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Novel scheme for graphical representation of positive mean-field interaction parameters in statistical copolymer blends

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Summary

A novel scheme for graphical representation of positive interaction parameters for binary blends consisting of two different statistical copolymers $P(A_xB_{1-x})$ and $P(C_yD_{1-y})$ is presented. The corresponding abstract parabolic equation, describing the interaction parameter as a function of x and y thus receives a pictorial meaning. The scheme is built by a pyramid shaped body where the corners represent the pure copolymer components A, B, C and D. Distances mirror the square root of corresponding positive interaction parameters. Copolymers are represented by positions on the respective edges depending on compositions.

Introduction

The miscibility of different polymers is one of the major problems in the field of polymers (1,2) in order to design polymer blends tailored for specific applications. Using statistical copolymers the miscibility can be tuned in a wide range. A quantity describing polymer miscibility is the Flory - Huggins - Stavermann interaction parameter χ within mean field theory and allows a quite detailed description of thermodynamics of phase separation for a particular polymer pair. The mean - field theory yields a parabolic dependence connecting the effective interaction parameter χ for blends of statistical copolymers $P(A_xB_{1-x})$ and $P(C_yD_{1-y})$ to the copolymer compositions x and y. The relevant prefactors of the parabolic dependency are given by 6, in general, different pair interaction parameters between the corresponding pure components, χ_{AB}, χ_{AC}, χ_{AD}, χ_{BC}, χ_{BD}, χ_{CD}. It is assumed that these relevant pair interaction parameters are all positive with respect to the solubility parameter approach (3,4). The presented scheme enables a graphical illustration of the interaction parameters where distances mirror the square root of respective positive interaction parameters. For the simplest case of a homopolymer blended with a statistical copolymer the scheme is a triangle where the sites are given by the 3 polymers and each side length is equal the square root of the interaction parameter of the polymers on the connected sites. For example the interaction parameter for a $P(A_xB_{1-x})$ / $P(C_yD_{1-y})$ blend can be directly read from the diagram for every possible copolymer composition x and y. In particular, one can see immediately a specific pair of x and y which minimizes the interaction parameter for a $P(A_xB_{1-x})$ / $P(C_yD_{1-y})$ blend system. Consequently, the presented scheme can be regarded as a helpful simple possibility for imagination and illustration of the abstract parabolic mean - field expressions.

Blends of a homopolymer and a statistical copolymer $P(A_{1-x}B_x)$

This particular scenario is shown in figure 1.The polymers are aligned in a triangle and distances represent the square root of corresponding interaction parameter. Additionally to positive interaction parameters it is also assumed that the suggested triangle construction is possible. Thus the lengths of the sides of a triangle a, b and c have to satisfy a - b$|$ $\leq c \leq a + b$ or for the particular case shown in figure 1

$$\left|\sqrt{\chi_{A/C}} - \sqrt{\chi_{B/C}}\right| \leq \sqrt{\chi_{A/B}} \leq \sqrt{\chi_{A/C}} + \sqrt{\chi_{B/C}}$$

The position of the $P(A_{1-x}B_x)$ copolymer, on the line connecting polymer A and B, is thus given by the fraction x of component B in the copolymer. The distance s represents the square root of the interaction parameter between polymer A and $P(A_{1-x}B_x)$. The height h in the triangle represents the possible minimum value of s.

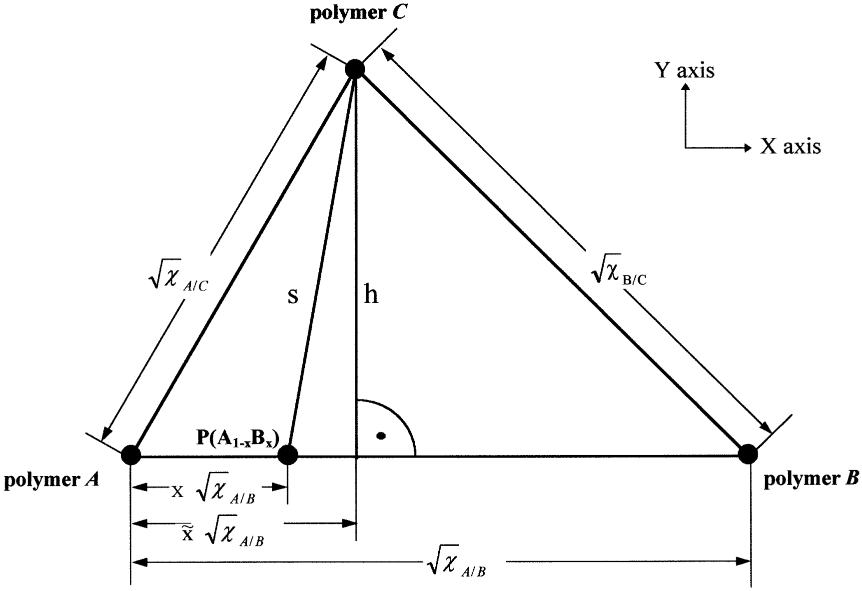

Fig. 1: Two dimensional scheme representing the interaction parameter between a homopolymer C and a statistical copolymer $P(A_{1-x}B_x)$ by the distance s.

The origin is given by polymer A, the vectors to polymer C and B are represented by

$$\vec{C} = \begin{pmatrix} \tilde{x}\sqrt{\chi_{A/B}} \\ h \end{pmatrix} \quad (1a)$$

and

$$\vec{B} = \begin{pmatrix} \sqrt{\chi_{A/B}} \\ 0 \end{pmatrix} \quad (1b)$$

respectively. From figure 1 the following relations are evident

$$\vec{C}^2 = \chi_{A/C} \quad (2a)$$

$$\vec{B}^2 = \chi_{A/B} \tag{2b}$$

$$|\vec{C} - \vec{B}|^2 = \chi_{B/C} \tag{3}$$

consequently the copolymer $P(A_{1-x}B_x)$ is represented by the vector

$$\vec{P}(A_{1-x}B_x) = x\vec{B} = \begin{pmatrix} x\sqrt{\chi}_{A/B} \\ 0 \end{pmatrix} \tag{4}$$

The relevant distance, describing the square root of the interaction parameter between polymer C and $P(A_{1-x}B_x)$ is given by s in figure 1. In order to demonstrate the equivalence between mean-field expression and the suggested geometrical representation an expression for s^2 has to be calculated. From the definitions above

$$s^2 = |\vec{C} - x\vec{B}|^2 \tag{5}$$

is evident and thus yields, utilizing equations 2a and 2b

$$s^2 = \vec{C}^2 - 2x\vec{C}\vec{B} + x^2\vec{B}^2 = \chi_{A/C} - 2x\vec{C}\vec{B} + x^2\chi_{A/B} \tag{6}$$

From equation 3 one obtains the identity

$$-2\vec{C}\vec{B} = \chi_{B/C} - \chi_{A/C} - \chi_{A/B} \tag{7}$$

Inserting equation 6 into 5 yields

$$s^2 = \chi_{A/C} + x\left(\chi_{B/C} - \chi_{A/C} - \chi_{A/B}\right) + x^2\chi_{A/B} \tag{8}$$

or rewritten

$$s^2 = x\chi_{B/C} + (1-x)\chi_{A/C} - x(1-x)\chi_{A/B} \tag{9}$$

The right side of equation 9 is equal to the mean - field interaction parameter for a blend of a homopolmer C with a statistical copolymer $P(A_{1-x}B_x)$ (5). Consequently the interpretation of the distance s and the suggested scheme is verified for this simple case.

The next step is focused on the extended, still, two dimensional case of two $P(A_{1-x}B_x)$ and $P(A_{1-y}C_y)$ statistical copolymers.

Blend of two statistical copolymers where one component is equal $P(A_{1-x}B_x)$ and $P(A_{1-y}C_y)$

In accordance to figure 1 and definitions of corresponding vectors, this case can be drawn in the following way, where the relevant distance is again s. Form figure 2 one see immediately

$$s^2 = |y\vec{C} - x\vec{B}|^2 = y^2\vec{C}^2 - 2xy\vec{C}\vec{B} + x^2\vec{B}^2 \tag{10}$$

utilizing again equation 7

$$s^2 = y^2\chi_{A/C} + xy\left(\chi_{B/C} - \chi_{A/C} - \chi_{A/B}\right) + x^2\chi_{A/B} \tag{11}$$

and rewritten

$$s^2 = xy\chi_{B/C} + y(y-x)\chi_{A/C} - x(y-x)\chi_{A/B} \tag{12}$$

The right side of equation 12 is equal to the interaction parameter given by mean field theory for this specific case (5). Extent to a three dimensional representation the general case of a blend of two statistical copolymers $P(A_{1-x}B_x)$.and $P(C_{1-y}D_y)$ can be illustrated as shown in the next section.

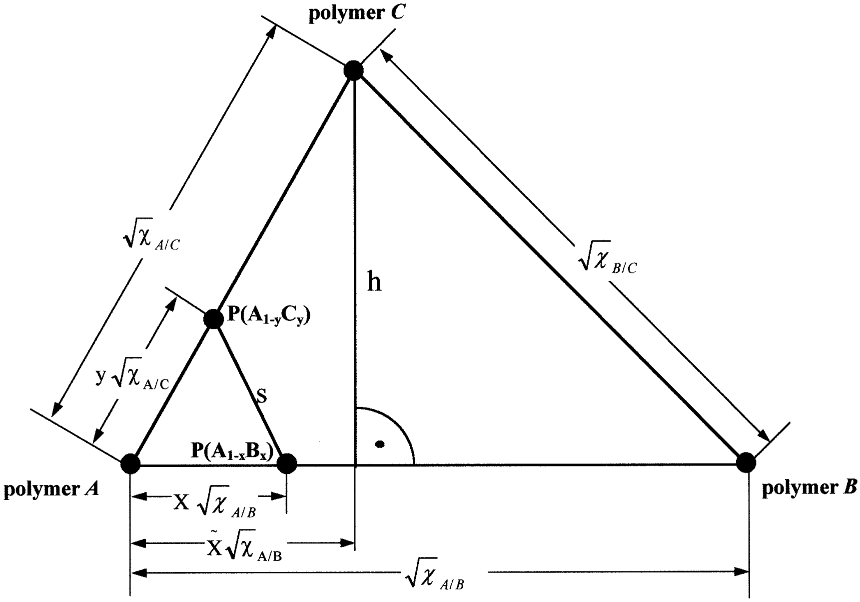

Fig. 2: Two dimensional scheme representing the interaction parameter between two statistical copolymer $P(A_{1-x}B_x)$ and $P(A_{1-y}C_y)$ by the distance s.

General case - Blend of two statistical copolymers $P(A_{1-x}B_x)$ and $P(C_{1-y}D_y)$

Again, distances in figure 3 represent the corresponding square root of interaction parameter and each triangle face of the body has to fulfil the relation $|a - b| \leq c \leq a + b$ as explained above.

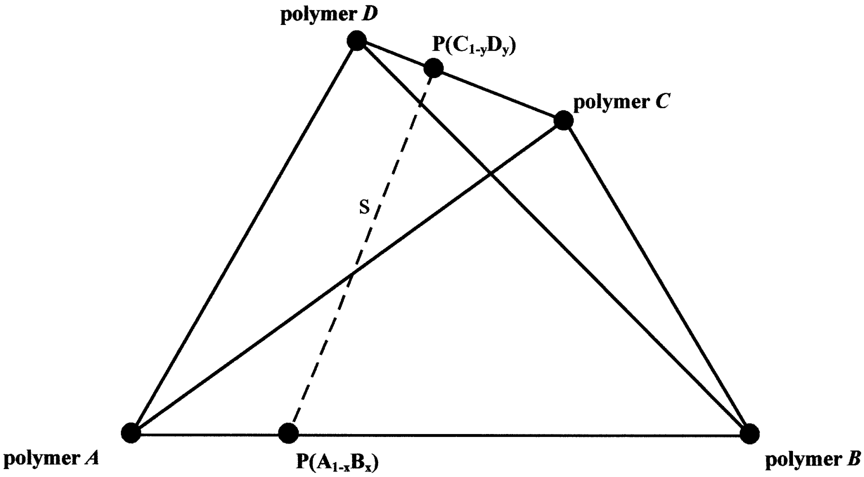

Fig. 3: Three dimensional scheme representing the interaction parameters between 4 polymer components. The interaction parameter between two statistical copolymer $P(A_{1-x}B_x)$ and $P(C_{1-y}D_y)$ is given by the distance s, as explained in the text.

The origin is again at polymer A and the vectors to polymer B and C are defined in the same way as in the sections above. Additional the vector from polymer A to polymer D is given by $\vec{D}$. The following relations can be seen from figure 3

$$\vec{C}^2 = \chi_{A/C} \tag{13}$$

$$\vec{B}^2 = \chi_{A/B} \tag{14}$$

$$\vec{D}^2 = \chi_{A/D} \tag{15}$$

$$\left|\vec{C} - \vec{B}\right|^2 = \chi_{C/B} \Rightarrow 2\vec{C}\vec{B} = \chi_{A/C} + \chi_{A/B} - \chi_{C/B} \tag{16}$$

$$\left|\vec{C} - \vec{D}\right|^2 = \chi_{C/D} \Rightarrow 2\vec{C}\vec{D} = \chi_{A/C} + \chi_{A/D} - \chi_{C/D} \tag{17}$$

$$\left|\vec{B} - \vec{D}\right|^2 = \chi_{B/D} \Rightarrow 2\vec{B}\vec{D} = \chi_{A/B} + \chi_{A/D} - \chi_{B/D} \tag{18}$$

The relevant value s^2 is thus given by

$$s^2 = \left|\vec{C} - x\vec{B} + y\left(\vec{D} - \vec{C}\right)\right|^2 = \left|(1-y)\vec{C} - x\vec{B} + y\vec{D}\right|^2 \tag{19}$$

$$s^2 = (1-y)^2\vec{C}^2 + 2(1-y)y\vec{C}\vec{D} - 2x(1-y)\vec{C}\vec{B} + y^2\vec{D}^2 - 2xy\vec{B}\vec{D} + x^2\vec{B}^2 \tag{20}$$

utilizing equations 13 to 18 yield

$$\begin{aligned} s^2 = &(1-x)(1-y)\chi_{A/C} + (1-x)y\chi_{A/D} + x(1-y)\chi_{B/C} + xy\chi_{B/D} \\ &- x(1-x)\chi_{A/B} - y(1-y)\chi_{D/C} \end{aligned} \tag{21}$$

This expression mirrors the mean -field interaction parameter in blends of $P(A_{1-x}B_x)$ and $P(C_{1-y}D_y)$ statistical copolymers (5).

It should be noted that minimal distance in the introduced scheme represents also the minimum of the interaction parameter for a specific choice of copolymer compositions x and y. For example the simple case of a homopolymer C blended with of $P(A_{1-x}B_x)$ as introduced by figure 1, is under consideration. The corresponding interaction parameter has a minimum for a particular composition x. Geometrically this value is given by $\tilde{x}$ in figure 1 where s is equal to h, the height in the triangle. This condition is fulfilled when

$$\left(\vec{C} - \tilde{x}\vec{B}\right)\perp\vec{B} \Rightarrow \left(\vec{C} - \tilde{x}\vec{B}\right)\vec{B} = 0 \tag{22}$$

$$\tilde{x} = \frac{\vec{B}\vec{C}}{\vec{B}^2} \tag{23}$$

and with equation 7

$$\tilde{x} = \frac{\chi_{A/B} + \chi_{A/C} - \chi_{B/C}}{2\chi_{A/B}} \tag{24}$$

Now this has to be compared with the particular value which minimizes the interaction parameter, differentiating equation 9 and equating zero

$$\frac{d(s^2)}{dx} = \frac{d\chi}{dx} = \frac{d}{dx}\left(x\chi_{B/C} + (1-x)\chi_{A/C} - x(1-x)\chi_{A/B}\right) = 0 \tag{25}$$

$$\chi_{B/C} - \chi_{A/C} - \chi_{A/B} + 2\tilde{x}\chi_{A/B} = 0 \tag{26}$$

$$\tilde{x} = \frac{\chi_{A/B} + \chi_{A/C} - \chi_{B/C}}{2\chi_{A/B}} \tag{27}$$

Equation 24 and 27 are equal, thus the equivalence of minimal distance and minimal interaction parameter is verified. The consequence of plotting and determining distances given by the square root of the interaction parameter has no influence on particular minimum values of corresponding interaction parameters. In other words, the minima of χ(x,y) are equal to the minima of $\sqrt{\chi(x, y)}$ which can be easily shown.

Consequently, all relevant information concerning the interaction parameters, also between the two statistical copolymers $P(A_{1-x}B_x)$.and $P(C_{1-y}D_y)$ are entirely represented by the suggested novel scheme.

Finally, the case of statistical copolymers consisting of tree components will be discussed. For simplification a blend of a homopolymer A and a statistical copolymer $P(A_{1-x-y}B_xC_y)$ is under consideration

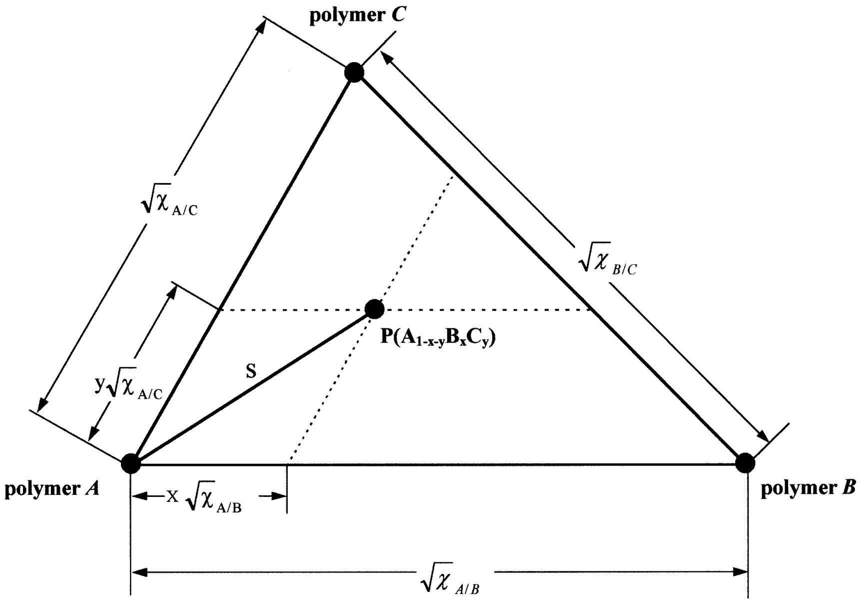

Fig. 4: Two dimensional scheme representing the interaction parameters between a homopolymer and a statisical copolymer consisting of three components *$P(A_{1-x-y}B_xC_y)$. The interaction parameter is given by distance s.*

The vector to $P(A_{1-x-v}B_xC_v)$ is given by

$$\vec{P}(A_{1-x-y}B_xC_y) = x\vec{B} + y\vec{C} \tag{28}$$

and thus

$$s^2 = x^2\vec{B}^2 + 2xy\vec{B}\vec{C} + y^2\vec{C}^2 \tag{29}$$

Utilizing equations 2a, 2b and 7 yields

$$s^2 = x^2\chi_{A/B} + xy(\chi_{A/B} + \chi_{A/C} - \chi_{B/C}) + y^2\chi_{A/C} \tag{30}$$

$$s^2 = x(x+y)\chi_{A/B} + y(x+y)\chi_{A/C} - xy\chi_{B/C} \tag{31}$$

In order to calculate the mean - field interaction parameter for this particular case one has to add the different combinations of interactions between the components in the two different polymers, first. Then one has to subtract the internal contact interactions in the copolymer.

$$\chi = \underbrace{(1-x-y)\chi_{AA} + x\chi_{AB} + y\chi_{A/C}}_{\text{homo} - \text{ copolymer contacts}} \underbrace{- x(1-x-y)\chi_{A/B} - y(1-x-y)\chi_{A/C} - xy\chi_{B/C}}_{\text{internal contacts}} \tag{32}$$

per definition χ_{AA} =0, rewriting equation 32 yields

$$\chi = x(x+y)\chi_{AB} + y(x+y)\chi_{A/C} - xy\chi_{B/C} \tag{33}$$

which is exactly the same result as obtained by analyzing the distance s, equation 31.

Furthermore, the interaction parameter for a blend of statistical copolymers $P(A_{1-x-y-z}B_xC_yD_z)$ and $P(A_{1-x'-y'-z'}B_{x'}C_{y'}D_{z'})$ can be read from the distance between the respective points.

$$\chi = \left|\vec{P}(A_{1-x-y-z}B_xC_yD_z) - \vec{P}(A_{1-x'-y'-z'}B_{x'}C_{y'}D_{z'})\right|^2 \tag{34}$$

with

$$\vec{P}(A_{1-x-y-z}B_xC_yD_z) = x\vec{B} + y\vec{C} + z\vec{D} \tag{35}$$

$$\vec{P}(A_{1-x'-y'-z'}B_{x'}C_{y'}D_{z'}) = x'\vec{B} + y'\vec{C} + z'\vec{D} \tag{36}$$

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