

Supporting Information

A Theoretical Study of Structure-Solubility Correlations of Carbon Dioxide in Polymers Containing Ether and Carbonyl Groups

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Computational Method

1. The Generator Matrix Method

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The second and the fourth moments $\langle r_{\alpha\gamma}^2 \rangle$ and $\langle r_{\alpha\gamma}^4 \rangle$ between the two points in the Koyama distribution function are calculated through the generator matrix method.¹ For the Cartesian coordinate system, suppose the supplementary angle of bond vector \vec{l}_i and \vec{l}_{i+1} to be θ_i in each macromolecule chain, and set $n = |\alpha - \gamma|$. The summation of the two sites α and γ can be expressed as

$$\vec{r}_{\alpha\gamma} = \sum_{i=1}^n \vec{l}_i \quad (1)$$

where $\vec{l}_i = (l_i, 0, 0)'$, l_i is the bond length and ' means transposing. Let T_i denote the matrix of the transformation between reference frames $i+1$ and i . For simplicity, the inner rotation of bond is supposed to be fully free, and independent between each other, thus

$$T_i = \begin{pmatrix} \cos \theta_i & \sin \theta_i & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2)$$

The square of the magnitude of the chain vector $r_{\alpha\gamma}^2$ between sites α and γ can be written as

$$\begin{aligned} r_{\alpha\gamma}^2 &= \vec{r}_{\alpha\gamma} \cdot \vec{r}_{\alpha\gamma} = \sum_{i=1}^n \vec{l}_i \cdot \sum_{j=1}^n \vec{l}_j = 2 \sum_{j>i=1}^n \vec{l}_i \cdot \vec{l}_j + \sum_{i=1}^n l_i^2 \\ &= 2 \sum_{j>i=1}^n \vec{l}_i T_i T_{i+1} \cdots T_{j-1} \vec{l}_j + \sum_{i=1}^n l_i^2 \end{aligned} \quad (3)$$

Here \vec{l}_i' is the transposed form of bond vector \vec{l}_i . The generator matrix with rows is

$$G_1 = (1 \quad 2\vec{l}_1' T_1 \quad l_1^2), \quad (4)$$

$$G_n = (l_n^2 \quad \vec{l}_n' \quad 1), \quad (5)$$

$$G_i = \begin{pmatrix} 1 & 2\vec{l}_i' T & l_i^2 \\ \vec{0} & T & \vec{l}_i' \\ 0 & \vec{0} & 1 \end{pmatrix}_i \quad (1 < i < n) \quad (6)$$

Therefore

$$r_{\alpha\gamma}^2 = \prod_{i=1}^n G_i \quad (7)$$

and the second moment can be symbolized by

$$\langle r_{\alpha\gamma}^2 \rangle = G_1 \left(\prod_{i=2}^{n-1} \langle G_i \rangle \right) G_n \quad (8)$$

with

$$\langle G_i \rangle = \begin{pmatrix} 1 & 2\vec{l}^i \langle T \rangle & l^2 \\ \vec{0} & \langle T \rangle & \vec{l} \\ 0 & \vec{0} & 1 \end{pmatrix}_i \quad (1 < i < n) \quad (9)$$

Set A and B to be $i \times j$ and $k \times l$ order matrix, respectively. The direct product $A \otimes B$ is $ik \times jl$ order matrix, which has the element $A_j B$ in the ith row and jth column. Correspondingly, the expression of $r_{\alpha\gamma}^4$ is obtained

$$r_{\alpha\gamma}^4 = \prod_{i=1}^n (G_i \otimes G_i) \triangleq \prod_{i=1}^n G_i^{\times 2} \quad (10)$$

The fourth moment can be given in the high order tensor form

$$\langle r_{\alpha\gamma}^4 \rangle = G_1^{\times 2} \left(\prod_{i=2}^{n-1} \langle G_i^{\times 2} \rangle \right) G_n^{\times 2} \quad (11)$$

2. Intramolecular Correlation Functions

For simplicity, PEC acts as an example. The repeat unit of PEC contains six sites. As shown in Figure 1, the sites A, B, C, D, E and F correspond to the CH₂, ether oxygen, carbonyl carbon, ether oxygen, emethylene and carbonyl oxygen, respectively. Accordingly, 21 independent intramolecular correlation

functions between the like sites as well as the unlike sites were obtained after some tedious algebraic summations. They were given as follows (due to the symmetry structure of PEC, 21 independent intramolecular correlation functions could be reduced to 13 independent intramolecular correlation functions)

$$\hat{\Omega}_{AA}(k) = \hat{\Omega}_{EE}(k) = 1 + \frac{2}{N} \sum_{i=1}^{N-1} (N-i) \hat{\omega}_{AA}(k) |_{n=5i} \quad (12)$$

$$\hat{\Omega}_{BB}(k) = \hat{\Omega}_{DD}(k) = 1 + \frac{2}{N} \sum_{i=1}^{N-1} (N-i) \hat{\omega}_{BB}(k) |_{n=5i} \quad (13)$$

$$\hat{\Omega}_{CC}(k) = 1 + \frac{2}{N} \sum_{i=1}^{N-1} (N-i) \hat{\omega}_{CC}(k) |_{n=5i} \quad (14)$$

$$\hat{\Omega}_{FF}(k) = 1 + \frac{2}{N} \sum_{i=1}^{N-1} (N-i) \hat{\omega}_{FF}(k) |_{n=5i+2} \quad (15)$$

$$\hat{\Omega}_{AB}(k) = \hat{\Omega}_{DE}(k) = \hat{\omega}_{AB}(k) |_{n=1} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{AB}(k) |_{n=5i+1} + \hat{\omega}_{AB}(k) |_{n=5i-1}] \quad (16)$$

$$\hat{\Omega}_{AC}(k) = \hat{\Omega}_{CE}(k) = \hat{\omega}_{AC}(k) |_{n=2} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{AC}(k) |_{n=5i+2} + \hat{\omega}_{AC}(k) |_{n=5i-2}] \quad (17)$$

$$\hat{\Omega}_{AD}(k) = \hat{\Omega}_{BE}(k) = \hat{\omega}_{AD}(k) |_{n=3} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{AD}(k) |_{n=5i+3} + \hat{\omega}_{AD}(k) |_{n=5i-3}] \quad (18)$$

$$\hat{\Omega}_{AE}(k) = \hat{\omega}_{AE}(k) |_{n=4} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{AE}(k) |_{n=5i+4} + \hat{\omega}_{AE}(k) |_{n=5i-4}] \quad (19)$$

$$\hat{\Omega}_{AF}(k) = \hat{\Omega}_{EF}(k) = \hat{\omega}_{AF}(k) |_{n=3} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{AF}(k) |_{n=5i+3} + \hat{\omega}_{AF}(k) |_{n=5i-1}] \quad (20)$$

$$\hat{\Omega}_{BC}(k) = \hat{\Omega}_{CD}(k) = \hat{\omega}_{BC}(k) |_{n=1} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{BC}(k) |_{n=5i+1} + \hat{\omega}_{BC}(k) |_{n=5i-1}] \quad (21)$$

$$\hat{\Omega}_{\text{BD}}(k) = \hat{\omega}_{\text{BD}}(k)|_{n=2} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{\text{BD}}(k)|_{n=5i+2} + \hat{\omega}_{\text{BD}}(k)|_{n=5i-2}] \quad (22)$$

$$\hat{\Omega}_{\text{BF}}(k) = \hat{\Omega}_{\text{DF}}(k) = \hat{\omega}_{\text{BF}}(k)|_{n=2} + \frac{1}{N} \sum_{i=1}^{N-1} (N-i) [\hat{\omega}_{\text{BF}}(k)|_{n=5i+2} + \hat{\omega}_{\text{BF}}(k)|_{n=5i-2}] \quad (23)$$

$$\hat{\Omega}_{\text{CF}}(k) = \hat{\omega}_{\text{CF}}(k)|_{n=1} + \frac{2}{N} \sum_{i=1}^{N-1} (N-i) \hat{\omega}_{\text{CF}}(k)|_{n=5i+1} \quad (24)$$

3. Reduced X-ray Scattering Intensity

The so called reduced X-ray scattering intensity is defined by

$$I(k) = k [i(k) - \langle f^2(k) \rangle] \quad (25)$$

here, k is scattering vector, and $k = 4\pi \sin \theta / \lambda$, λ is the wavelength of the scattered radiation, 2θ is the scattering angle, $i(k)$ is the scattering intensity per site, and $\langle f(k)^2 \rangle$ is the scattering factor squared averaged over all sites written in the form

$$\langle f^2(k) \rangle = \sum_{\alpha=1}^n x_{\alpha} f_{\alpha}^2(k) \quad (26)$$

In which n is the number of sites within a repeat unit of polymer, x_{α} and $f_{\alpha}(k)$ are the mole fraction and scattering factors of the sites, respectively. The scattering factors of different sites can be calculated following Narten's method²

$$f_{\alpha}(k) = \sum_{i=1}^4 a_{\alpha i} e^{-b_{\alpha i} k^2 / (16\pi^2)} + c_{\alpha} \quad (27)$$

The constants $a_{\alpha i}$, $b_{\alpha i}$ and c_{α} are also taken from reference.² The $i(k)$ can be written in terms of

$$i(k) = \sum_{\alpha\gamma} f_{\alpha}(k) f_{\gamma}(k) S_{\alpha\gamma}(k) / n \quad (28)$$

Here the $S_{\alpha\gamma}(k)$ is determined using the following equations

$$S_{\alpha\gamma}(k) = \omega_{\alpha\gamma}(k) + \rho_{\alpha} h_{\alpha\gamma}(k) \quad (29)$$

and ρ_{α} is the site density of type α

4. Densities for Polymers at Different Temperatures

The densities for PEO, PPO, PVAc, PEC, PPC at different temperatures are given in Table 1.

References

- 1 P. J. Flory, *Macromolecules*, 1974, **7**, 381.
- 2 A. H. Narten, *J. Chem. Phys.*, 1979, **70**, 299.

Table 1. Densities for polymers at different temperatures

<i>T</i> (K)	ρ (g/cm ³)				
	PEO	PPO	PVAc	PEC	PPC
298.15	1.19	0.986	1.19	1.32	1.20
318.15	1.17	0.971	1.17	1.30	1.18
338.15	1.15	0.956	1.15	1.28	1.17
358.15	1.12	0.941	1.14	1.26	1.16

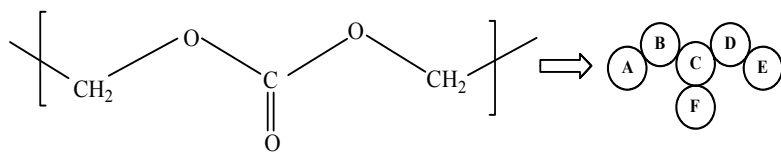


Figure 1. Graphic representation of PEC