Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Conformational Characteristics of Poly(3-hydroxyvalerate) (P3HV) and Structure-Property Relationships of P3HV and Poly(3-hydroxybutyrate)

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Appendix. Statistical Weight Matrices, U_j's (j: bond number), of Poly((*R*)-3-hydroxyvalerate)

For the bond designation, see Fig. 1. The U_j matrices of the first unit are

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

$$U_3 = C_1 \otimes R_3 \tag{A2}$$

$$U_4 = I_3 \otimes R_3 \otimes R_3 \otimes R_3 \tag{A3}$$

where $\otimes$ stands for the direct product,

$$C_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{A4}$$

$$R_1 = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \tag{A5}$$

$$R_3 = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \tag{A6}$$

and

$$I_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{A7}$$

The (l, m) $(l, m = 1 - 27)$ elemnts of U_6 are defined as follows:

(1,1)	(1,2)	(1,3)	(2,4)	(2,5)	(2,6)	(3,7)	(3,8)	(3,9)
$u_{\mathrm{tt(t)t}}$	$u_{\mathrm{tt(t)g^+}}$	$u_{\mathrm{tt(t)g^-}}$	$u_{\mathrm{tt(g^+)t}}$	$u_{\mathrm{tt(g^+)g^+}}$	$u_{\mathrm{tt(g^+)g^-}}$	$u_{\mathrm{tt(g^-)t}}$	$u_{\mathrm{tt(g^-)g^+}}$	$u_{\mathrm{tt(g^-)g^-}}$
(4,10)	(4,11)	(4,12)	(5,13)	(5,14)	(5,15)	(6,16)	(6,17)	(6,18)
$u_{\mathrm{tg^+(t)t}}$	$u_{\mathrm{tg^+(t)g^+}}$	$u_{\mathrm{tg^+(t)g^-}}$	$u_{\mathrm{tg^+(g^+)t}}$	$u_{\mathrm{tg^+(g^+)g^+}}$	$u_{\mathrm{tg^+(g^+)g^-}}$	$u_{\mathrm{tg^+(g^-)t}}$	$u_{\mathrm{tg^+(g^-)g^+}}$	$u_{\mathrm{tg^+(g^-)g^-}}$
(7,19)	(7,20)	(7,21)	(8,22)	(8,23)	(8,24)	(9,25)	(9,26)	(9,27)
$u_{\mathrm{tg^-(t)t}}$	$u_{\mathrm{tg^-(t)g^+}}$	$u_{\mathrm{tg^-(t)g^-}}$	$u_{\mathrm{tg^-(g^+)t}}$	$u_{\mathrm{tg^-(g^+)g^+}}$	$u_{\mathrm{tg^-(g^+)g^-}}$	$u_{\mathrm{tg^-(g^-)t}}$	$u_{\mathrm{tg^-(g^-)g^+}}$	$u_{\mathrm{tg^-(g^-)g^-}}$
(10,1)	(10,2)	(10,3)	(11,4)	(11,5)	(11,6)	(12,7)	(12,8)	(12,9)
$u_{\mathrm{g^+t(t)t}}$	$u_{\mathrm{g^+t(t)g^+}}$	$u_{\mathrm{g^+t(t)g^-}}$	$u_{\mathrm{g^+t(g^+)t}}$	$u_{\mathrm{g^+t(g^+)g^+}}$	$u_{\mathrm{g^+t(g^+)g^-}}$	$u_{\mathrm{g^+t(g^-)t}}$	$u_{\mathrm{g^+t(g^-)g^+}}$	$u_{\mathrm{g^+t(g^-)g^-}}$
(13,10)	(13,11)	(13,12)	(14,13)	(14,14)	(14,15)	(15,16)	(15,17)	(15,18)
$u_{\mathrm{g^+g^+(t)t}}$	$u_{\mathrm{g^+g^+(t)g^+}}$	$u_{\mathrm{g^+g^+(t)g^-}}$	$u_{\mathrm{g^+g^+(g^+)t}}$	$u_{\mathrm{g^+g^+(g^+)g^+}}$	$u_{\mathrm{g^+g^+(g^+)g^-}}$	$u_{\mathrm{g^+g^+(g^-)t}}$	$u_{\mathrm{g^+g^+(g^-)g^+}}$	$u_{\mathrm{g^+g^+(g^-)g^-}}$
(16,19)	(16,20)	(16,21)	(17,22)	(17,23)	(17,24)	(18,25)	(18,26)	(18,27)
$u_{\mathrm{g^+g^-(t)t}}$	$u_{\mathrm{g^+g^-(t)g^+}}$	$u_{\mathrm{g^+g^-(t)g^-}}$	$u_{\mathrm{g^+g^-(g^+)t}}$	$u_{\mathrm{g^+g^-(g^+)g^+}}$	$u_{\mathrm{g^+g^-(g^+)g^-}}$	$u_{\mathrm{g^+g^-(g^-)t}}$	$u_{\mathrm{g^+g^-(g^-)g^+}}$	$u_{\mathrm{g^+g^-(g^-)g^-}}$
(19,1)	(19,2)	(19,3)	(20,4)	(20,5)	(20,6)	(21,7)	(21,8)	(21,9)
$u_{\mathrm{g^-t(t)t}}$	$u_{\mathrm{g^-t(t)g^+}}$	$u_{\mathrm{g^-t(t)g^-}}$	$u_{\mathrm{g^-t(g^+)t}}$	$u_{\mathrm{g^-t(g^+)g^+}}$	$u_{\mathrm{g^-t(g^+)g^-}}$	$u_{\mathrm{g^-t(g^-)t}}$	$u_{\mathrm{g^-t(g^-)g^+}}$	$u_{\mathrm{g^-t(g^-)g^-}}$
(22,10)	(22,11)	(22,12)	(23,13)	(23,14)	(23,15)	(24,16)	(24,17)	(24,18)
$u_{\mathrm{g^-g^+(t)t}}$	$u_{\mathrm{g^-g^+(t)g^+}}$	$u_{\mathrm{g^-g^+(t)g^-}}$	$u_{\mathrm{g^-g^+(g^+)t}}$	$u_{\mathrm{g^-g^+(g^+)g^+}}$	$u_{\mathrm{g^-g^+(g^+)g^-}}$	$u_{\mathrm{g^-g^+(g^-)t}}$	$u_{\mathrm{g^-g^+(g^-)g^+}}$	$u_{\mathrm{g^-g^+(g^-)g^-}}$
(25,19)	(25,20)	(25,21)	(26,22)	(26,23)	(26,24)	(27,25)	(27,26)	(27,27)
$u_{\mathrm{g^-g^-(t)t}}$	$u_{\mathrm{g^-g^-(t)g^+}}$	$u_{\mathrm{g^-g^-(t)g^-}}$	$u_{\mathrm{g^-g^-(g^+)t}}$	$u_{\mathrm{g^-g^-(g^+)g^+}}$	$u_{\mathrm{g^-g^-(g^+)g^-}}$	$u_{\mathrm{g^-g^-(g^-)t}}$	$u_{\mathrm{g^-g^-(g^-)g^+}}$	$u_{\mathrm{g^-g^-(g^-)g^-}}$

where, for example,

$$u_{\mathrm{tg^+(g^-)t}} = \exp(-\Delta G_{\mathrm{tg^+(g^-)t}}/RT) \tag{A8}$$

is the statistical weight of the $\mathrm{tg^+(g^-)t}$ conformation, in which bonds 3, 4, 5 (side chain, in the parenthesis) and 6 adopt trans, gauche$^+$, (gauche$^-$) and trans states, respectively. $\Delta G_{\mathrm{tg^+(g^-)t}}$ is its conformational free energy, R is the gas constant and T is the absolute temperature. The other elements of U_6 and weights of the absent conformations are null.

The U_j matrices of the subsequent repeating unit are

$$U_{\mathrm{a}} = C_3 \otimes C_3 \otimes I_3 \otimes R_3 \tag{A9}$$

$$U_{\mathrm{b}} = C_3 \otimes C_3 \otimes R_3 \tag{A10}$$

$$U_{\mathrm{c}} = U_4 \tag{A11}$$

$$U_{\mathrm{e}} = U_6 \tag{A12}$$

$$U_{n-1} = U_a \tag{A13}$$

and

$$U_n = U_b \tag{A14}$$

where

$$C_3 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{A15}$$

Table S1 Optimized and experimental fractional coordinates and geometrical parameters of P3HB and P3HV crystals

	Optimized [a]			Experimental [b]		
			P3HB [c]			
Fractional Coordinates						
	x/a	y/b	z/c	x/a	y/b	z/c
C	0.458	−0.079	0.255	0.437	−0.068	0.217
C	0.292	−0.139	0.415	0.318	−0.139	0.389
C	0.112	−0.077	0.552	0.143	−0.077	0.513
C	0.606	−0.150	0.102	0.587	−0.140	0.052
O	0.197	0.015	0.611	0.232	0.017	0.585
O	−0.087	−0.109	0.606	−0.057	−0.105	0.558
H	0.576	−0.029	0.353	0.557	−0.020	0.294
H	0.407	−0.179	0.539	0.447	−0.171	0.499
H	0.191	−0.197	0.322	0.226	−0.200	0.301
H	0.718	−0.107	−0.020	0.667	−0.092	−0.076
H	0.489	−0.201	0.005	0.464	−0.192	−0.036
H	0.725	−0.196	0.210	0.710	−0.182	0.143
			$\Delta_{CHO} = 0.054$ [d]			
Geometrical Parameters						
Bond length (Å)						
C(=O)−O		1.341			1.42	
O−CH		1.462			1.42	
CH−CH_2		1.523			1.55	
CH−CH_3		1.522			1.62	
CH_2−C(=O)		1.513			1.49	
Bond angle (°)						
C(=O)−O−CH		117.2			110	
O−CH−CH_2		106.7			110	
CH−CH_2−C(=O)		116.3			107	
CH_2−C(=O)−O		112.9			113	
			P3HV [e]			
Fractional Coordinates						
	x/a	y/b	z/c	x/a	y/b	z/c
C	0.238	−0.132	0.937	0.240	−0.121	0.900
C	0.359	−0.164	0.762	0.358	−0.161	0.745
C	0.412	−0.048	0.600	0.398	−0.049	0.575
C	0.531	−0.098	0.429	0.527	−0.092	0.416
C	0.587	0.011	0.252	0.578	0.026	0.268
O	0.291	−0.003	0.453	0.282	−0.013	0.426
O	0.174	−0.221	0.049	0.160	−0.201	0.004
H	0.451	−0.203	−0.132			
H	0.322	−0.250	−0.349			
H	0.448	0.040	−0.293			
H	−0.380	−0.136	−0.457			
H	0.491	−0.186	0.328			
H	−0.335	−0.036	0.129			
H	0.500	0.053	0.142			
H	−0.360	0.097	0.345			
			$\Delta_{CO} = 0.029$ [f]			
Geometrical Parameters [g]						
Bond length (Å)						
C(=O)−O		1.339			1.36	
O−CH		1.460			1.41	
CH−$CH_{2,m}$		1.524			1.51	
CH−$CH_{2,s}$		1.531			1.55	
$CH_{2,m}$−C(=O)		1.514			1.46	
Bond angle (°)						
C(=O)−O−CH		119.0			115	
O−CH−$CH_{2,m}$		107.5			111	
CH−$CH_{2,m}$−C(=O)		117.4			111	
O−CH−$CH_{2,s}$		108.1			109	
$CH_{2,m}$−C(=O)−O		113.1			116	

[a]This study. At 0 K. [b](PH3B) M. Yokouchi, Y. Chatani, H. Tadokoro, K. Teranishi and H. Tani, *Polymer,* 1973, **14,** 267-272. (P3HV) M. Yokouchi, Y. Chatani, H. Tadokoro and H. Tani, *Polym. J. (Tokyo, Jpn),* 1974, **6,** 248-255. At room temperature. [c]Orthorhombic, space group $P2_12_12_1$. [d]Representing the difference between theory and experiment:

$$\Delta_{CHO} = \frac{1}{N_{atom}} \sum_{atom} \left\{ \left[\left(\frac{x}{a}\right)_{calc} - \left(\frac{x}{a}\right)_{expt} \right]^2 + \left[\left(\frac{y}{b}\right)_{calc} - \left(\frac{y}{b}\right)_{expt} \right]^2 + \left[\left(\frac{z}{c}\right)_{calc} - \left(\frac{z}{c}\right)_{expt} \right]^2 \right\}^{1/2}$$

which was calculated for carbon, hydrogen and oxygen atoms. [e]Orthorhombic, space group $P2_12_12_1$. [f]Calculated for carbon and oxygen atoms. [g]$CH_{2,m}$ and $CH_{2,s}$ stand for methylene groups of the main and side chains, respectively.

Table S2 Conformer free energies of M3AV, used in refined RIS calculations on P3HV

Bond [a]				ΔG (kcal mol^{-1})					
3	4	5	6	Gas	Benzene	Chloroform	Acetone	Methanol	DMSO
t	t	(t)	t	0.00	0.00	0.00	0.00	0.00	0.00
t	t	(t)	g^-	0.41	0.37	0.40	0.46	0.47	0.48
t	t	(g^+)	t	−0.85	−0.81	−0.78	−0.77	−0.76	−0.76
t	t	(g^+)	g^-	−0.56	−0.55	−0.51	−0.44	−0.43	−0.42
t	g^+	(t)	t	−0.98	−1.14	−1.23	−1.32	−1.34	−1.34
t	g^+	(t)	g^+	−1.18	−1.41	−1.51	−1.58	−1.59	−1.59
t	g^+	(g^+)	t	−0.92	−1.06	−1.15	−1.25	−1.27	−1.27
t	g^+	(g^+)	g^+	−0.64	−0.85	−0.95	−1.02	−1.03	−1.03
t	g^+	(g^-)	t	−1.11	−1.31	−1.48	−1.68	−1.70	−1.72
t	g^-	(t)	g^+	−0.33	−0.30	−0.26	−0.24	−0.23	−0.22
t	g^-	(t)	g^-	0.16	0.00	−0.07	−0.13	−0.14	−0.14
g^+	t	(t)	t	2.13	2.36	2.51	2.67	2.69	2.71
g^+	t	(t)	g^-	2.99	3.09	3.16	3.23	3.24	3.25
g^+	t	(g^+)	t	3.82	4.11	4.28	4.43	4.45	4.46
g^+	t	(g^+)	g^-	4.34	4.47	4.54	4.60	4.60	4.61
g^+	t	(g^-)	t	0.29	0.56	0.74	0.91	0.94	0.96
g^+	t	(g^-)	g^-	1.44	1.48	1.52	1.56	1.56	1.57
g^+	g^+	(t)	t	1.73	1.74	1.75	1.77	1.77	1.78
g^+	g^+	(t)	g^+	1.74	1.77	1.81	1.84	1.85	1.85
g^+	g^+	(g^+)	t	4.04	4.09	4.08	4.05	4.04	4.04
g^+	g^+	(g^+)	g^+	4.25	4.40	4.45	4.45	4.45	4.45
g^+	g^+	(g^-)	t	0.67	0.68	0.70	0.70	0.70	0.71
g^+	g^+	(g^-)	g^+	1.22	1.27	1.30	1.32	1.32	1.32
g^+	g^-	(t)	g^+	3.27	3.54	3.64	3.66	3.66	3.66
g^+	g^-	(t)	g^-	3.73	3.90	3.98	4.01	4.01	4.02
g^+	g^-	(g^+)	t	7.84	8.07	8.14	8.14	8.13	8.13
g^+	g^-	(g^+)	g^-	9.13	9.47	9.64	9.73	9.73	9.74
g^+	g^-	(g^-)	g^+	2.88	3.00	3.01	2.96	2.95	2.95
g^+	g^-	(g^-)	g^-	3.20	3.32	3.36	3.36	3.35	3.35
g^-	t	(t)	t	0.07	0.06	0.04	−0.03	−0.04	−0.04
g^-	t	(t)	g^-	0.34	0.25	0.21	0.18	0.18	0.18
g^-	t	(g^+)	t	−0.23	−0.05	0.05	0.16	0.17	0.18
g^-	t	(g^+)	g^-	−0.97	−0.94	−0.90	−0.85	−0.85	−0.84
g^-	t	(g^-)	t	−1.46	−1.32	−1.23	−1.14	−1.13	−1.13
g^-	t	(g^-)	g^-	−1.40	−1.47	−1.49	−1.48	−1.48	−1.48
g^-	g^+	(t)	g^+	−0.93	−0.89	−0.85	−0.82	−0.82	−0.81
g^-	g^+	(t)	g^-	−0.26	−0.41	−0.49	−0.59	−0.60	−0.60
g^-	g^+	(g^+)	g^+	−1.01	−0.91	−0.85	−0.81	−0.81	−0.81
g^-	g^+	(g^+)	g^-	−0.20	−0.30	−0.36	−0.44	−0.45	−0.45
g^-	g^+	(g^-)	g^+	−1.51	−1.44	−1.40	−1.37	−1.37	−1.37
g^-	g^+	(g^-)	g^-	−0.95	−1.08	−1.15	−1.24	−1.25	−1.26
g^-	g^-	(t)	g^+	−0.76	−0.62	−0.53	−0.44	−0.43	−0.42
g^-	g^-	(t)	g^-	−0.33	−0.30	−0.26	−0.21	−0.21	−0.20
g^-	g^-	(g^+)	g^+	1.68	1.79	1.87	1.95	1.96	1.97
g^-	g^-	(g^+)	g^-	1.70	1.88	1.99	2.07	2.08	2.09
g^-	g^-	(g^-)	g^+	−1.03	−0.99	−0.95	−0.89	−0.88	−0.87
g^-	g^-	(g^-)	g^-	−0.87	−0.84	−0.82	−0.79	−0.79	−0.79

[a] See Fig. 1.

Table S3 NMR vicinal coupling constants of M3AV-^{13}C [a]

Solvent	Temp (°C)	$^3J_{AX}$		$^3J_{AB}$	$^3J_{AC}$	$^3J_{AD}$	$^3J_{AE}$
		Obs	Clac	Obs			
Benzene-d_6	15	3.36	3.46	7.58	5.00	5.12	6.99
	25	3.36	3.47	7.55	5.03	5.15	6.96
	35	3.36	3.48	7.53	5.05	5.16	6.95
	45	3.36	3.48	7.48	5.10	5.17	6.94
	55	3.36	3.48	7.43	5.13	5.19	6.91
Chloroform-d	15	3.39	3.45	7.83	5.16	5.33	7.16
	25	3.39	3.46	7.75	5.20	5.34	7.15
	35	3.39	3.46	7.71	5.22	5.37	7.12
	45	3.39	3.47	7.66	5.24	5.40	7.09
	55	3.39	3.47	7.58	5.30	5.42	7.07
Acetone-d_6	5	3.42	3.45	7.90	4.81	5.10	7.04
	15	3.42	3.45	7.89	4.82	5.13	7.01
	25	3.42	3.45	7.85	4.86	5.15	6.98
	35	3.42	3.46	7.82	4.89	5.17	6.96
	45	3.42	3.47	7.79	4.92	5.18	6.95
Methanol-d_4	5	3.42	3.45	8.21	4.43	5.08	7.12
	15	3.42	3.45	8.11	4.48	5.11	7.08
	25	3.42	3.45	8.02	4.54	5.14	7.05
	35	3.42	3.46	7.99	4.57	5.16	7.02
	45	3.42	3.46	7.95	4.61	5.19	6.99
	55	3.42	3.47	7.92	4.64	5.21	6.97
DMSO-d_6	25	3.42	3.45	8.15	4.89	5.19	7.16
	35	3.42	3.46	8.10	4.95	5.23	7.12
	45	3.42	3.47	8.03	5.01	5.24	7.11
	55	3.43	3.46	7.96	5.08	5.29	7.04

[a] In Hz. A−E stand for hydrogen atoms (protons), and X represents the ^{13}C labeled carbonyl atom (see Fig. 1c).

Table S4 Bond conformations of (*R*)-M3AV, evaluated from NMR vicinal coupling constants

		Bond [a]					
		4			5		
Solvent	Temp (°C)	p_{t}	$p_{\mathrm{g+}}$	$p_{\mathrm{g-}}$	p_{t}	$p_{\mathrm{g+}}$	$p_{\mathrm{g-}}$
Benzene-d_6	15	0.30	0.56	0.14	0.29	0.23	0.48
	25	0.30	0.56	0.14	0.29	0.23	0.48
	35	0.31	0.55	0.14	0.29	0.24	0.47
	45	0.31	0.55	0.14	0.29	0.24	0.47
	55	0.31	0.54	0.15	0.29	0.24	0.47
Chloroform-*d*	15	0.34	0.57	0.09	0.32	0.19	0.49
	25	0.34	0.57	0.09	0.32	0.19	0.49
	35	0.34	0.56	0.10	0.33	0.19	0.49
	45	0.34	0.56	0.10	0.33	0.19	0.48
	55	0.34	0.55	0.11	0.33	0.19	0.48
Acetone-d_6	5	0.29	0.59	0.12	0.29	0.23	0.48
	15	0.29	0.59	0.12	0.29	0.23	0.48
	25	0.29	0.59	0.12	0.29	0.23	0.48
	35	0.30	0.58	0.12	0.29	0.23	0.48
	45	0.30	0.58	0.12	0.29	0.23	0.48
Methanol-d_4	5	0.26	0.63	0.11	0.29	0.22	0.49
	15	0.26	0.62	0.12	0.29	0.22	0.49
	25	0.26	0.61	0.13	0.29	0.22	0.49
	35	0.26	0.61	0.13	0.30	0.22	0.48
	45	0.27	0.60	0.13	0.30	0.23	0.47
	55	0.27	0.60	0.13	0.30	0.23	0.47
DMSO-d_6	25	0.32	0.61	0.07	0.31	0.20	0.49
	35	0.32	0.61	0.07	0.31	0.20	0.49
	45	0.33	0.60	0.07	0.31	0.20	0.49
	55	0.33	0.59	0.08	0.31	0.20	0.49

[a] See Fig. 1.

Table S5 Geometrical parameters of P3HV, used in refined RIS calculations [a]

Conformation [b]					
$j-1$	j	$j+1$	l_j [c]	$\angle j \wedge (j+1)$ [d]	ϕ_j [e]
			Bond a		
1	1	1	1.353	117.4	0.3
2	1	1	1.353	117.4	0.3
3	1	1	1.353	117.4	0.3
1	1	2	1.348	120.1	2.4
2	1	2	1.348	120.1	2.4
3	1	2	1.348	120.1	2.4
1	1	3	1.351	117.7	−2.2
2	1	3	1.351	117.7	−2.2
3	1	3	1.351	117.7	−2.2
			Bond b		
1	1	1	1.459	105.2	−29.0
1	2	1	1.462	111.5	119.6
1	3	1	1.458	108.7	−97.8
1	1	2	1.459	104.7	−31.9
1	2	2	1.465	112.9	132.4
1	3	2	1.459	108.2	−98.0
1	1	3	1.455	107.6	−34.5
1	2	3	1.463	110.9	117.6
1	3	3	1.458	108.3	−96.9
1	1	4	1.456	105.3	−28.4
1	2	4	1.462	110.9	113.6
1	3	4	1.452	108.3	−80.3
1	1	5	1.457	105.6	−29.0
1	2	5	1.465	113.7	130.9
1	3	5	1.452	108.7	−80.2
1	1	6	1.455	106.1	−44.8
1	2	6	1.463	111.0	113.8
1	3	6	1.451	108.6	−80.5
1	1	7	1.456	106.0	−38.6
1	2	7	1.463	111.9	108.9
1	3	7	1.455	109.1	−97.2
1	1	8	1.455	107.6	−34.5
1	2	8	1.463	114.0	129.9
1	3	8	1.450	111.2	−101.1
1	1	9	1.455	107.6	−34.5
1	2	9	1.463	112.0	109.0
1	3	9	1.455	109.5	−96.6
			Bond c		
1	1	1	1.528	113.6	26.1
1	2	1	1.526	113.4	9.4
1	3	1	1.531	113.5	6.6
1	4	1	1.521	113.1	113.3
1	5	1	1.521	113.0	111.3
1	6	1	1.523	113.7	114.6
1	7	1	1.531	113.5	−123.3
1	8	1	1.531	113.5	−123.3
1	9	1	1.531	113.5	−123.3
2	1	1	1.533	112.8	37.8
2	2	1	1.530	111.8	26.4
2	3	1	1.529	112.3	24.8
2	4	1	1.527	112.5	114.1
2	5	1	1.527	112.9	114.8
2	6	1	1.527	112.4	114.6
2	7	1	1.531	113.5	−123.3
2	8	1	1.540	120.1	−90.2
2	9	1	1.531	113.5	−123.3
3	1	1	1.530	113.8	21.8
3	2	1	1.528	113.5	7.0
3	3	1	1.527	113.4	10.3
3	4	1	1.531	113.5	113.7
3	5	1	1.531	113.5	113.7
3	6	1	1.531	113.5	113.7
3	7	1	1.531	113.5	−123.3
3	8	1	1.531	113.5	−123.3
3	9	1	1.531	113.5	−123.3
1	1	2	1.531	113.5	6.6
1	2	2	1.531	113.5	6.6
1	3	2	1.531	113.5	6.6
1	4	2	1.525	114.6	119.8
1	5	2	1.526	114.5	117.6
1	6	2	1.531	113.5	113.7
1	7	2	1.533	114.3	−120.5
1	8	2	1.531	113.5	−123.3
1	9	2	1.531	113.5	−123.3
2	1	2	1.531	113.5	6.6
2	2	2	1.531	113.5	6.6
2	3	2	1.531	113.5	6.6
2	4	2	1.534	112.4	124.9
2	5	2	1.535	111.8	123.1
2	6	2	1.534	112.4	125.0
2	7	2	1.540	117.3	−96.4
2	8	2	1.531	113.5	−123.3
2	9	2	1.539	117.4	−96.2
3	1	2	1.531	113.5	6.6
3	2	2	1.531	113.5	6.6
3	3	2	1.531	113.5	6.6
3	4	2	1.535	112.4	115.0
3	5	2	1.536	112.2	113.5
3	6	2	1.536	112.6	115.3
3	7	2	1.538	113.6	−119.9
3	8	2	1.542	117.7	−124.4
3	9	2	1.538	113.5	−122.6

1	1	3	1.532	116.0	16.5
1	2	3	1.533	113.2	2.6
1	3	3	1.531	113.5	6.6
1	4	3	1.531	113.5	113.7
1	5	3	1.531	113.5	113.7
1	6	3	1.531	113.5	113.7
1	7	3	1.535	115.7	−125.2
1	8	3	1.531	113.5	−123.3
1	9	3	1.531	113.5	−123.3
2	1	3	1.538	115.0	29.3
2	2	3	1.537	111.7	19.0
2	3	3	1.535	113.5	17.2
2	4	3	1.531	113.5	113.7
2	5	3	1.531	113.5	113.7
2	6	3	1.531	113.5	113.7
2	7	3	1.539	117.9	−112.2
2	8	3	1.547	117.5	−132.4
2	9	3	1.539	117.8	−113.0
3	1	3	1.535	116.3	10.5
3	2	3	1.535	113.9	−1.9
3	3	3	1.533	114.6	1.3
3	4	3	1.536	113.1	104.2
3	5	3	1.537	112.7	103.2
3	6	3	1.536	113.1	104.5
3	7	3	1.540	114.0	−125.5
3	8	3	1.542	116.6	−131.1
3	9	3	1.540	114.0	−126.8
			Bond e		
1	1	1	1.513	111.1	28.4
1	2	1	1.513	111.3	108.3
1	3	1	1.514	111.7	−130.4
2	1	1	1.512	110.8	15.7
2	2	1	1.513	111.3	108.3
2	3	1	1.513	111.3	−118.0
3	1	1	1.513	110.8	11.2
3	2	1	1.513	111.3	108.3
3	3	1	1.514	111.7	−127.6
4	1	1	1.514	111.0	−26.6
4	2	1	1.514	111.6	130.6
4	3	1	1.513	111.9	−90.1
5	1	1	1.515	110.9	−23.3
5	2	1	1.515	111.7	131.6
5	3	1	1.513	111.9	−89.6
6	1	1	1.513	110.8	−21.2
6	2	1	1.512	111.2	96.4
6	3	1	1.513	112.0	−90.0
7	1	1	1.513	111.3	−12.9
7	2	1	1.514	111.6	61.9
7	3	1	1.515	111.9	−106.5
8	1	1	1.514	111.0	43.3
8	2	1	1.513	111.6	100.2
8	3	1	1.516	112.7	−77.7
9	1	1	1.513	111.3	−12.9
9	2	1	1.515	111.6	63.6
9	3	1	1.515	111.9	−104.7

[a]Obtained from the geometrical optimization for (*R*)-M3AV at the B3LYP/6-311+G(2d,p) level. $j-1$, j and $j+1$ denote the previous, current and next bonds, respectively. [b]The conformations are represented by numbers: bond a, 1 = t; bond b, 1 = t, 2 = g^+ and 3 = g^-; bonds c and (d); 1 = t(t), 2 = t(g^+), 3 = t(g^-), 4 = g^+(t), 5 = g^+(g^+), 6 = g^+(g^-), 7 = g^-(t), 8 = g^-(g^+) and 9 = g^-(g^-); bond e, 1 = t, 2 = g^+ and 3 = g^-. [c]Length of bond j. [d]Angle formed between bonds j and $j+1$. [e]Dihedral angle of bond j, defined as follows: ϕ (t) ∼ 0°, ϕ (g^+) ∼ 120° and ϕ (g^-) ∼ −120°.

Table S6 Average bond lengths and bond angles of P3HV at 25 °C, derived from the RIS calculations [a]

Bond length (Å)	
C(=O)−O	1.352
O−CH	1.455
CH−$CH_{2,m}$	1.530
$CH_{2,m}$−C(=O)	1.514
Bond angle (°)	
C(=O)−O−CH	117.6
O−CH−$CH_{2,m}$	107.3
CH−$CH_{2,m}$−C(=O)	113.6
$CH_{2,m}$−C(=O)−O	111.4

[a]With the Gibbs free energies in the chloroform environment. $CH_{2,m}$ represents the methyl group of the main chain.