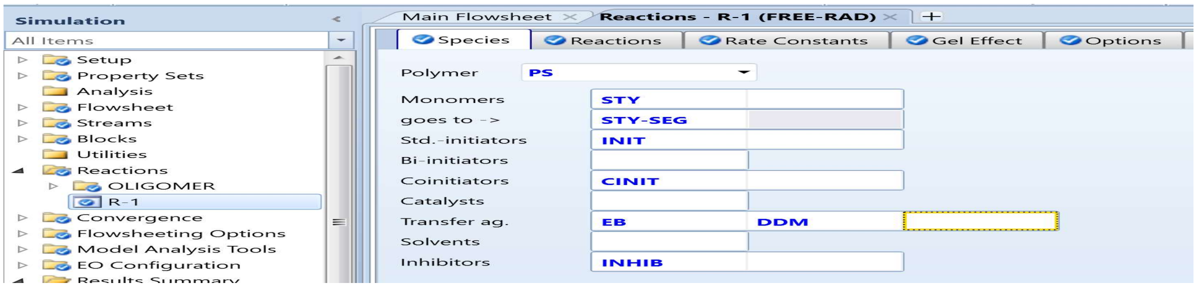
Reaction	**Representation**	**Notes**
1. Initiator decomposition	Initiator -> Radicals INIT -> ε n R* + aA + bB (no byproducts A and B for this initiator)	ε is the decomposition efficiency, typically assumed to be 0.8. Our INIT or DTBP (di-t-butyl peroxide) generates two radicals (n=2).
2. Special (thermal) initiation	Monomer + Coinitiator -> Growing monomer STY + CINIT -> P1[STY-SEG]	P1[STY-SEG] is a growing polymer chain of length 1 having an active STY segment. Thermal initiation reaction rate is proportional to the monomer concentration to the third power [4].
3. Chain initiation	Monomer + Radical -> Growing monomer Sty + R*-> P1[Sty]	
4. Chain propagation	Growing polymer chain + Monomer -> Propagating polymer chain Pn[Sty] + Sty -> Pn+1[Sty]	Pn[STY] is a growing polymer chain of length n having an active STY segment
5. Chain transfer to monomer	Growing polymer chain +Monomer -> Dead chain + Growing monomer Pn[Sty] + Sty -> Dn + R*	Dn is a dead polymer chain of length n that does not have an attached radical.
6. Chain transfer to agent	Growing polymer chain + transfer agent-> Dead chain + Growing monomer Pn[Sty] + A -> Dn + R*	A represents the chain transfer agent
7. Chain termination by combination	Growing polymer chain Pm + growing polymer chain Pn -> Dead polymer chain Dm+n Pn[Sty]+ Pm[Sty] -> Dn+m	
8. Inhibition reaction	Growing polymer chain + inhibition agent-> Dead polymer chain Pn[Sty] + X -> Dn	

To generate these reactions within Aspen Polymers, follow the path: Reactions -> New: R-1 FREE-RAD type -> OK. See Figures. 6.24 to 6.29. Based on the species defined in Figure 6.25, we click on the "generate reactions" button displayed in Figure 6.26. Aspen Polymers automatically generates the ten reactions in Figure 6.26. For our current simulation, we delete reaction 8, termination by disproportionation, and reaction 10, inhibition reaction. This results in the reaction set in Figure 6.27. For the reaction rate constants in Figure 6.28, we use the pre-exponential factor and activation energy for the reaction rate constant from reference [6] as our initial values. For the initiator decomposition rate parameters, we can also follow Section 4.4.6, and Figures 4.25a to 4.25b, to retrieve the same values as in Figure 6.28 from Aspen Polymers initiator database. For reaction calculations, we do not assume the quasi-steady state approximation; for reaction 2, we specify the dependence of special (thermal) initiation reaction rate (see Section 4.2.2) on the third power of the monomer concentration [9]. We demonstrate both aspects in Figure 6.29.

Enter ID: R-1

Select Type: FREE-RAD

Figure 6.24 Create free radical polymerization reactions.



Polymer PS

Monomers STY

goes to -> STY-SEG

Std.-initiators INIT

Bi-initiators

Coinitiators CINIT

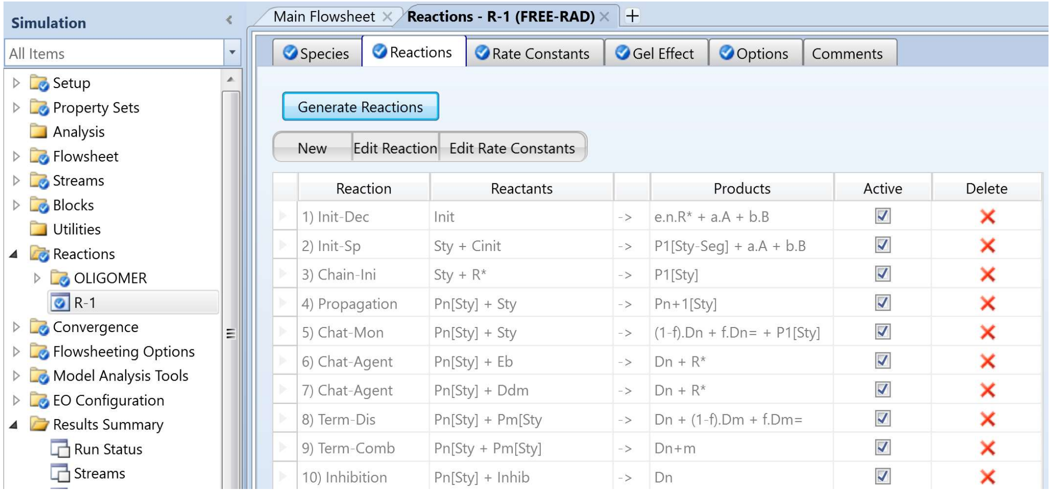
Catalysts

Transfer ag. EB DDM

Solvents

Inhibitors INHIB

Figure 6.25 Specification of species for generating free radical polymerization reactions for PS

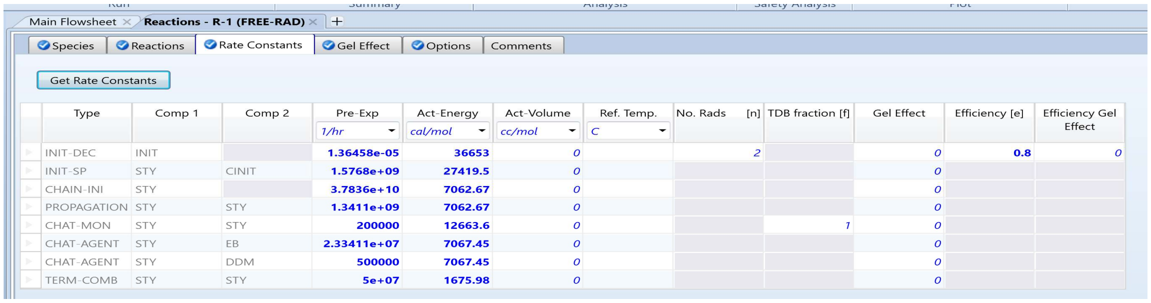


Reaction	Reactants		Products	Active	Delete
1) Init-Dec	Init	->	e.n.R* + a.A + b.B	☑	✗
2) Init-Sp	Sty + Cinit	->	P1[Sty-Seg] + a.A + b.B	☑	✗
3) Chain-Ini	Sty + R*	->	P1[Sty]	☑	✗
4) Propagation	Pn[Sty] + Sty	->	Pn+1[Sty]	☑	✗
5) Chat-Mon	Pn[Sty] + Sty	->	(1-f).Dn + f.Dn= + P1[Sty]	☑	✗
6) Chat-Agent	Pn[Sty] + Eb	->	Dn + R*	☑	✗
7) Chat-Agent	Pn[Sty] + Ddm	->	Dn + R*	☑	✗
8) Term-Dis	Pn[Sty] + Pm[Sty	->	Dn + (1-f).Dm + f.Dm=	☑	✗
9) Term-Comb	Pn[Sty + Pm[Sty]	->	Dn+m	☑	✗
10) Inhibition	Pn[Sty] + Inhib	->	Dn	☑	✗

Figure 6.26. Ten free radical reactions generated automatically by Aspen Polymers.

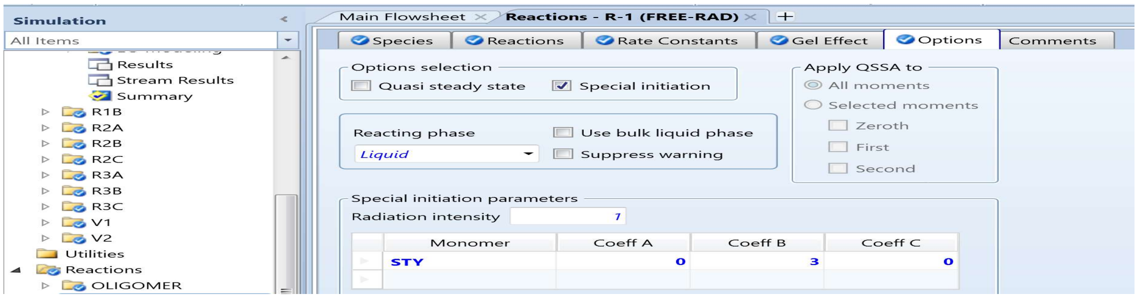
Reaction	Reactants		Products	Active
1) Init-Dec	Init	->	e.n.R* + a.A + b.B	☑
2) Init-Sp	Sty + Cinit	->	P1[Sty-Seg] + a.A + b.B	☑
3) Chain-Ini	Sty + R*	->	P1[Sty]	☑
4) Propagation	Pn[Sty] + Sty	->	Pn+1[Sty]	☑
5) Chat-Mon	Pn[Sty] + Sty	->	(1-f).Dn + f.Dn= + P1[Sty]	☑
6) Chat-Agent	Pn[Sty] + Eb	->	Dn + R*	☑
7) Chat-Agent	Pn[Sty] + Ddm	->	Dn + R*	☑
8) Term-Comb	Pn[Sty + Pm[Sty]	->	Dn+m	☑

Figure 6.27. Final free radical polymerization reactions for the current PS simulation.



Type	Comp 1	Comp 2	Pre-Exp 1/hr	Act-Energy cal/mol	Act-Volume cc/mol	Ref. Temp. C	No. Rads [n]	TDB fraction [f]	Gel Effect	Efficiency [e]	Efficiency Gel Effect
INIT-DEC	INIT		1.36458e-05	36653	0		2		0	0.8	0
INIT-SP	STY	CINIT	1.5768e+09	27419.5	0				0		
CHAIN-INI	STY		3.7836e+10	7062.67	0				0		
PROPAGATION	STY	STY	1.3411e+09	7062.67	0				0		
CHAT-MON	STY	STY	200000	12663.6	0			1	0		
CHAT-AGENT	STY	EB	2.33411e+07	7067.45	0				0		
CHAT-AGENT	STY	DDM	500000	7067.45	0				0		
TERM-COMB	STY	STY	5e+07	1675.98	0				0		

Figure 6.28 Initial values of pre-exponential factors and activation energies, together with the number of radicals and initiator decomposition efficiency [9].



Options selection
☐ Quasi steady state ☑ Special initiation

Reacting phase: Liquid
☐ Use bulk liquid phase
☐ Suppress warning

Apply QSSA to
● All moments
○ Selected moments
☐ Zeroth
☐ First
☐ Second

Special initiation parameters
Radiation intensity: 1

Monomer	Coeff A	Coeff B	Coeff C
STY	0	3	0

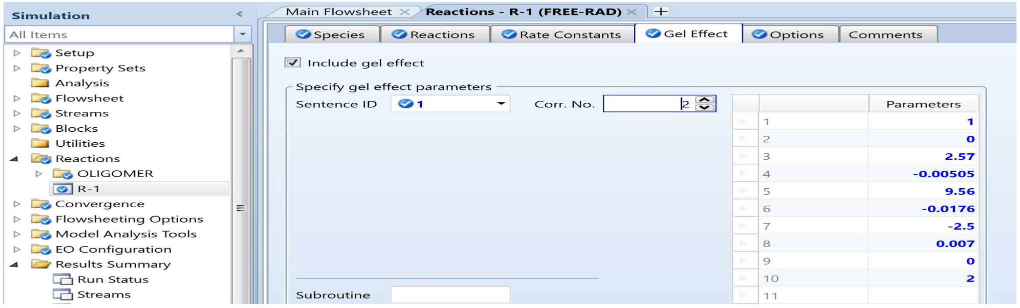
Figure 6.29 Specification of no quasi-steady state assumption and special (thermal) initiation dependency on monomer concentration to the third power (Coeff B =3).

Next, we consider the gel effect on the free radical polymerization reactions and the resulting polymer molecular weights. Specifically, as the monomer conversion to PS increases, the viscosity of the liquid reaction mixture continues to increase. The termination and other reactions eventually become diffusion-limited. This affects the polymerization rate and polymer molecular weight [2]. Aspen Polymers multiplies the reaction rate constant without gel effect, *k,* by a correction factor *GF* to obtain the effective reaction rate constant k_{eff} and presents two correlations for *GF* as a function of conversion X_p. We use correlation two and input the values of parameters a_1 to a_{10} provided by the Aspen Polymers online help by following the path: Help -> Search "Gel effect" ->correlation two.

Correlation Number 2: $k_{eff} = k{*}\, GF \quad GF = \left(\left[A / (1 - a_9 X_p) \right] \exp\left[-(B X_p + C X_p^2 + D X_p^3) \right] \right)^{a_{10}}$

- *With* $A = a_1 + a_2 T$, $B = a_3 + a_4 T$, $C = a_5 + a_6 T$, $D = a_7 + a_8 T$

Figure 6.30 shows our input of the recommended parameter values of a_1 to a_{10} [3,6].



☑ Include gel effect

Specify gel effect parameters

Sentence ID: 1

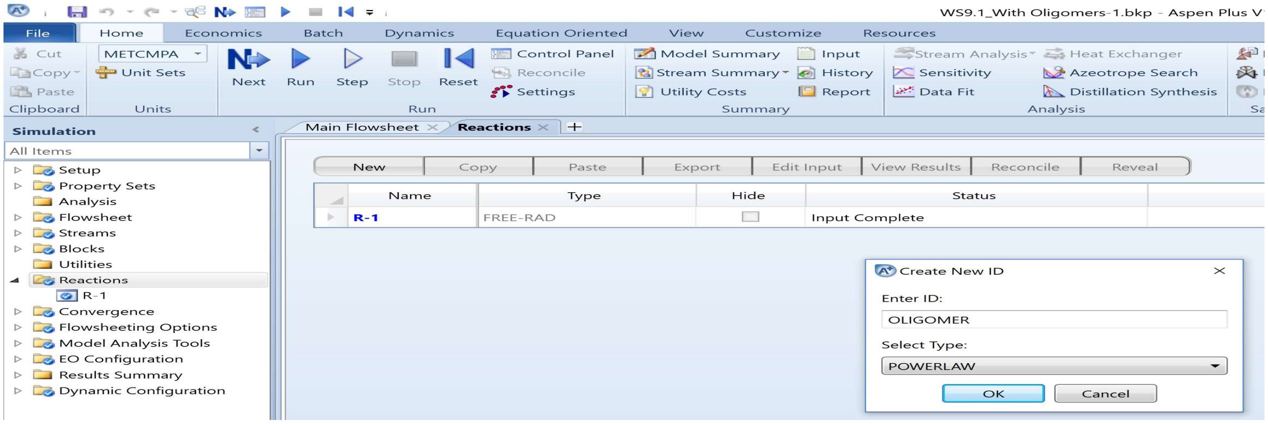
Corr. No.: 2

	Parameters
1	1
2	0
3	2.57
4	-0.00505
5	9.56
6	-0.0176
7	-2.5
8	0.007
9	0
10	2
11	

Subroutine

Figure 6.30. Entering parameter values for gel effect correlation number 2.

Finally, we define the oligomer formation reactions. We specify a power-law type of reactions named oligomer (see Figure 6.31), and then define the first kinetic reaction, 2 STY -> DCB, and quantify its kinetics according to reaction information in Table 6.3. See Figures 6.32 to 6.34. The pre-exponential factor for oligomer reaction number 6 is assumed to be zero, indicating that we ignore this reaction.



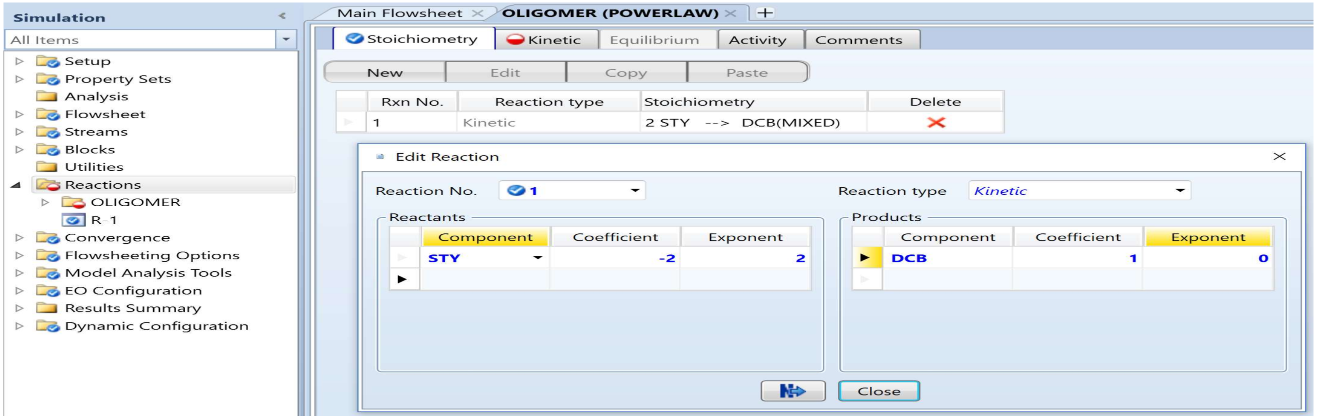
Name	Type	Hide	Status
R-1	FREE-RAD	☐	Input Complete

Create New ID

Enter ID: OLIGOMER

Select Type: POWERLAW

Figure 6.31 Defining a power-law type of reactions named Oligomer.



Rxn No.	Reaction type	Stoichiometry	Delete
1	Kinetic	2 STY --> DCB(MIXED)	✕

Edit Reaction

Reaction No.: 1

Reaction type: Kinetic

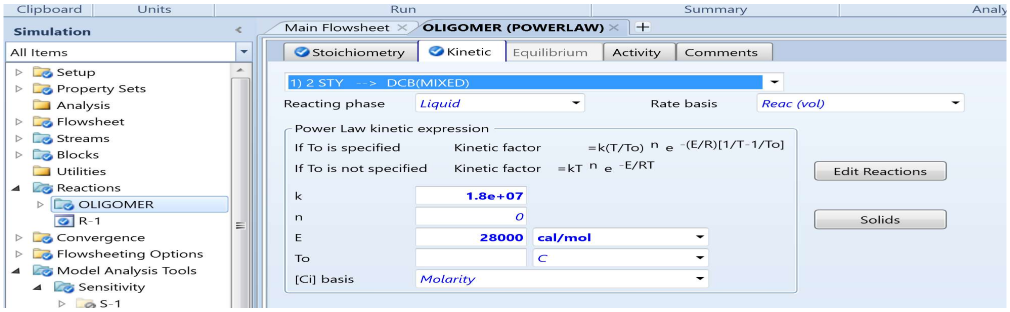
Reactants

Component	Coefficient	Exponent
STY	-2	2

Products

Component	Coefficient	Exponent
DCB	1	0

Figure 6.32 Stoichiometry of oligomer reaction no. 1.



1) 2 STY --> DCB(MIXED)

Reacting phase: Liquid

Rate basis: Reac (vol)

Power Law kinetic expression

If To is specified: Kinetic factor $=k(T/To)^{n}\, e^{-(E/R)[1/T-1/To]}$

If To is not specified: Kinetic factor $=kT^{n}\, e^{-E/RT}$

k: 1.8e+07

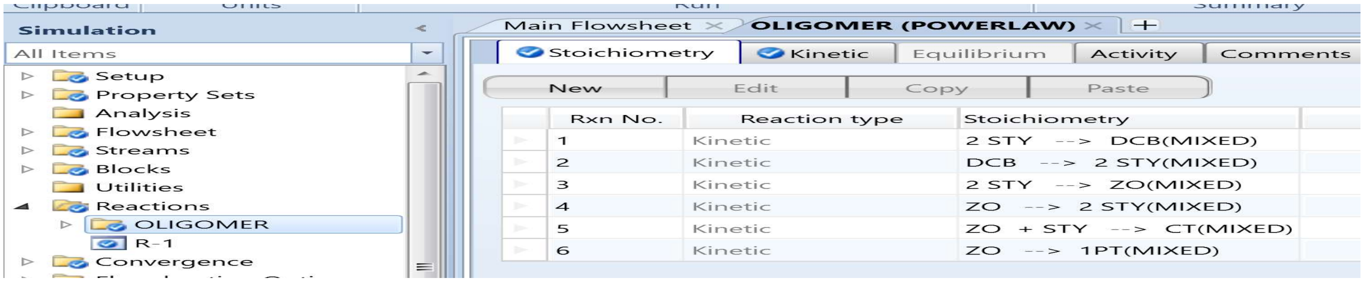
n: 0

E: 28000 cal/mol

To: C

[Ci] basis: Molarity

Figure 6.33 Kinetics of oligomer reaction no. 1.



Rxn No.	Reaction type	Stoichiometry
1	Kinetic	2 STY --> DCB(MIXED)
2	Kinetic	DCB --> 2 STY(MIXED)
3	Kinetic	2 STY --> ZO(MIXED)
4	Kinetic	ZO --> 2 STY(MIXED)
5	Kinetic	ZO + STY --> CT(MIXED)
6	Kinetic	ZO --> 1PT(MIXED)

Figure 6.34 Stoichiometry of six oligomer reactions.

Table 6.3 Specification of six oligomer reactions [9,10].

Reaction number	Reaction	Reaction rate	Pre-exponential factor	Activation energy, cal/mol
1	2 STY -> DCB	$R_1 = K_1 C^2_{STY}$	1.8E7	28000
2	1 DCB -> 2 STY	$R_2 = K_2 C_{DCB}$	1E10	28000
3	2 STY -> 1 ZO	$R_3 = K_3 C^2_{STY}$	3909	20000
4	1 ZO -> 2 STY	$R_4 = K_4 C_{ZO}$	20	20000
5	1 ZO + STY -> CT	$R_5 = K_5 C_{ZO}C_{STY}$	1E7	20000
6	1 ZO -> 1 1PT	$R_6 = K_6 C_{ZO}$	0	20000

6.1.8 Specification of Inlet Process Streams and Unit Operation and Reactor Blocks.

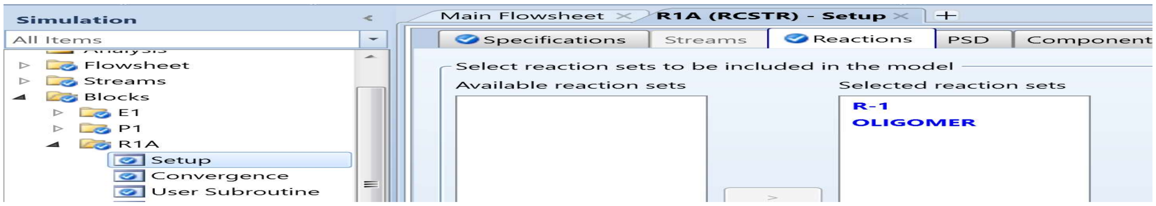
Table 6.4 shows the inlet stream specifications. Table 6.5 gives the specifications for unit operation and reactor blocks. For each reactor, we need to activate the relevant reactions. See Figure 6.35. Additionally, for reactor simulation, we do not assume quasi-steady state approximation (see Figure 6.29) and use Broyden method for convergence calculation with 500 iterations and initialize the calculation by integration (see Figure 6.36).

Table 6.4 Specifications of inlet process streams.

Stream	Input Specifications
T2	12°C, 2.033 MPa, mass flow (kg/hr): STY=5915, EB=144.306
R2	12°C, 2.033 MPa, mass flow (kg/hr): STY=615, DCB=1, EB=2, DDM=2
C2	12°C, 7.033 MPa, mass flow (kg/hr): INIT=1, CINIT=1, EB=2
A6	12°C, 5.033 MPa, mass flow (kg/hr): STY =55, EB =2

Table 6.5 Specifications of Unit Operation and Reactor Blocks

Block	R1A	R1B	R2A	R2B	R2C	R3A	R3B	R3C
Volume, m^3	5.5	11	5.5	5.5	5.5	5.5	5.5	5.5
Temperature, C	112	113	115	118	123	135	152	160
Pressure, MPa	5.233	5.233	4.833	4.833	4.833	3.833	3.833	3.833
Phase	L	L	L	L	L	L	L	L
Reacting phase	L	L	L	L	L	L	L	L
Other blocks: (1) E1: 90 C, 0 MPa (no pressure drop); (2) P1: exit pressure, 5.233 MPa; (3) V1: 4.533 MPa, 0 MPa; (4) V2: 3.833 MPa, 0 MPa.								

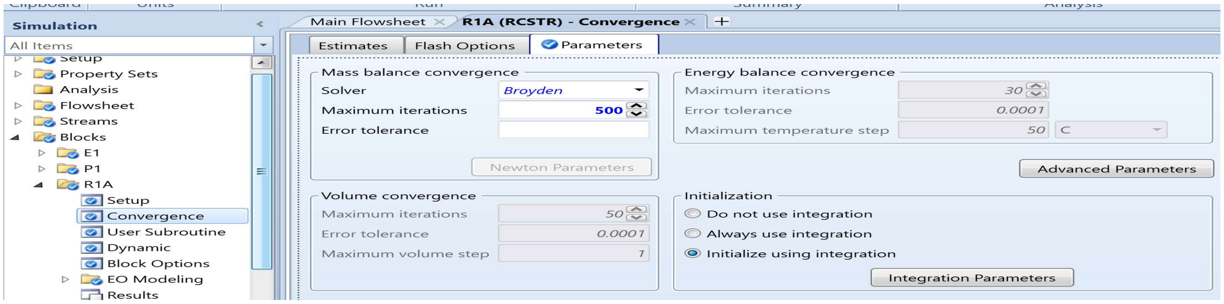


Select reaction sets to be included in the model

Available reaction sets

Selected reaction sets: R-1, OLIGOMER

Figure 6.35 Specification of reactions for each reactor.



Mass balance convergence
Solver: Broyden
Maximum iterations: 500
Error tolerance:

Energy balance convergence
Maximum iterations: 30
Error tolerance: 0.0001
Maximum temperature step: 50 C

Volume convergence
Maximum iterations: 50
Error tolerance: 0.0001
Maximum volume step: 1

Initialization
○ Do not use integration
○ Always use integration
● Initialize using integration

Figure 6.36 Specification of reactor convergence method and initiation by integration.

6.1.9 Kinetic Parameter Estimation and Model Validation

Table 6.6 lists the major kinetic parameters and independent variables affecting the simulation targets for free radical polymerization for our kinetic parameter estimation below.

Table 6.6 Major kinetic parameters and independent variables affecting simulation targets of free radical polymerization of PS

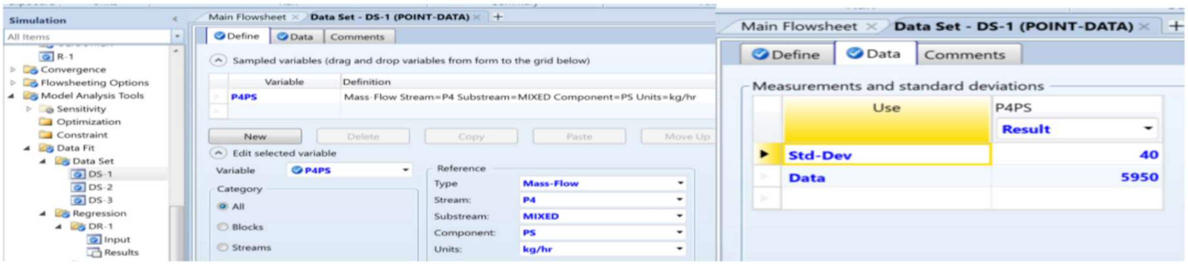
Simulation target	Major affecting kinetic parameters and independent variables
1. Production rate or monomer conversion	Propagation rate constant
2. MWN, MWW	Rate constants for chain transfer to monomer and to chain transfer agent; mass flow rate of chain transfer agent

Table 6.6 results from the following kinetic relationship for degree of polymerization (DPN) for free radical polymerization [2]:

$$1/MWN \propto 1/DPN = k_{tr,m}/k_p + (k_{tr,A} * C_A)/(k_p * C_m) \qquad (6.1)$$

where the subscripts *p, tr,m,* and *tr,A* represent propagation, chain transfer to monomer, and chain transfer to chain transfer agent, respectively; C_A and C_m represent the concentration of chain transfer agent and monomer, respectively. This relationship suggests as k_p increases and as $k_{tr,m}$ and $k_{tr,A}$ decrease, MWN and MWW increase. We find this guidance to be sufficient for the kinetic parameter estimation for the current PS simulation using the data fit tool. Previously, in Section 4.4.8, Figure 4.26, we presented an expanded list of major affecting parameters for free radical polymerization of high-pressure LDPE, considering a different set of reactions involved.

We define three datasets for our simulation targets. Figures 6.37 to 6.38 show how to define two datasets (point data), namely, PS production rate (dataset DS-1) and PS MWN (dataset DS-2). Following Figure 6.38, we define the dataset DS-3 for PS MWW by choosing the attribute MWW. We then define data regression run DR-1 for dataset DS-1, and data regression run DR-2 for datasets DS-2 and DS-3 together. See Figures 6.39 and 6.40.



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
P4PS	Mass-Flow Stream=P4 Substream=MIXED Component=PS Units=kg/hr

Edit selected variable

Variable: P4PS

Category: ● All ○ Blocks ○ Streams

Reference

Type: Mass-Flow

Stream: P4

Substream: MIXED

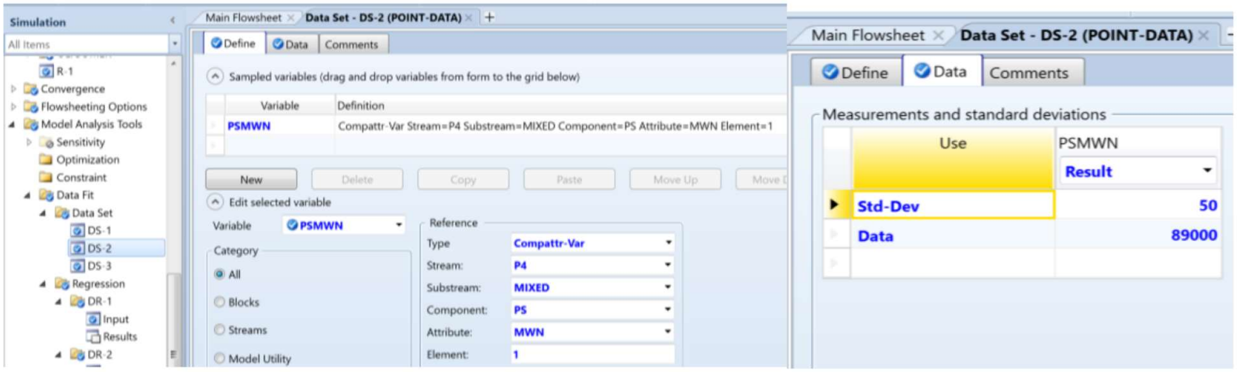
Component: PS

Units: kg/hr

Measurements and standard deviations

Use	P4PS Result
Std-Dev	40
Data	5950

Figure 6.37 Defining the dataset DS-1 for PS production rate



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
PSMWN	Compattr-Var Stream=P4 Substream=MIXED Component=PS Attribute=MWN Element=1

Edit selected variable

Variable: PSMWN

Category: ● All ○ Blocks ○ Streams ○ Model Utility

Reference

Type: Compattr-Var

Stream: P4

Substream: MIXED

Component: PS

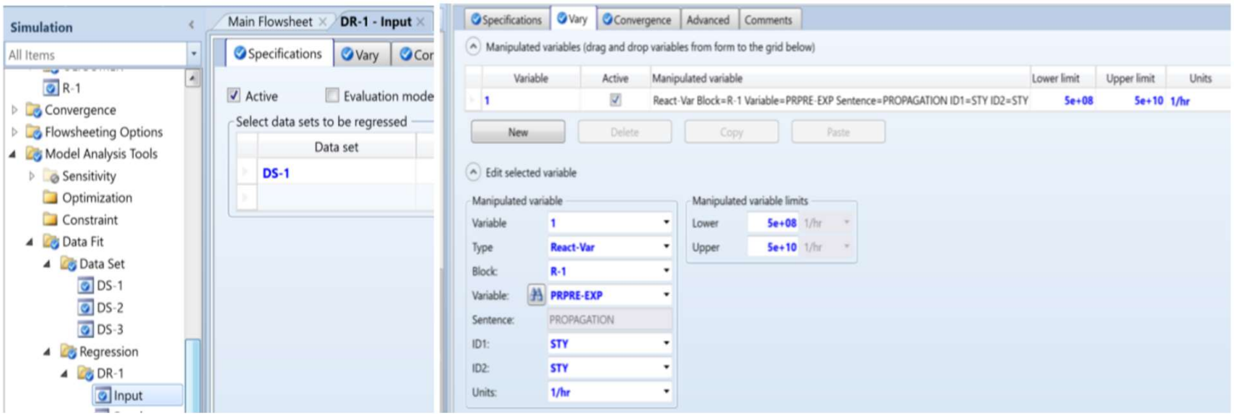
Attribute: MWN

Element: 1

Measurements and standard deviations

Use	PSMWN
	Result
Std-Dev	50
Data	89000

Figure 6.38 Defining the dataset DS-2 for PS MWN



☑ Active ☐ Evaluation mode

Select data sets to be regressed

Data set
DS-1

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Lower limit	Upper limit	Units
1	☑	React-Var Block=R-1 Variable=PRPRE-EXP Sentence=PROPAGATION ID1=STY ID2=STY	5e+08	5e+10	1/hr

Edit selected variable

Manipulated variable

Variable: 1

Type: React-Var

Block: R-1

Variable: PRPRE-EXP

Sentence: PROPAGATION

ID1: STY

ID2: STY

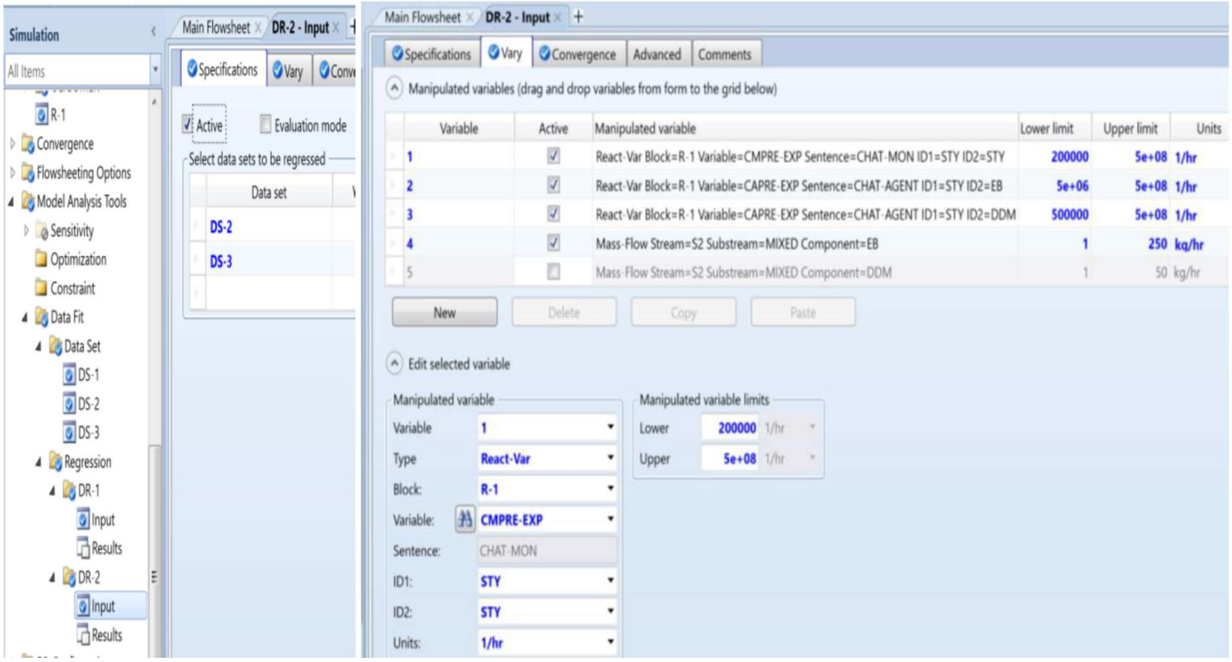
Units: 1/hr

Manipulated variable limits

Lower: 5e+08 1/hr

Upper: 5e+10 1/hr

Figure 6.39 Defining data regression DR-1 for PS production rate



☑ Active ☐ Evaluation mode

Select data sets to be regressed

Data set
DS-2
DS-3

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Lower limit	Upper limit	Units
1	☑	React-Var Block=R-1 Variable=CMPRE-EXP Sentence=CHAT-MON ID1=STY ID2=STY	200000	5e+08	1/hr
2	☑	React-Var Block=R-1 Variable=CAPRE-EXP Sentence=CHAT-AGENT ID1=STY ID2=EB	5e+06	5e+08	1/hr
3	☑	React-Var Block=R-1 Variable=CAPRE-EXP Sentence=CHAT-AGENT ID1=STY ID2=DDM	500000	5e+08	1/hr
4	☑	Mass-Flow Stream=S2 Substream=MIXED Component=EB	1	250	kg/hr
5	☐	Mass-Flow Stream=S2 Substream=MIXED Component=DDM	1	50	kg/hr

Edit selected variable

Manipulated variable

Variable: 1

Type: React-Var

Block: R-1

Variable: CMPRE-EXP

Sentence: CHAT-MON

ID1: STY

ID2: STY

Units: 1/hr

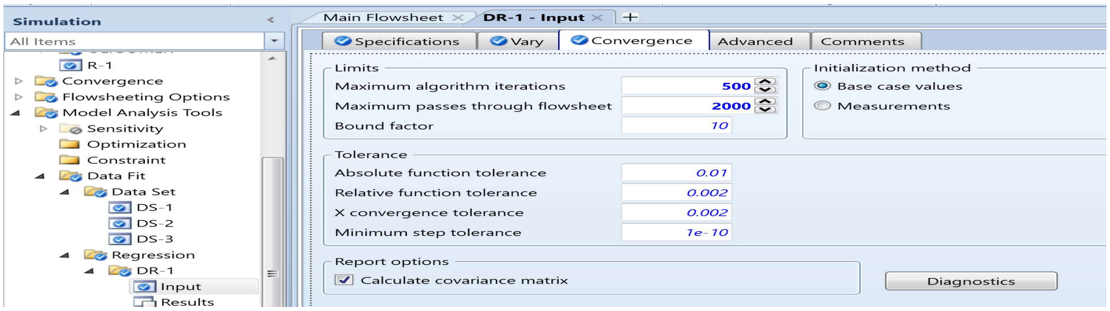
Manipulated variable limits

Lower: 200000 1/hr

Upper: 5e+08 1/hr

Figure 6.40 Defining data regression DR-2 for PS MWN (dataset DS-2) and MWW (dataset DS-3).

We increase the number of iterations and flowsheet passes for both regression runs DR-1 and DR-2. See Figure 6.41.



Limits
Maximum algorithm iterations 500
Maximum passes through flowsheet 2000
Bound factor 10

Initialization method
● Base case values
○ Measurements

Tolerance
Absolute function tolerance 0.01
Relative function tolerance 0.002
X convergence tolerance 0.002
Minimum step tolerance 1e-10

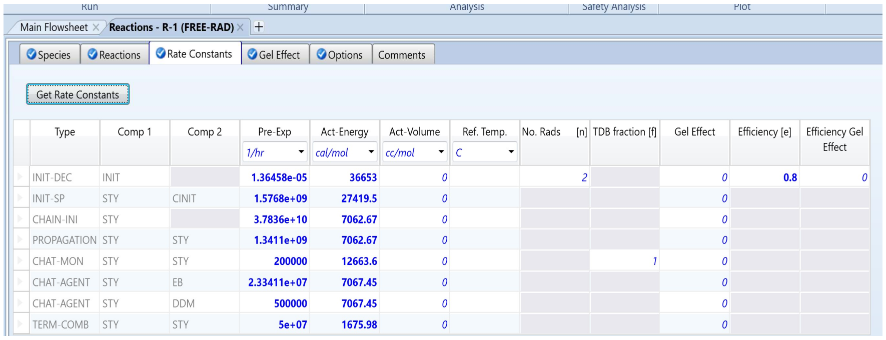
Report options
☑ Calculate covariance matrix

Figure 6.41 Increasing the number of iterations and flowsheet passes in data regression runs.

Table 6.7 lists the computed manipulated variables and fitted data from regression runs. Figure 6.42 shows the final kinetic parameters for the base case.

Table 6.7 Comparison of simulation targets (datasets) with model results

	PS production rate, kg/hr (DS-1)	**PS MWN (DS-2)**	**PS MWW (DS-3)**
1. Simulation target	5950	89000	256000
2. Model result	5926	92645	250635
3. Error	0.4%	4.1%	2.1%
4. Key manipulated variables	Pre-exponential factor for propagation reaction rate constant	Pre-exponential factors for rate constant for chain transfer to: (1) monomer STY, (2) to chain transfer agents EB, and (3) to chain transfer agent DDM. (4) Mass flow rate of chain transfer agent EB	
5. Variable range	5E8 to 5E10 1/hr	2E5 to 5E8 1/hr; (2) 5E6 to 5E8 1/hr; (3) 5E5 to 5E8 1/hr; (4) 1 to 250 kg/hr	
6. Data regression result	1.3411E9 1/hr	(1) 2E5 1/hr; (2) 2.33272E7 1/hr (3) 5E5 1/hr; (4) 143.376 kg/hr	



Type	Comp 1	Comp 2	Pre-Exp 1/hr	Act-Energy cal/mol	Act-Volume cc/mol	Ref. Temp. C	No. Rads [n]	TDB fraction [f]	Gel Effect	Efficiency [e]	Efficiency Gel Effect
INIT-DEC	INIT		1.36458e-05	36653	0		2		0	0.8	0
INIT-SP	STY	CINIT	1.5768e+09	27419.5	0				0		
CHAIN-INI	STY		3.7836e+10	7062.67	0				0		
PROPAGATION	STY	STY	1.3411e+09	7062.67	0				0		
CHAT-MON	STY	STY	200000	12663.6	0			1	0		
CHAT-AGENT	STY	EB	2.33411e+07	7067.45	0				0		
CHAT-AGENT	STY	DDM	500000	7067.45	0				0		
TERM-COMB	STY	STY	5e+07	1675.98	0				0		

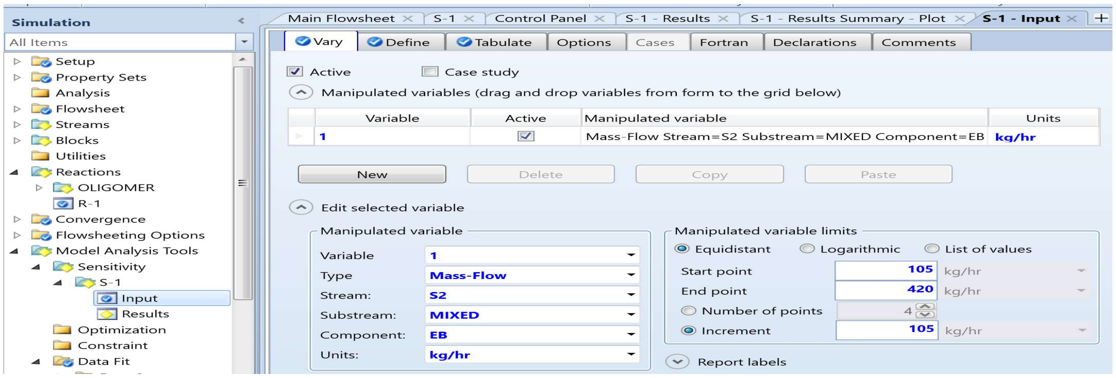
Figure 6.42 Kinetic parameter values of base-case model.

This concludes our base-case model development, and we save the simulation as ***WS7.1_With Oligomers_BaseCase.bkp.***

6.1.10 Model Applications

A PS simulation model validated by plant data can have many useful applications. The model will be useful for the capacity expansion of the current plant. We can use the validated model to study the effects of changes in key independent variables on production targets.

As an example, we study the effects of varying the mass flow rate of chain transfer agent EB in feed steam S1 from 105 kg/hr to 420 kg/hr, with an increment of 105 kg/hr, on the PS mass flow rate, and MWN and MWW of product steam P4 exiting reactor V3C. See Figure 6.43 to 6.45.



☑ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

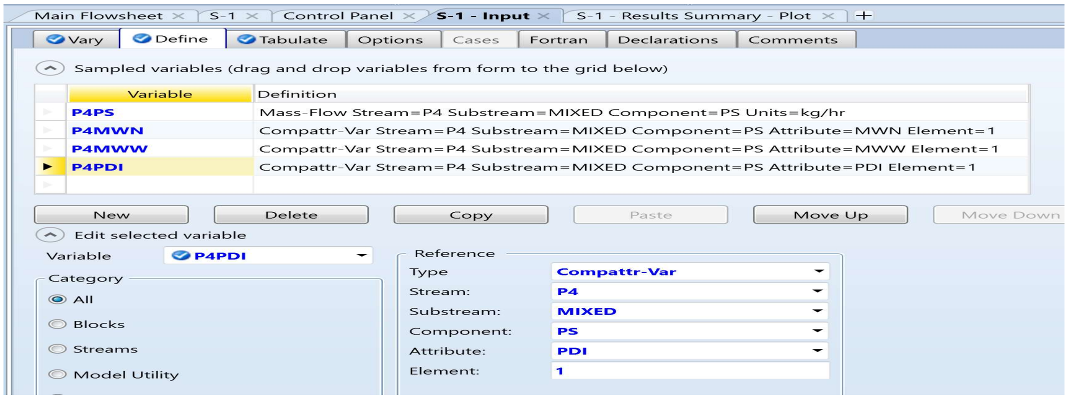
Variable	Active	Manipulated variable	Units
1	☑	Mass-Flow Stream=S2 Substream=MIXED Component=EB	kg/hr

Edit selected variable

Manipulated variable
Variable: 1
Type: Mass-Flow
Stream: S2
Substream: MIXED
Component: EB
Units: kg/hr

Manipulated variable limits
● Equidistant ○ Logarithmic ○ List of values
Start point: 105 kg/hr
End point: 420 kg/hr
○ Number of points: 4
● Increment: 105 kg/hr

Figure 6.43 Defining the independent variable ("Vary") of sensitivity study S-1



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
P4PS	Mass-Flow Stream=P4 Substream=MIXED Component=PS Units=kg/hr
P4MWN	Compattr-Var Stream=P4 Substream=MIXED Component=PS Attribute=MWN Element=1
P4MWW	Compattr-Var Stream=P4 Substream=MIXED Component=PS Attribute=MWW Element=1
P4PDI	Compattr-Var Stream=P4 Substream=MIXED Component=PS Attribute=PDI Element=1

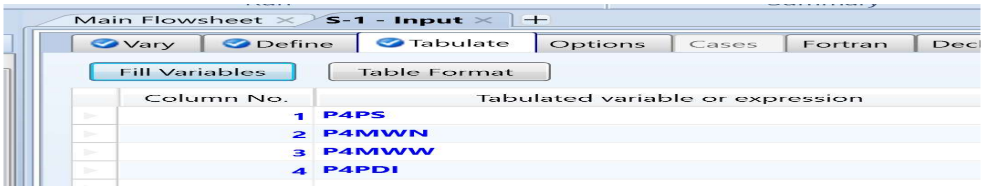
Edit selected variable

Variable: P4PDI

Category
● All
○ Blocks
○ Streams
○ Model Utility

Reference
Type: Compattr-Var
Stream: P4
Substream: MIXED
Component: PS
Attribute: PDI
Element: 1

Figure 6.44 Defining the dependent variables ("Define") of sensitivity study S-1



Column No.	Tabulated variable or expression
1	P4PS
2	P4MWN
3	P4MWW
4	P4PDI

Figure 6.45 Defining the dependent variables to be tabulated in sensitivity study S-1

We see from Figures 6.46 and 6.47 that the mass flow rate of chain transfer agent EB has only a minor effect on the mass flow rate and PDI of PS in the product polymer, stream P4, but it has a significant effect on the resulting MWN and MWW.

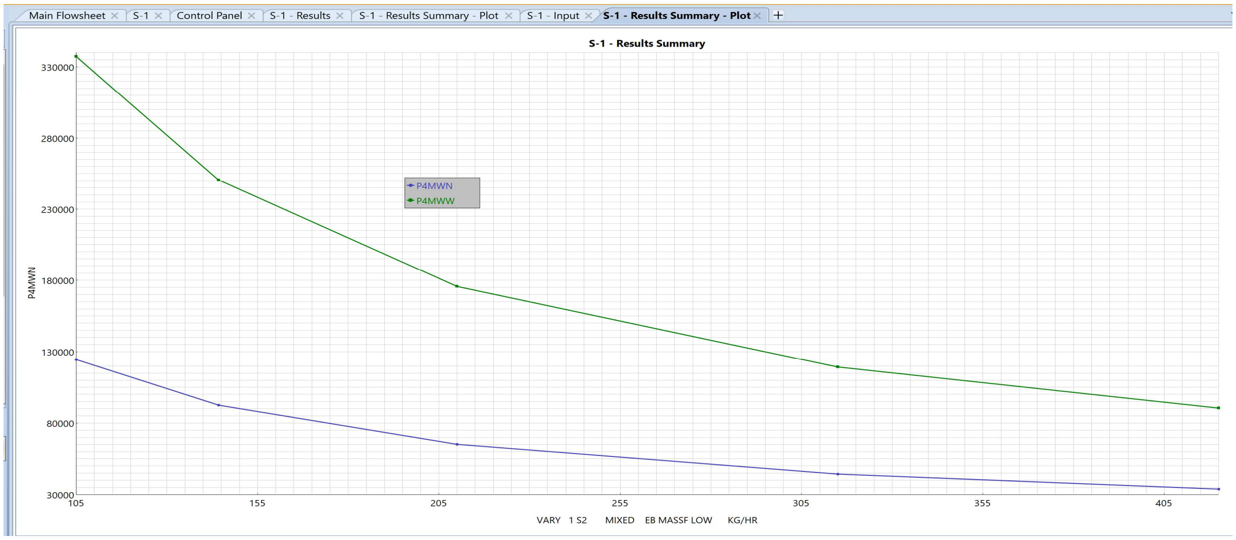


Figure 6.46 Effect of mass flow rate of chain transfer agent EB on the MWN and MWW of product polymer, stream P4.

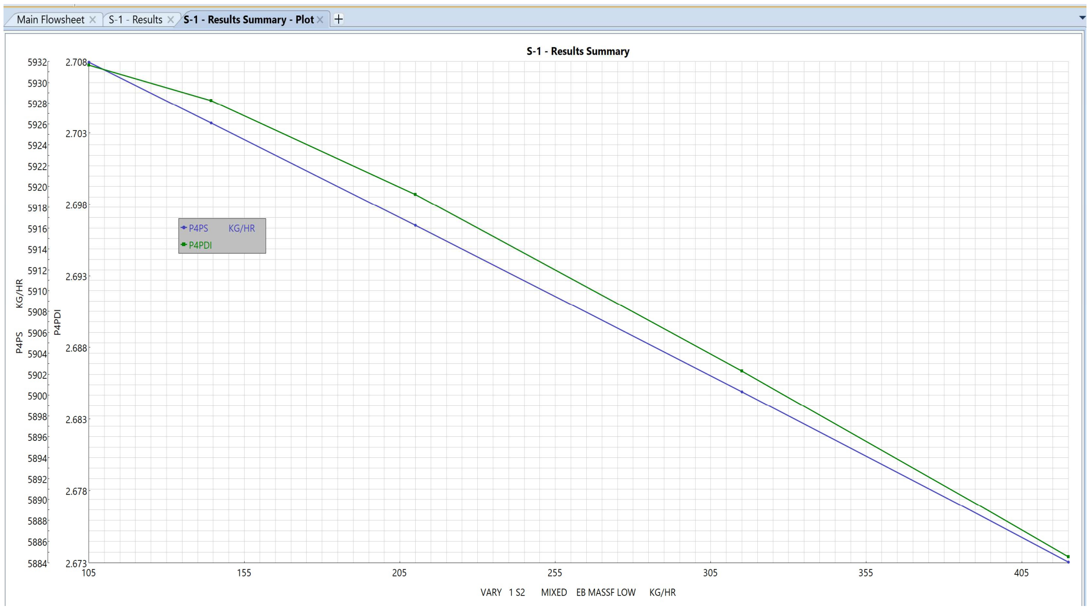
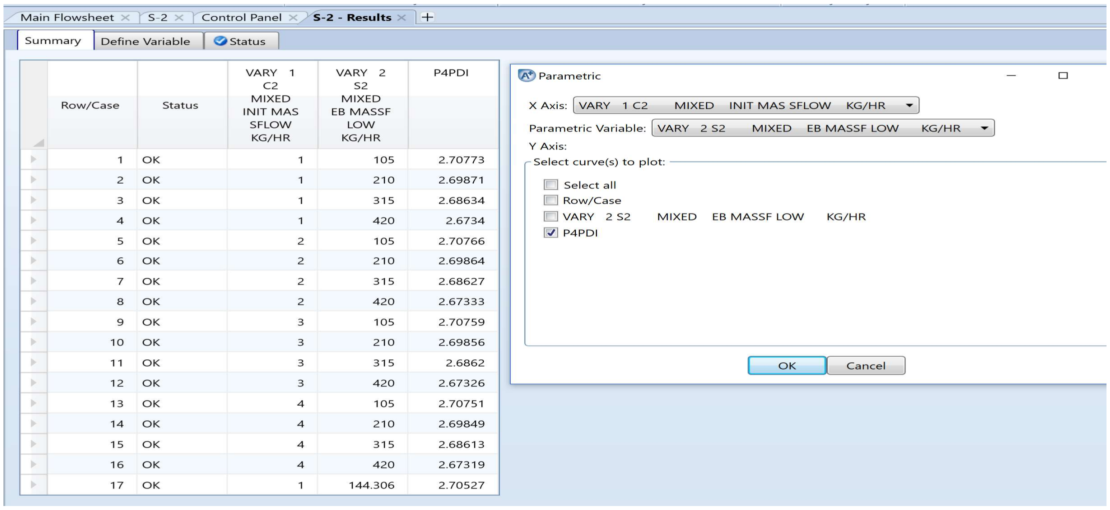


Figure 6.47 Effect of mass flow rate of chain transfer agent EB on the PS mass flow rate and PDI of product polymer, stream P4.

As another example, we investigate the interactive effect of varying the INIT mass flow within feed stream C2 from 1 to 4 kg/hr and varying the mass flow rate of chain transfer agent EB within feed stream S2 from 105 to 420 kg/hr on the PDI of PS in the product stream P4. We make a parametric plot of the result, with x-variable being the INIT mass flow in stream S2, parametric variable being the mass flow of chain transfer agent EB in stream C2, and y-variable being the PDI of PS in product P4. See Figures 6.48 and 6.49.



Row/Case	Status	VARY 1 C2 MIXED INIT MAS SFLOW KG/HR	VARY 2 S2 MIXED EB MASSF LOW KG/HR	P4PDI
1	OK	1	105	2.70773
2	OK	1	210	2.69871
3	OK	1	315	2.68634
4	OK	1	420	2.6734
5	OK	2	105	2.70766
6	OK	2	210	2.69864
7	OK	2	315	2.68627
8	OK	2	420	2.67333
9	OK	3	105	2.70759
10	OK	3	210	2.69856
11	OK	3	315	2.6862
12	OK	3	420	2.67326
13	OK	4	105	2.70751
14	OK	4	210	2.69849
15	OK	4	315	2.68613
16	OK	4	420	2.67319
17	OK	1	144.306	2.70527

X Axis: VARY 1 C2 MIXED INIT MAS SFLOW KG/HR

Parametric Variable: VARY 2 S2 MIXED EB MASSF LOW KG/HR

Y Axis:

Select curve(s) to plot:

☐ Select all
☐ Row/Case
☐ VARY 2 S2 MIXED EB MASSF LOW KG/HR
☑ P4PDI

Figure 6.48 Defining the parametric plot of sensitivity analysis result.

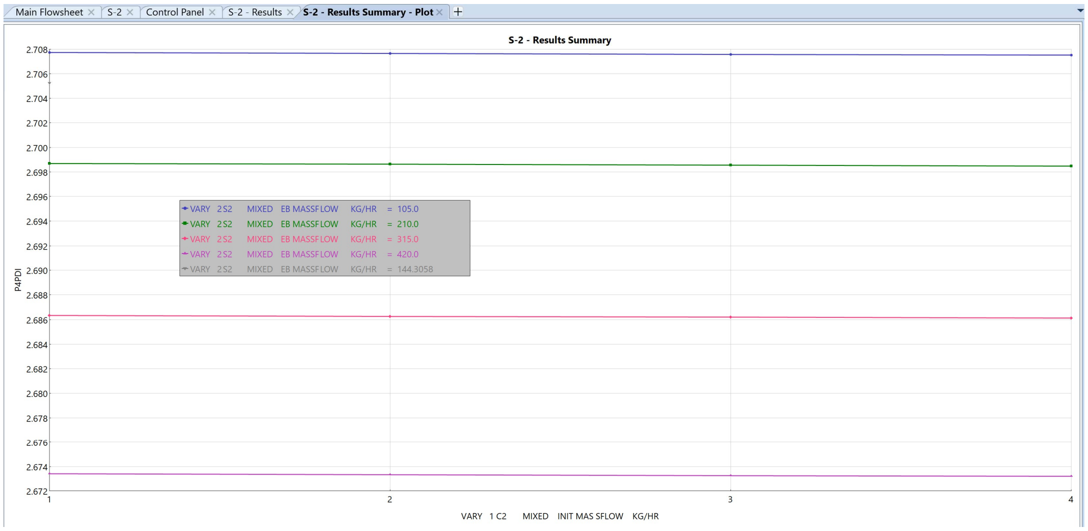


Figure 6.49 PDI of PS in product P4 does not change much when INIT varies from 1 to 4 kg/hr, but drops when mass flow of chain transfer agent EB increases from 105 to 420 kg/hr.

This concludes the current workshop for PS simulation with gel effect and oligomer formation.

6.2 Workshop 6.2-Production of Poly(Styrene-Butadiene-Styrene) or SBS Rubber by Ionic Polymerization

6.2.1 Motivation and Objective for Modeling Ionic Polymerization Processes

As discussed previously, polystyrene is an important class of unsaturated polyolefins. PS and its copolymers, such as SBS rubber, represent approximately 10% of commercial polymer production. In two classic papers, Chang et al. [15,16] presented a convincing argument to study the fundamental modeling of anionic polymerization processes, using the SBS rubber as an example. We summarize their reasoning below.

Elastomers refer to natural or synthetic polymers having elastic properties, such as rubber. Ziegler-Natta catalysts, discussed in Chapter 5, are used widely to produce elastomers of given stereo-specific microstructure (e.g., isotactic, syndiotactic and atatactic aspects) that are relatively insensitive to process variations and environmental impurities. However, it is difficult to produce customized polymers for new or unique applications. Fortunately, significant research achievements by polymer chemists on living anionic polymerization systems, especially with alkyllithium initiators, have opened doors for highly customized polymer architectures. We note that a living polymerization refers to a polymerization without any termination reactions taking place. Specifically, the tire and rubber industries have tailor-made elastomers of controlled molecular weight and molecular weight distribution, microstructure, sequence distribution, and branching, in order to meet to meet the market's requirements for tire and rubber qualities.

Living anionic polymerization systems with alkyllithium initiators are sensitive to many process and chemistry variables, such as temperature, catalyst modifier, and the type and configuration of reactor systems, among others. The need to control many variables presents problems of reproducibility and scale-up for research chemists and process engineers. Chang et al. [15,16] were among the first to demonstrate the power of fundamental process modeling to accurately predict conversion, microstructure, molecular weights and distributions, as a function of process and chemistry variables.

6.2.2 Reactor Configurations and Copolymer Products

Anionic copolymerization of styrene and butadiene takes place in a batch, semi-batch, or continuous reactors from 50 to 100°C using *n-, sec- or tert*-butyllithium initiators in hydrocarbon solvents, such as hexane and cyclohexane. Activators, such as tetrahydrofuran (THF), are also introduced into the reactor. THF promotes initial increases in chain propagation rate of the polymerization. It also serves as a chain transfer agent. Chain termination is very rare in anionic polymerization, but can occur at the very end of a process to prevent any further polymer growth through the adding a small amount of a chain terminating agent, such as water.

There are three different types of styrene-butadiene copolymers produced by anionic polymerization [17,18]:

(1) Tapered block copolymer

In a *batch* reactor with styrene, butadiene and alkyllithium, a tapered block copolymer is formed. One block would be a butadiene-styrene (B/S) copolymer with only small amount of styrene, and the other a polystyrene (S) block, resulting in *an overall B/S-S structure.*

(2) Di/tri-block copolymer and a star-shaped block copolymer

In a *semi-batch* reactor with sequential addition of styrene and butadiene, we can produce a di/tri block copolymer by first polymerizing styrene to form the "S" block, followed by addition of half of butadiene to form the half "B" block. We then add a di-functional coupling agent, such as iodine, to link the living polymer chains and form *a tri-block copolymer, SBS.*

We note that a star-shaped block copolymer could be produced by adding a tetravalent coupling agent such as silicone tetrachloride ($SiCl_4$) to unite two living di-blocks and to form a star-shaped *styrenic block copolymer (SBC).* A star-shaped polymer is the simplest class of branched polymers with a general structure consisting of several (at least three) linear chains connected to a central core. The core, or the center, of the polymer can be an atom, molecule, or macromolecule; the chains, or "arms", consist of variable-length organic chains.

(3) Random copolymer

In a *continuous* reactor, polymerization of styrene and butadiene produces a random copolymer. The copolymer composition varies with flow rates of styrene and butadiene feeds.

6.2.3 Components, Segments and Polymer in Anionic Copolymerization of Styrene and Butadiene

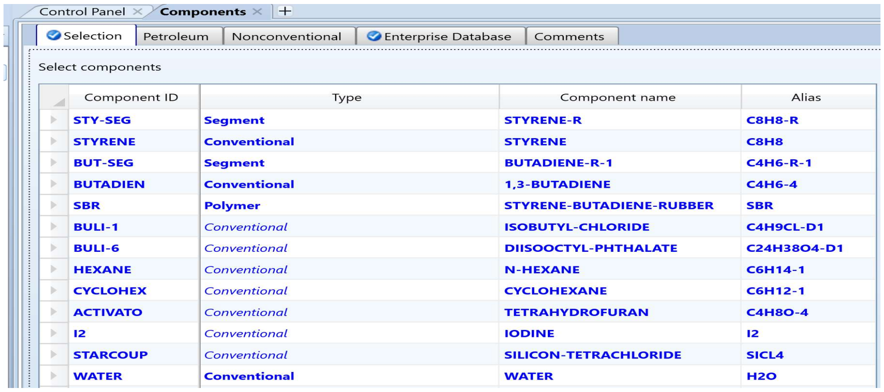
Table 6.8 summarizes the relevant species in the anionic copolymerization.

Table 6.8 component specification in anionic copolymerization of styrene and butadiene

Component ID	Type	Component name	Alias in Aspen Polymers	Function
Styrene	Conventional	Styrene	C8H8	Monomer
Sty-seg	Segment	Styrene-R	C8H8-R	Monomer segment
Butadiene	Conventional	1,3-Butadiene	C4H6-4	Monomer
But-seg	Segment	Butadiene-R-1	C4H6-R-1	Monomer segment
SBR	Polymer	Styrene-Butadiene-Rubber	SBR	Polymer
Buli-6	Conventional	Butyl-lithium-hexamer*	C24H38O4-D1*	Associated initiator
Buli-1	Conventional	n-Butyl-lithium*	C4H9CL-D1*	Initiator
Hexane	Conventional	n-Hexane	C6H14-	Solvent
Cyclohex	Conventional	Cyclohexane	C6H12-1	Solvent
THF	Conventional	Tetrahydrofuran	C4H8O-4	Activator, or chain transfer agent
I2	Conventional	Iodine	I2	Coupling agent
StarCoup	Conventional	Silica-tetrachloride	SiCl4	Star-shaped coupling agent
H2O	Conventional	Water	H2O	Terminating agent

*Buli-6 and Buli-1 are both not available within Aspen Polymers databank. Use diisooctyl-phthalate (C24H38O4-D1) to represent Buli-6 and specify its molecular weight as 384 (true molecular weight of BuLi-6); and use isobutyl chloride (C4H9CL-D1) to represent Buli-1, and specify its molecular weight as 64 (true molecular weight of BuLi-1).

Figure 6.50 shows the component specifications for anionic copolymerization of styrene and butadiene in Aspen Polymers.



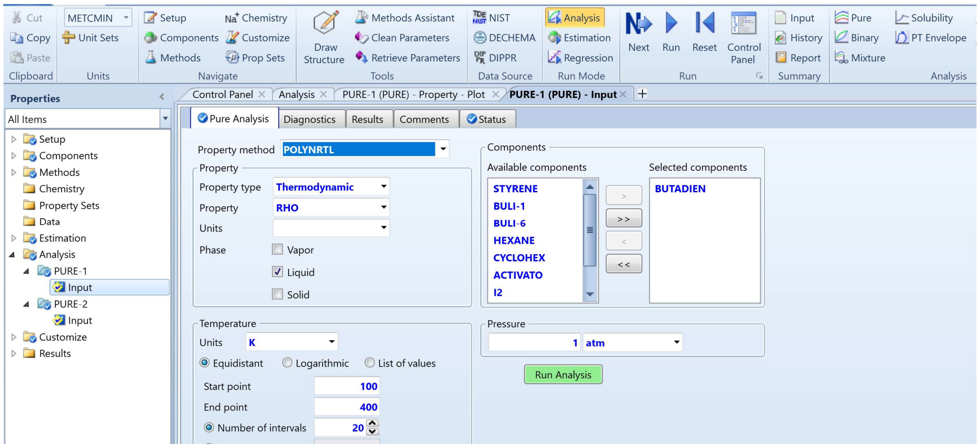
Select components

Component ID	Type	Component name	Alias
STY-SEG	Segment	STYRENE-R	C8H8-R
STYRENE	Conventional	STYRENE	C8H8
BUT-SEG	Segment	BUTADIENE-R-1	C4H6-R-1
BUTADIEN	Conventional	1,3-BUTADIENE	C4H6-4
SBR	Polymer	STYRENE-BUTADIENE-RUBBER	SBR
BULI-1	*Conventional*	ISOBUTYL-CHLORIDE	C4H9CL-D1
BULI-6	*Conventional*	DIISOOCTYL-PHTHALATE	C24H38O4-D1
HEXANE	*Conventional*	N-HEXANE	C6H14-1
CYCLOHEX	*Conventional*	CYCLOHEXANE	C6H12-1
ACTIVATO	*Conventional*	TETRAHYDROFURAN	C4H8O-4
I2	*Conventional*	IODINE	I2
STARCOUP	*Conventional*	SILICON-TETRACHLORIDE	SICL4
WATER	Conventional	WATER	H2O

Figure 6.50 Component specifications for anionic copolymerization of styrene and butadiene.

6.2.4 Thermodynamic Method and Property Parameters of Components and Polymer

Following Figure 6.11, we choose POLYNRTL thermodynamic method (Section 2.2.4 and Table 4.3) for anionic copolymerization of styrene and butadiene. To validate the accuracy of the POLYNRTL model in predicting the pure component properties, we use the "Analysis" tool within the Properties environment of Aspen Polymers to predict the densities and ideal gas heat capacities of styrene, butadiene and THF, and compare the predicted values with experimental data from the Design Institute for Physical Property Research (DIPPR) [19]. Figures 6.51 to 6.53 show the analysis input and predicted results for butadiene density at 1 atm from 100 to 400 K with 20 increments.



Property method: POLYNRTL

Property

Property type: Thermodynamic

Property: RHO

Units:

Phase

☐ Vapor

☑ Liquid

☐ Solid

Components

Available components: STYRENE, BULI-1, BULI-6, HEXANE, CYCLOHEX, ACTIVATO, I2

Selected components: BUTADIEN

Temperature

Units: K

● Equidistant ○ Logarithmic ○ List of values

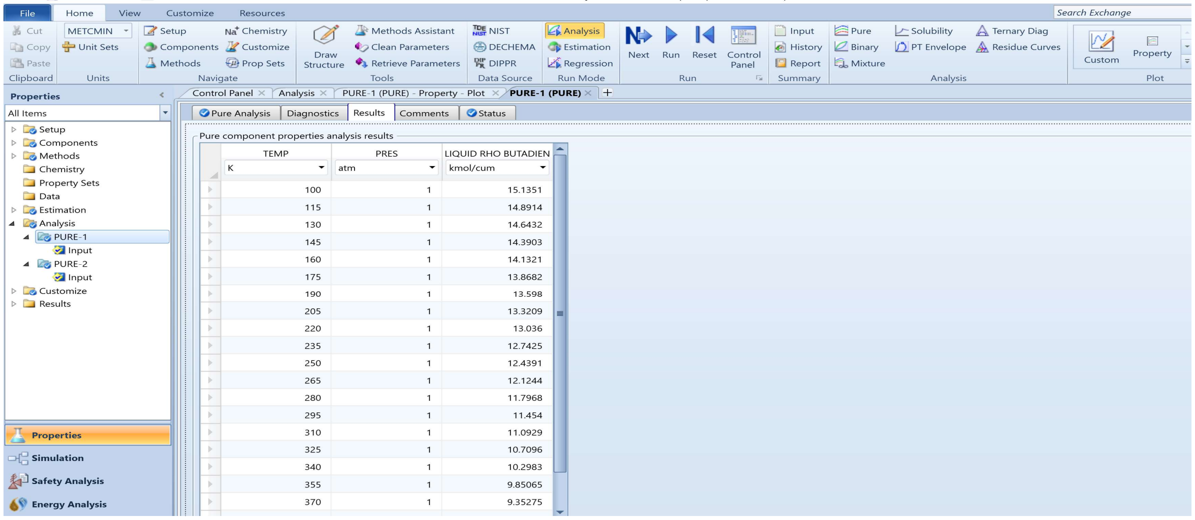
Start point: 100

End point: 400

● Number of intervals: 20

Pressure: 1 atm

Figure 6.51 Analysis input for predicting the density of butadiene



Pure component properties analysis results

TEMP	PRES	LIQUID RHO BUTADIEN
K	atm	kmol/cum
100	1	15.1351
115	1	14.8914
130	1	14.6432
145	1	14.3903
160	1	14.1321
175	1	13.8682
190	1	13.598
205	1	13.3209
220	1	13.036
235	1	12.7425
250	1	12.4391
265	1	12.1244
280	1	11.7968
295	1	11.454
310	1	11.0929
325	1	10.7096
340	1	10.2983
355	1	9.85065
370	1	9.35275

Figure 6.52 Predicted density of butadiene. Clicking on Plot->Property on the upper right corner will show the plot of Figure 6.75.

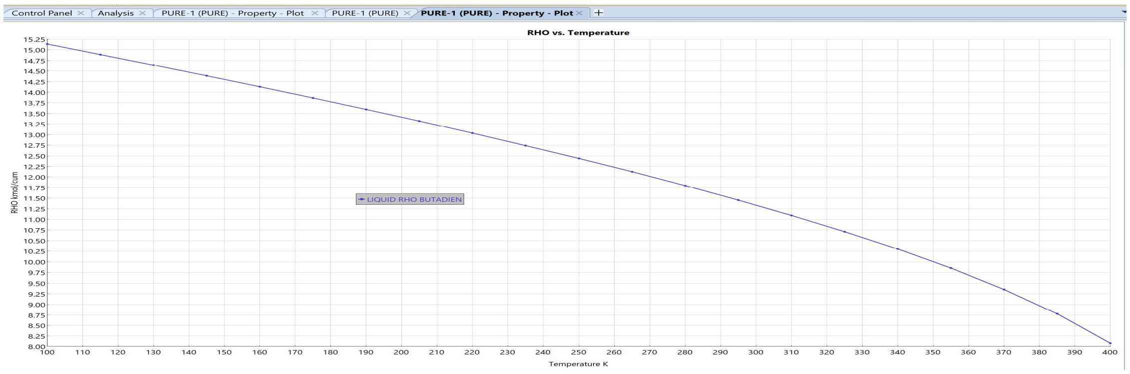


Figure 6.53 Predicted density of butadiene as a function of temperature

Figures 6.54 to 6.56 compare the predicted property values with experimental data from DIPPR [14]. The POLYNRTL thermodynamic method gives accurate prediction.

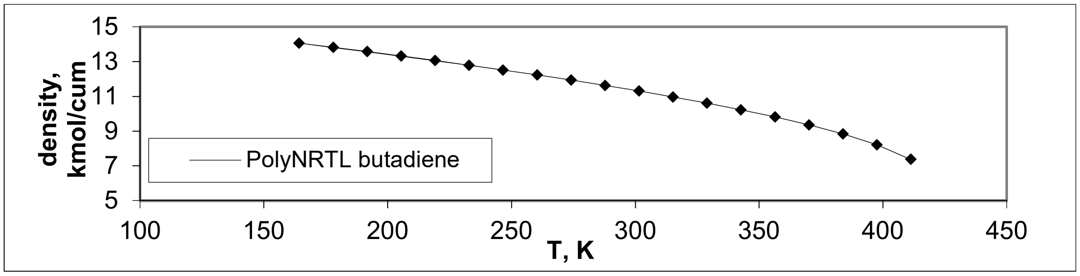


Figure 6.54 Comparing experimental data with PolyNRTL predictions for the densities of 1,3 butadiene. The literature values are from DIPPR [14].

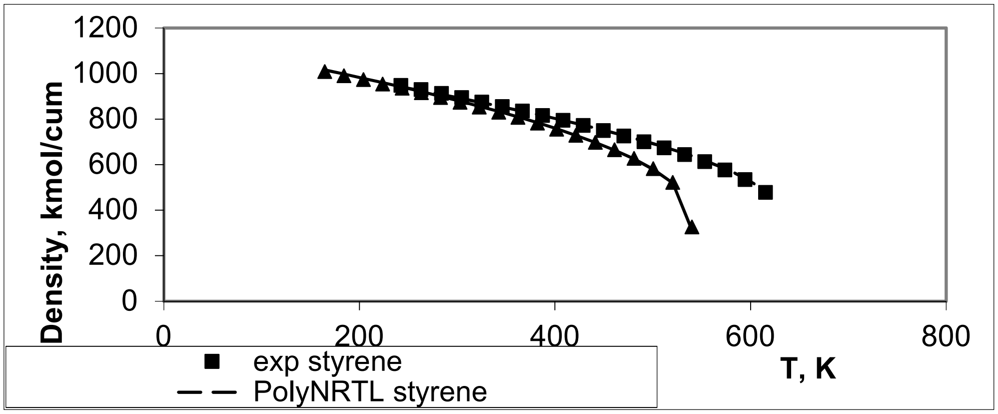


Figure 6.55 Comparing experimental data with PolyNRTL predictions for the densities of styrene and THF. The literature values are from DIPPR [19].

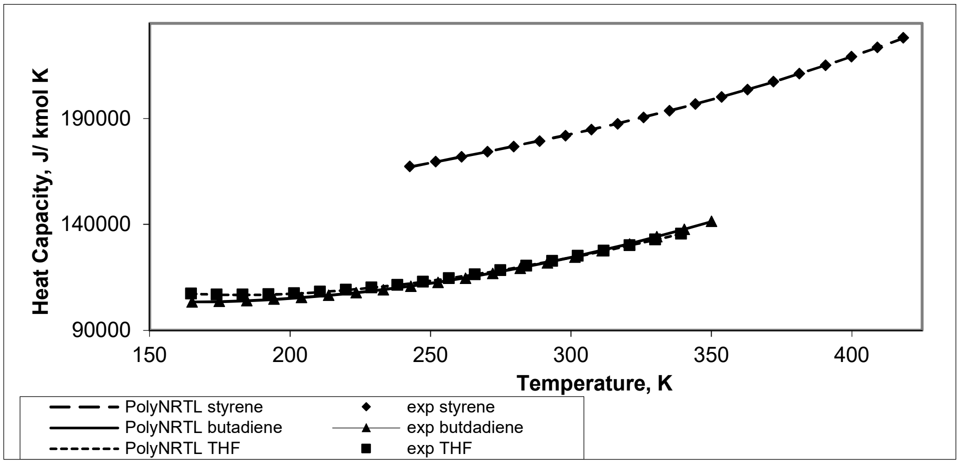


Figure 6.56 Comparing experimental data with PolyNRTL predictions for heat capacity of styrene, butadiene, and tetrahydrofuran. The literature values are from Caruthers et al [20].

We also use molecular structures to estimate all missing property parameters. First, to define the molecular structure of BULI-6, currently being represented by diisooctyl phthalate, we follow the procedure previously demonstrated in Figures 4.18, 4.19a to 4.19c. Specifically, we search the component on the website of Chemical Book (www.chemicalbook.com). We Google for the entry: “Chemical Book, diisooctyl phthalate”, and see the component ACS number 27554-26-2 together with the molecular file ***27554-26-3.mol***. We download and save the molecular structure file and import it into Aspen Polymers by following the path: Properties -> Components -> Molecular Structure -> BULI-6 -> Structure (Graphical Structure) -> Draw/Import/Edit -> Molecule Editor -> Import Mol File -> 27554-26-3.mol -> Structure shown in Figure 6.56.

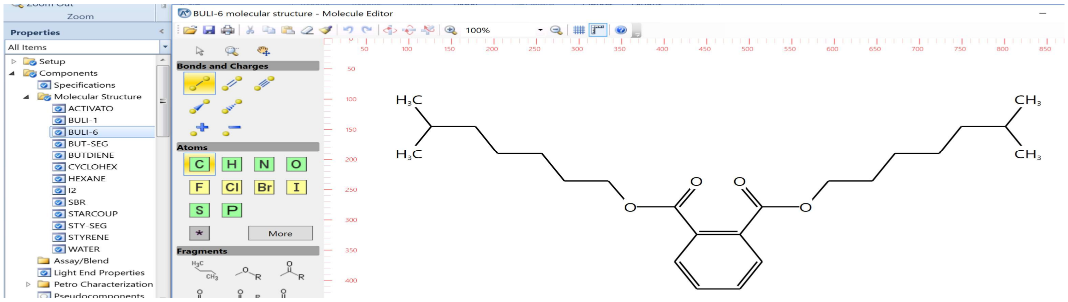
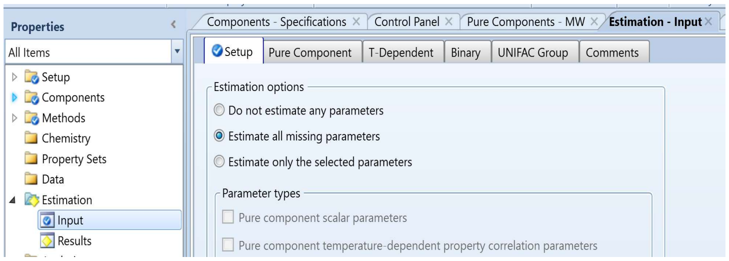


Figure 6.56 Structure of diisooctyl phthalate, representing the associated initiator BULI-6.

We follow Figures 4.19a to 4.19c to quantify the structure of BULI-6 in terms of atoms C, H and O. After defining all the molecular structures, we estimate the missing property parameters. See Figures 6.58 to 6.60.



Estimation options

○ Do not estimate any parameters

● Estimate all missing parameters

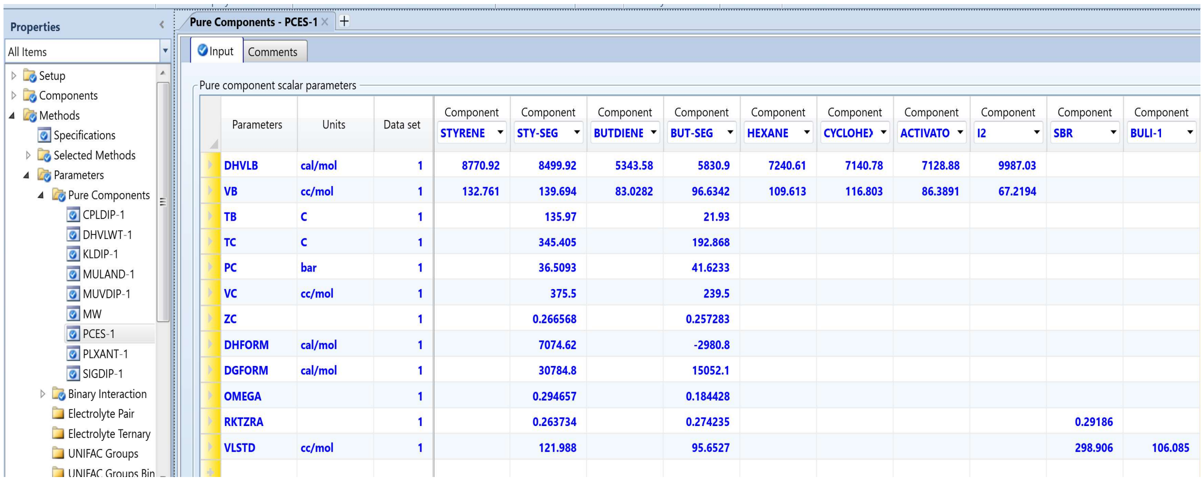
○ Estimate only the selected parameters

Parameter types

☐ Pure component scalar parameters

☐ Pure component temperature-dependent property correlation parameters

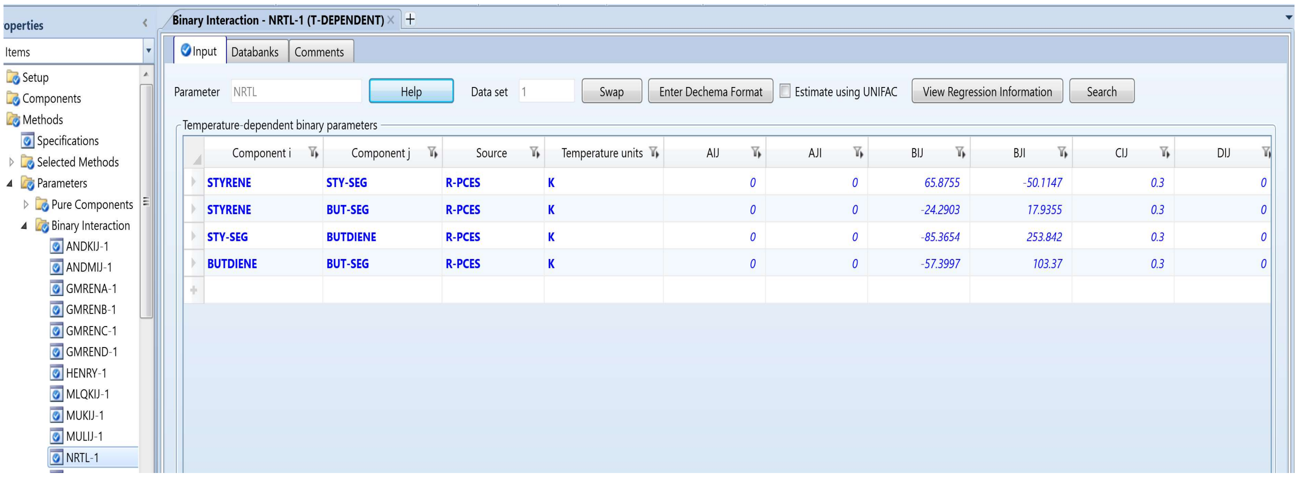
Figure 6.58 Estimation of all missing parameters.



Pure component scalar parameters

Parameters	Units	Data set	Component STYRENE	Component STY-SEG	Component BUTDIENE	Component BUT-SEG	Component HEXANE	Component CYCLOHE)	Component ACTIVATO	Component I2	Component SBR	Component BULI-1
DHVLB	cal/mol	1	8770.92	8499.92	5343.58	5830.9	7240.61	7140.78	7128.88	9987.03		
VB	cc/mol	1	132.761	139.694	83.0282	96.6342	109.613	116.803	86.3891	67.2194		
TB	C	1		135.97		21.93						
TC	C	1		345.405		192.868						
PC	bar	1		36.5093		41.6233						
VC	cc/mol	1		375.5		239.5						
ZC		1		0.266568		0.257283						
DHFORM	cal/mol	1		7074.62		-2980.8						
DGFORM	cal/mol	1		30784.8		15052.1						
OMEGA		1		0.294657		0.184428						
RKTZRA		1		0.263734		0.274235					0.29186	
VLSTD	cc/mol	1		121.988		95.6527					298.906	106.085

Figure 6.59 Estimated pure component property parameters.



Parameter NRTL

Data set 1

☐ Estimate using UNIFAC

Temperature-dependent binary parameters

Component i	Component j	Source	Temperature units	AIJ	AJI	BIJ	BJI	CIJ	DIJ
STYRENE	STY-SEG	R-PCES	K	0	0	65.8755	-50.1147	0.3	0
STYRENE	BUT-SEG	R-PCES	K	0	0	-24.2903	17.9355	0.3	0
STY-SEG	BUTDIENE	R-PCES	K	0	0	-85.3654	253.842	0.3	0
BUTDIENE	BUT-SEG	R-PCES	K	0	0	-57.3997	103.37	0.3	0

Figure 6.60 Estimated binary interaction parameters NRTL-1.

6.2.5 Kinetics of Anionic Copolymerization of Styrene and Butadiene [21,22]

6.2.5.1 Initiator Disassociation (INIT-DISSOC)

For anionic polymerization, the active species is the initiator in a dissociated form. We observe the association and disassociation of initiator in an alkyl-lithium type of initiators in nonpolar solvents.

INIT-DISSOC: Buli-6 <-> 6 Buli-1 (6.2)

BuLi-6 is the associated initiator. 6 is the degree of ionization. Buli-1 is the disassociated initiator.

6.2.5.2 Chain Initiation (CHAIN-INI)

The ionic polymerization model within Aspen Polymers adopts the same kinetic framework as in the Ziegler-Natta multisite kinetic model. In the ionic polymerization model, each active site refers a unique type of active species, which corresponds to an initiator in a disassociated form. For example, to model three propagating species for an initiator, the model considers three active sites or active species (*particularly active site or species 1 for free ion; 2 for ion pairs; and 3 for dormant esters*) with each corresponding to a unique propagating active species type. We consider three types of chain initiation reactions.

(1) CHAIN-INI-1: The initiator in a disassociated form is an active species of a chain length zero, Po[1], which can react with a monomer to form a propagating species (a live polymer molecular chain) with a unit chain length, P1[1,Sty-Seg] or P1[1,But-Seg], with an active segment, Sty-Seg or But-Seg, attached to it. Here, "1" refers to active site or active species 1 corresponding to *a free ion*. Thus, this chain initiation reaction involves *a monomer and an active species.*

Po[1] + Styrene -> P1[1,Sty-Seg] (6.3)

Po[1] + Butadiene -> P1[1,But-Seg] (6.4)

(2) CHAIN-INI-2: This chain initiation reaction involves *a monomer and a disassociated initiator*, and it may produce a C-ion (when the stoichiometric coefficient d is not zero). A C-ion represents a counter ion that accompanies an ionic species in order to maintain electric neutrality. As an example, in table salt, the sodium ion is the counter ion for the chlorine ion and vice versa. We commonly call a counter ion as *an anion or a cation*, depending on whether it is negatively or positively charged. We note that for the anionic copolymerization of styrene and butadiene, more ion pairs (type 2 active species or site) are initiated than free ions (type 1 active species or site) [21].

Buli-1 + Styrene -> P1[1, Sty-Seg] + d · C-Ion (6.5)

Buli-1 + Butadiene -> P1[1, But-Seg] + d · C-Ion (6.6)

(3) CHAIN-INI-T: The third chain initiation reaction involves *a monomer and a transfer active species*, PTo[1], which results from a chain transfer reaction of a growing polymer chain (see Section 6.2.5.5 below), to form a propagating species with a unit chain length with an active segment, Sty-Seg or But-Seg, attached to it.

PTo[1] + Styrene -> P1[1,Sty-Seg] (6.7)

PTo[1] + Butadiene -> P1[1,But-Seg] (6.8)

6.2.5.3 Chain Propagation (PROPAGATION)

Polymer chains grow by means of chain propagation. A growing polymer, with an active species at the end of the chain, propagates through the addition of monomer to create longer polymer chains. Increasing the amount of monomer in the system yields larger polymer chains.

PROPAGATION: Pn[1, Sty-Seg] + Styrene -> Pn+1[1,Sty-Seg] (6.9)

Pn[1, Sty-Seg] + Butadiene -> Pn+1[1,But-Seg] (6.10)

Pn[1, But-Seg] + Styrene -> Pn+1[1,Sty-Seg] (6.11)

Pn[1,But-Seg] + Butadiene -> Pn+1[1,But-Seg] (6.12)

The propagation reaction accounts for the total amount of polymer produced. We observe that an increase in the rate constant result in a linear increase in polymer molecular weight.

6.2.5.4 Association or Aggregation (ASSOCIATION)

In anionic polymerization by alkyllithium type initiators, propagating species also exhibit an association phenomenon like the initiator. The association of the live polymer species is usually dimeric and creates the associate polymer, Qn+m[1,Sty-Seg] and Qn+m[1,But-Seg] . The associated polymer does not participate in any other reactions.

ASSOCIATION: Pn[1, Sty-Seg] + Pm[1,Sty-Seg] <-> Qn+m[1,Sty-Seg] (6.13)

Pn[1, But-Seg] + Pm[1,But-Seg] <-> Qn+m[1,But-Seg] (6.14)

6.2.5.5 Chain Transfer (CHAT)

Chain transfer can lead to the formation of dead polymer chains, D_n. This process limits the molecular weight of the polymer. We also fine-tune chain-transfer rate constants to match the MWW. Specifically, we consider three types of chain-transfer reactions. The first reaction we incorporate is a reaction with an activator or a chain-transfer agent, **CHAT-AGENT**. For anionic copolymerization of styrene and butadiene, our activator ("Activato") or chain-transfer agent is tetrahydrofuran (THF).

We also consider the spontaneous chain transfer, **CHAT-SPON**, and the chain transfer to monomer, **CHAT-MONOMER.** We ignore the chain-transfer reaction that leads to the formation of dormant polymer (**CHAT-DORM-P**) [17].

(1) CHAT-AGENT: A growing polymer chain, Pn[1, Sty-Seg] or Pn[1,But-Seg], can be transferred to an activator or a chain-transfer agent, leading to the formation of a dead polymer chain of n segments, Dn, and a transfer active species, PTo[1], of the same type. PTo[1] can then participate in new chain-initiation reaction, **CHAIN-INI-T.** See Eqs. (6.7) and (6.8).

Pn[1, Sty-Seg] + Activato^order -> Dn [1] + PTo[1] (6.15)

Pn[1, But-Seg] + Activato^order -> Dn [1] + PTo[1] (6.16)

The reaction order with respect to the activator or chain-transfer agent, "order", is set by the user.

(2) CHAT-SPON: A spontaneous chain transfer is the third type of chain transfer in our model. This reaction leads to the formation of a dead polymer molecule Dn[1] and a polymer active species Po[1] by proton loss.

Pn[1, Sty-Seg] -> Dn[1] + Po[1] (6.17)

Pn[1, But-Seg] -> Dn[1] + Po[1] (6.18)

(3) CHAT-MONOMER: This reaction results in the formation of a dead polymer molecule Dn[1] and a propagating species with a unit chain length with an active segment, Sty-Seg or But-Seg, attached to it, that is, P1[1,Sty-Seg] or P1[1,But-Seg].

Pn[1, Sty-Seg] + Styrene -> Dn[1] + P1[1,Sty-Seg] (6.19)

Pn[1, Sty-Seg] + Butadien -> Dn[1] + P1[1,Sty-Seg] (6.20)

Pn[1, But-Seg] + Styrene -> Dn[1] + P1[1,But-Seg] (6.21)

Pn[1, But-Seg] + Butadien -> Dn[1] + P1[1,But-Seg] (6.22)

6.2.5.6 Chain Termination (TERM-AGENT)

Chain-termination reaction is very rare in anionic polymerization reactions, but can occur at the very end of a process to prevent any further polymer growth. We can use water as a terminating agent to terminate a growing polymer Pn[1, Sty-Seg] or Pn[1,But-Seg], thus creating a dead polymer chain Dn[1].

TERM-AGENT: Pn[1,Sty-Seg] + T_m-> Dn[1] (6.23)

Pn[1,But-Seg] + T_m -> Dn[1] (6.24)

T_m is the termination agent, and in our workshop, it is water. Since the amount of initiators far exceeds the amount of water in the system, we disregard this reaction in our model. There is 369 ppm of initiators entering the system, and only 30 ppm of water in the system. We assume that the initiation rate is of the same order of the termination rate.

6.2.5.7 Equilibrium with Counter-Ion or Reversible Ionization (EQUILIB-CION)

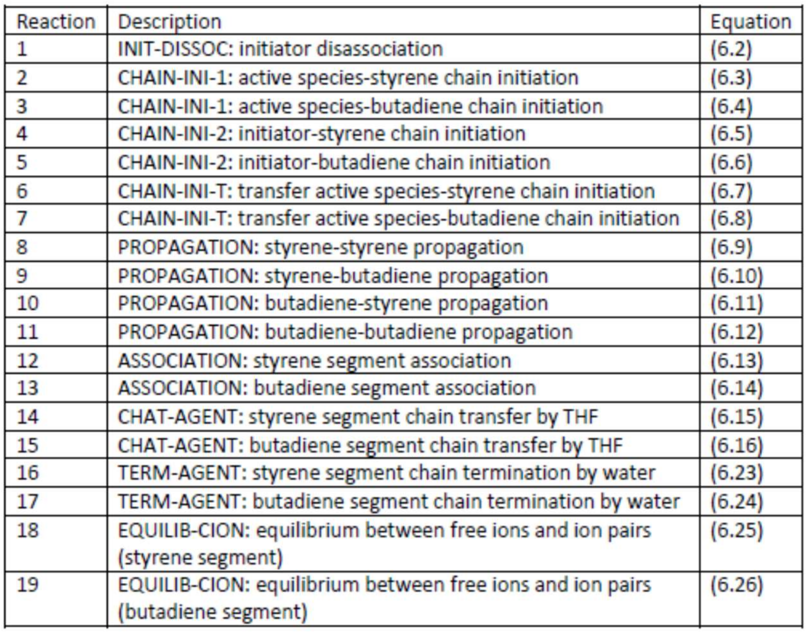
The following reactions represent the equilibrium between free ions (active site or species type 1) and ion pairs (active site or species type 2), hence the name equilibrium with counter ion.

EQUILIB-CION: Pn[2,Sty-Seg] <-> Pn[1,Sty-Seg] + C-Ion (6.25)

Pn[2,But-Seg] <-> Pn[1,But-Seg] + C-Ion (6.26)

Table 6.9 summarizes our reactions for the anionic copolymerization of styrene and butadiene.

Table 6.9 Reactions for the anionic copolymerization of styrene and butadiene



Reaction	Description	Equation
1	INIT-DISSOC: initiator disassociation	(6.2)
2	CHAIN-INI-1: active species-styrene chain initiation	(6.3)
3	CHAIN-INI-1: active species-butadiene chain initiation	(6.4)
4	CHAIN-INI-2: initiator-styrene chain initiation	(6.5)
5	CHAIN-INI-2: initiator-butadiene chain initiation	(6.6)
6	CHAIN-INI-T: transfer active species-styrene chain initiation	(6.7)
7	CHAIN-INI-T: transfer active species-butadiene chain initiation	(6.8)
8	PROPAGATION: styrene-styrene propagation	(6.9)
9	PROPAGATION: styrene-butadiene propagation	(6.10)
10	PROPAGATION: butadiene-styrene propagation	(6.11)
11	PROPAGATION: butadiene-butadiene propagation	(6.12)
12	ASSOCIATION: styrene segment association	(6.13)
13	ASSOCIATION: butadiene segment association	(6.14)
14	CHAT-AGENT: styrene segment chain transfer by THF	(6.15)
15	CHAT-AGENT: butadiene segment chain transfer by THF	(6.16)
16	TERM-AGENT: styrene segment chain termination by water	(6.23)
17	TERM-AGENT: butadiene segment chain termination by water	(6.24)
18	EQUILIB-CION: equilibrium between free ions and ion pairs (styrene segment)	(6.25)
19	EQUILIB-CION: equilibrium between free ions and ion pairs (butadiene segment)	(6.26)

Figures 6.61 to 6.62 show how to implement these reactions within Aspen Polymers our selected reactions for our workshop of styrene-butadiene copolymerization below. Depending on our feeds and reactor type, we may add or delete some reactions in the examples below.

Polymer: SBR

Monomers: STYRENE, BUTADIEN

goes to ->: STY-SEG, BUT-SEG

Assoc. init.: BULI-6

Initiators: BULI-1

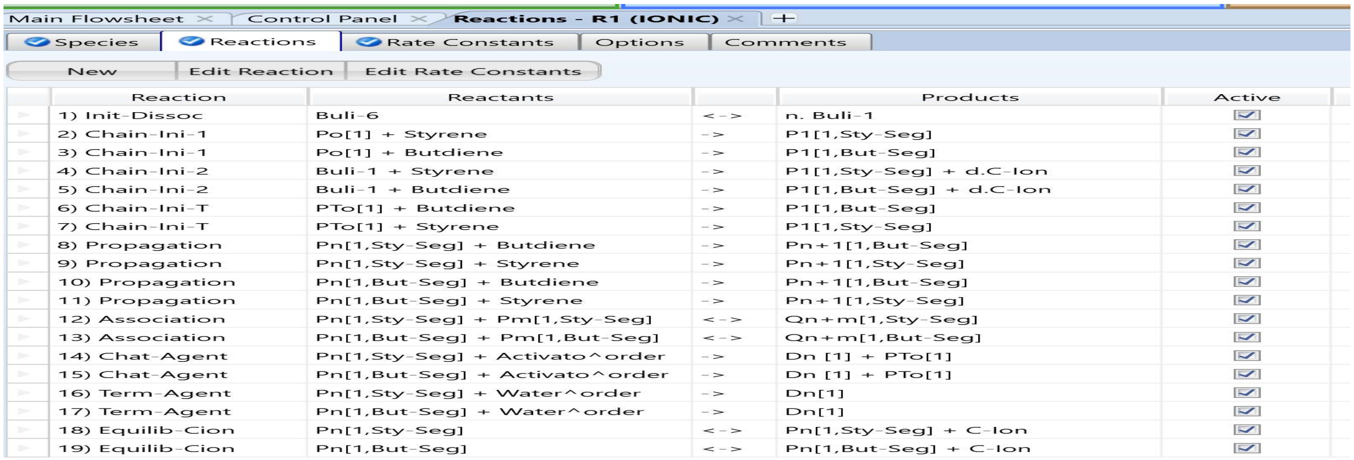
Catalysts:

Transfer ag.: ACTIVATO

Exch. ag.:

Term. ag.: WATER

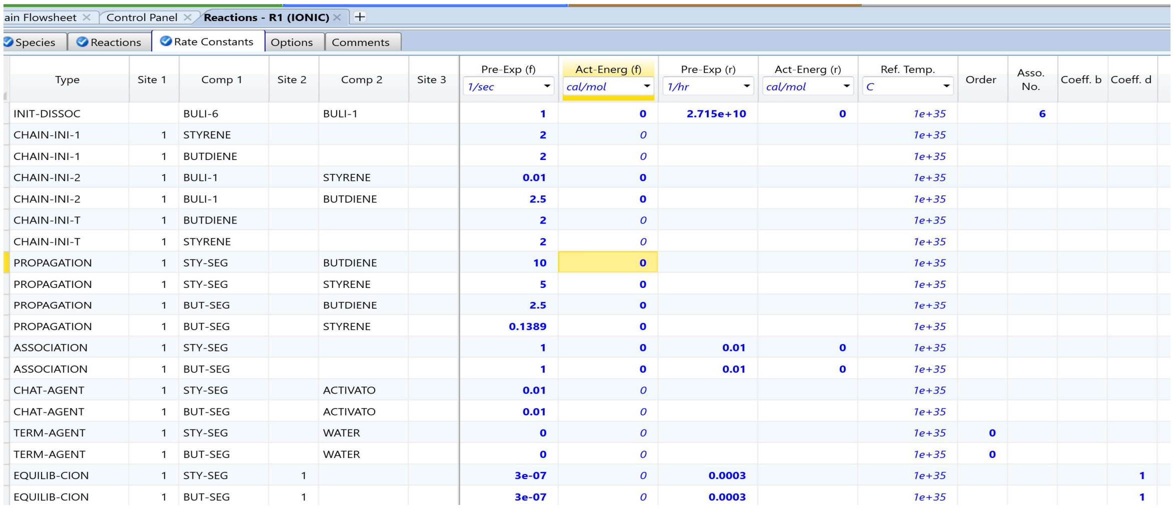
Figure 6.61 Species specification of the ionic reaction set R-1 for anionic copolymerization of styrene and butadiene.



Reaction	Reactants		Products	Active
1) Init-Dissoc	Buli-6	<->	n. Buli-1	☑
2) Chain-Ini-1	Po[1] + Styrene	->	P1[1,Sty-Seg]	☑
3) Chain-Ini-1	Po[1] + Butdiene	->	P1[1,But-Seg]	☑
4) Chain-Ini-2	Buli-1 + Styrene	->	P1[1,Sty-Seg] + d.C-Ion	☑
5) Chain-Ini-2	Buli-1 + Butdiene	->	P1[1,But-Seg] + d.C-Ion	☑
6) Chain-Ini-T	PTo[1] + Butdiene	->	P1[1,But-Seg]	☑
7) Chain-Ini-T	PTo[1] + Styrene	->	P1[1,Sty-Seg]	☑
8) Propagation	Pn[1,Sty-Seg] + Butdiene	->	Pn+1[1,But-Seg]	☑
9) Propagation	Pn[1,Sty-Seg] + Styrene	->	Pn+1[1,Sty-Seg]	☑
10) Propagation	Pn[1,But-Seg] + Butdiene	->	Pn+1[1,But-Seg]	☑
11) Propagation	Pn[1,But-Seg] + Styrene	->	Pn+1[1,Sty-Seg]	☑
12) Association	Pn[1,Sty-Seg] + Pm[1,Sty-Seg]	<->	Qn+m[1,Sty-Seg]	☑
13) Association	Pn[1,But-Seg] + Pm[1,But-Seg]	<->	Qn+m[1,But-Seg]	☑
14) Chat-Agent	Pn[1,Sty-Seg] + Activato^order	->	Dn [1] + PTo[1]	☑
15) Chat-Agent	Pn[1,But-Seg] + Activato^order	->	Dn [1] + PTo[1]	☑
16) Term-Agent	Pn[1,Sty-Seg] + Water^order	->	Dn[1]	☑
17) Term-Agent	Pn[1,But-Seg] + Water^order	->	Dn[1]	☑
18) Equilib-Cion	Pn[1,Sty-Seg]	<->	Pn[1,Sty-Seg] + C-Ion	☑
19) Equilib-Cion	Pn[1,But-Seg]	<->	Pn[1,But-Seg] + C-Ion	☑

Figure 6.62 Reactions for anionic copolymerization of styrene and butadiene following Table 6.9 and ignoring CHAT-SPON, CHAT-MONOMER and TERM-AGENT reactions

Figure 6.63 shows the initial values of the reaction rate constants and activation energies [16].



Type	Site 1	Comp 1	Site 2	Comp 2	Site 3	Pre-Exp (f) 1/sec	Act-Energ (f) cal/mol	Pre-Exp (r) 1/hr	Act-Energ (r) cal/mol	Ref. Temp. C	Order	Asso. No.	Coeff. b	Coeff. d
INIT-DISSOC		BULI-6		BULI-1		1	0	2.715e+10	0	1e+35		6		
CHAIN-INI-1	1	STYRENE				2	0			1e+35				
CHAIN-INI-1	1	BUTDIENE				2	0			1e+35				
CHAIN-INI-2	1	BULI-1		STYRENE		0.01	0			1e+35				
CHAIN-INI-2	1	BULI-1		BUTDIENE		2.5	0			1e+35				
CHAIN-INI-T	1	BUTDIENE				2	0			1e+35				
CHAIN-INI-T	1	STYRENE				2	0			1e+35				
PROPAGATION	1	STY-SEG		BUTDIENE		10	0			1e+35				
PROPAGATION	1	STY-SEG		STYRENE		5	0			1e+35				
PROPAGATION	1	BUT-SEG		BUTDIENE		2.5	0			1e+35				
PROPAGATION	1	BUT-SEG		STYRENE		0.1389	0			1e+35				
ASSOCIATION	1	STY-SEG				1	0	0.01	0	1e+35				
ASSOCIATION	1	BUT-SEG				1	0	0.01	0	1e+35				
CHAT-AGENT	1	STY-SEG		ACTIVATO		0.01	0			1e+35				
CHAT-AGENT	1	BUT-SEG		ACTIVATO		0.01	0			1e+35				
TERM-AGENT	1	STY-SEG		WATER		0	0			1e+35	0			
TERM-AGENT	1	BUT-SEG		WATER		0	0			1e+35	0			
EQUILIB-CION	1	STY-SEG	1			3e-07	0	0.0003		1e+35				1
EQUILIB-CION	1	BUT-SEG	1			3e-07	0	0.0003		1e+35				1

Figure 6.63 Initial values of pre-exponential factors and activation energies.

Research [17] shows that the order of propagation rate constants for anionic polymerization of styrene and butadiene, reactions 8 to 11, in Figure 6.63, is as follows: ***k_{SB} (Sty-Seg-Butadiene)> k_{SS} (Sty-Seg-Styrene)> k_{BB} (But-Seg-Butadiene)> k_{BS} (But-Seg-Butadiene),*** or 10>5 >2.5 >0.1389. In the figure, we purposely set the pre-exponential factors for TERM-AGENT reactions to zero. Water is the termination agent in this batch reaction; however, since the amount of initiators far exceeds the amount of water in the system, we can disregard the two termination reactions in our model. As dated previously, there is 369 ppm of initiators entering our industrial process, and only 30 ppm of water entering the process.

6.2.5.8 Batch Reactor for Producing a Tapered Block Copolymer

(1) Reactor Flowsheet, and Feed and Operating Conditions

Figure 6.64 shows the simple batch reactor flowsheet for producing a tapered block polymer. We save the simulation file as ***WS6.2_SBC Batch.bkp***.

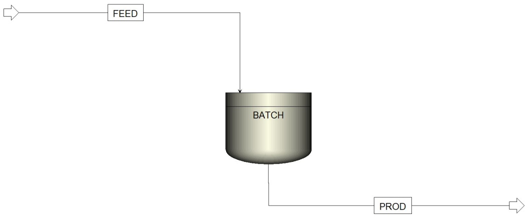
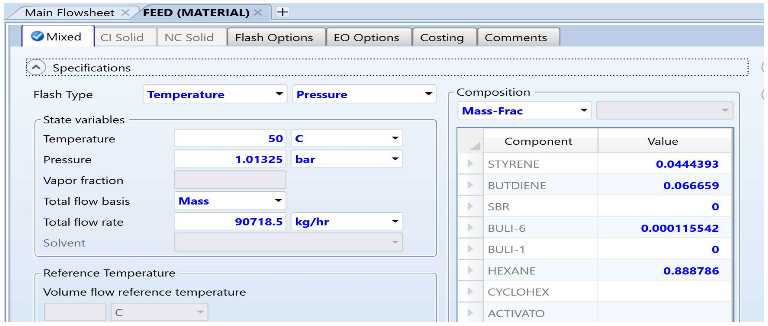


Figure 6.64 A batch reactor for producing a tapered block copolymer

We use the METCBAR unit system, and Figure 6.65 specifies our feed.



Flash Type: Temperature, Pressure

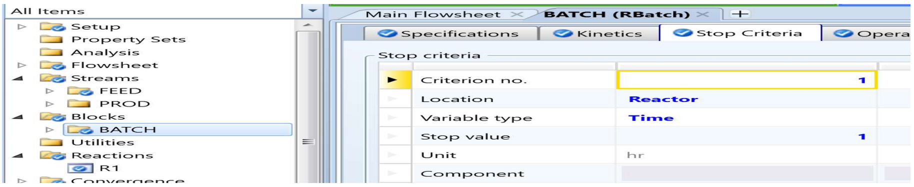
State variables
Temperature: 50 C
Pressure: 1.01325 bar
Vapor fraction:
Total flow basis: Mass
Total flow rate: 90718.5 kg/hr
Solvent:

Composition: Mass-Frac

Component	Value
STYRENE	0.0444393
BUTDIENE	0.066659
SBR	0
BULI-6	0.000115542
BULI-1	0
HEXANE	0.888786
CYCLOHEX	
ACTIVATO	

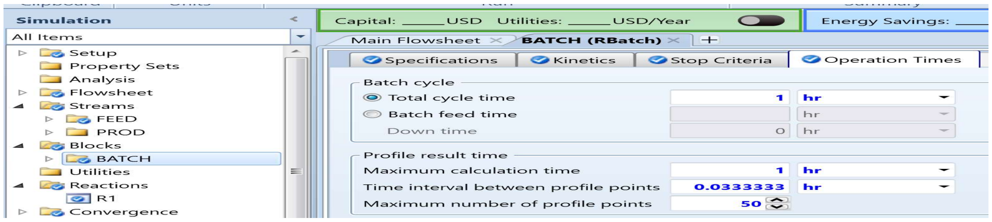
Figure 6.65 Feed specifications.

We specify the reactor at constant temperature of 50°C with the valid phases being the reactor phase with liquid only. We fix the reactor pressure at 0 bar (meaning no pressure drop). There is 0 kg of catalyst loading. We set the reaction set as R1 (see Figures 6.61 and 6.62). For the batch reactor operation, our specifications of stop criteria and operating times appear in Figures 6.66 and 6.67.



Stop criteria
Criterion no.: 1
Location: Reactor
Variable type: Time
Stop value: 1
Unit: hr
Component:

Figure 6.66 Stop criteria for batch reactor operation.



Batch cycle

● Total cycle time: 1 hr

○ Batch feed time: hr

Down time: 0 hr

Profile result time

Maximum calculation time: 1 hr

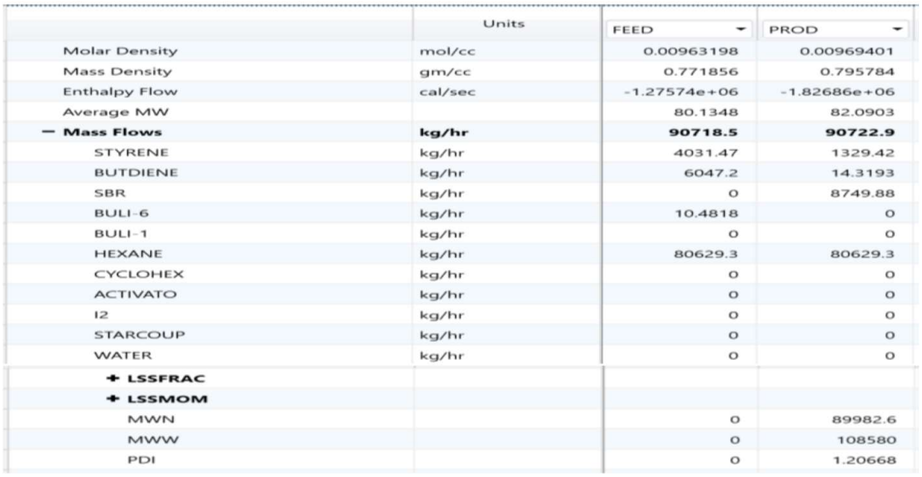
Time interval between profile points: 0.0333333 hr

Maximum number of profile points: 50

Figure 6.67 Operation times for the batch reactor.

(2) Simulation Results:

Figure 6.68 shows the calculated mass balance and polymer molecular weights based on the kinetics polymerization of Figures 6.61 to 6.63.



	Units	FEED	PROD
Molar Density	mol/cc	0.00963198	0.00969401
Mass Density	gm/cc	0.771856	0.795784
Enthalpy Flow	cal/sec	-1.27574e+06	-1.82686e+06
Average MW		80.1348	82.0903
− Mass Flows	**kg/hr**	**90718.5**	**90722.9**
STYRENE	kg/hr	4031.47	1329.42
BUTDIENE	kg/hr	6047.2	14.3193
SBR	kg/hr	0	8749.88
BULI-6	kg/hr	10.4818	0
BULI-1	kg/hr	0	0
HEXANE	kg/hr	80629.3	80629.3
CYCLOHEX	kg/hr	0	0
ACTIVATO	kg/hr	0	0
I2	kg/hr	0	0
STARCOUP	kg/hr	0	0
WATER	kg/hr	0	0
+ LSSFRAC			
+ LSSMOM			
MWN		0	89982.6
MWW		0	108580
PDI		0	1.20668

Figure 6.68 Simualted results of tapered SBR block polymer using a batch reactor.

We see that 86.8% of monomers, styrene and butadiene, is converted to SBR polymer with a MWN of 89983, a MWW of 108580, and a PDI of 1.2066. In the next example, we will use a semi-batch reactor with sequential additions of monomers to produce a tri-block copolymer. We will also fine-tune the reaction kinetics to match plant data.

Figure 6.69 shows the composition profiles of styrene, butadiene, and SBR block polymer versus the batch reaction time.

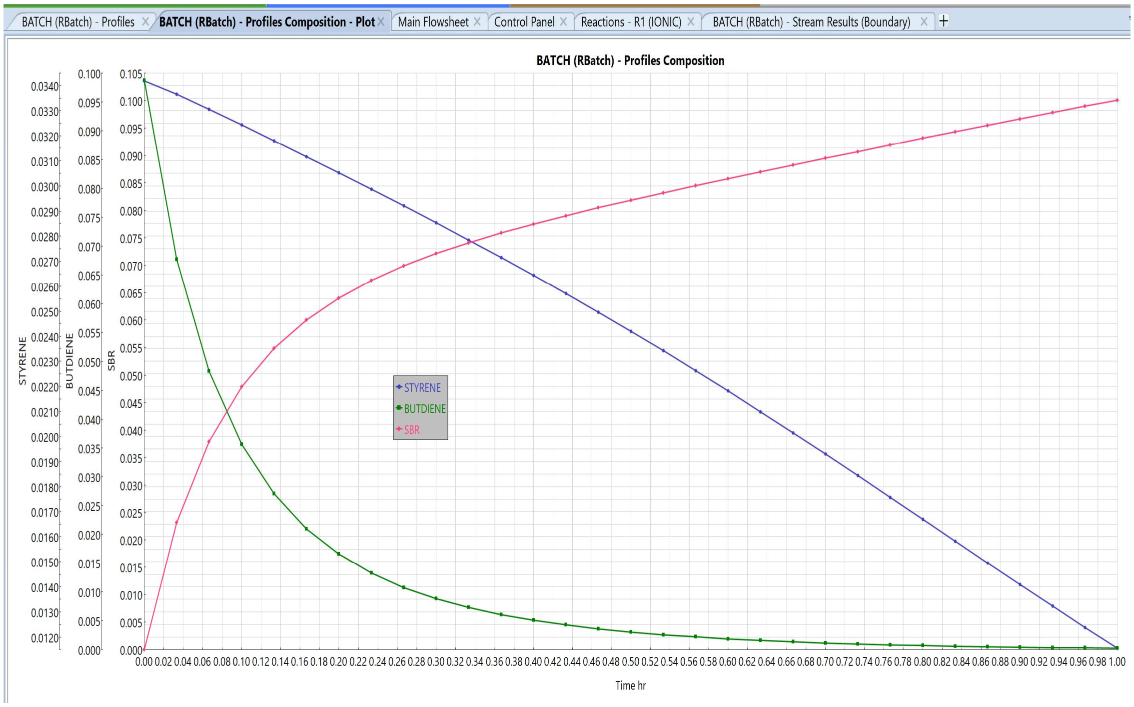


Figure 6.69 Composition profiles of styrene, butadiene, and SBR block polymer vs batch reaction time

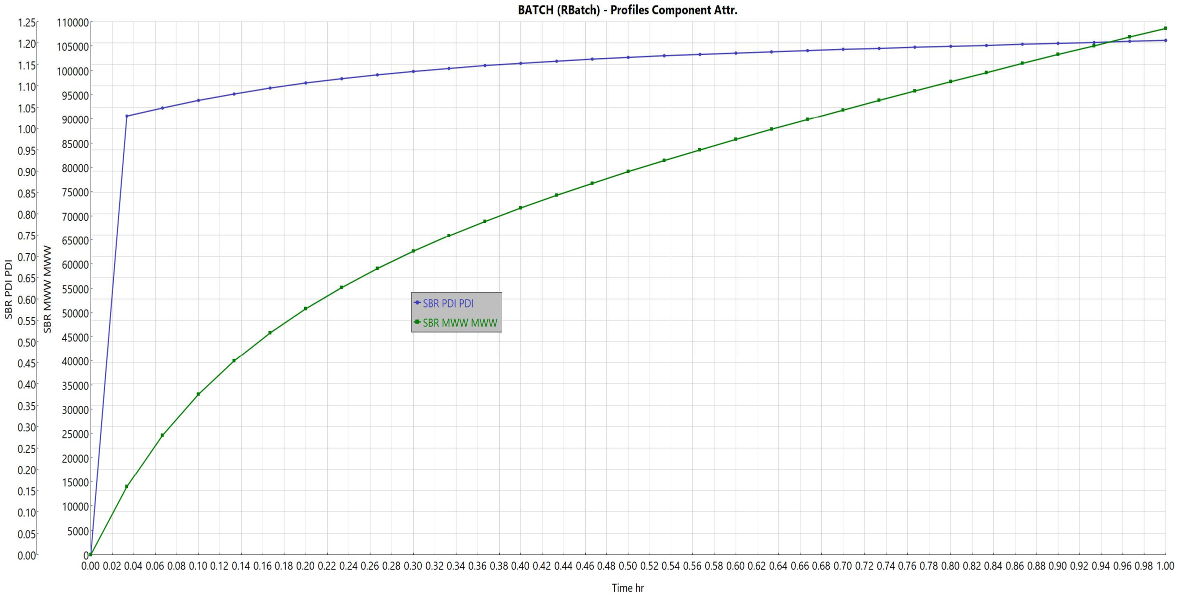


Figure 6.70 MWW and PDI of the SBR block polymer as a function of the batch reaction time.

6.2.5.9 Semi-Batch Reactor for Producing a Tri-Block SBS Copolymer by an Industrial Batch Sequence Recipe

(1) Reactor Flowsheet, and Feed and Operating Conditions

Figure 6.71 shows the simple semi-batch reactor flowsheet for producing a tri-block SBS copolymer. We save the simulation file as ***WS6.2_SBC Semi-Batch.bkp***.

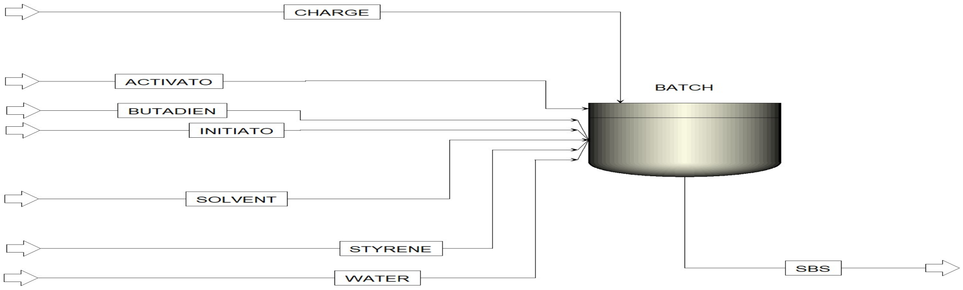
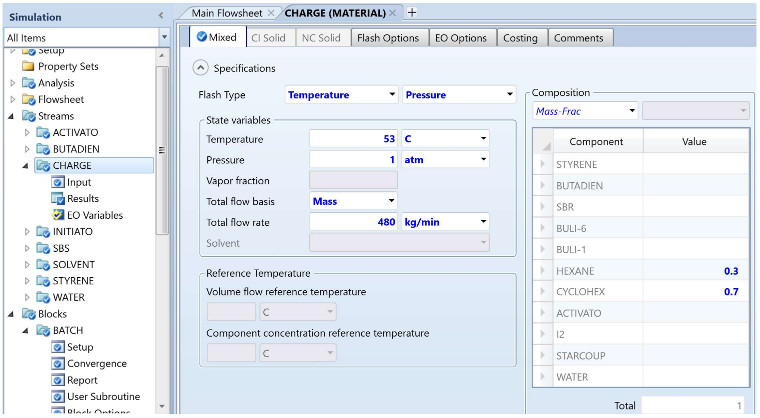


Figure 6.71 A semi-batch reactor for producing a triblock SBS copolymer

Figure 6.72 specifies the solvent mixture as our initial charge to the semi-batch reactor.



Flash Type: Temperature, Pressure

State variables

Temperature: 53 C

Pressure: 1 atm

Vapor fraction:

Total flow basis: Mass

Total flow rate: 480 kg/min

Solvent:

Reference Temperature

Volume flow reference temperature: C

Component concentration reference temperature: C

Composition: Mass-Frac

Component	Value
STYRENE	
BUTADIEN	
SBR	
BULI-6	
BULI-1	
HEXANE	0.3
CYCLOHEX	0.7
ACTIVATO	
I2	
STARCOUP	
WATER	
Total	1

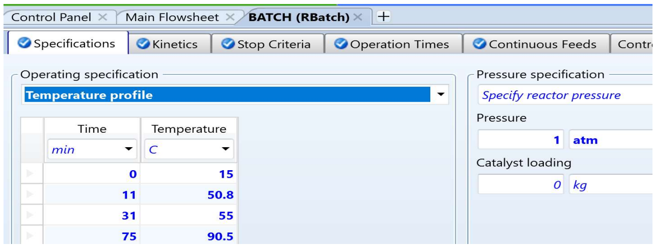
Figure 6.72 Specification of the initial charge stream, CHARGE.

Table 6.9 shows the specifications of continuous feeds.

Table 6.9 Specifications of continuous feeds.

Stream	Temp, °C	Pressure, atm	Mass flow, kg/min	Composition, mass fraction
Styrene	10	1	12.667	styrene = 0.99998, water = 2E-5
Butadien	10	1	19	Butadiene = 0.999988, water =1.2E-5
Initiato	15	1	2.06	buli-6 = 1
Solvent	53	1	0.667	hexane = 0.3, cyclohex = 0.7
Activato	25	1	1.2	activato= 0.99997, water = 3E-5
Water	25	1	0.38	Water = 1

Figure 6.73a shows the specifications of the semi-batch reactor. Remember to specify the valid phases as reactor phase, liquid-only. Specify the reaction set R-1 (Figure 6.62).



Operating specification: Temperature profile

Time	Temperature
min	C
0	15
11	50.8
31	55
75	90.5

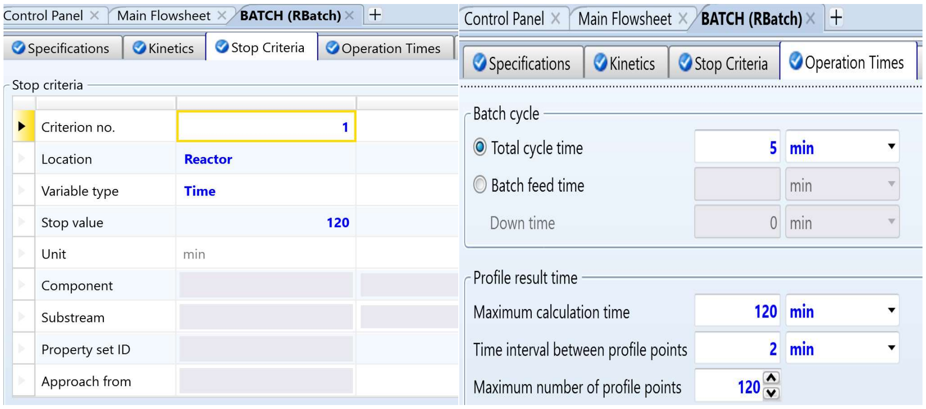
Pressure specification: Specify reactor pressure

Pressure: 1 atm

Catalyst loading: 0 kg

Figure 6.73a Specifications of the semi-batch reactor.

Figure 6.73b illustrates the stopping criterion and operation times for the batch reactor simulation.



Stop criteria

Criterion no.	1
Location	Reactor
Variable type	Time
Stop value	120
Unit	min
Component	
Substream	
Property set ID	
Approach from	

Batch cycle

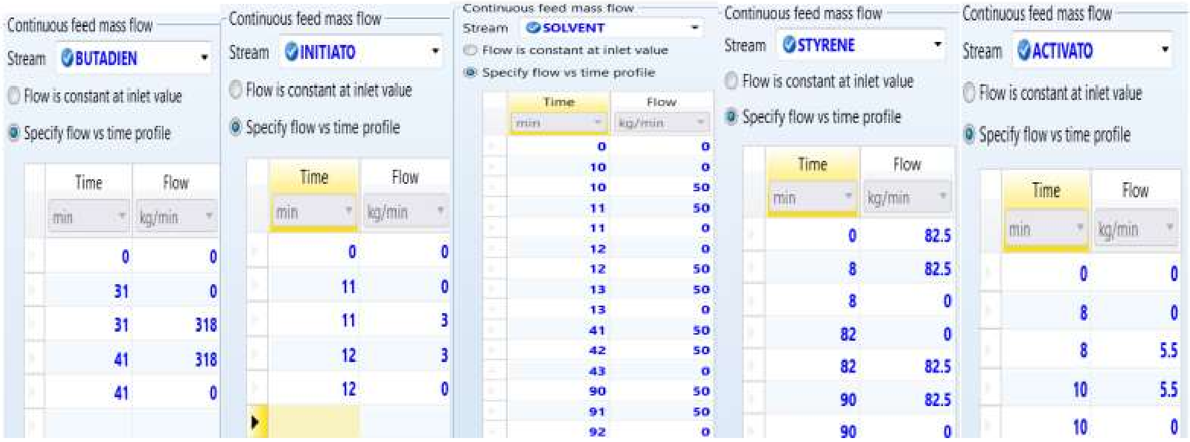
● Total cycle time: 5 min
○ Batch feed time: min
Down time: 0 min

Profile result time

Maximum calculation time: 120 min
Time interval between profile points: 2 min
Maximum number of profile points: 120

Figure 6.73b Specification of stopping criterion and operation times of batch reactor simulation.

Figure 6.73c shows the sequential addition of continuous feeds as a function of operation times.



Continuous feed mass flow
Stream: BUTADIEN
○ Flow is constant at inlet value
● Specify flow vs time profile

Time (min)	Flow (kg/min)
0	0
31	0
31	318
41	318
41	0

Continuous feed mass flow
Stream: INITIATO
○ Flow is constant at inlet value
● Specify flow vs time profile

Time (min)	Flow (kg/min)
0	0
11	0
11	3
12	3
12	0

Continuous feed mass flow
Stream: SOLVENT
○ Flow is constant at inlet value
● Specify flow vs time profile

Time (min)	Flow (kg/min)
0	0
10	0
10	50
11	50
11	0
12	0
12	50
13	50
13	0
41	50
42	50
43	0
90	50
91	50
92	0

Continuous feed mass flow
Stream: STYRENE
○ Flow is constant at inlet value
● Specify flow vs time profile

Time (min)	Flow (kg/min)
0	82.5
8	82.5
8	0
82	0
82	82.5
90	82.5
90	0

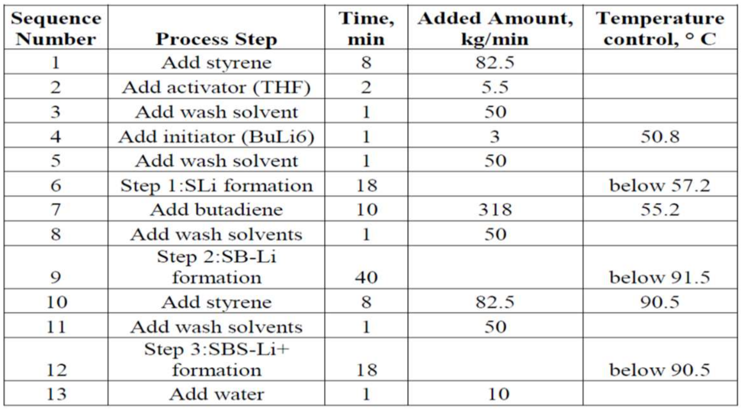
Continuous feed mass flow
Stream: ACTIVATO
○ Flow is constant at inlet value
● Specify flow vs time profile

Time (min)	Flow (kg/min)
0	0
8	0
8	5.5
10	5.5
10	0

Figure 6.73c Sequential addition of continuous feeds as a function of operation times.

Table 6.10 shows an industrial batch sequence recipe for this workshop. Because of the sequential addition of continuous feeds, the component mass flows of essential feed components as illustrated in Figure 6.73c represent the actual mass flows to the semi-batch reactor at different times. These values take precedence over the mass flow rate entered in the stream input form (Figure 6.72) or specified in Table 6.10.

Table 6.10 Batch sequence recipe



Sequence Number	Process Step	Time, min	Added Amount, kg/min	Temperature control, ° C
1	Add styrene	8	82.5	
2	Add activator (THF)	2	5.5	
3	Add wash solvent	1	50	
4	Add initiator (BuLi6)	1	3	50.8
5	Add wash solvent	1	50	
6	Step 1:SLi formation	18		below 57.2
7	Add butadiene	10	318	55.2
8	Add wash solvents	1	50	
9	Step 2:SB-Li formation	40		below 91.5
10	Add styrene	8	82.5	90.5
11	Add wash solvents	1	50	
12	Step 3:SBS-Li+ formation	18		below 90.5
13	Add water	1	10	

(2) Simulation Results

We wish to fine-tune kinetic parameters of the model to match the average plant data of **SBS mass production of 910 kg/min, MWN of 104310, and MWW of 108800.** Figure 6.74 illustrates our methodology for kinetic parameter estimation for the anionic polymerization of styrene and butadiene to produce SBS block copolymer.

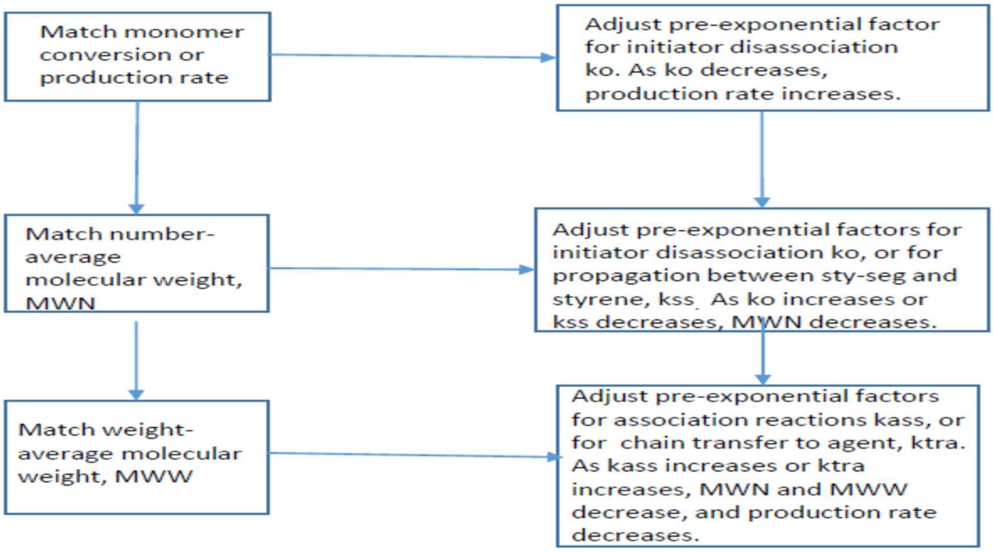
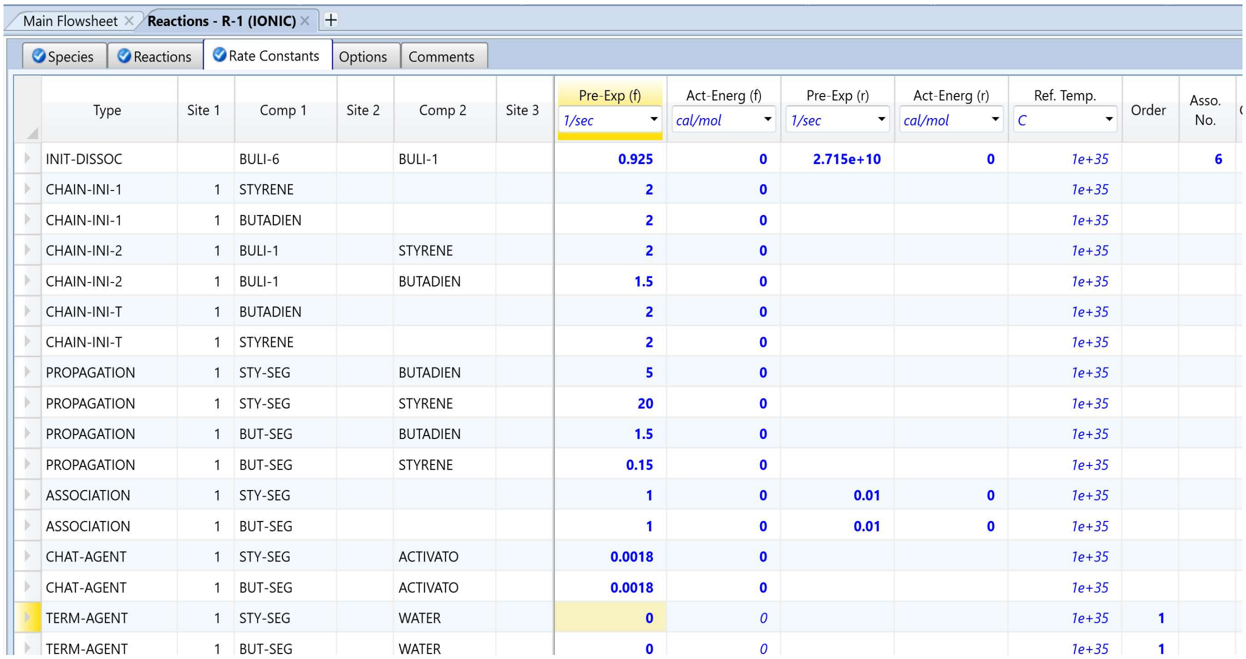


Figure 6.74 Methodology for kinetic parameter estimation for anionic polymerization of styrene and butadiene to produce SBS block copolymer.

Following this methodology to fine-tune the kinetic parameters, we obtain the simulation results along with their comparison with plant data in Table 6.11. Figure 6.75 shows the resulting set of kinetic parameters. We note that fine-tuning the kinetic parameters to match both MWW and MWN exactly is a challenging task. While we can easily find the set of kinetic parameters to match either MWN or MWN exactly, it is difficult to identify the set of kinetic parameters to match both MWW and MWN exactly.

Table 6.11 Comparison of simulation results with plant data

Simulation target	**Plant data**	**Simulation result**	**% Error**
MWW (g/mol)	108800	116461	6.96%
MWN (g/mol)	104310	99507	4.60%
SBS production rate, kg/min	910	900.95	0.99%



Type	Site 1	Comp 1	Site 2	Comp 2	Site 3	Pre-Exp (f) 1/sec	Act-Energ (f) cal/mol	Pre-Exp (r) 1/sec	Act-Energ (r) cal/mol	Ref. Temp. C	Order	Asso. No.
INIT-DISSOC		BULI-6		BULI-1		0.925	0	2.715e+10	0	1e+35		6
CHAIN-INI-1	1	STYRENE				2	0			1e+35		
CHAIN-INI-1	1	BUTADIEN				2	0			1e+35		
CHAIN-INI-2	1	BULI-1		STYRENE		2	0			1e+35		
CHAIN-INI-2	1	BULI-1		BUTADIEN		1.5	0			1e+35		
CHAIN-INI-T	1	BUTADIEN				2	0			1e+35		
CHAIN-INI-T	1	STYRENE				2	0			1e+35		
PROPAGATION	1	STY-SEG		BUTADIEN		5	0			1e+35		
PROPAGATION	1	STY-SEG		STYRENE		20	0			1e+35		
PROPAGATION	1	BUT-SEG		BUTADIEN		1.5	0			1e+35		
PROPAGATION	1	BUT-SEG		STYRENE		0.15	0			1e+35		
ASSOCIATION	1	STY-SEG				1	0	0.01	0	1e+35		
ASSOCIATION	1	BUT-SEG				1	0	0.01	0	1e+35		
CHAT-AGENT	1	STY-SEG		ACTIVATO		0.0018	0			1e+35		
CHAT-AGENT	1	BUT-SEG		ACTIVATO		0.0018	0			1e+35		
TERM-AGENT	1	STY-SEG		WATER		0	0			1e+35	1	
TERM-AGENT	1	BUT-SEG		WATER		0	0			1e+35	1	

Figure 6.75 Final kinetic parameters for the tri-block SBS copolymer

By plotting selected items from the RBATCH profile results, we see in Figures 6.76a to 6.76e: (1) feed mass flow rate profiles of styrene and butadiene; (2) MWW and MWN of the resulting copolymer; (3) variation of mole composition of monomers and SBS copolymer within the reactor as a function of reaction times; and (4) accumulated mass of monomers and SBS copolymer within the reactor as a function of reaction times. We save the completed simulation as ***WS6.2 SBC_Semi-Batch_Good.bkp.***

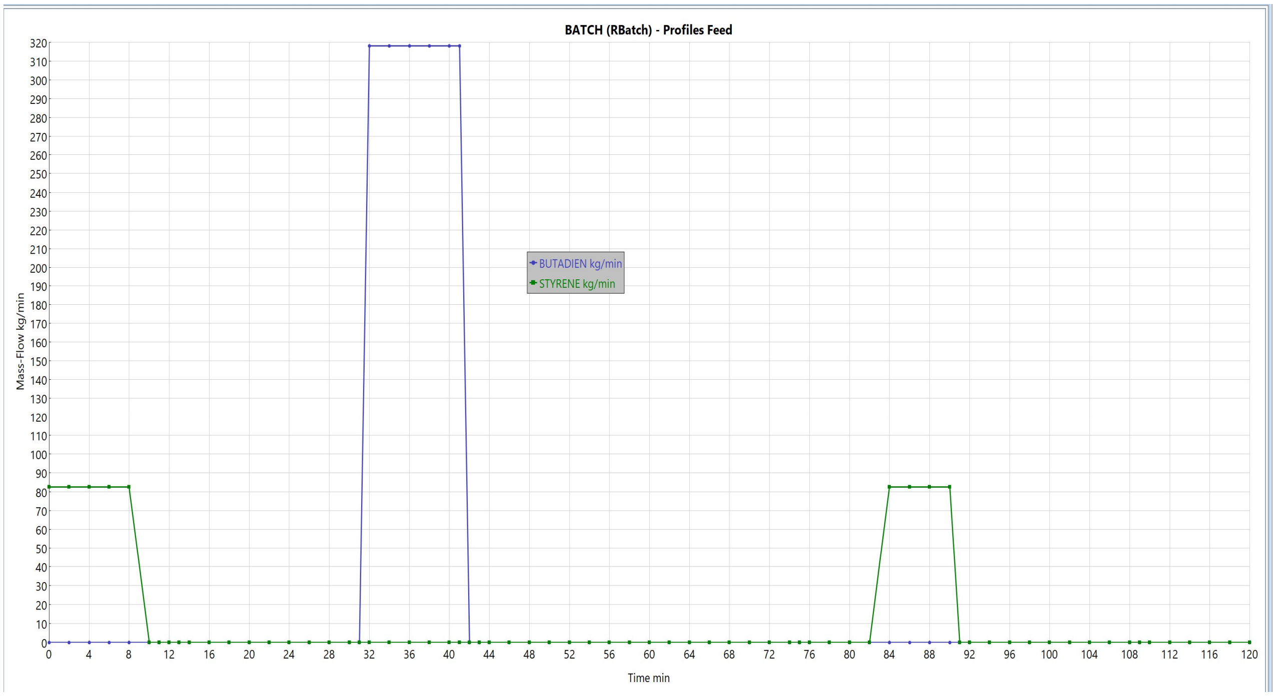


Figure 6.76a   Feed mass flow rate profiles for styrene and butadiene.

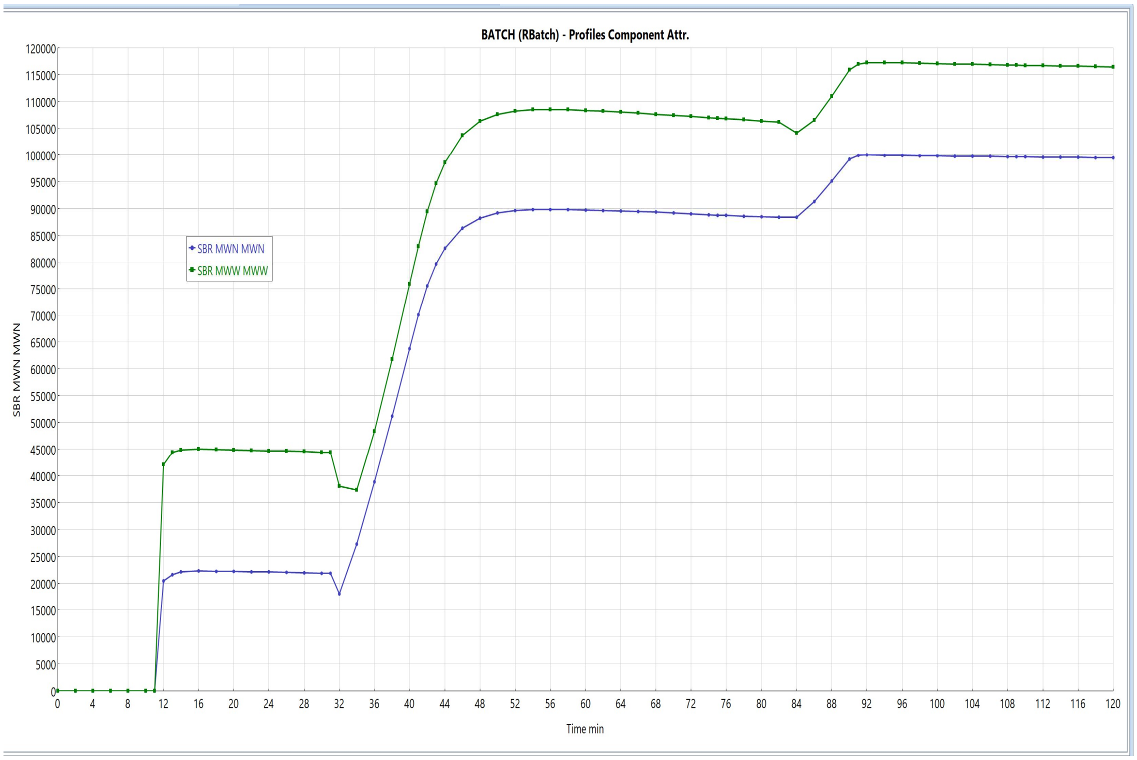


Figure 6.76b   MWW and MWN of tri-block SBS copolymer

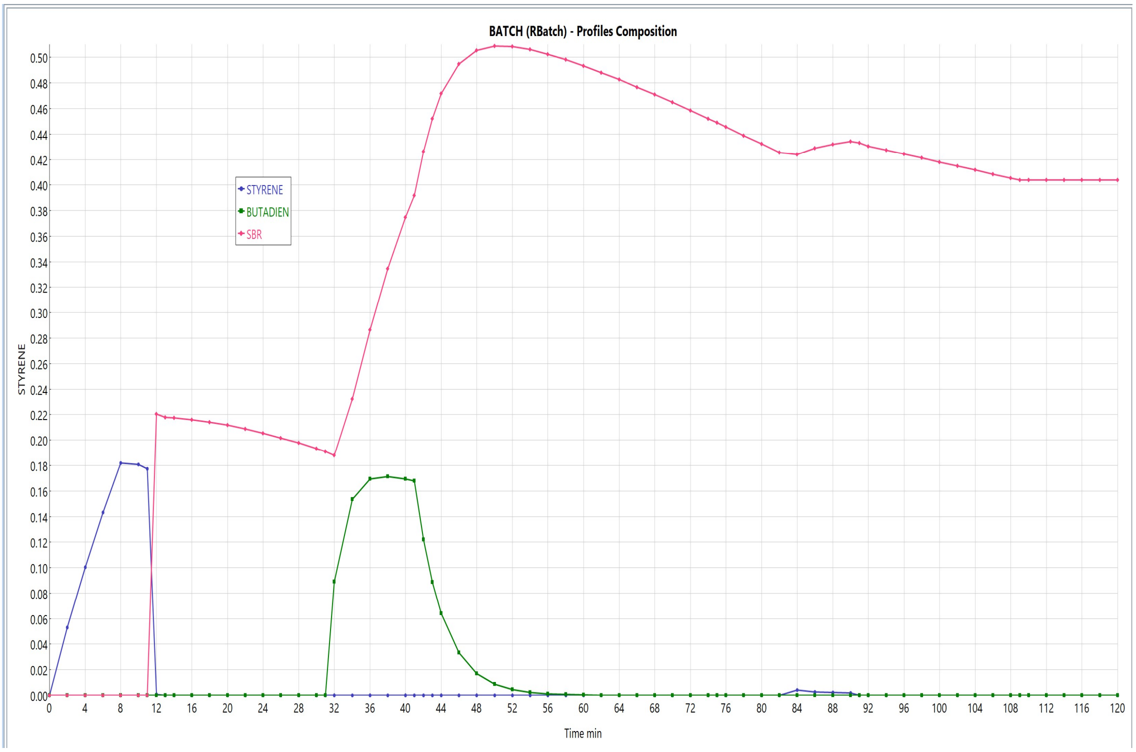


Figure 6.76c Variation of mole compositions of monomers and SBS copolymer within the reactor as a function of reaction times

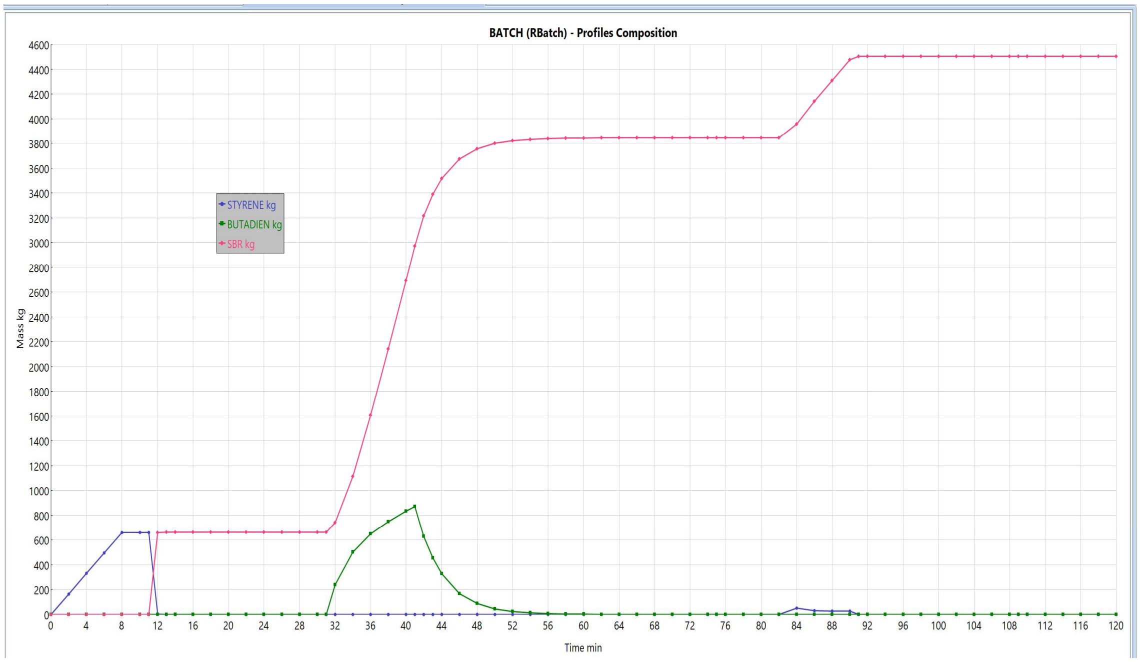


Figure 6.76d. Accumulated mass of monomers and SBS copolymer within the reactor as a function of reaction times.

(3) Model Application:

What happens if we change the amount of initiator addition in Figure 6.73c during min 11 to 12 of te bach? Table 6.12 compares the results.

Table 6.12 Effect of the amount of initiator BuLi-6 addition on simulation results

Initiator BuLi-6 addition from 11 to 12 min, kg	3 kg	6 kg	9 kg
MWW (g/mol)	116461	61977	43667
MWN (g/mol)	99507	49671	34460
SBS copolymer production, kg/min	900.95	901.818	902.795

Increasing the initiator addition significantly decreases the resulting molecular weights of the SBS copolymer, but it only slightly affects the mass flow rate of copolymer produced.

6.2.5.10 Semi-Batch Reactor for Producing a Tri-Block SBS Copolymer by a Literature Batch Sequence Recipe [17,18,24]

Sirohi and Ravindranath [18] simulated the batch sequence recipe of Hsieh [17,24] to produce a tri-block SBS copolymer consisting of the following batch sequence recipe: 1) charge the batch reactor with styrene and solvent; 2) add a BuLi initiator and allow styrene to polymerize for an hour; 3) add butadiene and let it also polymerize for an hour; 4) add *a coupling agent* (COUPLING), such as iodine, and allow 40 minutes for coupling; and 5) add *a terminating agent or a short stopper (S-STOP), such as* water, to kill the remaining initiator and live polymer chains. We simulate this semi-batch reactor operation below.

(1) Component List, Reactor Flowsheet, and Feed and Operating Conditions

We open file, ***WS6.2 SBC_Semi-Batch_Good.bkp,*** and save it as a new name, ***WS6.2 SBC_Semi-Batch_Hsieh.bkp.*** We slightly modify the flowsheet as Figure 6.77.

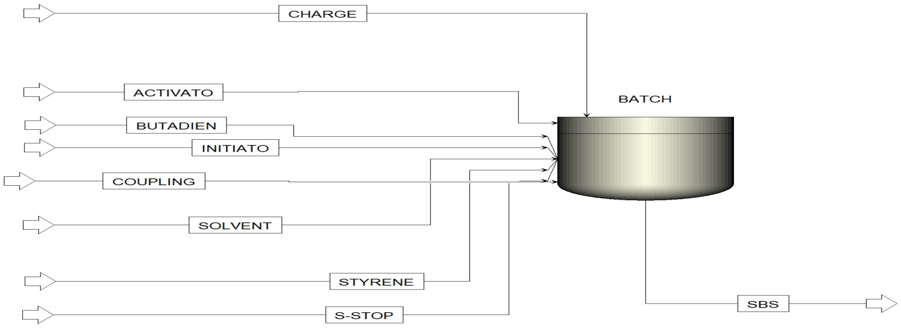
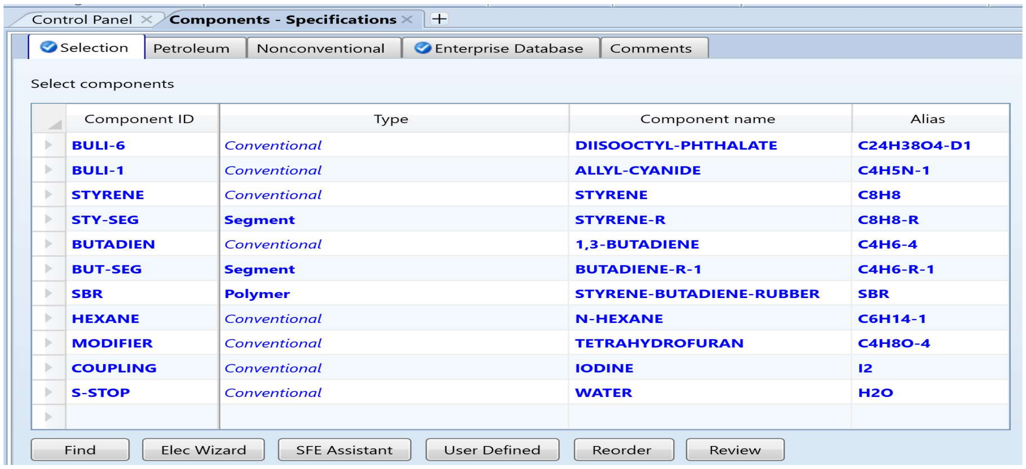


Figure 6.77 A modified flowsheet with the addition of feed streams, COUPLING and S-STOP.

Figure 6.78 shows the modified component list. Note the coupling agent (COUPLING), iodine, and the terminating agent or short stopper (S-STOP), water. We use a unit system of METCATM, with temperature at °C and pressure at atm.



Select components

Component ID	Type	Component name	Alias
BULI-6	Conventional	DIISOOCTYL-PHTHALATE	C24H38O4-D1
BULI-1	Conventional	ALLYL-CYANIDE	C4H5N-1
STYRENE	Conventional	STYRENE	C8H8
STY-SEG	Segment	STYRENE-R	C8H8-R
BUTADIEN	Conventional	1,3-BUTADIENE	C4H6-4
BUT-SEG	Segment	BUTADIENE-R-1	C4H6-R-1
SBR	Polymer	STYRENE-BUTADIENE-RUBBER	SBR
HEXANE	Conventional	N-HEXANE	C6H14-1
MODIFIER	Conventional	TETRAHYDROFURAN	C4H8O-4
COUPLING	Conventional	IODINE	I2
S-STOP	Conventional	WATER	H2O

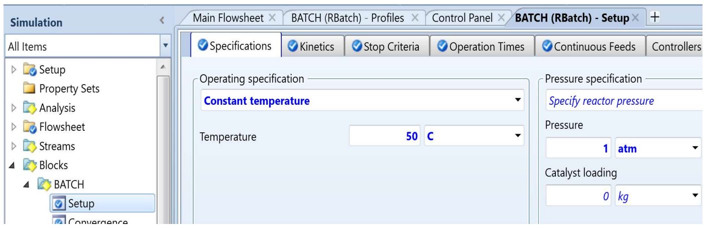
Figure 6.78 Modified component list for ***WS6.2 SBC_Semi-Batch_Hsieh***

Table 6.13 specifies our initial charge, and continuous feeds to the batch reactor.

Table 6.13 Stream specifications

Stream	Temp, °C	Pressure, atm	Mass flow, kg/hr	Composition, mass fraction
Charge	50	5	25,000	styrene= 0.04762, solvent =0.95238
Styrene	50	5	760.02	styrene = 0.99998, s-stop = 2E-5
Butadiene	50	5	1136	butadiene= 0.995, s-stop = 0.005
Initiato	50	5	13.75	buLi-6 =1
Solvent	50	5	40.02	hexane = 1
Coupling	50	5	22.264	coupling = 1
Activato	50	5	72	modifier = 0.99997, s-stop = 3E-5
S-Stop	50	5	500	s-stop = 1

Figures 6.79a to 6.79c specify the semi-batch reactor. The valid reactor phase is the liquid phase. The reaction set is R-1 displayed in Figures 6.80a and 6.80b.



Operating specification: Constant temperature

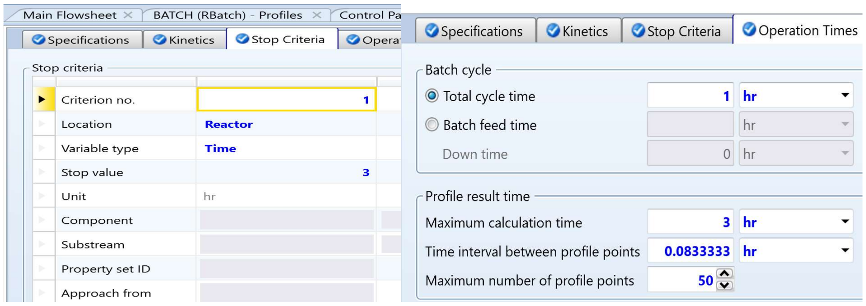
Temperature: 50 C

Pressure specification: Specify reactor pressure

Pressure: 1 atm

Catalyst loading: 0 kg

Figure 6.79a Specifications of the semi-batch reactor



Stop criteria

Criterion no.	1
Location	Reactor
Variable type	Time
Stop value	3
Unit	hr
Component	
Substream	
Property set ID	
Approach from	

Batch cycle

● Total cycle time: 1 hr

○ Batch feed time: hr

Down time: 0 hr

Profile result time

Maximum calculation time: 3 hr

Time interval between profile points: 0.0833333 hr

Maximum number of profile points: 50

Figure 6.79b Specifications of stop criterion and operational times

Stream: BUTADIEN

Time (hr)	Flow (kg/hr)
0	0
1	0
1	11360
1.1	11360
1.1	0

Stream: INITIATO

Time (hr)	Flow (kg/hr)
0	230
0.03	230
0.03	0

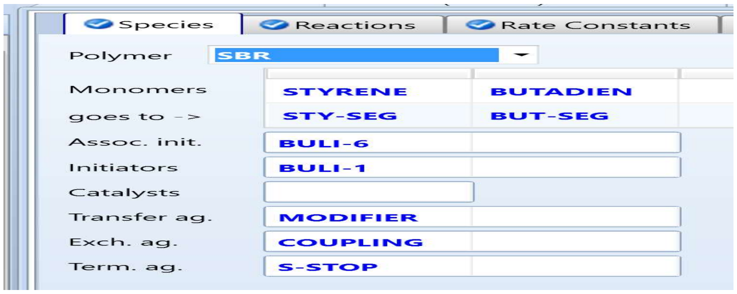
Stream: S-STOP

Time (hr)	Flow (kg/hr)
0	0
2.65	0
2.65	5
2.68	5
2.68	0

Stream: COUPLING

Time (hr)	Flow (kg/hr)
0	0
2	0
2	111.3
2.1	111.3
2.1	0

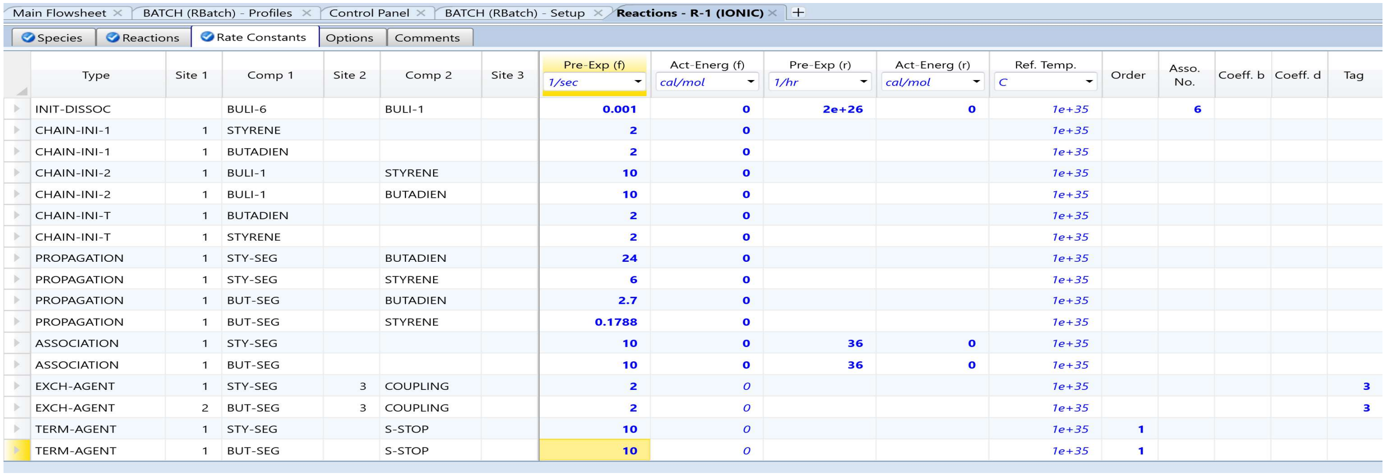
Figure 6.79c Sequential addition of continuous feeds as a function of operational time.



Polymer: SBR

Monomers	STYRENE	BUTADIEN
goes to ->	STY-SEG	BUT-SEG
Assoc. init.	BULI-6	
Initiators	BULI-1	
Catalysts		
Transfer ag.	MODIFIER	
Exch. ag.	COUPLING	
Term. ag.	S-STOP	

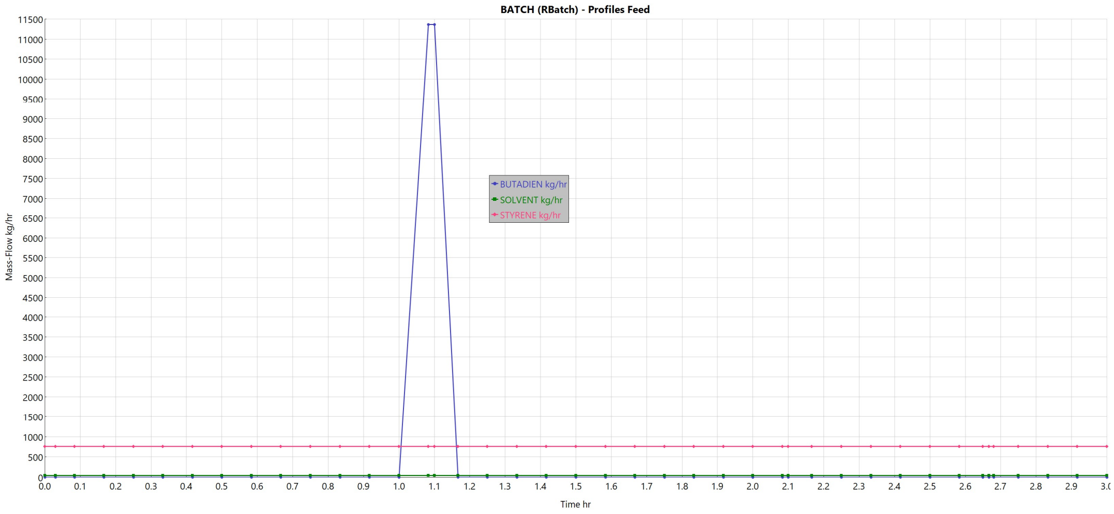
Figure 6.80a. Specifications of Species for the reaction set



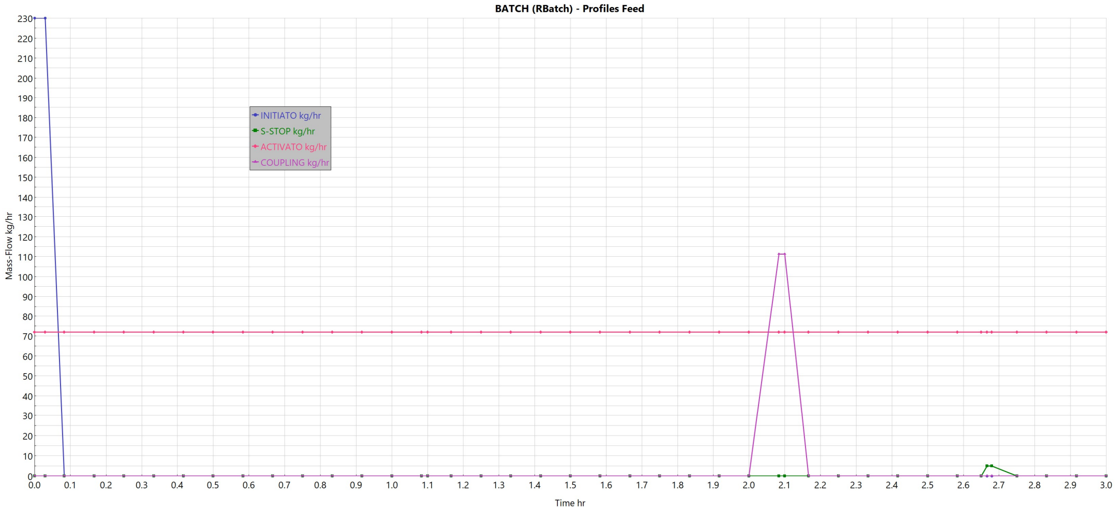
Type	Site 1	Comp 1	Site 2	Comp 2	Site 3	Pre-Exp (f) 1/sec	Act-Energ (f) cal/mol	Pre-Exp (r) 1/hr	Act-Energ (r) cal/mol	Ref. Temp. C	Order	Asso. No.	Coeff. b	Coeff. d	Tag
INIT-DISSOC		BULI-6		BULI-1		0.001	0	2e+26	0	1e+35		6			
CHAIN-INI-1	1	STYRENE				2	0			1e+35					
CHAIN-INI-1	1	BUTADIEN				2	0			1e+35					
CHAIN-INI-2	1	BULI-1		STYRENE		10	0			1e+35					
CHAIN-INI-2	1	BULI-1		BUTADIEN		10	0			1e+35					
CHAIN-INI-T	1	BUTADIEN				2	0			1e+35					
CHAIN-INI-T	1	STYRENE				2	0			1e+35					
PROPAGATION	1	STY-SEG		BUTADIEN		24	0			1e+35					
PROPAGATION	1	STY-SEG		STYRENE		6	0			1e+35					
PROPAGATION	1	BUT-SEG		BUTADIEN		2.7	0			1e+35					
PROPAGATION	1	BUT-SEG		STYRENE		0.1788	0			1e+35					
ASSOCIATION	1	STY-SEG				10	0	36	0	1e+35					
ASSOCIATION	1	BUT-SEG				10	0	36	0	1e+35					
EXCH-AGENT	1	STY-SEG	3	COUPLING		2	0			1e+35					3
EXCH-AGENT	2	BUT-SEG	3	COUPLING		2	0			1e+35					3
TERM-AGENT	1	STY-SEG		S-STOP		10	0			1e+35	1				
TERM-AGENT	1	BUT-SEG		S-STOP		10	0			1e+35	1				

Figure 6.80b. Specifications of reaction rate constants

After running the simulation, we can plot the time-dependent profiles of feeds and SBS copolymer product by plotting the "profiles" section of the semi-batch reactor, BATCH. Figures 6.81a and 6.81b illustrate the profiles of the mass flow rates of feed components.



Figures 6.81a Profiles of the mass flow rates of feed components.



Figures 6.81b Profiles of the mass flow rates of feed components (continued).

Figure 6.82 shows the accumulated reactor mass varying with time, and Figure 6.83 illustrates the resulting MWN and MWW of the SBS copolymer product.

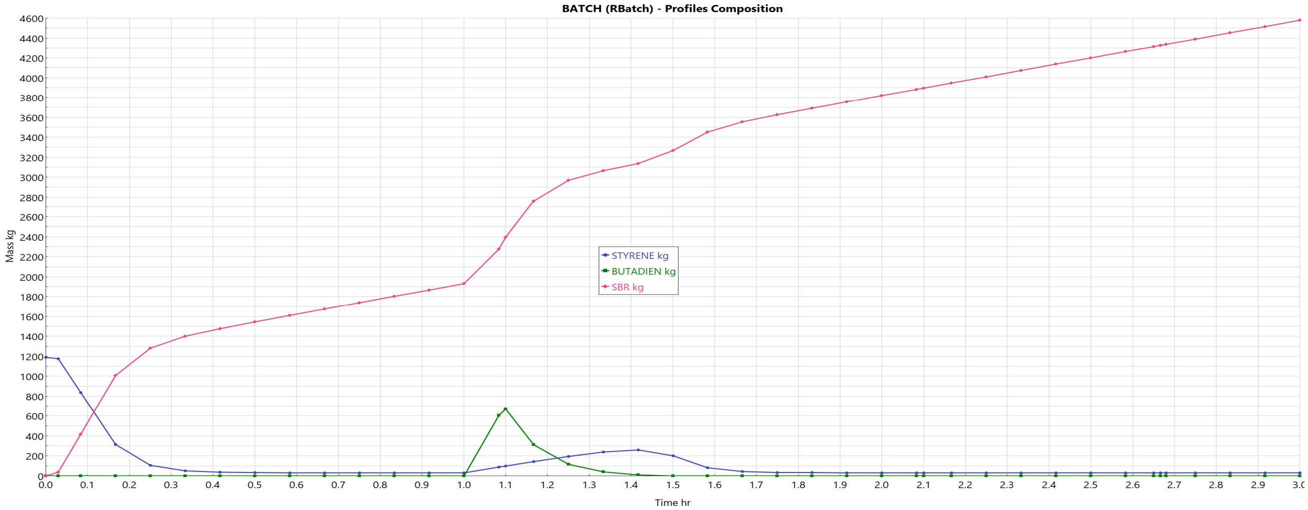


Figure 6.82 The accumulated reactor mass varying with time

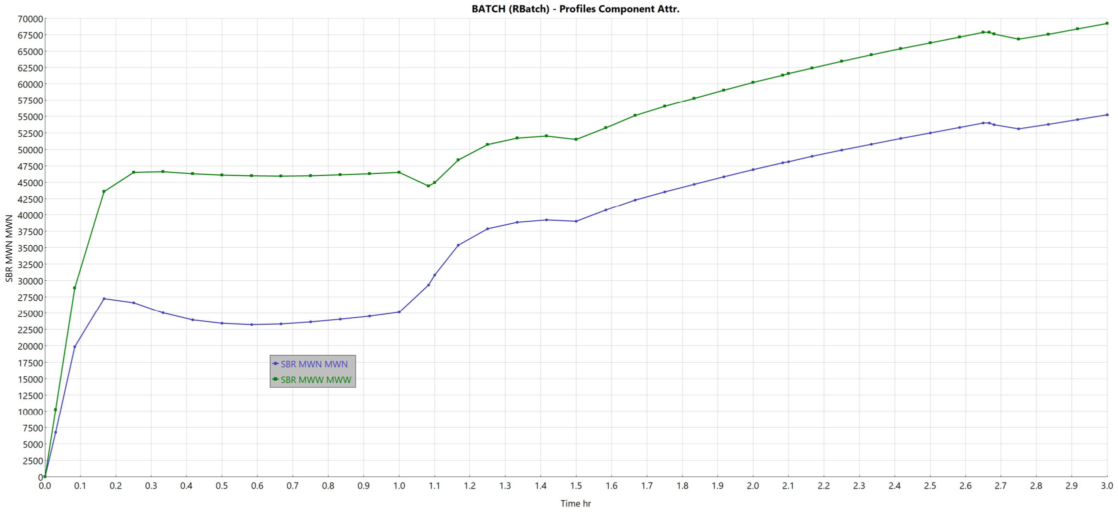


Figure 6.83 The MWN and MWW of the SBS copolymer product. Note the noticeable effects of adding butadiene from 1 to 1.1 hr, and terminating agent (S-Stop) from 2.65 to 2.68 hr. The effect of adding a coupling agent (COUPLING) from 2 to 2.1 hr is not noticeable.

This concludes the current workshop. We save the simulation as ***WS7.2 SBC_Semi-Batch_Hsieh.bkp.***

This chapter is published with Wiley publication in the book *Integrated Process Modeling, Advanced Control and Data Analytics for Optimizing Polyolefin Manufacturing by Liu & Sharma[25-36].*

6.3 Bibliography

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