Getting started with Simulis® Thermodynamics

Use Case 14: Definition and properties calculation of a polymer/solvent mixture

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Introduction

A polymer is not considered as a classic component because:

- **Its properties depend on the length of its chain (represented by the number and the weight average molar mass),**
- **Its properties depend on the considered repeat units (segments),**
- **All properties of classical component are not defined for a polymer (no critical point, no saturation pressure…),**
- **Predictive methods available for property calculations of classical components are not adapted.**

Moreover, high molar mass value of polymers leads to particular behaviors of mixtures containing this type of component. As an example, the vapor phase of this type of mixture at vapor-liquid equilibria will never contain polymer.

Consequently, the treatment of polymer/solvent mixtures requires a specific approach in Simulis Thermodynamics. This document presents in details the different steps to follow in order to perform calculation concerning this type of mixture.

Introduction

The following steps are described in this document:

- Step 1: Add a new polymer component
  (Which data are required? How to supply them?)
- Step 2: Calculation of pure polymer properties
  (Which properties can be calculated? How to calculate them?)
- Step 3: Calculation of polymer/solvent mixture properties
  (Which thermodynamic model to use? How to calculate these properties?)

The example presented in this document is based on the following mixture:
Acetone / poly(Styrene5%molar-Butadiene95%molar) with a weight average molar mass of 300 kg/mol and a number average molar mass of 40 kg/mol

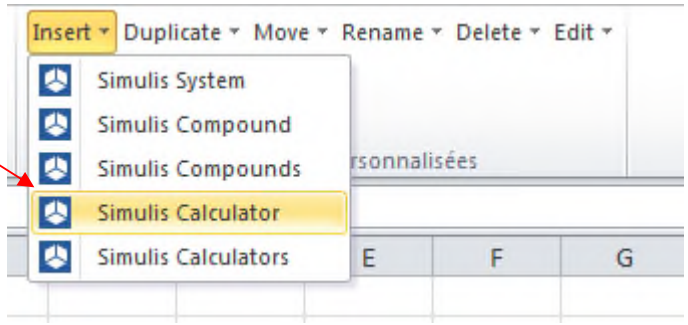
Before studying this chapter, it is recommended to consult:
- « Getting Started with Simulis Thermodynamics: Use Case 1 » that explains the method to select components and configure a thermodynamic profile,
- « Getting Started with Simulis Thermodynamics: Use Case 4 » that explains the method to calculate thermodynamic properties of pure components and mixtures in Simulis Thermodynamics.

Step 1: Add a new polymer component

ACCESS THE THERMODYNAMIC CALCULATOR EDITOR:

- **<u>If you are using Simulis Thermodynamics in Excel</u>:**

Create the calculator object in a spreadsheet



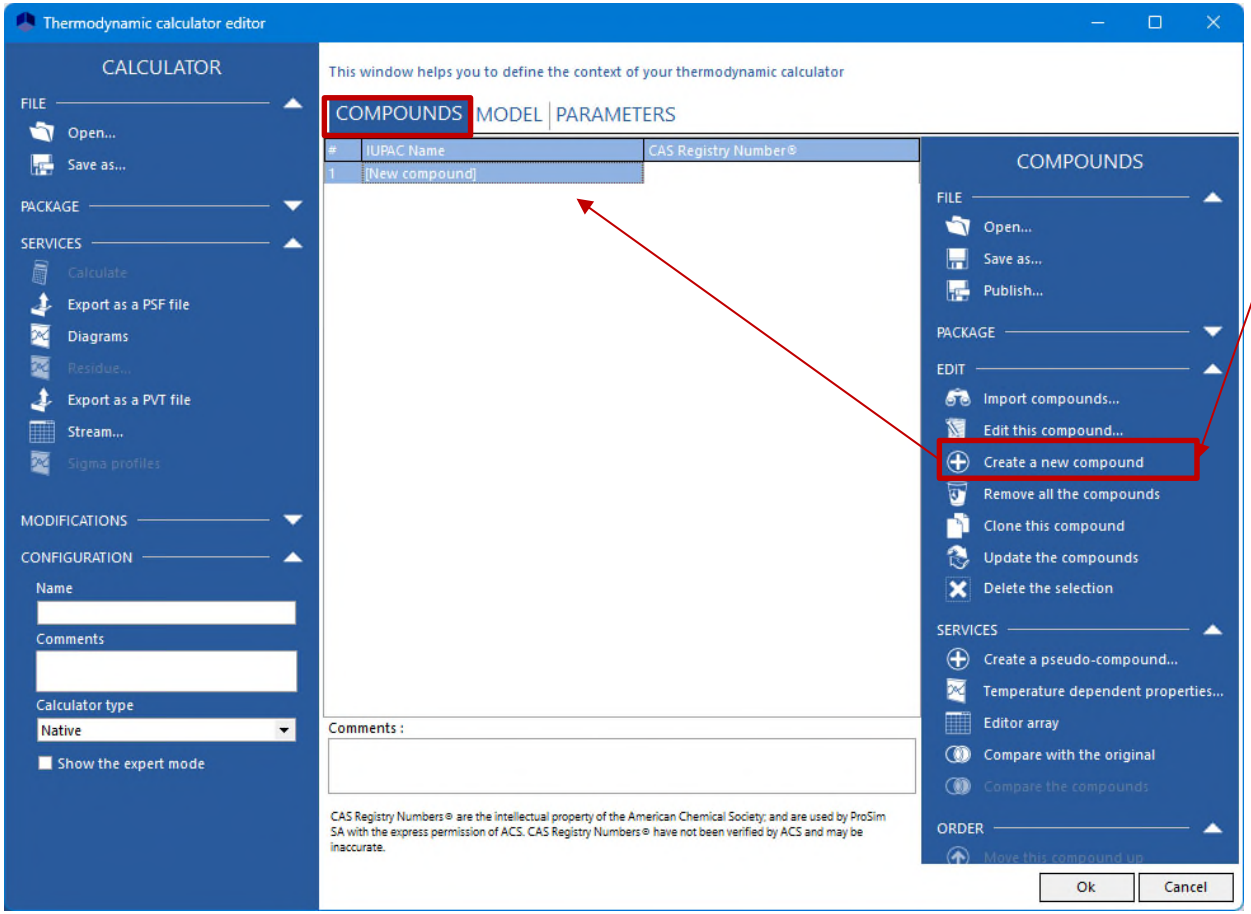
- **<u>If you are using Simulis Thermodynamics within another ProSim environment</u> (ProSimPlus, BatchReactor, BatchColumn etc…):**

Click on the thermodynamic icon to open the calculator editor:

or

Simulis Thermodynamics is a « software component » that you can integrate into different applications: ProSim software, Excel, Matlab, your own software, etc…

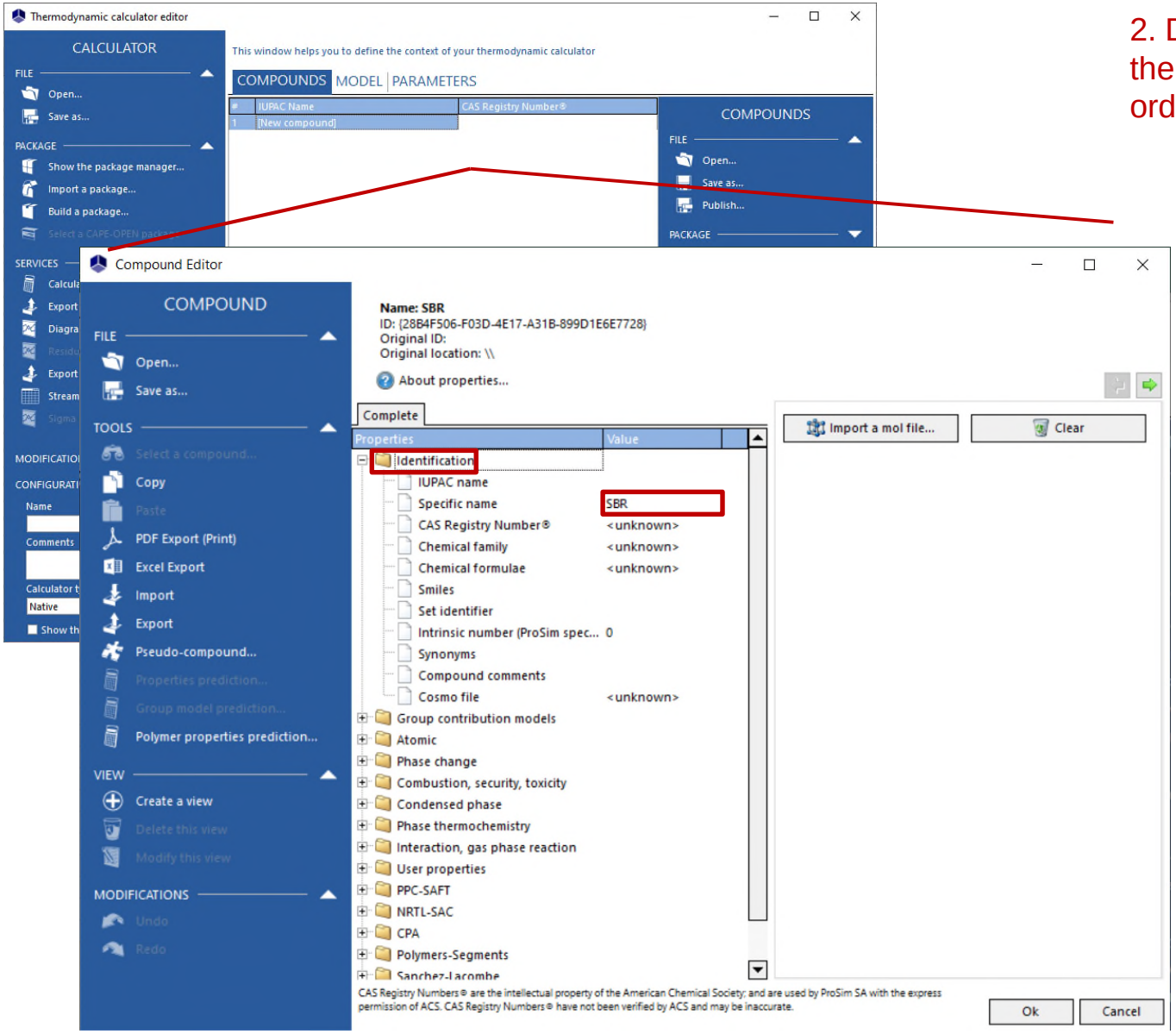
Step 1: Add a new polymer component



1. In « COMPOUNDS » tab: Click on « Create a new compound »

For more details about the creation of a new compound, please consult:
« Getting started with Simulis Thermodynamics, use case 9 »

Step 1: Add a new polymer component



2. Double-click or right-click on the [New compound] added in order to define the polymer

3. In the « identification » folder, give a name to the polymer (« SBR » in this example for Styrene-Butadiene-Rubber)

Step 1: Add a new polymer component

In order to:
- Predict pure polymer properties,
- Perform calculations of thermodynamic or transport properties of mixtures containing polymers,

the following data must be filled in:

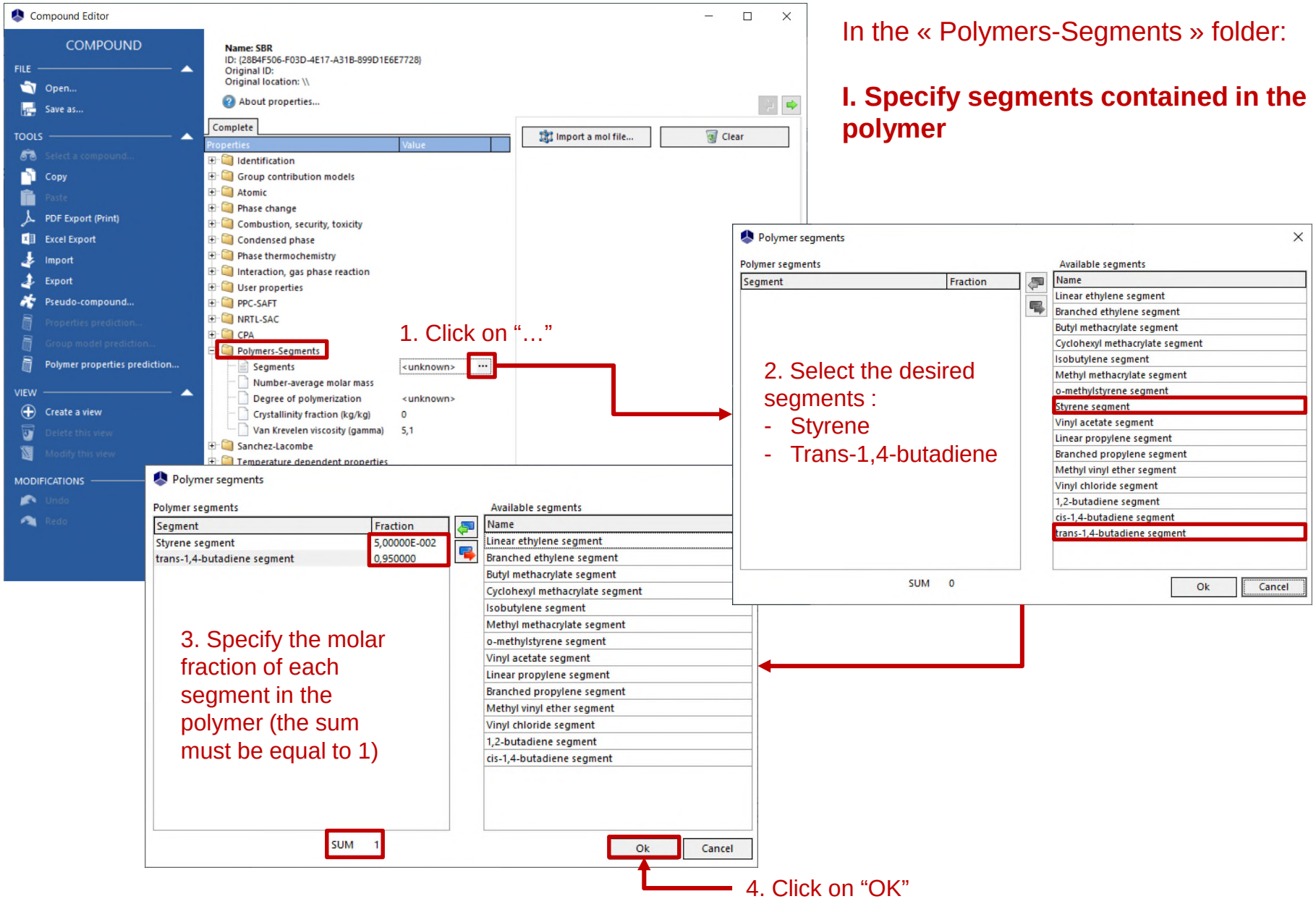
- Segments and segment molar fractions of the polymer,
- The number average molar mass of the polymer (Mn),
- The weight average molar mass of the polymer (Mw).

The following slides explain how to supply these data for the new “SBR” polymer component

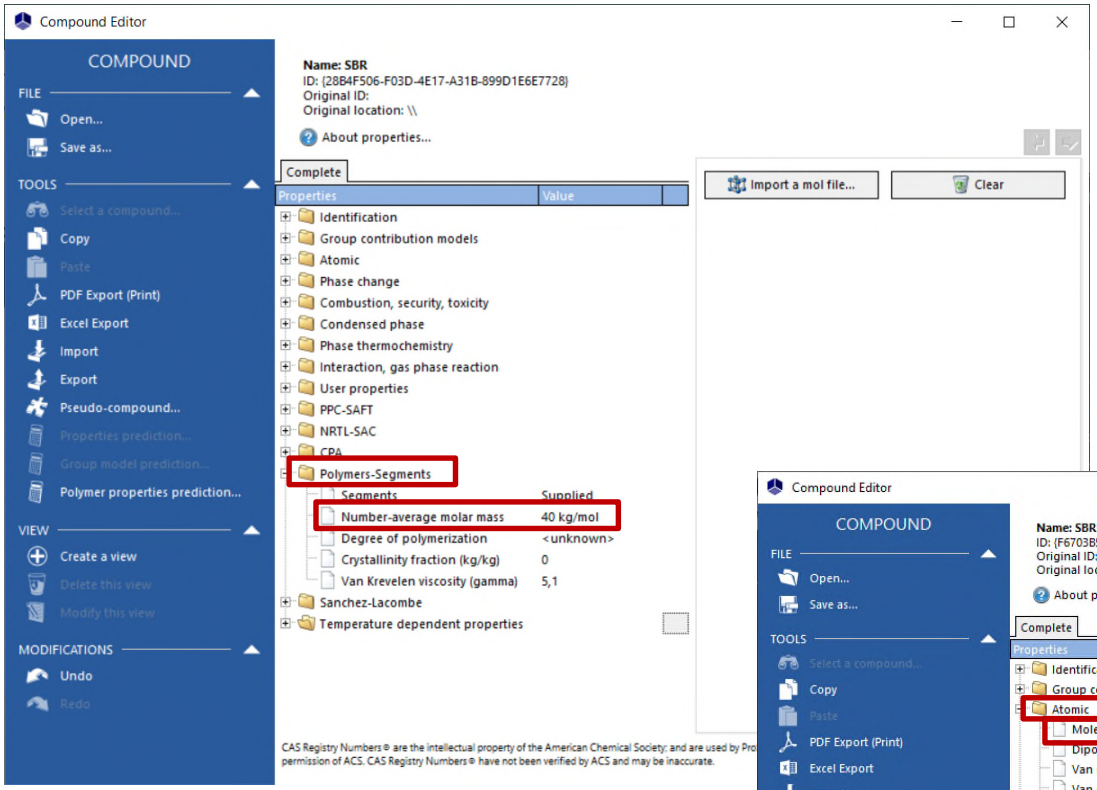
Step 1: Add a polymer component

In the « Polymers-Segments » folder:

I. Specify segments contained in the polymer

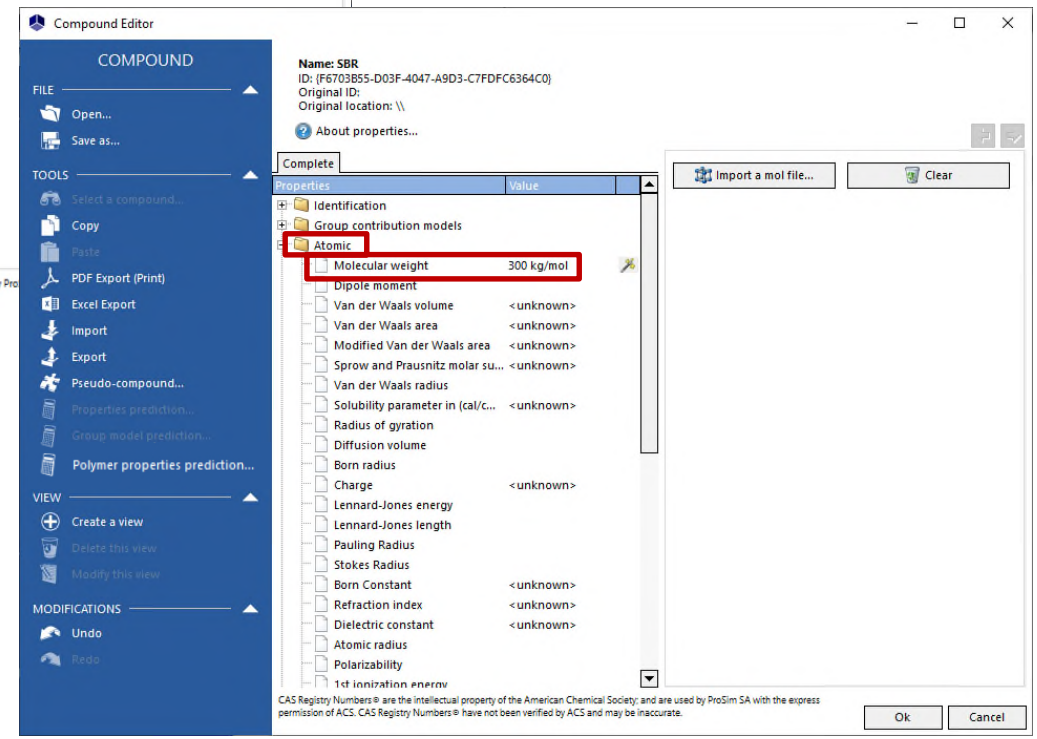


Step 1: Add a polymer component



In the « Polymers-Segments » folder:

II. Specify the number average molar mass of the polymer



In the « Atomic » folder:

III. Specify the weight average molar mass of the polymer

Step 2: Calculation of pure polymer properties

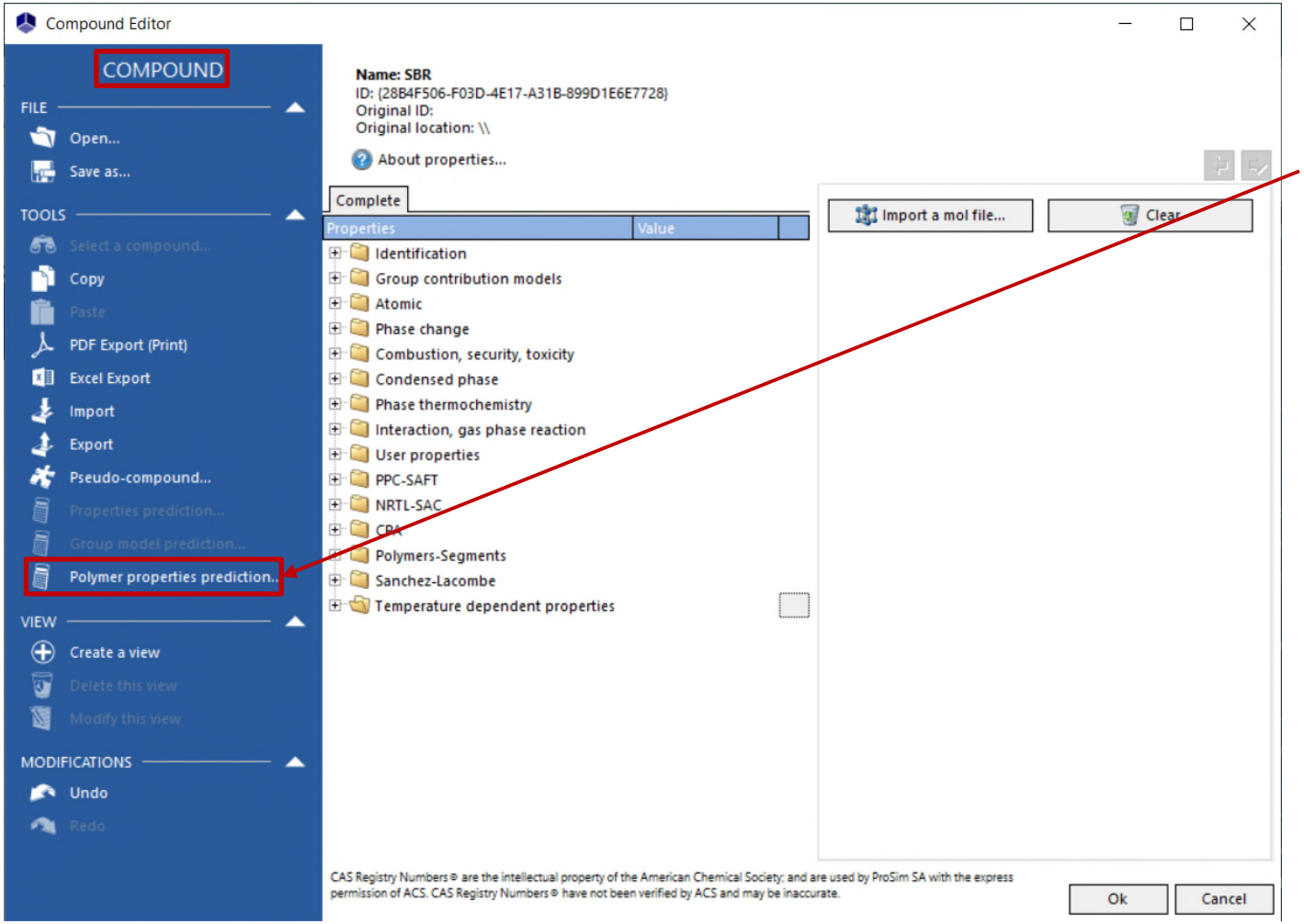
The temperature-independent properties and the correlations of temperature-dependent properties of a pure polymer can be:

- Directly provided by the user
- Or predicted from data supplied at step 1

Temperature-independent properties used for a polymer are:
- The glass-transition temperature (« Phase change » folder)
- The melting temperature (« Phase change » folder)
- The van der Waals volume (« Atomic » folder)
- The ideal gas enthalpy and Gibbs energy of formation at 25°C (« Phase thermochemistry » folder)
- The vaporization and fusion enthalpies (« Phase change » folder)
- The parachor (« Condensed phase » folder)
- The degree of polymerization (« Polymers-Segments » folder)
- The *hypothetical* critical temperature (« Phase change » folder)
- The *hypothetical* critical pressure (« Phase change » folder)
- The *hypothetical* boiling temperature (« Phase change » folder)
- The *hypothetical* acentric factor (« Phase change » folder)

For temperature-dependent properties, correlations called « Polymers », specific to polymers are available for calculation of:
- Vapor pressure (fixed to avoid polymer in vapor phase)
- The ideal gas specific heat
- The liquid specific heat
- The solid specific heat
- The liquid density
- The solid density
- The liquid viscosity
- The liquid thermal conductivity
- The solid thermal conductivity
- The surface tension

Step 2: Calculation of pure polymer properties



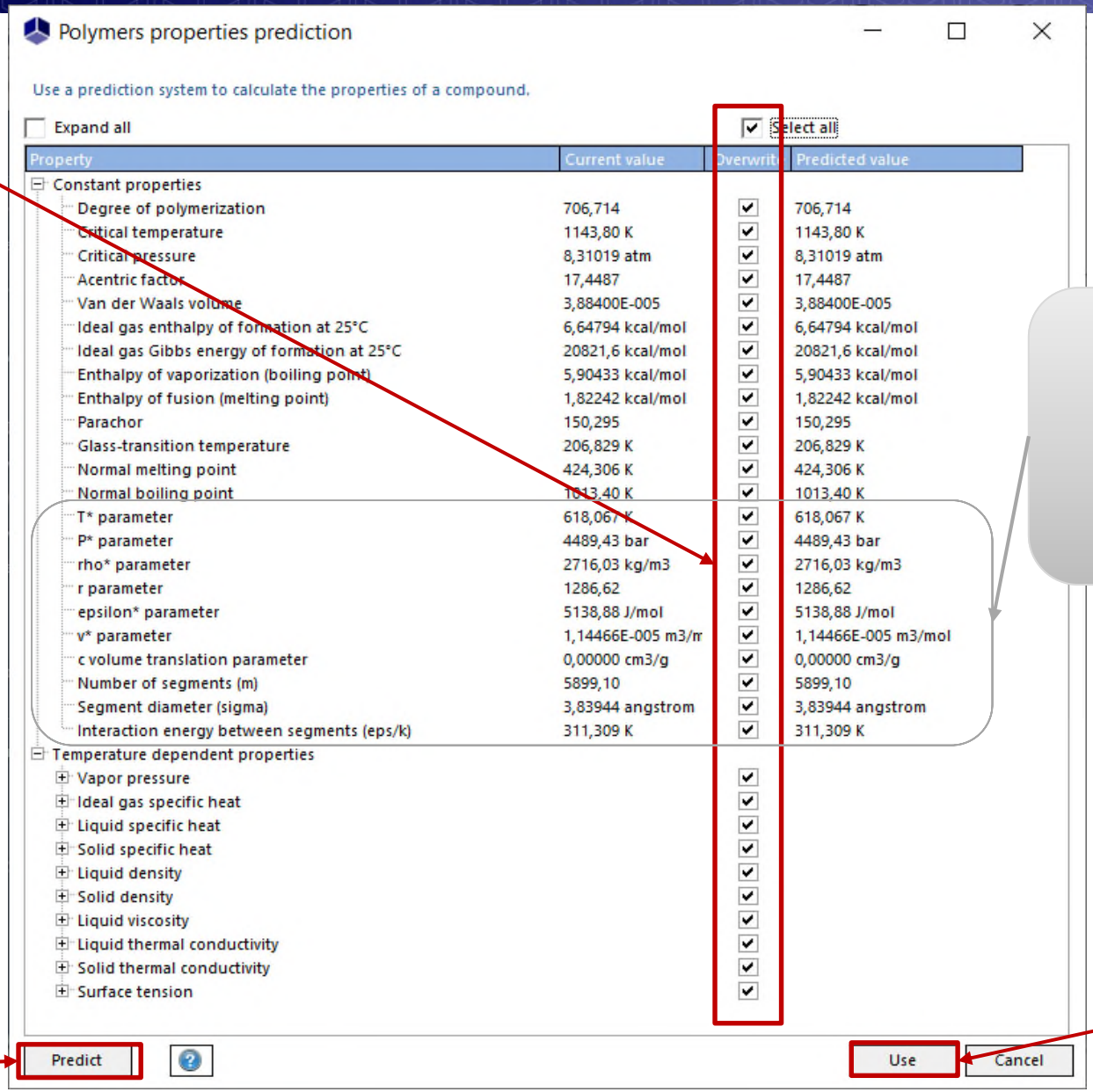
In order to predict pure polymer properties:

- On the "COMPOUND" tab, click on "Polymer properties prediction…"

The predictions of the properties of a pure polymer can only be made correctly if step 1 has been carried out previously

Step 2: Calculation of pure polymer properties

2. Select the properties you want to predict

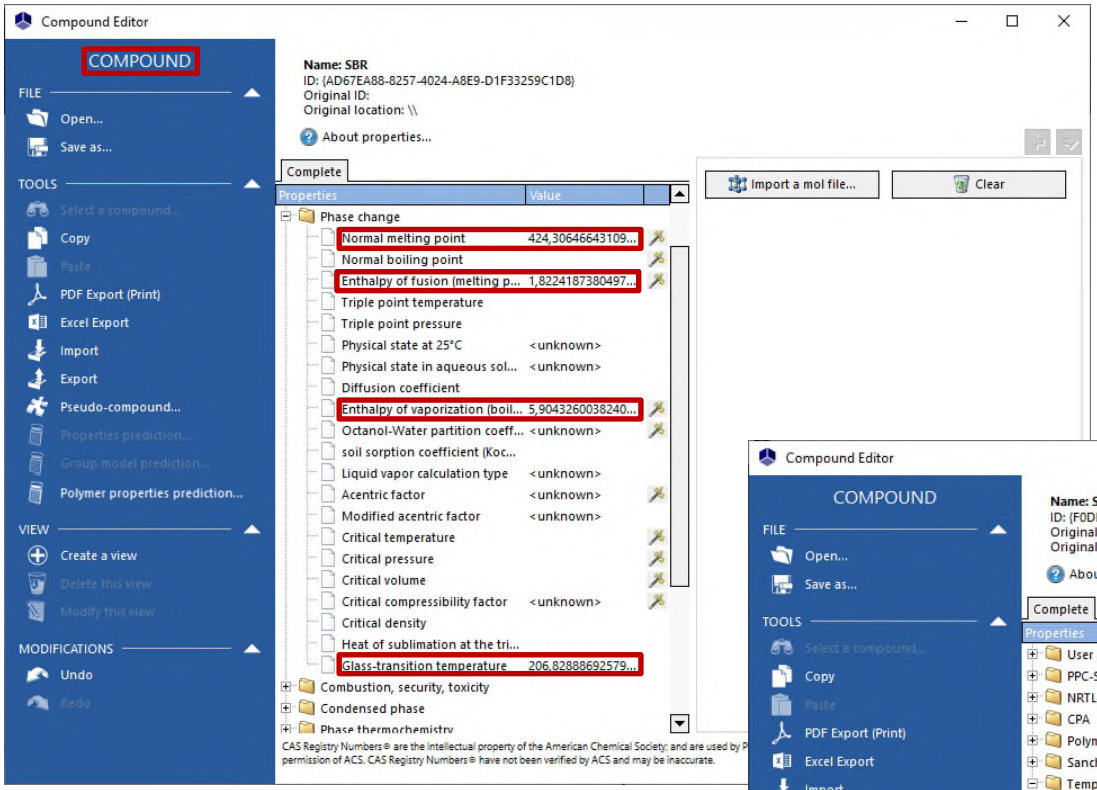


Note that it is also possible to predict values of Sanchez-Lacombe and GC-PPC-SAFT equations of state pure polymer parameters

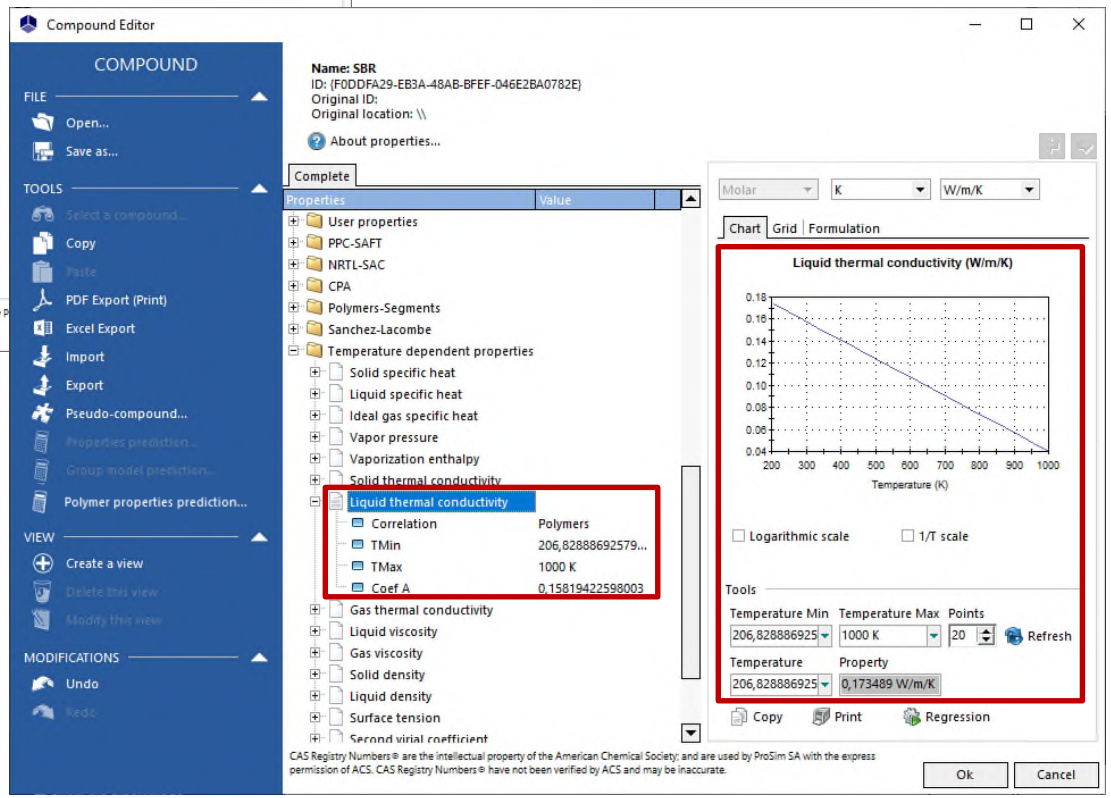
1. Predict

3. Use

Step 2: Calculation of pure polymer properties



The predicted properties can be viewed in the different folders of “COMPOUND” tab

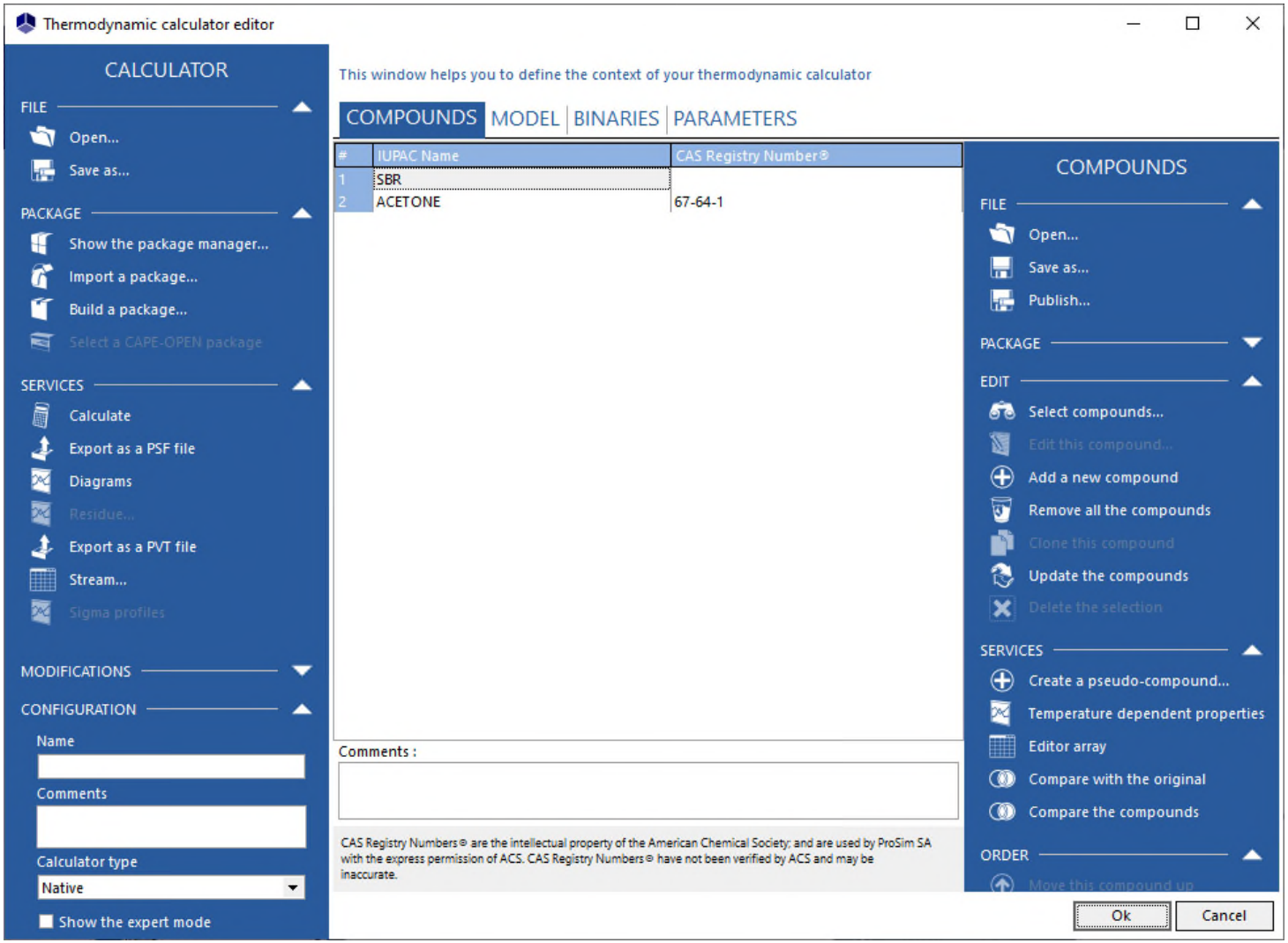


For more details about the component properties, please consult:
« Getting started with Simulis Thermodynamics, use case 4 »

Step 3: Calculation of polymer/solvent mixture properties

Add the solvent component (acetone in this example)

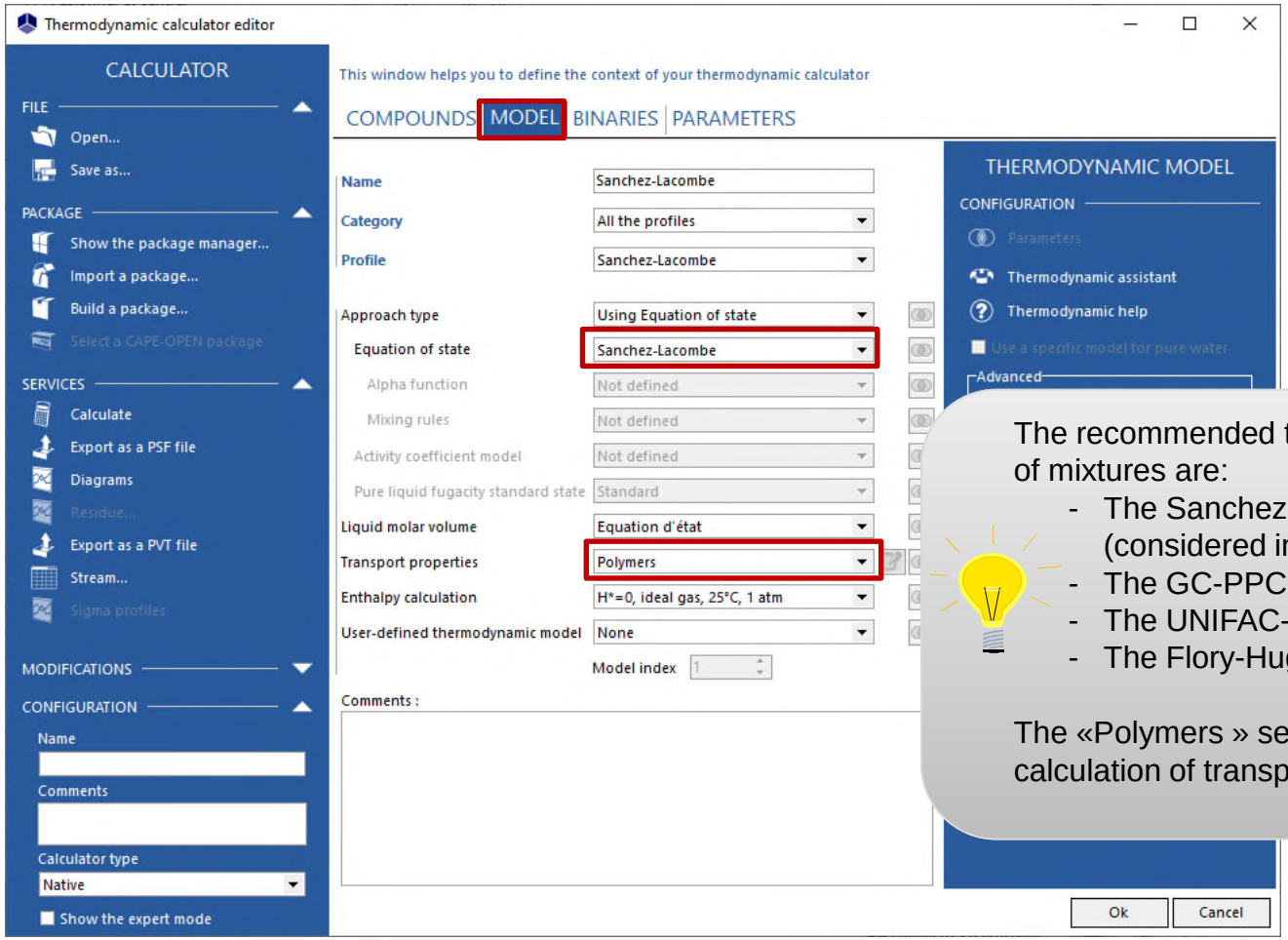
(For a detailed description of this step, please consult: « Getting started with Simulis Thermodynamics: use case 1 »)



Step 3: Calculation of polymer/solvent mixture properties

In the “MODEL” tab:

1. Select a thermodynamic model well suited to mixtures containing polymers
2. Select a set of methods for transport properties calculation which is adapted to mixtures containing polymers



The recommended thermodynamic models for this type of mixtures are:

- The Sanchez-Lacombe equation of state (considered in this example)
- The GC-PPC-SAFT equation of state
- The UNIFAC-FV activity coefficients model
- The Flory-Huggins activity coefficients model

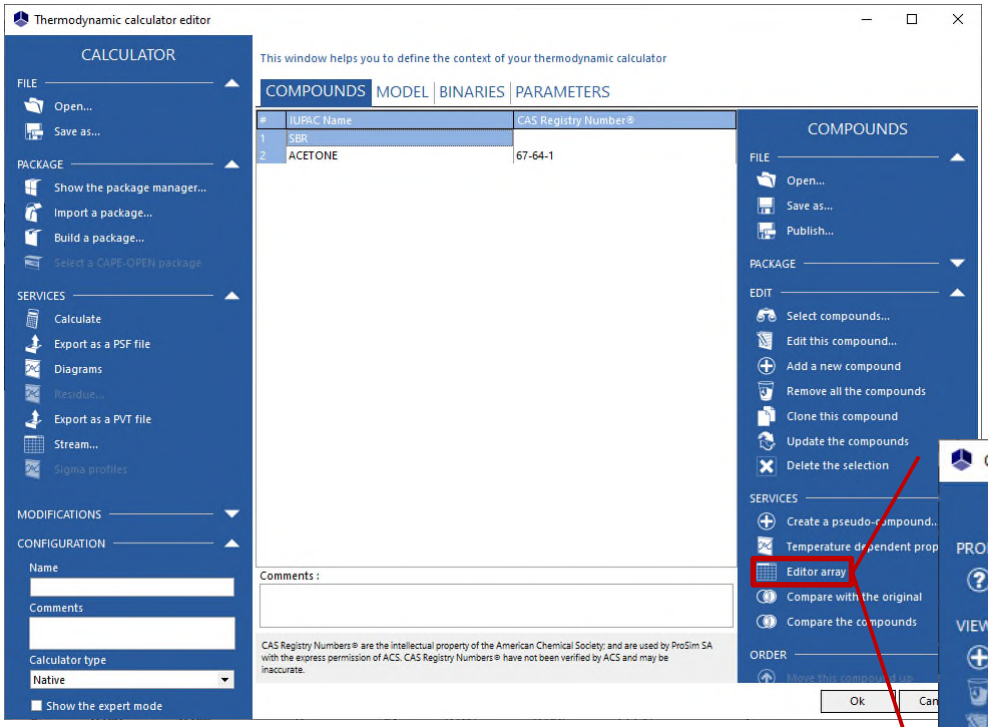
The «Polymers » set of properties is well suited to calculation of transport properties of this type of mixture

Step 3: Calculation of polymer/solvent mixture properties

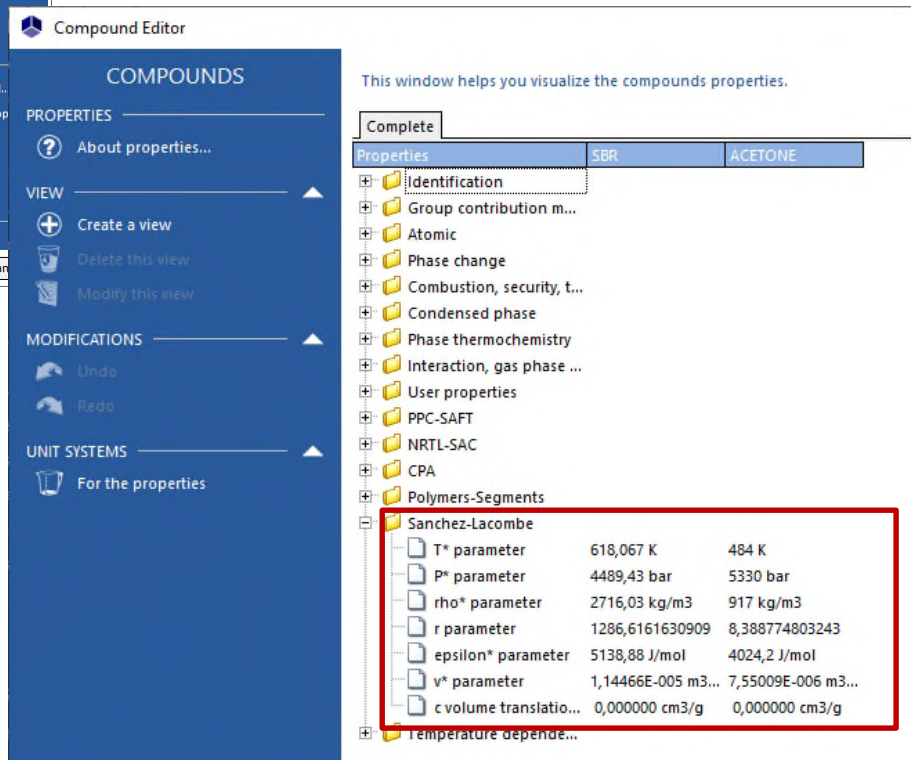
In the “BINARIES” tab:

- Add the binary interaction parameter of the equation of state by providing a value to the Akij coefficient (Akij = 0.035)

Step 3: Calculation of polymer/solvent mixture properties



Before using a thermodynamic model (Sanchez-Lacombe equation of state in this case), the user must be sure that all the required parameters are available for all components



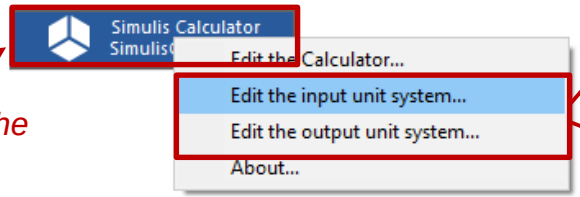
If one of these parameters is not available:

- For a polymer component, the « polymer prediction » method presented on step 2 can be employed
- For a solvent component, these parameters are implicitly estimated from other data during the calculation of a property. *(For more details about these estimation methods, please consult the Sanchez-Lacombe paragraph of the thermodynamic models manual, available from the « MODEL » tab of the calculator)*

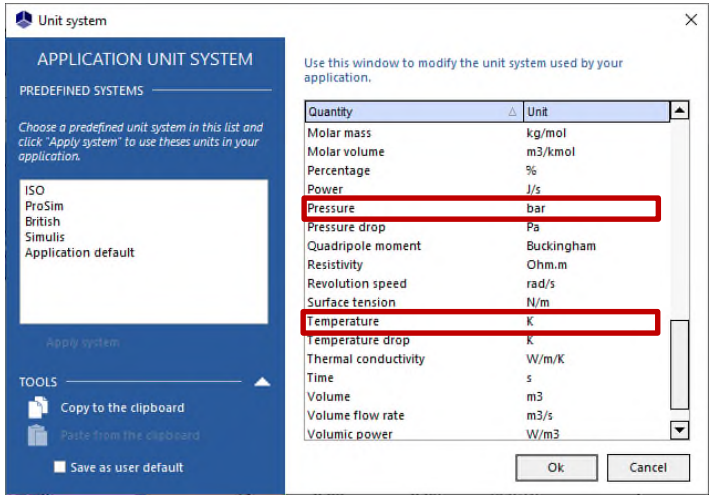
Step 3: Calculation of polymer/solvent mixture properties

In the excel sheet of your calculator:

1. Select the « bar » unit for the pressure and the « K » unit for the temperature for the input and output unit systems



Right-clic on the calculator



For more details about the modification of unit systems, please consult:
« Getting started with Simulis Thermodynamics, use case 1 »

2. Display the name of the components and the selected units

Index compo	Name compound
1	SBR
2	=stCALCompoundDisplayName(C5;B9)

	input	output
	1	2
Temperatur	K	K
Pressure	bar	=stCALGetUnitNameInSystem(;G$7;$E9)

Notes :
- *The index of the polymer is 1, the index of the solvent is 2*
- *In this example, the weight fraction is employed. As the polymer is a heavy molecule, its weight fraction is high even if its molar fraction is very low*

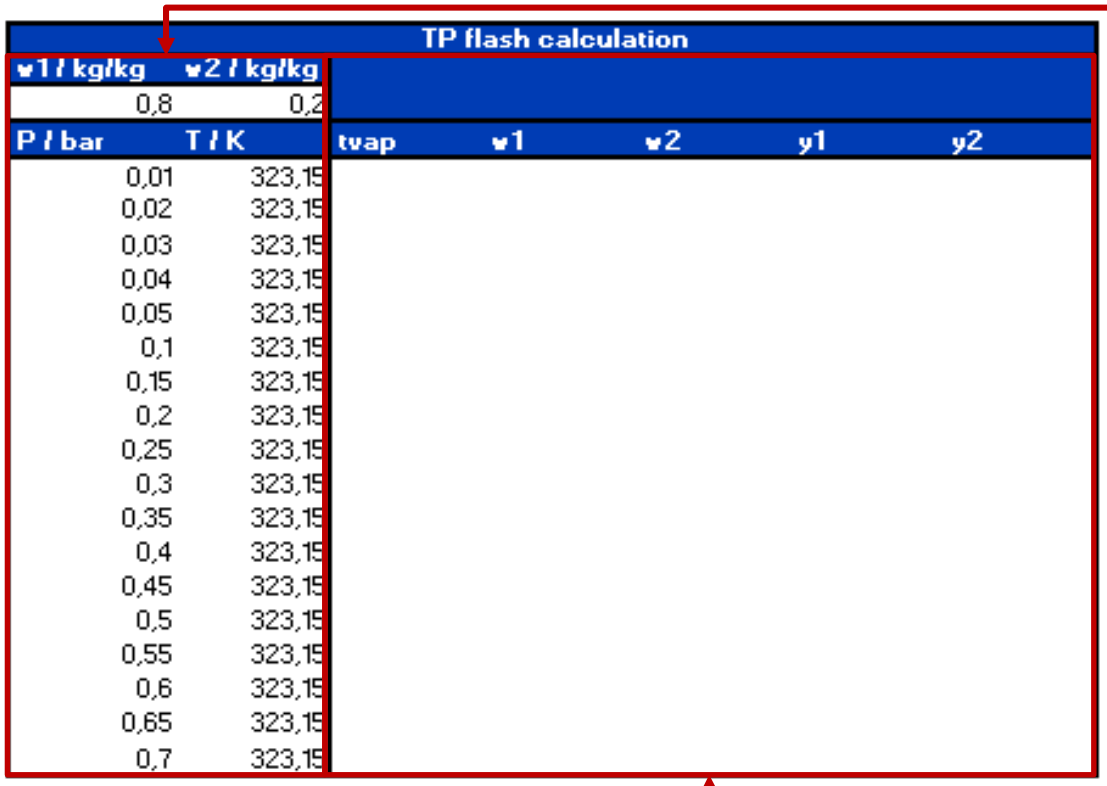
3. Provide the experimental data (bubble pressure data in this example)

EXP	
Liquid Equilibria of Coplymer + Solvent and Homopolymer + Solvent Binaries: New Experimental Data and Their Correlation", J. Chem. Eng.	
T / K	*323,15*
w2 / kg/kg	*P Bubble / bar*
0,003	0,137
0,023	0,265
0,04	0,363
0,056	0,415
0,067	0,453
0,072	0,465
0,067	0,472
0,066	0,473
0,078	0,511
0,079	0,523
0,08	0,533
0,091	0,552
0,115	0,596
0,11	0,597
0,12	0,613

Step 3: Calculation of polymer/solvent mixture properties

4. Perform a TP-Flash calculation with the Sanchez-Lacombe equation of state (calculation of the vapor ratio, the liquid and vapor phases compositions at fixed temperature, pressure and global composition)

4.1. Preparation of the calculation in the Excel sheet: Create the following table



TP flash calculation

w1 / kg/kg	w2 / kg/kg
0,8	0,2

P / bar	T / K	twap	w1	w2	y1	y2
0,01	323,15					
0,02	323,15					
0,03	323,15					
0,04	323,15					
0,05	323,15					
0,1	323,15					
0,15	323,15					
0,2	323,15					
0,25	323,15					
0,3	323,15					
0,35	323,15					
0,4	323,15					
0,45	323,15					
0,5	323,15					
0,55	323,15					
0,6	323,15					
0,65	323,15					
0,7	323,15					

Provide the global weight composition of the mixture, the temperature and the pression for the calculation

Define a table area dedicated to the calculated values

Step 3: Calculation of polymer/solvent mixture properties

4. Perform a TP-Flash calculation with the Sanchez-Lacombe equation of state (calculation of the vapor ratio, the liquid and vapor phases compositions at fixed temperature, pressure and global composition)

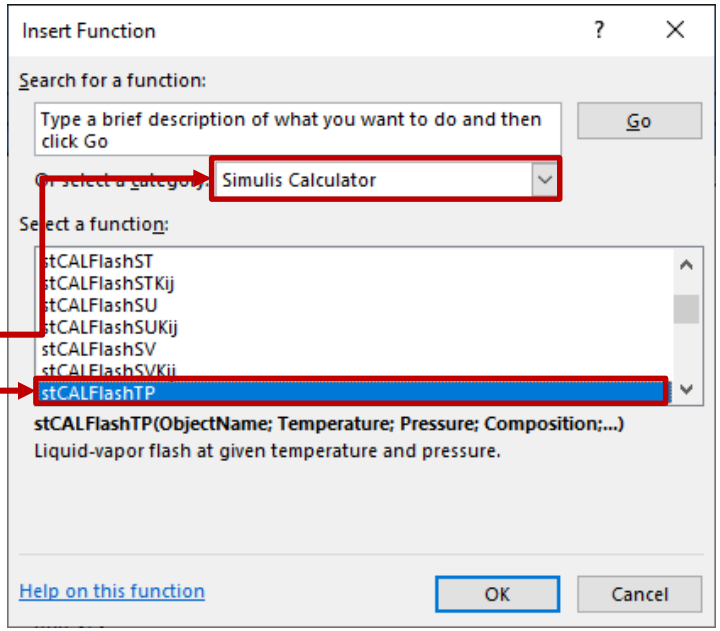
4.2. Add the calculation function

TP flash calculation						
w1 / kg/kg	w2 / kg/kg					
0,8	0,2					
P / bar	T / K	twap	w1	w2	y1	y2
0,01	323,15					
0,02	323,15					
0,03	323,15					
0,04	323,15					
0,05	323,15					
0,1	323,15					
0,15	323,15					
0,2	323,15					
0,25	323,15					
0,3	323,15					
0,35	323,15					
0,4	323,15					
0,45	323,15					
0,5	323,15					
0,55	323,15					
0,6	323,15					
0,65	323,15					
0,7	323,15					

1. Select the first line of the table and click on the excel button dedicated to the insertion of a function

2. In "Insert Function" window, select "Simulis Calculator"

3. In the list of functions, select "stCALFlashTP"

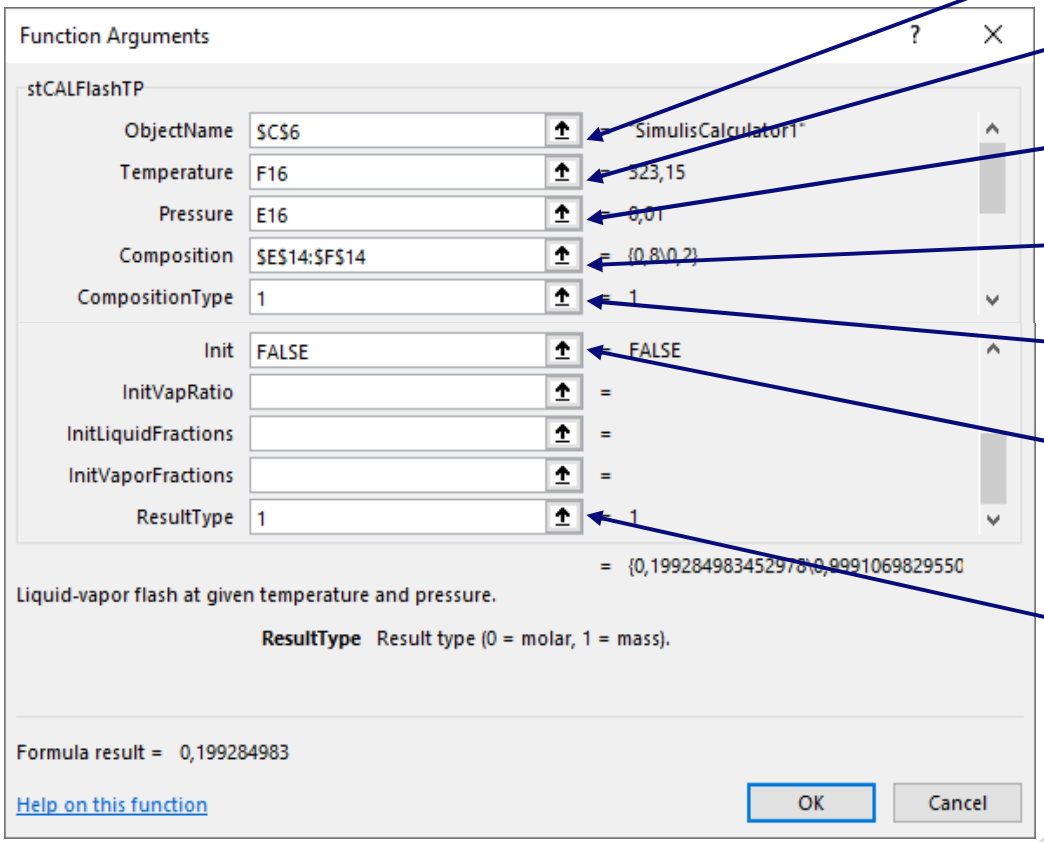


Step 3: Calculation of polymer/solvent mixture properties

4. Perform a TP-Flash calculation with the Sanchez-Lacombe equation of state (calculation of the vapor ratio, the liquid and vapor phases compositions at fixed temperature, pressure and global composition)

4.2. Add the calculation function

4. Provide the function arguments



Provide the name of the calculator

Provide the temperature for the TP Flash calculation

Provide the pressure for the TP Flash calculation

Provide the global composition of the mixture for the TP Flash

Provide the type of the input composition (1 = weight composition)

Provide if initial values must be taken into account (here FALSE)

Provide the type of the output composition

5. Validate the matrix function with Ctrl+Shift+Enter

Some arguments must be set by adding « $ » in order to extend the function in the table (see next slide)

Step 3: Calculation of polymer/solvent mixture properties

4. Perform a TP-Flash calculation with the Sanchez-Lacombe equation of state (calculation of the vapor ratio, the liquid and vapor phases compositions at fixed temperature, pressure and global composition)

4.2. Add the calculation function

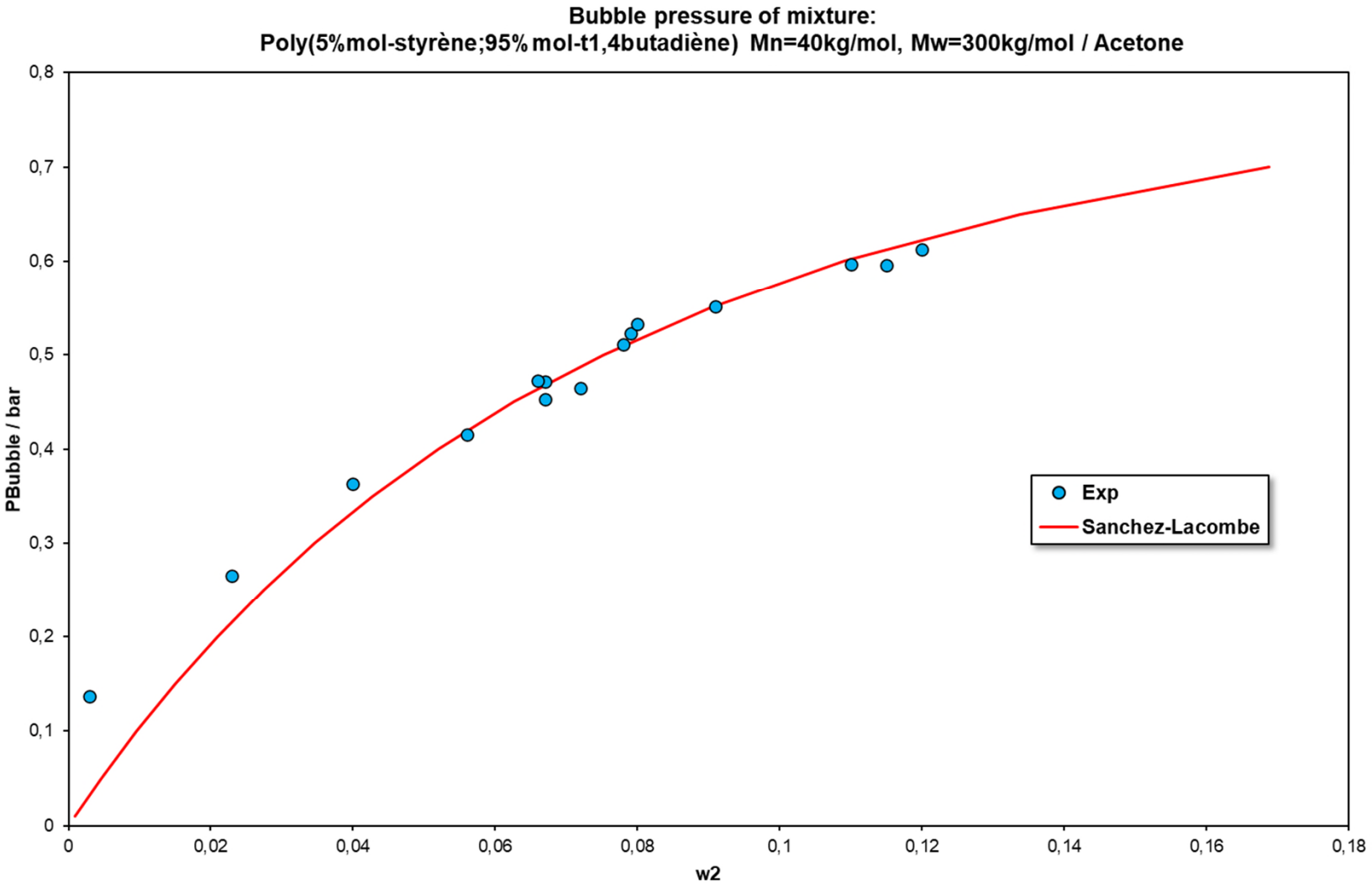
TP flash calculation							
w1 / kg/kg	w2 / kg/kg						
0,8	0,2						
P / bar	T / K	tvap	w1	w2	y1	y2	
0,01	323,15	0,199285	0,999107	0,000893	0	1	
0,02	323,15						
0,03	323,15						
0,04	323,15						
0,05	323,15						
0,1	323,15						
0,15	323,15						
0,2	323,15						
0,25	323,15						
0,3	323,15						
0,35	323,15						
0,4	323,15						
0,45	323,15						
0,5	323,15						
0,55	323,15						
0,6	323,15						
0,65	323,15						
0,7	323,15						

6. Extend the calculation vertically over the whole table

TP flash calculation						
w1 / kg/kg	w2 / kg/kg					
0,8	0,2					
P / bar	T / K	tvap	w1	w2	y1	y2
0,01	323,15	0,199285	0,999107	0,000893	0	1
0,02	323,15	0,198558	0,998201	0,001799	0	1
0,03	323,15	0,197819	0,997281	0,002719	0	1
0,04	323,15	0,197067	0,996346	0,003654	0	1
0,05	323,15	0,196301	0,995398	0,004602	0	1
0,1	323,15	0,192263	0,990422	0,009578	0	1
0,15	323,15	0,187827	0,985012	0,014988	0	1
0,2	323,15	0,18292	0,979096	0,020904	0	1
0,25	323,15	0,177443	0,972577	0,027423	0	1
0,3	323,15	0,171272	0,965335	0,034665	0	1
0,35	323,15	0,164236	0,957208	0,042792	0	1
0,4	323,15	0,156097	0,947976	0,052024	0	1
0,45	323,15	0,146512	0,93733	0,06267	0	1
0,5	323,15	0,134958	0,924817	0,075183	0	1
0,55	323,15	0,120625	0,909737	0,090263	0	1
0,6	323,15	0,102046	0,890925	0,109075	0	1
0,65	323,15	0,076462	0,866247	0,133753	0	1
0,7	323,15	0,037399	0,831133	0,168867	0	1

Step 3: Calculation of polymer/solvent mixture properties

The results obtained are plotted on the following graph



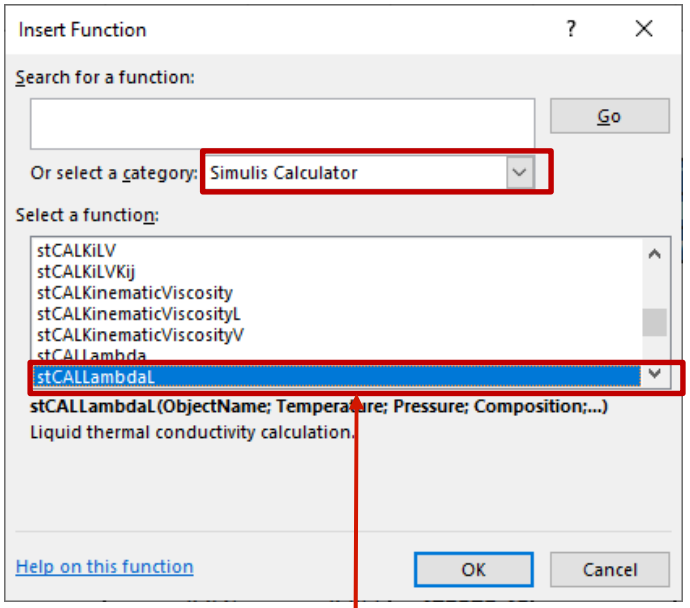
Step 3: Calculation of polymer/solvent mixture properties

Calculation of transport properties can also be performed.
An example of liquid thermal conductivity calculation is presented here.

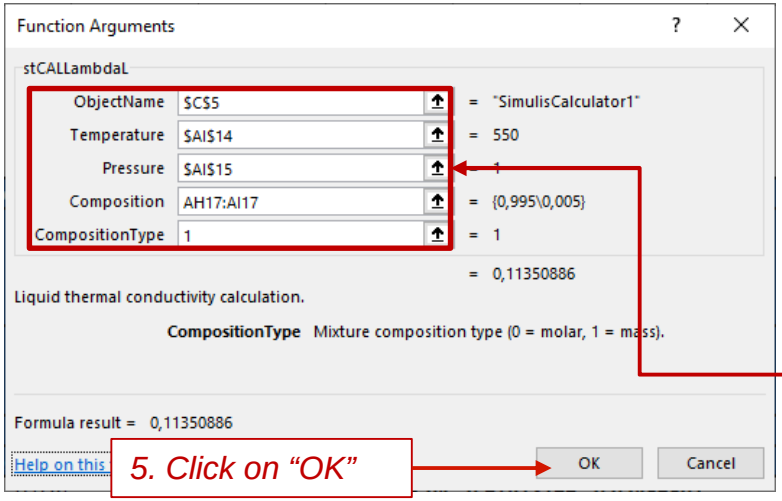
1. Create the following table

T / K	550	
P / bar	1	
w1 / kg/kg	w2 / kg/kg	λL / W/m/K
0,995	0,005	
0,99	0,01	
0,985	0,015	
0,98	0,02	
0,975	0,025	
0,97	0,03	
0,965	0,035	
0,96	0,04	
0,955	0,045	
0,95	0,05	
0,945	0,055	
0,94	0,06	
0,935	0,065	
0,93	0,07	
0,925	0,075	
0,92	0,08	
0,915	0,085	
0,91	0,09	
0,905	0,095	
0,9	0,1	
0,895	0,105	
0,89	0,11	
0,885	0,115	
0,88	0,12	

2. Select the first line of this table and click on the excel button dedicated to the insertion of a function



3. In the "Simulis Calculator" category, select the function "stCALLambdaL"



4. Provide the arguments of the function :
- *The name of the calculator*
- *The temperature*
- *The pressure*
- *The composition of the mixture*
- *The type of the composition*

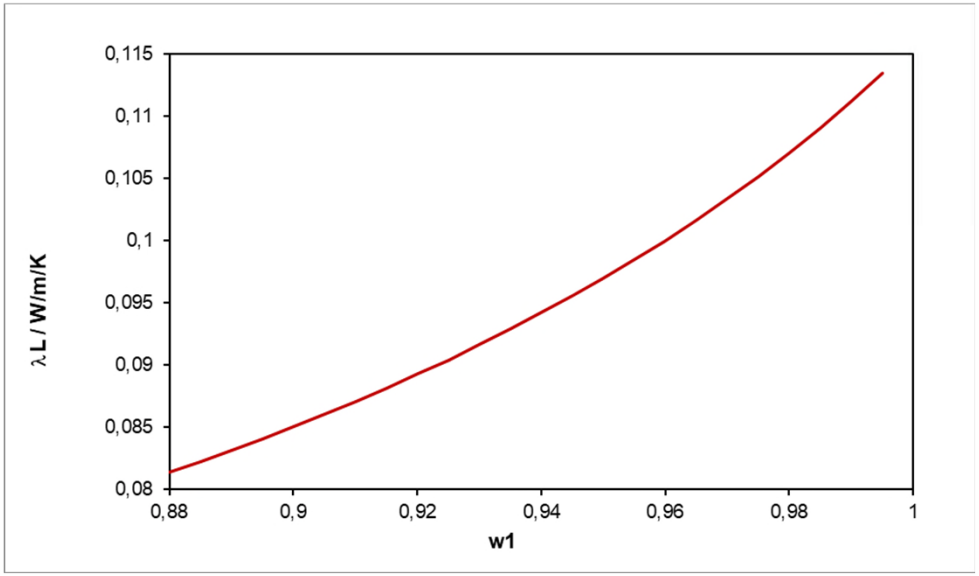
5. Click on "OK"

Step 3: Calculation of polymer/solvent mixture properties

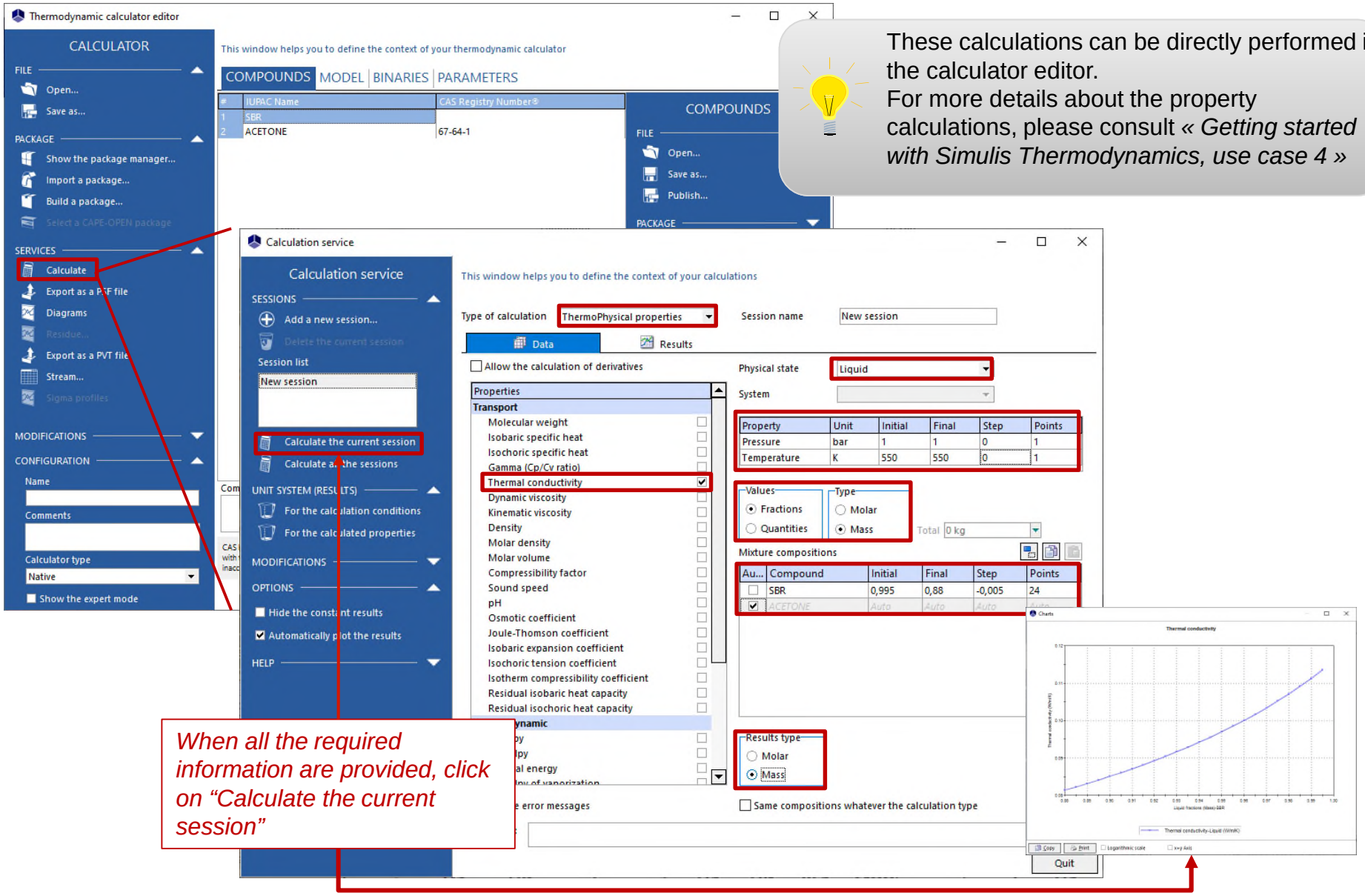
T / K	550	
P / bar	1	
w1 / kg/kg	w2 / kg/kg	λL / W/m/K
0,995	0,005	0,11350886
0,99	0,01	
0,985	0,015	
0,98	0,02	
0,975	0,025	
0,97	0,03	
0,965	0,035	
0,96	0,04	
0,955	0,045	
0,95	0,05	
0,945	0,055	
0,94	0,06	
0,935	0,065	
0,93	0,07	
0,925	0,075	
0,92	0,08	
0,915	0,085	
0,91	0,09	
0,905	0,095	
0,9	0,1	
0,895	0,105	
0,89	0,11	
0,885	0,115	
0,88	0,12	

6. Extend vertically the calculation in all the table

T / K	550	
P / bar	1	
w1 / kg/kg	w2 / kg/kg	λL / W/m/K
0,995	0,005	**0,11350886**
0,99	0,01	**0,11124356**
0,985	0,015	**0,10910869**
0,98	0,02	**0,10709219**
0,975	0,025	**0,10518352**
0,97	0,03	**0,10337339**
0,965	0,035	**0,10165361**
0,96	0,04	**0,10001691**
0,955	0,045	**0,0984568**
0,95	0,05	**0,09696748**
0,945	0,055	**0,09554377**
0,94	0,06	**0,09418099**
0,935	0,065	**0,0928749**
0,93	0,07	**0,09162168**
0,925	0,075	**0,09041787**
0,92	0,08	**0,08926029**
0,915	0,085	**0,08814606**
0,91	0,09	**0,08707255**
0,905	0,095	**0,08603732**
0,9	0,1	**0,08503816**
0,895	0,105	**0,08407302**
0,89	0,11	**0,08314002**
0,885	0,115	**0,0822374**
0,88	0,12	**0,08136356**



Step 3: Calculation of polymer/solvent mixture properties



These calculations can be directly performed in the calculator editor.
For more details about the property calculations, please consult *« Getting started with Simulis Thermodynamics, use case 4 »*

When all the required information are provided, click on “Calculate the current session”

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