Supporting Information

Structure-Property Relationships of Poly(ethylene carbonate) and Poly(propylene carbonate)

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Appendix A. Statistical weight matrices U_j's of poly(ethylene carbonate) (PEC).

For bond numbers of PEC, see Figure 1. Herein, the symbol ⊗ stands for direct product.

$$U_1 = U_2 = U_3 = C_1 \otimes R_1 \tag{A1}$$

$$U_4 = C_1 \otimes R_3 \tag{A2}$$

$$U_5 = I_3 \otimes R_3 \tag{A3}$$

$$U_6 = \begin{pmatrix} u_{\mathrm{ttt}} & u_{\mathrm{ttg^+}} & u_{\mathrm{ttg^-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_{\mathrm{tg^+t}} & u_{\mathrm{tg^+g^+}} & u_{\mathrm{tg^+g^-}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_{\mathrm{tg^-t}} & u_{\mathrm{tg^-g^+}} & u_{\mathrm{tg^-g^-}} \\ u_{\mathrm{g^+tt}} & u_{\mathrm{g^+tg^+}} & u_{\mathrm{g^+tg^-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_{\mathrm{g^+g^+t}} & u_{\mathrm{g^+g^+g^+}} & u_{\mathrm{g^+g^+g^-}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_{\mathrm{g^+g^-t}} & u_{\mathrm{g^+g^-g^+}} & u_{\mathrm{g^+g^-g^-}} \\ u_{\mathrm{g^-tt}} & u_{\mathrm{g^-tg^+}} & u_{\mathrm{g^-tg^-}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_{\mathrm{g^-g^+t}} & u_{\mathrm{g^-g^+g^+}} & u_{\mathrm{g^-g^+g^-}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_{\mathrm{g^-g^-t}} & u_{\mathrm{g^-g^-g^+}} & u_{\mathrm{g^-g^-g^-}} \end{pmatrix} \tag{A4}$$

$$U_{\mathrm{a}} = C_3 \otimes I_3 \otimes R_1 \tag{A5}$$

The U_{b} and U_{c} matrices are 9×9 in size. The (1,1), (4,1), and (7,1) elements of U_{b} are unity, and the others are null. The (1,1), (1,2), and (1,3) elements of U_{c} are unity, and the others are null.

$$U_{\mathrm{d}} = C_1 \otimes U_5 \tag{A6}$$

$$U_{\mathrm{e}} = U_6 \tag{A7}$$

$$U_{\mathrm{l}} = U_{\mathrm{a}} \tag{A8}$$

$$U_{\mathrm{m}} = U_{\mathrm{b}} \tag{A9}$$

and

$$U_{\mathrm{n}} = U_{\mathrm{c}} \tag{A10}$$

where

$$C_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{A11}$$

$$C_3 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{A12}$$

$$R_1 = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \tag{A13}$$

$$R_3 = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \tag{A14}$$

and

$$I_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{A15}$$

For example, the element $u_{tg^+g^-}$ of the U_6 matrix is the Boltzmann factor of the corresponding conformer free energy: $u_{tg^+g^-} = \exp(-\Delta G_{tg^+g^-}/RT)$, where tg^+g^- is the conformation in bonds 4−6 (viz., bonds 4, 5, and 6 are in the trans, gauche$^+$, and gauche$^-$ states, respectively), R is the gas constant, T is the absolute temperature, and the $\Delta G_{tg^+g^-}$ value was taken from that of E_model.

Appendix B. Statistical weight matrices of poly(propylene carbonate) (PPC).

The U matrices except U_6 and U_e are the same as those of PEC. The U_6 and U_e matrices of the (*R*)-orthodromic (T→H) form are expressed as

$$U^R_{\text{ortho, 6}} = U^R_{\text{ortho, e}} = \begin{array}{c} \\ t\ t \\ t\ g^+ \\ t\ g^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \end{array} \\ \begin{pmatrix} u_1 & u_2 & u_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_4 & u_5 & u_6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_7 & u_8 & u_9 \\ u_{10} & u_{11} & u_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_{13} & u_{14} & u_{15} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_{16} & u_{17} & u_{18} \\ u_{19} & u_{20} & u_{21} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_{22} & u_{23} & u_{24} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_{25} & u_{26} & u_{27} \end{pmatrix} \end{array} \tag{A16}$$

Here, the element is the Boltzmann factor of the free energy of the corresponding conformation; e.g., $u_6 = \exp(-\Delta G_{tg^+g^-}/RT)$. The U_6 and U_e matrices of the (*S*)-orthodromic (T→H) form can be derived from

$$U^S_{\text{ortho, 6}} = U^S_{\text{ortho, e}} = Q_9 \left(U^R_{\text{ortho, 6}} \right) Q_9 \tag{A17}$$

where

$$Q_9 = Q_3 \otimes Q_3 \tag{A18}$$

with

$$Q_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{A19}$$

The U_6 and U_e matrices of the (R)-antidromic (H→T) form are given as

$$U^{R}_{\text{anti, 6}} = U^{R}_{\text{anti, e}} = \begin{array}{c} \\ \text{t t} \\ \text{t g}^{+} \\ \text{t g}^{-} \\ \text{g}^{+}\text{t} \\ \text{g}^{+}\text{g}^{+} \\ \text{g}^{+}\text{g}^{-} \\ \text{g}^{-}\text{t} \\ \text{g}^{-}\text{g}^{+} \\ \text{g}^{-}\text{g}^{-} \end{array} \begin{array}{c} \begin{array}{ccccccccc} \text{t} & \text{g}^{+} & \text{g}^{-} & \text{t} & \text{g}^{+} & \text{g}^{-} & \text{t} & \text{g}^{+} & \text{g}^{-} \end{array} \\ \begin{pmatrix} u_1 & u_{10} & u_{19} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_4 & u_{13} & u_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_7 & u_{16} & u_{25} \\ u_2 & u_{11} & u_{20} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_5 & u_{14} & u_{23} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_8 & u_{17} & u_{26} \\ u_3 & u_{12} & u_{21} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & u_6 & u_{15} & u_{24} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & u_9 & u_{18} & u_{27} \end{pmatrix} \end{array} \tag{A20}$$

The elements here, $u_1 - u_{27}$, are the same as those in eq A16. The U_6 and U_e matrices of the (S)-antidromic (H→T) form can be derived from

$$U^{S}_{\text{anti, 6}} = U^{S}_{\text{anti, e}} = Q_9 \left(U^{R}_{\text{anti, 6}} \right) Q_9 \tag{A21}$$

Table S1. Geometrical Parameters of PEC, Used in the Refined RIS Calculations[a]

conformation						
bond						
$j-1$	j	$j+1$	l_j [b]	$\angle j \wedge (j+1)$ [c]	$\angle(j-1) \wedge j$ [d]	ϕ_j [e]
				bond a		
t	t	t	1.336	107.9	114.9	0.0
				bond b		
t	t	t	1.341	115.1	107.9	0.0
	t	g^+	1.343	116.1	107.7	0.3
	t	g^-	1.343	116.1	107.7	−0.3
				bond c (e)		
t	t	t	1.439	105.6	115.1	0.0
	g^+		1.439	109.6	116.1	91.1
	g^-		1.439	109.6	116.1	−91.1
	t	g^+	1.440	108.1	115.0	−2.4
	g^+		1.441	112.6	115.8	95.0
	g^-		1.439	112.2	115.6	−98.1
	t	g^-	1.440	108.1	115.0	2.4
	g^+		1.439	112.2	115.6	98.1
	g^-		1.441	112.6	115.8	−95.0
				bond d		
t	t	t	1.515	105.6	105.6	0.0
	g^+		1.504	108.1	108.1	108.4
	g^-		1.504	108.1	108.1	−108.4
g^+	t		1.519	105.6	109.6	5.4
	g^+		1.509	108.0	112.6	111.9
	g^-		–	–	–	–
g^-	t		1.519	105.6	109.6	−5.4
	g^+		–	–	–	–
	g^-		1.509	108.0	112.6	−111.9
t	t	g^+	1.519	109.6	105.6	5.4
	g^+		1.509	112.6	108.0	111.9
	g^-		–	–	–	–
g^+	t		1.522	108.8	108.8	12.3
	g^+		1.514	112.7	112.7	118.4
	g^-		–	–	–	–
g^-	t		1.523	109.8	109.8	0.0
	g^+		1.514	112.2	110.5	114.4
	g^-		1.514	110.5	112.2	−114.4
t	t	g^-	1.519	109.6	105.6	−5.4
	g^+		–	–	–	–
	g^-		1.509	112.6	108.0	−111.9
g^+	t		1.523	109.8	109.8	0.0
	g^+		1.514	110.5	112.2	114.4
	g^-		1.514	112.2	110.5	−114.4
g^-	t		1.522	108.8	108.8	−12.3
	g^+		–	–	–	–
	g^-		1.514	112.7	112.7	−118.4

[a]Obtained from the geometrical optimization for E_model at the B3LYP/6-311+G(2d,p) level. For the terminal CH_3-O bonds, the bond length and bond angle were, respectively, set equal to 1.439 Å and 114.9°, and the 3-fold rotational symmetry was assumed. j denotes the current bond. [b]Length of bond j. [c]Angle formed between bonds j and $j+1$. [d]Angle formed between bonds $j-1$ and j. [e]Dihedral angle of bond j. For the bond numbers, see Figure 1.

Table S2. Geometrical Parameters of PPC, Used in the Refined RIS Calculations[a]

conformation					
bond					
$j-1$	j	$j+1$	l_j [b]	$\angle j \wedge (j+1)$ [c]	ϕ_j [d]
				bond a	
t	t	t	1.337	107.9	0.0
				bond b	
t	t	t	1.340	115.2	0.1
	t	g^+	1.340	115.7	−0.6
	t	g^-	1.343	116.2	0.6
				bond c	
t	t	t	1.439	106.6	−0.3
	g^+		–	–	–
	g^-		1.439	110.4	−89.1
	t	g^+	1.439	108.0	−2.5
	g^+		1.440	112.2	93.7
	g^-		1.442	110.3	−77.9
	t	g^-	1.440	109.2	3.0
	g^+		1.440	111.2	74.8
	g^-		1.441	111.9	−67.0
				bond d	
t	t	t	1.522	103.6	4.7
	g^+		1.512	106.2	110.4
	g^-		1.513	106.7	−110.4
g^+	t		–	–	–
	g^+		1.517	106.2	112.8
	g^-		–	–	–
g^-	t		1.527	103.5	1.4
	g^+		–	–	–
	g^-		1.517	106.8	−111.9
t	t	g^+	1.527	110.7	21.1
	g^+		1.517	112.7	120.4
	g^-		1.518	110.3	−104.2
g^+	t		–	–	–
	g^+		1.523	112.4	124.9
	g^-		–	–	–
g^-	t		1.532	111.0	17.3
	g^+		1.522	111.3	111.9
	g^-		1.523	110.1	−111.9
t	t	g^-	1.524	106.9	3.1
	g^+		1.512	106.2	110.4
	g^-		1.518	110.5	−113.1
g^+	t		–	–	–
	g^+		1.522	108.2	120.8
	g^-		1.522	109.9	−114.4
g^-	t		–	–	–
	g^+		–	–	–
	g^-		1.522	110.7	−115.5
				bond e	
t	t	t	1.452	116.5	−30.0
	g^+		1.455	119.1	116.6
	g^-		1.452	116.7	−92.4
g^+	t		1.452	116.5	−31.1
	g^+		1.455	119.5	116.7
	g-		1.449	116.9	−76.6
g^-	t		1.454	116.2	−31.2
	g^+		1.456	122.2	90.5
	g^-		1.453	116.5	−97.9

[a]Obtained from the geometrical optimization for (*R*)-P_model at the B3LYP/6-311+G(2d,p) level. For the terminal CH_3-O bonds, the bond length and bond angle were, respectively, set equal to 1.439 Å and 114.9°, and the 3-fold rotational symmetry was assumed. j denotes the current bond. [b]Length of bond j. [c]Angle formed between bonds j and $j+1$. [d]Dihedral angle of bond j. For the bond numbers, see Figure 1.

Table S3. Fractions of Reigo- and Stereosequences in Bernoulli and Markov Statistics for PPC

					stereosequence					
		regiosequence			diad		triad			
	probability[a]	H-T	H-H	T-T	*meso*	*racemo*	*mm*	*mr*	*rm*	*rr*
Bernoulli	0.00	1.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00
	0.10	0.82	0.09	0.09	0.82	0.18	0.73	0.09	0.09	0.09
	0.20	0.68	0.16	0.16	0.68	0.32	0.52	0.16	0.16	0.16
	0.30	0.58	0.21	0.21	0.58	0.42	0.37	0.21	0.21	0.21
	0.40	0.52	0.24	0.24	0.52	0.48	0.28	0.24	0.24	0.24
	0.50	0.50	0.25	0.25	0.50	0.50	0.25	0.25	0.25	0.25
	0.60	0.52	0.24	0.24	0.52	0.48	0.28	0.24	0.24	0.24
	0.70	0.58	0.21	0.21	0.58	0.42	0.37	0.21	0.21	0.21
	0.80	0.68	0.16	0.16	0.68	0.32	0.52	0.16	0.16	0.16
	0.90	0.82	0.09	0.09	0.82	0.18	0.73	0.09	0.09	0.09
	1.00	1.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00
Markov	0.00	0.00	0.50	0.50	0.00	1.00	0.00	0.00	0.00	1.00
	0.10	0.10	0.45	0.45	0.10	0.90	0.01	0.09	0.09	0.81
	0.20	0.20	0.40	0.40	0.20	0.80	0.04	0.16	0.16	0.64
	0.30	0.30	0.35	0.35	0.30	0.70	0.09	0.21	0.21	0.49
	0.40	0.40	0.30	0.30	0.40	0.60	0.16	0.24	0.24	0.36
	0.50	0.50	0.25	0.25	0.50	0.50	0.25	0.25	0.25	0.25
	0.60	0.60	0.20	0.20	0.60	0.40	0.36	0.24	0.24	0.16
	0.70	0.70	0.15	0.15	0.70	0.30	0.49	0.21	0.21	0.09
	0.80	0.80	0.10	0.10	0.80	0.20	0.64	0.16	0.16	0.04
	0.90	0.90	0.05	0.05	0.90	0.10	0.81	0.09	0.09	0.01
	1.00	1.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00

[a] For the Bernoulli trial, p_{ortho} (regiosequence) and p_R (stereosequence). For the Markov process, $p_{\mathrm{H-T}}$ (regiosequence) and p_{meso} (stereosequence).