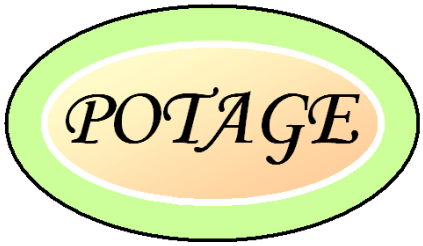
OCTA

Integrated simulation system for soft materials

Phase diagram utility Of Ternary AGEnts



version 3.0

USER'S MANUAL

OCTA User's Group

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Developper of program

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Chapter 1

Introduction

Solubilities between polymers and, polymers and solvents are important properties and easily estimations of these properties have been desired. POTAGE (Phase diagram utility Of Ternary AGEnts) is one of programs for such estimations. POTAGE generates triangle phase diagrams of polymers/solvents mixture with three components. The feature of POTAGE is the usage of extended Flory-Huggins theory and the theory enables us generating phase diagrams with random copolymers and block copolymers. Parameters for calculations with POTAGE are polymer architectures (topologies of constructing chains and numbers of segments for each constructing chains) and Flory-Huggins interaction energy between segments (Flory-Huggins χ parameters).

χ parameters can be estimated by a python script using PolymerDatabase , which includes solubility parameters, generated by OCTA project.

The latest version of POTAGE draws spinodal curves and critical points only on triangle phase diagrams. The functional of drawing binodal curves will be impremented in future.

Chapter 2

Theoretical background

2.1 Mixing energy of Flory-Huggins theory

We can calculate the free energy of mixture of polymers/solvents with Flory-Huggins theory, which uses the lattice theory. The derivation of the theory is written in many letartures, please refer these letartures in detail [1].

The mixing free energy of Flory-Huggins theory with n components can be written by the generalized form

$$\frac{\Delta G}{RT} = \sum_{i}^{n} \frac{\phi_i}{N_i} \ln \phi_i + \sum_{i}^{n} \sum_{j>i}^{n} \chi_{ij} \phi_i \phi_j, \tag{2.1}$$

$$\sum_{i}^{n} \phi_i = 1, \tag{2.2}$$

where R is gas constant, T is thermodynamic temperature, N_i is the number of segments of i-th chain, ϕ_i is the volume fraction of i-th chain, and χ_{ij} is the Flory-Huggins interaction energy between segments composing i-th and j-th chains. Basic Flory-Huggins equation (2.1) was derivered for systems of homopolymer blends and the theory has been modified for random copolymer blends. [2] [3] [4]. The mixing energy of random copolymer can be considered as follows. The i-th chain of random copolymer is composed of k_i kinds of segments and each k_i segments volume fracrtion is $\{y_p\}$. The mixing energy of the system of random copolymer is considered as [Mixing energy of segment-segment interactions]

= [Whole segment-segment interactions energy] - [Internal energy of segment-segment interactions in random copolymers]

Therefore, equation (2.1) can be modified by

$$\begin{aligned} \frac{\Delta G}{RT} &= \sum_{i}^{n} \frac{\phi_i}{N_i} \ln \phi_i + \sum_{i}^{n} \sum_{j\geq i}^{n} \sum_{p}^{k_i} \sum_{q>p}^{k_j} \chi_{pq} y_p y_q \phi_i \phi_j - \sum_{i}^{n} \sum_{p}^{k_i} \sum_{q>p}^{k_i} \chi_{pq} y_p y_q \phi_i & (2.3) \\ &= \sum_{i}^{n} \frac{\phi_i}{N_i} \ln \phi_i + \sum_{i}^{n} \sum_{j\geq i}^{n} \chi'_{ij} \phi_i \phi_j - \sum_{i}^{n} \chi'_{ii} \phi_i, & (2.4) \end{aligned}$$

where, in right-hand side, the second term is the whole segment-segment interaction energy, the third term is the internal energy of segment-segment interactions in random copolymers. Take care to the relation of i and j in the sum, it is different with equation (2.1) and the sum is done between the same volume fraction ϕ_i. In equation (2.4), χ'_{ij} is the effective χ parameter for randomness written by

$$\chi'_{ij} = \sum_{p}^{k_i} \sum_{q>p}^{k_j} \chi_{pq} y_p y_q. \tag{2.5}$$

Using the equaiton (2.4), the phenomena of miscibility windows of polymer arroys composed of random copolymers can be explained [2] [3] [4] [5] [6]. The following sections, we use the equation (2.1) as the standard equation for derivation instead of equation (2.4).

2.1.1 Partial differential equation of mixing energy of Flory-Huggins equation

The partial differentiation of Flory-Huggins equation (2.4) by the i-th volume fraction ϕ_i gives the own chemical potential μ_i. Using such the manner, several theories using partial differentiations deriverd based on Flory-Huggins equation are considered for generating spinodal, binodal and critical conditions. However, these partial differentiations must be done under the imcompressibility condition and the introducing the imcompressibility condition demands asymmetric treatments in equations. Derived equations introducing the imcompressibility condition explicitly tends to be complex, therefore we use implicit method to introduce the imcompressibility condition that we differentiate Flory-Huggins equation (2.4) with the variable $\{s_i\}$ which is implicitlty a componet of ϕ_i and the imcompressibility condition introduced to the final derived equation, which is symmetric equation for eqch components, with $\{s_i\}$. This implicit method reduces complexities in numerical treatments.

First, we express equation (2.4) as $\mathbf{G}$ and partially differentiation it by s_1 gives

$$\frac{\partial \mathbf{G}}{\partial s_1} = \sum_i^n \frac{1}{N_i}\big(\ln\phi_i + 1\big)\frac{\partial \phi_i}{\partial s_1} + \sum_i^n \sum_{j\geq i}^n \chi'_{ij}\Big(\frac{\partial \phi_i}{\partial s_1}\phi_j + \phi_i \frac{\partial \phi_j}{\partial s_1}\Big) - \sum_i^n \chi'_{ii}\frac{\partial \phi_i}{\partial s_1}. \tag{2.6}$$

This equation means the chemical potential of i-th components. Fathermore, we continue to differentiate partially to this equation by $s_2, s_3, ...$, and get higher order differentiate equations using the extinction rule of the imcompressibility condition that over secondally differentiated terms by the same $\{s_i\}$ are vanished as follows.

$$\frac{\partial^2 \mathbf{G}}{\partial s_2 \partial s_1} = \sum_i^n \Big(\frac{1}{N_i\phi_i}\frac{\partial \phi_i}{\partial s_2}\frac{\partial \phi_i}{\partial s_1}\Big) + \sum_i^n \sum_{j\geq i}^n \chi'_{ij}\Big(\frac{\partial \phi_i}{\partial s_1}\frac{\partial \phi_j}{\partial s_2} + \frac{\partial \phi_i}{\partial s_2}\frac{\partial \phi_j}{\partial s_1}\Big) \tag{2.7}$$

$$\frac{\partial^3 \mathbf{G}}{\partial s_3 \partial s_2 \partial s_1} = \sum_i^n \Big(-\frac{1}{N_i\phi_i^2}\frac{\partial \phi_i}{\partial s_3}\frac{\partial \phi_i}{\partial s_2}\frac{\partial \phi_i}{\partial s_1}\Big) \tag{2.8}$$

.....

$$\frac{\partial^m \mathbf{G}}{\partial s_m ....\partial s_3 \partial s_2 \partial s_1} = \sum_i^n \Big(\frac{1}{N_i}(-1)^{m-2}(m-2)!\frac{1}{\phi_i^{m-1}}\prod_j^m \frac{\partial \phi_i}{\partial s_j}\Big), \tag{2.9}$$

where equation (2.9) is the m-th order partial differential equation over third degree partial differentiation.

We introduce the imcompressibility condition to the implicit partially differentiate equations derived above. We define the number of components as n and can select any component as a dependent component under the imcompressibility condition. We choose the dependent component as $s_j = \phi_j$ and the expression of $\partial\phi_i/\partial s_k$ is written as follows.

$$\frac{\partial \phi_i}{\partial s_k} = 1 \quad (k = i) \tag{2.10}$$

$$\frac{\partial \phi_i}{\partial s_k} = 0 \quad (k \neq i,\ k \neq j) \tag{2.11}$$

$$\frac{\partial \phi_i}{\partial s_k} = -1 \quad (k = j). \tag{2.12}$$

Consequently, $\partial\phi_k/\partial s_k$ has the values 1,0, or -1. For example, ternally systems need a simple impricit rule for any higher order partially differentiate equation such as
$i = 1, j = 3, s_1 = \phi_1$

$$\frac{\partial \phi_1}{\partial s_1} = 1 \tag{2.13}$$

$$\frac{\partial \phi_2}{\partial s_1} = 0 \tag{2.14}$$

$$\frac{\partial \phi_3}{\partial s_1} = -1 \tag{2.15}$$

$i = 2, j = 1, s_2 = \phi_2$

$$\frac{\partial \phi_1}{\partial s_2} = -1 \tag{2.16}$$

$$\frac{\partial \phi_2}{\partial s_2} = 1 \tag{2.17}$$

$$\frac{\partial \phi_3}{\partial s_2} = 0 \tag{2.18}$$

$i = 3, j = 2, s_3 = \phi_3$

$$\frac{\partial \phi_1}{\partial s_3} = 0 \tag{2.19}$$

$$\frac{\partial \phi_2}{\partial s_3} = -1 \tag{2.20}$$

$$\frac{\partial \phi_3}{\partial s_3} = 1 \tag{2.21}$$

2.1.2 The method of calculating χ parameters

We introduced the group contribution method by van Krevelen to estimate χ parameters [7].

χ_{ij} is estimated with the equation

$$\chi_{ij} = \chi_s + \frac{V_s}{RT}(\delta_i - \delta_j)^2 \tag{2.22}$$

where χ_s is the constatn (=0.34), V_s is the segment volume, δ_i and δ_j are the solubility parameters for segment i and segment j, respectively. The detail is descrived in SUSHI manual [8].

2.2 The method to estimate the phase diagram with three components

The method to estimate the phase diagram with three components are summarized as the literature by Koningsveld at el [9]. Please refer the literature.

The method to estimate the phase diagram with many components is also summarized by Kamide [10]. Please refer the literature.

Fathermore a tool using the method by Koningsveld was developped as a program named PDFT in OCTA project. Please refer the manual of PDFT.

The latest version of POTAGE can draw spinodal curves and critical points on triangle phase diagrams. We will esplain the method as following sections.

2.2.1 Spinodal curves

Spinodal curves is the trace of points where the value of partial differentiation of chemical potential by each $\{\phi_i\}$ is zero. For simpicity, we define the general partial differentiate form as

$$G_{m....321} = \frac{\partial^m \mathbf{G}}{\partial s_m ....\partial s_3 \partial s_2 \partial s_1}. \tag{2.23}$$

The condition of spinodal points can be written by the determinant

$$J_{Sij} = \begin{vmatrix} G_{ii} & G_{ij} \\ G_{ji} & G_{jj} \end{vmatrix} = 0. \tag{2.24}$$

2.2.2 Critical point

The condition of critical points satisfies $G_{iii} = 0$ on spinodal curves. This condition demands the additional equation to equation (2.24) as

$$\begin{vmatrix} \partial J_{Sij}/\partial \phi_i & \partial J_{Sij}/\partial \phi_j \\ G_{ji} & G_{jj} \end{vmatrix} + \begin{vmatrix} G_{ii} & G_{ij} \\ \partial J_{Sij}/\partial \phi_i & \partial J_{Sij}/\partial \phi_j \end{vmatrix} = 0 \tag{2.25}$$

2.2.3 Tie-line and binodal curve

Tie-line is a line connecting two coexisting compositions on phase diagram. Binodal curve is the curve connecting ends of tie-lines. Macro phase separation is cuased within the binodal curve.

The chemical potentials of two coexisting compositions match the values.

Using the extend Flory-Huggins theory descrived in the section 2.1, The eq. (2.4) can be written with three compositions

$$\begin{aligned}\frac{\Delta G}{k_BTN} &= \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \frac{\phi_C}{N_C}\ln\phi_C \\ &+ \chi_{AB}\phi_A\phi_B + \chi_{BC}\phi_B\phi_C + \chi_{CA}\phi_C\phi_A \\ &+ \chi_{AA}\phi_A\phi_A + \chi_{BB}\phi_B\phi_B + \chi_{CC}\phi_C\phi_C \\ &- \chi_{AA}\phi_A - \chi_{BB}\phi_B - \chi_{CC}\phi_C, \end{aligned} \tag{2.26}$$

where、N is the total segment number in the sysytem defined as

$$N = n_AN_A + n_BN_B + n_CN_C, \tag{2.27}$$

where n_i is the number of i-th polymer. The binodal condition of coexisting points ϕ_A, ϕ_B, ϕ_C and $\phi'_A, \phi'_B, \phi'_C$ must satisfy the condition

$$\mu_A(\phi_A,\phi_B,\phi_C) = \mu_A(\phi'_A,\phi'_B,\phi'_C) \tag{2.28}$$
$$\mu_B(\phi_A,\phi_B,\phi_C) = \mu_B(\phi'_A,\phi'_B,\phi'_C) \tag{2.29}$$
$$\mu_C(\phi_A,\phi_B,\phi_C) = \mu_C(\phi'_A,\phi'_B,\phi'_C) \tag{2.30}$$
$$\phi_A + \phi_B + \phi_C = 1 \tag{2.31}$$
$$\phi'_A + \phi'_B + \phi'_C = 1. \tag{2.32}$$

Chemical potential μ_i is defined as the difference of the free energy of the system when adding one polymer chain as

$$\mu_i = \frac{\partial G_i^0}{\partial n_i} + \frac{\partial \Delta G}{\partial n_i}|_{n_j\neq n_i} = \mu_i^0 + \Delta\mu_i. \tag{2.33}$$

Therefore the binodal condition be be got by solving these equations

$$\Delta\mu_A(\phi_A,\phi_B,\phi_C) = \Delta\mu_A(\phi'_A,\phi'_B,\phi'_C) \tag{2.34}$$
$$\Delta\mu_B(\phi_A,\phi_B,\phi_C) = \Delta\mu_B(\phi'_A,\phi'_B,\phi'_C) \tag{2.35}$$
$$\Delta\mu_C(\phi_A,\phi_B,\phi_C) = \Delta\mu_C(\phi'_A,\phi'_B,\phi'_C). \tag{2.36}$$

$\Delta G/k_BT$ is obtained with multiplying N to both side of eq.(2.26) as

$$\begin{aligned}\frac{\Delta G}{k_BT} &= n_A\ln\phi_A + n_B\ln\phi_B + n_C\ln\phi_C \\ &+ \chi_{AB}n_AN_A\phi_B + \chi_{BC}n_BN_B\phi_C + \chi_{CA}n_CN_C\phi_A \\ &+ \chi_{AA}n_AN_A\phi_A + \chi_{BB}n_BN_B\phi_B + \chi_{CC}n_CN_C\phi_C \\ &- \chi_{AA}n_AN_A - \chi_{BB}n_BN_B - \chi_{CC}n_CN_C\phi_C. \end{aligned} \tag{2.37}$$

Concequentry the chemical potentional of A polymer $\Delta\mu_A/k_BT$ is given by [9]

$$\begin{aligned}\frac{\Delta\mu_A}{k_BT} &= \frac{1}{k_BT}\frac{\partial\Delta G}{\partial\phi_A}|_{n_i\neq n_A} \\ &= \ln\phi_A + (1-\phi_A) - \frac{N_A\phi_B}{N_B} - \frac{N_A\phi_C}{N_C} \\ &+ (1-\phi_A)N_A(\chi_{AB}\phi_B + \chi_{CA}\phi_C + \chi_{AA}\phi_A - \chi_{AA}) \\ &- \chi_{BC}N_A\phi_B\phi_C - \chi_{BB}N_A\phi_B\phi_B - \chi_{CC}N_A\phi_C\phi_C. \end{aligned} \tag{2.38}$$

Chemical potentials of B and C polymers also obtained with same manner. Under the binoal condition, the values of chemical potentials of each components match.

2.2.4 Numerical calculations

Spinodal condition

The spinodal condition equation (2.24) can be reduced to simultaneous linear equations and it can be solved analitycally. However the critical point condition equation (2.25) can not be solved analitycally. Thus we introduce numerical methods for these calculations as follows.

Mesh sysytems are introduced to triangle phase diagrams and select a grid point. We verify the inversion of the sign of spinodal condition equation (2.24) on arounds a grid points to the selected grid point. If the inversion is occured, a spinodal point exsists near the selected grid point. and we start to seach the spinodal point numerically near the point then after seraching the spinodal point, as same sa the spinodal point, we verify the inversion of the sign of critical condition equation (2.25) on arounds the point, if we can detect the possibility of the existance of the critical point, we start to seach the critcal point. We introduced the bisection method for numerical searching for both spinodal and critical points

Binodal condition

The spinodal condition eq. (2.38) can be modified to symmetric form by dividing by N as

$$\begin{aligned}
&\frac{1}{N_A}\ln\phi_A - \frac{(\phi_A-1)}{N_A} - \frac{\phi_B}{N_B} - \frac{\phi_C}{N_C} + (1-\phi_A)(\chi_{AB}\phi_B + \chi_{CA}\phi_C + \chi_{AA}\phi_A - \chi_{AA}) \\
&-\chi_{BC}\phi_B\phi_C - \chi_{BB}\phi_B\phi_B - \chi_{CC}\phi_C\phi_C \\
= \;& \frac{1}{N_A}\ln\phi'_A - \frac{(\phi'_A-1)}{N_A} - \frac{\phi'_B}{N_B} - \frac{\phi'_C}{N_C} + (1-\phi'_A)(\chi_{AB}\phi'_B + \chi_{CA}\phi'_C + \chi_{AA}\phi'_A - \chi_{AA}) \\
&-\chi_{BC}\phi'_B\phi'_C - \chi_{BB}\phi'_B\phi'_B - \chi_{CC}\phi'_C\phi'_C. \qquad (2.39)
\end{aligned}$$

Further, this equation can be transformed to

$$\begin{aligned}
X_A = 1 - \frac{\phi'_A}{\phi_A}\exp N_A[\quad \{ \quad & \frac{\phi_A}{N_A} + \frac{\phi_B}{N_B} + \frac{\phi_C}{N_C} \\
- \quad & \frac{\phi'_A}{N_A} - \frac{\phi'_B}{N_B} - \frac{\phi'_C}{N_C} \\
+ \quad & \chi_{AB}\phi_A\phi_B + \chi_{BC}\phi_B\phi_C + \chi_{CA}\phi_C\phi_A - \chi_{AB}\phi_B - \chi_{CA}\phi_C \\
- \quad & \chi_{AB}\phi'_A\phi'_B - \chi_{BC}\phi'_B\phi'_C - \chi_{CA}\phi'_C\phi'_A + \chi_{AB}\phi'_B + \chi_{CA}\phi'_C \\
+ \quad & \chi_{AA}\phi_A\phi_A + \chi_{BB}\phi_B\phi_B + \chi_{CC}\phi_C\phi_C - 2\chi_{AA}\phi_A \\
- \quad & \chi_{AA}\phi'_A\phi'_A - \chi_{BB}\phi'_B\phi'_B - \chi_{CC}\phi'_C\phi'_C + 2\chi_{AA}\phi'_A\}] = 0. \qquad (2.40)
\end{aligned}$$

Such transformation can be done for both B and C polymers as followings

$$\begin{aligned}
X_B = 1 - \frac{\phi'_B}{\phi_B}\exp N_B[\quad \{ \quad & \frac{\phi_A}{N_A} + \frac{\phi_B}{N_B} + \frac{\phi_C}{N_C} \\
- \quad & \frac{\phi'_A}{N_A} - \frac{\phi'_B}{N_B} - \frac{\phi'_C}{N_C} \\
+ \quad & \chi_{AB}\phi_A\phi_B + \chi_{BC}\phi_B\phi_C + \chi_{CA}\phi_C\phi_A - \chi_{BC}\phi_C - \chi_{AB}\phi_A \\
- \quad & \chi_{AB}\phi'_A\phi'_B - \chi_{BC}\phi'_B\phi'_C - \chi_{CA}\phi'_C\phi'_A + \chi_{BC}\phi'_C + \chi_{AB}\phi'_A \\
+ \quad & \chi_{AA}\phi_A\phi_A + \chi_{BB}\phi_B\phi_B + \chi_{CC}\phi_C\phi_C - 2\chi_{BB}\phi_B \\
- \quad & \chi_{AA}\phi'_A\phi'_A - \chi_{BB}\phi'_B\phi'_B - \chi_{CC}\phi'_C\phi'_C + 2\chi_{BB}\phi'_B\}] = 0, \qquad (2.41)
\end{aligned}$$

$$\begin{aligned}
X_C = 1 - \frac{\phi'_C}{\phi_C}\exp N_C[\quad \{ \quad & \frac{\phi_A}{N_A} + \frac{\phi_B}{N_B} + \frac{\phi_C}{N_C} \\
- \quad & \frac{\phi'_A}{N_A} - \frac{\phi'_B}{N_B} - \frac{\phi'_C}{N_C} \\
+ \quad & \chi_{AB}\phi_A\phi_B + \chi_{BC}\phi_B\phi_C + \chi_{CA}\phi_C\phi_A - \chi_{CA}\phi_C - \chi_{BC}\phi_B \\
- \quad & \chi_{AB}\phi'_A\phi'_B - \chi_{BC}\phi'_B\phi'_C - \chi_{CA}\phi'_C\phi'_A + \chi_{CA}\phi'_C + \chi_{BC}\phi'_B \\
+ \quad & \chi_{AA}\phi_A\phi_A + \chi_{BB}\phi_B\phi_B + \chi_{CC}\phi_C\phi_C - 2\chi_{CC}\phi_C \\
- \quad & \chi_{AA}\phi'_A\phi'_A - \chi_{BB}\phi'_B\phi'_B - \chi_{CC}\phi'_C\phi'_C + 2\chi_{CC}\phi'_C\}] = 0. \qquad (2.42)
\end{aligned}$$

Consequently the problem of the binodal condition of three components reaches to the minimizaion problem of the equation

$$X(\phi_A, \phi_B, \phi'_A, \phi'_B) = X_A^2 + X_B^2 + X_C^2. \tag{2.43}$$

where the incompressibility condition requires only 4 parameters. Newton method can be used to solve the problem because the eq. (2.43) can be partial differentiated by ϕ_i.

2.3 Phase diagrams for block polymers

We applied the extend Flory-Huggins (F-H) theory and Random Phase Approximation (RPA) to the mixture of block polymers.

2.3.1 Linear self-consistent field theory with RPA

We will derive the linear responce equation of polymer melts with RPA [13] . RPA solves the linear self-consistent field equation given by

$$\begin{aligned} \mathbf{x} &= \mathbf{S}^0(\mathbf{u} + \mathbf{C}\mathbf{x} + u^*\mathbf{e}) && (2.44)\\ x_{ij} &= \delta\phi_i(\mathbf{q}) && (2.45)\\ C_{ij} &= z\epsilon_{ij}. && (2.46) \end{aligned}$$

where $\{\delta\phi_i(\mathbf{q})\}$ is the fluctuation of the segment density of $\{\phi_i(\mathbf{r}) - \bar{\phi_i}\}$ in Fourier space.

$\mathbf{S}^0$ is the Scattering function matrix between sub-chains.

$\mathbf{C}$ is the χ parameters matrix.

u^* is the pressure on demand of incompressibility condition.

$\mathbf{e}$ is the unit vector of which all elements are unity.

z is the coordinate number of segment(=6).

ϵ_{ij} is the segment-segment interaction energy between i-th and j-th segments.

2.3.2 The scattering functions between subchains

The scattering functions between subchains are obtained with Gaussian chain theory and given by

$$\begin{aligned} \mathcal{S}^{0p}_{i'i'}(\mathbf{q}) &= \frac{2N^{(p)}_{i'}}{N^{(p)}x^2}(e^{-x} - 1 + x) && (2.47)\\ \mathcal{S}^{0p}_{i'j'}(\mathbf{q}) &= \frac{N^{(p)}_{i'}N^{(p)}_{j'}e^{-z}}{N^{(p)}xy}(e^{-x} - 1)(e^{-y} - 1)(i' \neq j'), && (2.48) \end{aligned}$$

$$x \equiv R^2_{Gi'}|\mathbf{q}|^2,\ y \equiv R^2_{Gj'}|\mathbf{q}|^2,\ z \equiv R^2_{Gi'j'}|\mathbf{q}|^2, \tag{2.49}$$

where N is the chain length、 p is the index of chain, and i' and j' are the index of subchains. $R_{Gi'}$ and $R_{Gi'j'}$ are the radius of gyration of subchains.

To get the phase diagram of spinodal decomposition of block polymers, we use the scattering functions matrix between segment kinds given by

$$S^0_{KK'}(\mathbf{q}) = \sum_{i\in K, j\in K'} \sum_{i',j'} \bar{\phi}_p \mathcal{S}^{0p}_{i'j'}(\mathbf{q}). \tag{2.50}$$

2.3.3 The information of spinodal decomposition with RPA

We solve the eq. 2.44 between segment kinds and get the linear equation in Fourier space as

$$\mathbf{u} = -\frac{1}{\beta}\widetilde{\mathbf{S}}^{-1}\mathbf{x} \tag{2.51}$$

with one-dimensional mesh systtem and following information of spinodal decomposition are obtained from the eigenvalue problem of the matrix $-(1/\beta)\widetilde{\mathbf{S}}^{-1}$.

The existance of negative eigenvalue of $-(1/\beta)\widetilde{\mathbf{S}}^{-1}$ means the sysytem is under a spinodal condition. where

$q = 0$ measn macro-phase separation,

$q > 0$ means micro-phase separation.

Chapter 3

Basic Operation

3.1 Preparation of GOURMET environment

Copy all files on Potage/action directory to $PF_ENGINE/action directory. Copy Potage/bin/win*/potage2.exet to $PF_ENGINE/bin/win*, where * means wild cards.

3.2 Basic operation

We copy the POTAGE/def_udf/POTAGE.udf to our working directory and change the name for our work. Open the udf with GOURMET and change to the View/Table mocde and insert date array to pd_data[] (use Edit/Insert... か Ctrl-i) then input parameters to each pd_data[]. For name1, name2, and name3, input names of polymers. The n1, n2, and n3 are the number of segments of each polymers. chi_{ij} is the χparameter between i-th and j-th components. We can add many elements to pd_data[] and draw all phase diagrams as a one sheet.

The parametes in control_parameters subholder are the control parameters of numerical calculations. The num_dev is the parameteres of mesh grids. The error_sp, error_cr, and error_bi is numerical criterion of *phi* for spinodal points, critical points and binodal points (not used), respectively. The max_iter is the maximum trial number of numerical calculations. The values of recomendation are num_dev=400, error_sp=error_cr=error_bi=$1e^{-12}$, and max_iter=300 , respectively.

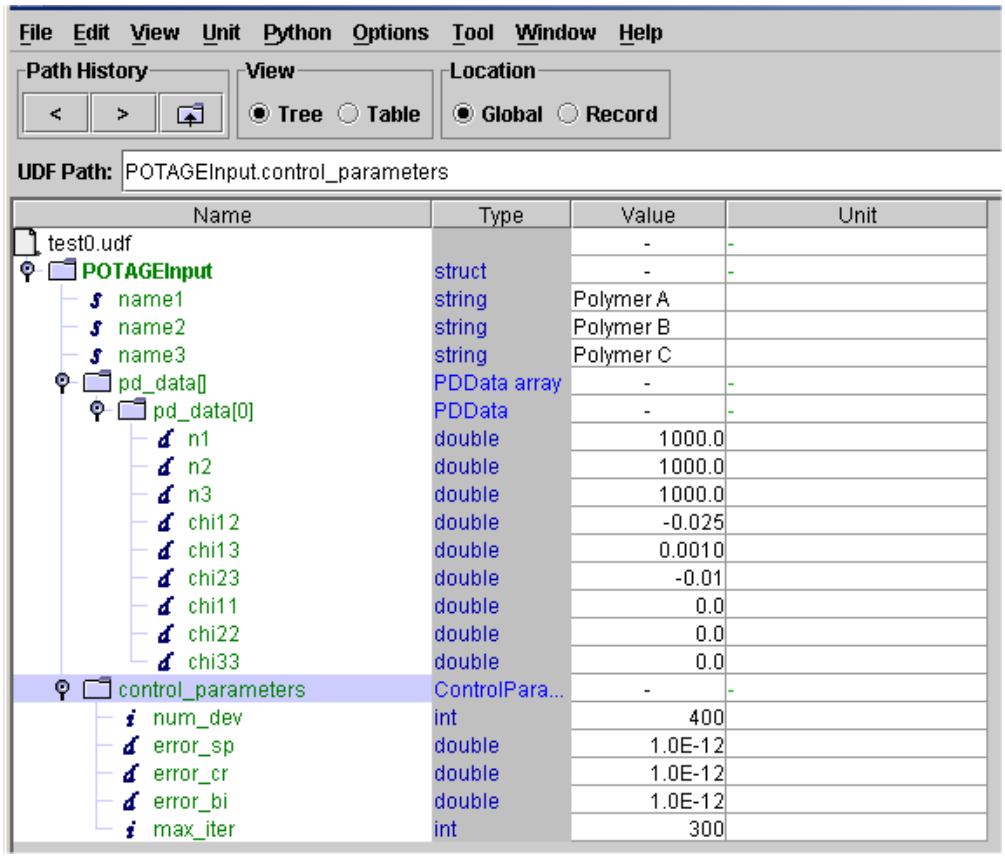

Figure 3.1: An example of POTAGE input UDF

After finishing the input, crick the right mouse button on the POTAGEInput subholder and invoke PotageRun action. An action window will appear with empty parameter boxes for workingdir and run_name. We can input the path of working directory to the workingdir and the name of inptu UDF file path to run_name. No need to input data to both empty parameter boxes for the default runs. The default run copys the opened UDF file to the default working directory GOURMET/tmp and invoke the potage on the working directory. After invoking normally, command file run_name.gp and data file run_name.pd3 for gnuplot are written on the working directory and gnuplot is automatically invoked and a phase diagram window is drawed. The drawed pahase diagram is shown in Figure **??** [12]. The regions within the red curves are spinodal regions. Grid points "*" in the spinodal regions are colored red and other grid points are colored blue. The red circle points on spinodal curves are the critical points.

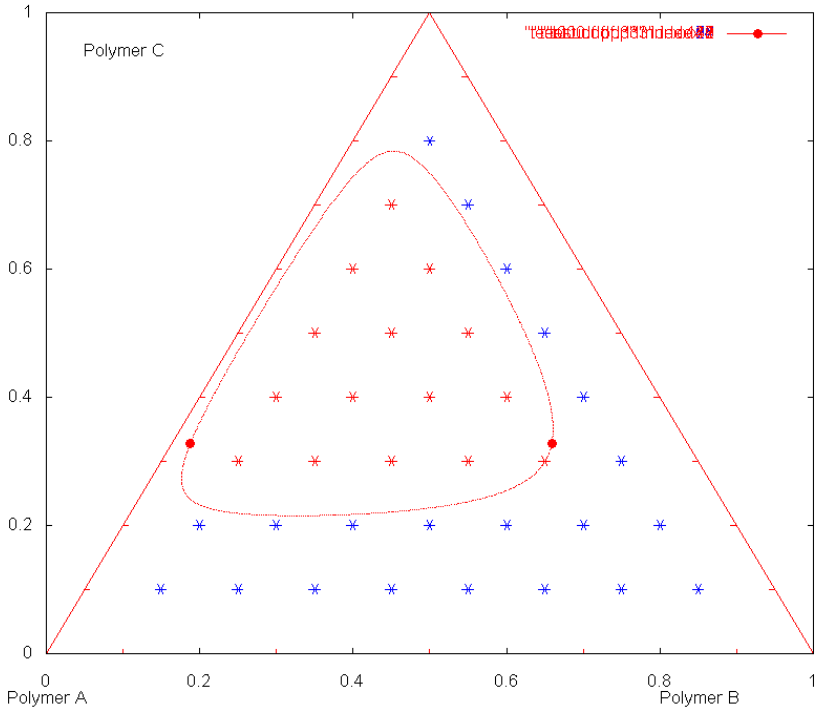

Figure 3.2: An example of phase diagram by a POTAGE run

POTAGE can be invoked on shell. The method is as

```
> potage -Iinput.udf
```

After finishing the run, input.udf.gp and input.udf.pd3 files are generated for gnuplot. We can draw phase diagram using both files on gnuplot as

```
> load 'input.udf.gp'
```

3.3 Execution with POTAGE Ver.2 and Ver.3

There are differences in the UDF data structures of ver 1, 2, 3 of POTAGE because ver. 2 and 3 use RPA for any archtecture of polymers.

One example of the UDF of ver.3 is shown in the fig. 3.3.

```
POTAGEInput.recipe   the point datga to plot as a recipe
POTAGEInput.recipe.phi1 recipe of component 1
POTAGEInput.recipe.phi2 recipe of component 2
            Component 3 can be obtained with incompressibility condition.

POTAGEInput.meshForRPA   Mesh data for RPA calculation.
POTAGEInput.meshForRPA.mesh_width   mesh width      default:0.5
POTAGEInput.meshForRPA.num_mesh     number of mesh  default:64

POTAGEInput.pd_data_for_RPA[]   UDF data array for ver. 2 and 3.
The UDF data is the same of SUSHI UDF, please refer SUSHI manual.

POTAGEInput.control_parameters   added date for ver. 3
POTAGEInput.control_parameters.error_bi    convergence error for binodal calculation
POTAGEInput.control_parameters.num_dev_bi   number of division of the system area for
                                           binodal condition
```

```
Please try both values as 1.0E-6 and 40.
```

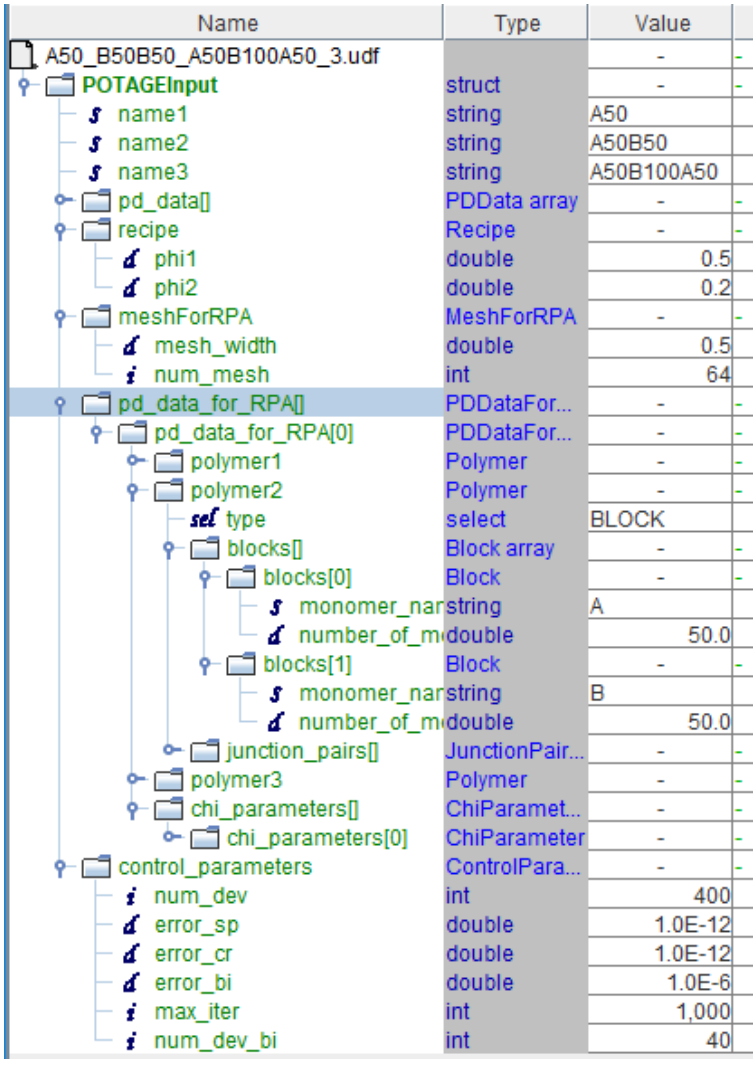

Figure 3.3: UDF data structure for POTAGE3

potage2_run action gives triangle phase daiagram shown as fig. 3.4.

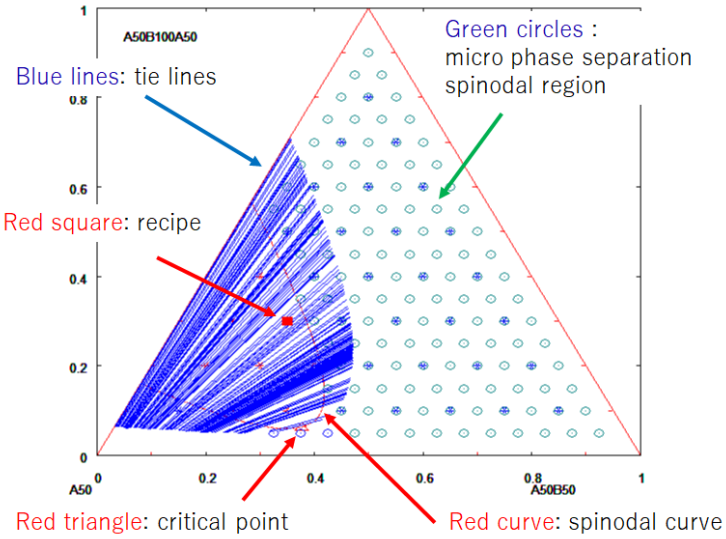

Figure 3.4: Typical triangle phase daiagram obtained with POTAGE3

3.4 Method to use PolymerDatabase(for homo and randompolymer only)

Opne GOURMET and read $PF_ENGINE/POLYMERDATABASE/polymerdatabase.udf file. Open File/Header and write "potage.act" to the Action File as figure 3.5.

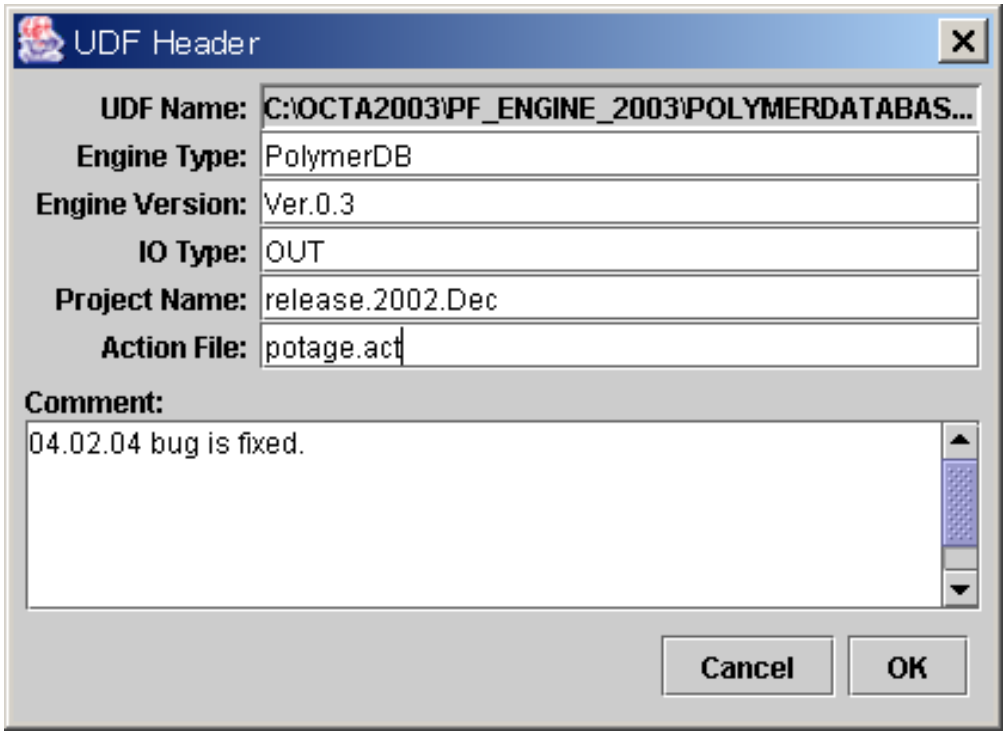

Figure 3.5: dd the potage action file to polymerdatabase UDF

Crick the right mouse button on the PolymerDatabase subholder and invoke potage action POTAGEIn-

putMaker. Action window with empty parameter of workingdir is appeared. The default of the workingdir is empty which uses the GOURMET/tmp as the working directory.

After invoking the potage action, POTAGE_input_maker.udf file with SP values is written on the working directory. Read the POTAGE_input_maker.udf with GOURMET. We can see the two subholders POTAGEInput and POTAGEInputMaker on the UDF file. We modify the date in the POTAGEInputMaker with Table mode on GOURMET, crick the polymer_parameter_for_potage[] subholder, we can see the date of SP values.

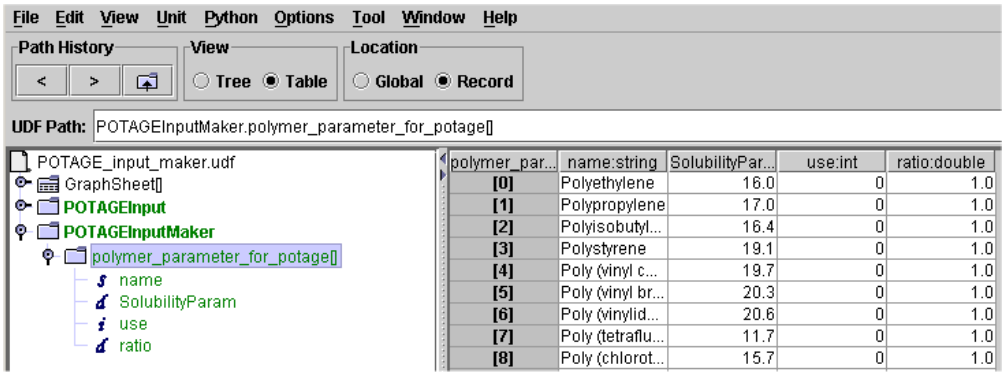

Figure 3.6: Polymer parameter for potage subholder

We can see the data use:int and ratio:double in a raw. Put the value 1, 2, or 3 to the use:int cell and the value 1. to the ratio:double cell for homopolymers. The number means the id of components on the ternaly phase diagram. If we set a random copolymer's data, put the same id number for the components composing the random copolymer. And put the values of the random ratio to the each ratio:double cell where the sum of all values must be one. If we need to use the same polymer data for different components, insert the same data as a new raw and use the same data for the different components. The input UDF file is not saved to the original polymerdatabase.udf file thus mdification is kept on the run.

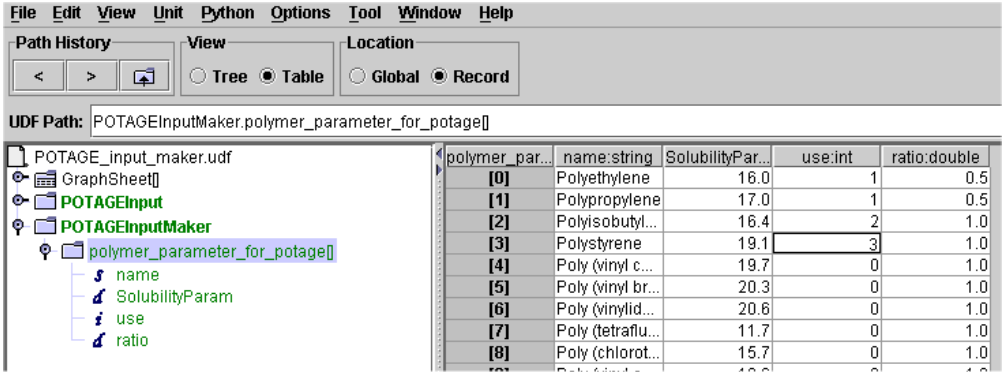

Figure 3.7: polymer parameter for potage

Crick the right mouse button on the POTAGEInputMaker subholder and invoke POTAGESetChi action. A action windows with parameter boxes of segment molar volume $V_r[cm^3/mol]$ and thermodynammic temperatrure $T[^\circ C]$、constant parameter χ_s. The default values are 100,150 and 0., respectively. In the manual of CPC, the value $\chi_s = 0.34$ but the value 0. does not so influence to results.

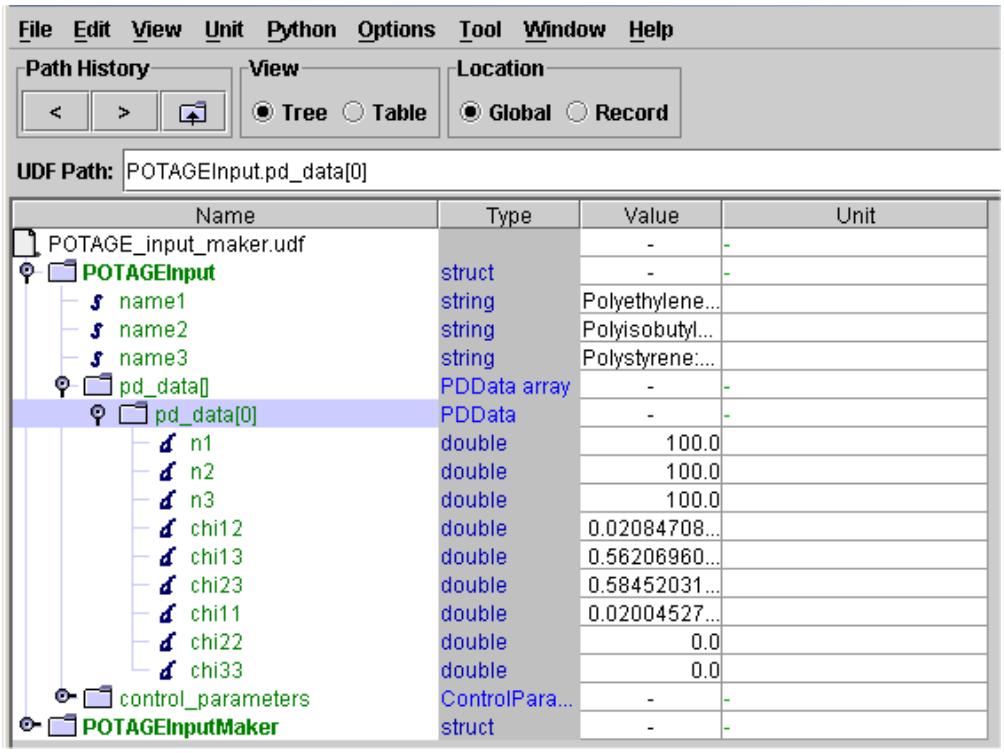

Figure 3.8: POTAGEInput subholder

The action write the data to the POTAGEInput subholder. We can see the estimated χ parameters as mentioned in the previous section 3.2.

For the default value of number of segments n1, n2 and n3, $10000/V_r$ is inputted. This value sould be changed for our purpose.

The figure 3.9 shows an example of potage run. This example is the phase diagram of random copolymer with Polyethylene:Polypropylene=0.5:0.5 , Polyisobutylene and Polystyrene blends.

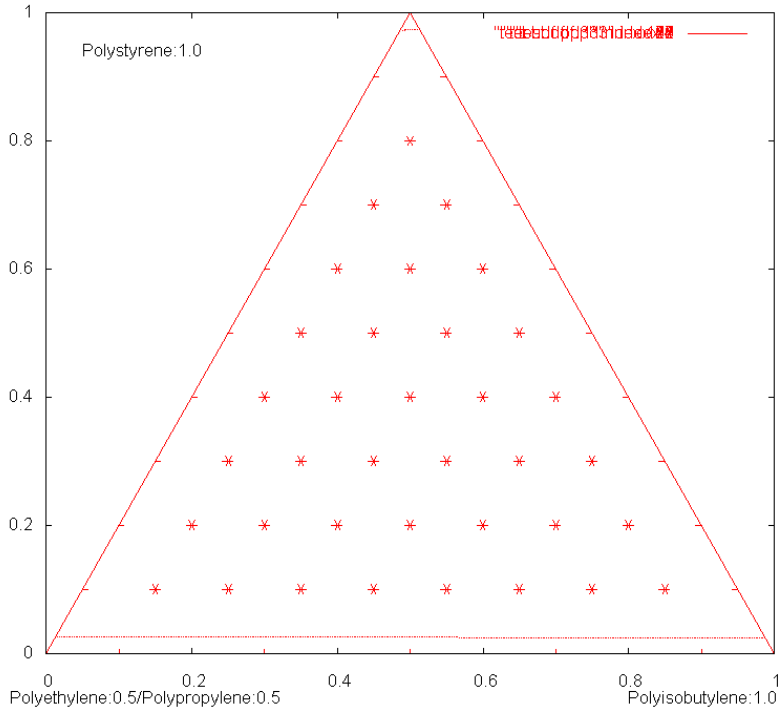

Figure 3.9: Calculation results of POTAGE

Name	Type	Value	
A50_B50_A50B50.udf		-	-
POTAGEInput	struct	-	-
name1	string	A50	
name2	string	B50	
name3	string	A50B50	
pd_data[]	PDData array	-	-
recipe	Recipe	-	-
meshForRPA	MeshForRPA	-	-
pd_data_for_RPA[]	PDDataFor...	-	-
pd_data_for_RPA[0]	PDDataFor...	-	-
polymer1	Polymer	-	-
type	select	HOMO	
blocks[]	Block array	-	-
junction_pairs[]	JunctionPair...	-	-
polymer2	Polymer	-	-
polymer3	Polymer	-	-
chi_parameters[]	ChiParamet...	-	-
control_parameters	ControlPara...	-	-

Figure 3.10: UDF of POTAGE2

Appendix A

Compiling method

A.1 The structure of source file directory

The structure of source file directory of POTAGE is as follows.

```
SUSHI+
     |
   POTAGE
        |
        +--def_udf--+--POTAGE.udf             UDF file for Input
        |           +--POTAGE_input_maker.udf UDF file for action
        |
        +--bin      executable modules
        |
        +--sample   sample files
        |
        +--src      source files and include files
        |
        +--action   action files
```

When compiling POTAGE, compilers use the source codes of SUSHI and libraries of SUSHI thus the compiling POTAGE must be done after compiling SUSHI as one core version and the position of POTAGE directory must not be moved.

A.2 Compiling method

Use gmake for compiling on Linux (Cygwin).
Make on the directory POTAGE/src as

```
> cd POTAGE/src
> make all
```

A.3 Install method

On POTAGE/src directory

```
> make install
```

A.4 Clear method

On POTAGE/src directory

```
> make clean
```

References

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