

Supplementary information

Conformational characteristics and conformation-dependent properties of poly(ϵ -caprolactone)

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Appendix A Statistical weight matrices U_j 's (j , bond number) of PCL

$$U_1 = C_1 \otimes R_1 \quad (\text{A1})$$

$$U_2 = C_1 \otimes R_1 \quad (\text{A2})$$

$$U_3 = C_1 \otimes R_3 \quad (\text{A3})$$

$$U_4 = I_3 \otimes R_3 \quad (\text{A4})$$

$$U_5 = I_9 \otimes R_3 \quad (\text{A5})$$

$$U_6 = I_{27} \otimes R_3 \quad (\text{A6})$$

$$U_7 = I_{81} \otimes R_3 \quad (\text{A7})$$

$$U_8 = \begin{bmatrix} u_{tttt} & u_{tttg^+} & u_{tttg^-} & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & u_{tttg^+t} & u_{tttg^+g^+} & u_{tttg^+g^-} & \\ & \vdots & & & \vdots & & \ddots \\ & & & & & & \cdots & u_{g^-g^-g^-g^-g^-t} & u_{g^-g^-g^-g^-g^-g^+} & u_{g^-g^-g^-g^-g^-g^-} \end{bmatrix} \quad (\text{A8})$$

$$U_a = C_3 \otimes I_{81} \otimes R_1 \quad (\text{A9})$$

$$U_b = C_3 \otimes I_{81} \otimes R_3 \quad (\text{A10})$$

$$U_c = U_d = U_e = U_f = U_b \quad (\text{A11})$$

$$U_g = U_8 \quad (\text{A12})$$

$$U_m = U_a \quad (\text{A13})$$

and

$$U_n = U_b \quad (\text{A14})$$

where \otimes stands for the direct product,

$$C_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A15})$$

$$C_3 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad (\text{A16})$$

$$R_1 = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \quad (\text{A17})$$

$$R_3 = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \quad (\text{A18})$$

I_i stands for the identity matrix of size i ($i = 3, 9, 27$, or 81), and, for example,

$$u_{tttg^+t} = \exp(-\Delta G_{tttg^+t}/RT) \quad (\text{A19})$$

is the statistical weight of the $tttg^+t$ conformation with R and T being the gas constant and absolute temperature, respectively. The size of $U_8 - U_n$ is 243×243 .

Appendix B Stiffness (C) and compliance (S) tensors of PES and PBS

(a) Stiffness (C) and compliance (S) tensors of PES

$$C = \begin{bmatrix} 21.864 & 12.391 & 14.756 & 0.000 & 0.000 & 0.000 \\ & 19.514 & 17.097 & 0.000 & 0.000 & 0.000 \\ & & 64.645 & 0.000 & 0.000 & 0.000 \\ & & & 15.018 & 0.000 & 0.000 \\ & & & & 5.700 & 0.000 \\ & & & & & 17.299 \end{bmatrix} \text{ (GPa)} \quad (\text{B1})$$

$$S = \begin{bmatrix} 73.0488 & -41.3600 & -5.7355 & 0.0000 & 0.0000 & 0.0000 \\ & 90.1182 & -14.3937 & 0.0000 & 0.0000 & 0.0000 \\ & & 20.5852 & 0.0000 & 0.0000 & 0.0000 \\ & & & 66.5860 & 0.0000 & 0.0000 \\ & & & & 175.4493 & 0.0000 \\ & & & & & 57.8069 \end{bmatrix} \text{ (TPa}^{-1}\text{)} \quad (\text{B2})$$

The above S tensor yields the crystalline moduli in the a -, b -, and c -axis directions as $E_a = 13.69$, $E_b = 11.10$, and $E_c = 48.58$ GPa.

(b) Stiffness and compliance tensors of PBS

$$C = \begin{bmatrix} 26.115 & 11.761 & 29.132 & 0.000 & -11.669 & 0.000 \\ & 22.132 & 13.127 & 0.000 & 0.311 & 0.000 \\ & & 50.815 & 0.000 & -16.395 & 0.000 \\ & & & 10.266 & 0.000 & -0.832 \\ & & & & 7.818 & 0.000 \\ & & & & & 5.915 \end{bmatrix} \text{ (GPa)} \quad (\text{B3})$$

$$S = \begin{bmatrix} 133.2536 & -39.4397 & -53.8006 & 0.0000 & 38.4527 & 0.0000 \\ & 70.1819 & -6.0408 & 0.0000 & -32.6114 & 0.0000 \\ & & 57.9558 & 0.0000 & 18.1985 & 0.0000 \\ & & & 98.5341 & 0.0000 & 13.8623 \\ & & & & 98.6212 & 0.0000 \\ & & & & & 171.0094 \end{bmatrix} \text{ (TPa}^{-1}\text{)} \quad (\text{B4})$$

The above S tensor yields the crystalline moduli in the a -, b -, and c -axis directions as $E_a = 7.51$, $E_b = 14.25$, and $E_c = 67.24$ GPa.

Table S1 Gibbs free energies of MAH

Conformation ^a	ΔG_k (kcal mol ⁻¹)			Conformation	ΔG_k (kcal mol ⁻¹)		
	Gas	Benzene	DMSO		Gas	Benzene	DMSO
ttttt	0.000	0.000	0.000	tg ⁺ g ⁺ g ⁺ g ⁺ g ⁺	0.366	0.536	0.781
ttttg ⁺ t	-0.152	-0.005	0.175	tg ⁺ g ⁺ g ⁺ g ⁻ t	1.102	1.418	1.718
ttttg ⁺ g ⁺	0.130	0.085	0.067	tg ⁺ g ⁺ g ⁺ g ⁻ g ⁻	1.116	1.330	1.656
tttg ⁺ tt	0.550	0.569	0.573	tg ⁺ g ⁺ g ⁻ tt	1.903	2.040	2.197
tttg ⁺ g ⁺ t	0.283	0.415	0.552	tg ⁺ g ⁺ g ⁻ tg ⁻	1.972	2.026	2.161
tttg ⁺ g ⁺ g ⁺	0.066	0.135	0.274	tg ⁺ g ⁺ g ⁻ g ⁺ t	2.206	2.647	3.206
tttg ⁺ g ⁺ t	0.692	0.828	0.980	tg ⁺ g ⁺ g ⁻ g ⁻ t	1.285	1.536	1.807
tttg ⁺ g ⁻ g ⁻	1.304	1.330	1.438	tg ⁺ g ⁺ g ⁻ g ⁻ g ⁺	1.692	2.308	2.934
ttg ⁺ ttt	0.378	0.388	0.377	tg ⁺ g ⁺ g ⁻ g ⁻ g ⁻	1.584	2.129	2.735
ttg ⁺ tg ⁺ t	0.590	0.734	0.849	tg ⁺ g ⁻ ttt	0.727	0.853	0.970
ttg ⁺ tg ⁺ g ⁺	0.893	0.883	0.950	tg ⁺ g ⁻ tg ⁺ t	0.982	1.221	1.465
ttg ⁺ tg ⁺ t	0.599	0.746	0.964	tg ⁺ g ⁻ tg ⁺ g ⁺	0.976	1.032	1.126
ttg ⁺ tg ⁻ g ⁻	0.954	0.938	0.994	tg ⁺ g ⁻ tg ⁻ t	0.514	0.734	0.981
ttg ⁺ g ⁺ tt	0.877	0.889	0.854	tg ⁺ g ⁻ tg ⁻ g ⁻	0.916	0.972	1.096
ttg ⁺ g ⁺ tg ⁻	1.383	1.298	1.254	tg ⁺ g ⁻ g ⁺ tg ⁺	1.959	2.128	2.317
ttg ⁺ g ⁺ g ⁺ t	1.060	1.203	1.372	tg ⁺ g ⁻ g ⁺ tg ⁻	3.114	3.626	4.219
ttg ⁺ g ⁺ g ⁺ g ⁺	1.285	1.354	1.485	tg ⁺ g ⁻ g ⁺ g ⁺ t	2.549	2.795	3.044
ttg ⁺ g ⁺ g ⁺ t	1.253	1.473	1.694	tg ⁺ g ⁻ g ⁺ g ⁺ g ⁺	2.558	2.853	3.162
ttg ⁺ g ⁺ g ⁻ g ⁻	1.574	1.685	1.869	tg ⁺ g ⁻ g ⁻ tt	1.070	1.540	2.071
ttg ⁺ g ⁻ tt	2.568	2.643	2.720	tg ⁺ g ⁻ g ⁻ tg ⁻	1.081	1.272	1.518
ttg ⁺ g ⁻ g ⁺ t	2.528	3.247	4.007	tg ⁺ g ⁻ g ⁻ g ⁺ t	2.329	2.821	3.390
ttg ⁺ g ⁻ g ⁻ t	1.894	2.132	2.427	tg ⁺ g ⁻ g ⁻ g ⁺ g ⁺	2.692	2.968	3.250
tg ⁺ tttt	-0.025	0.037	0.112	tg ⁺ g ⁻ g ⁻ g ⁻ t	1.122	1.413	1.739
tg ⁺ ttg ⁺ t	-0.500	-0.303	-0.044	tg ⁺ g ⁻ g ⁻ g ⁻ g ⁻	0.824	1.098	1.434
tg ⁺ ttg ⁺ g ⁺	0.204	0.218	0.290	g ⁺ ttttt	0.206	0.327	0.465
tg ⁺ ttg ⁻ t	-0.377	-0.234	-0.103	g ⁺ tttg ⁺ t	0.294	0.502	0.655
tg ⁺ ttg ⁻ g ⁻	0.014	0.012	0.061	g ⁺ tttg ⁺ g ⁺	0.673	0.768	0.960
tg ⁺ tg ⁺ tt	0.253	0.316	0.393	g ⁺ tttg ⁻ t	0.137	0.407	0.809
tg ⁺ tg ⁺ g ⁺ t	0.439	0.582	0.721	g ⁺ tttg ⁻ g ⁻	0.516	0.600	0.800
tg ⁺ tg ⁺ g ⁺ g ⁺	0.161	0.213	0.248	g ⁺ ttg ⁺ tt	0.574	0.700	0.840
tg ⁺ tg ⁺ g ⁻ t	0.207	0.441	0.737	g ⁺ ttg ⁺ g ⁺ t	0.775	1.033	1.368
tg ⁺ tg ⁺ g ⁻ g ⁻	1.232	1.329	1.456	g ⁺ ttg ⁺ g ⁺ g ⁺	0.872	1.081	1.426
tg ⁺ tg ⁻ tt	0.254	0.317	0.359	g ⁺ ttg ⁺ g ⁻ t	1.362	1.572	1.776
tg ⁺ tg ⁻ g ⁺ t	0.707	0.917	1.168	g ⁺ ttg ⁺ g ⁻ g ⁻	1.347	1.502	1.765
tg ⁺ tg ⁻ g ⁺ g ⁺	1.127	1.263	1.487	g ⁺ ttg ⁻ tt	0.504	0.646	0.852
tg ⁺ tg ⁻ g ⁻ t	0.238	0.398	0.561	g ⁺ ttg ⁻ g ⁺ t	0.983	1.244	1.587
tg ⁺ tg ⁻ g ⁻ g ⁻	0.222	0.396	0.667	g ⁺ ttg ⁻ g ⁺ g ⁺	1.719	1.795	1.830
tg ⁺ g ⁺ ttt	0.082	0.154	0.213	g ⁺ ttg ⁻ g ⁻ t	0.574	0.839	1.148
tg ⁺ g ⁺ ttg ⁺	0.594	0.587	0.645	g ⁺ ttg ⁻ g ⁻ g ⁻	0.993	1.015	0.950
tg ⁺ g ⁺ g ⁺ t	-0.341	-0.107	0.091	g ⁺ tg ⁺ ttt	0.843	0.952	0.969
tg ⁺ g ⁺ g ⁺ g ⁺	0.585	0.589	0.629	g ⁺ tg ⁺ ttg ⁻	1.139	1.186	1.296
tg ⁺ g ⁺ g ⁺ t	0.047	0.261	0.544	g ⁺ tg ⁺ tg ⁺ t	0.299	0.602	1.047
tg ⁺ g ⁺ g ⁻ g ⁻	0.477	0.510	0.606	g ⁺ tg ⁺ tg ⁺ g ⁺	1.026	1.136	1.350
tg ⁺ g ⁺ g ⁺ tt	0.783	0.846	0.865	g ⁺ tg ⁺ tg ⁻ t	0.833	1.086	1.335
tg ⁺ g ⁺ g ⁺ g ⁺ t	0.612	0.794	0.963	g ⁺ tg ⁺ tg ⁻ g ⁻	1.029	1.124	1.304

Conformation	ΔG_k (kcal mol ⁻¹)			Conformation	ΔG_k (kcal mol ⁻¹)		
	Gas	Benzene	DMSO		Gas	Benzene	DMSO
g ⁺ tg ⁺ g ⁺ tt	0.625	0.942	1.300	g ⁺ g ⁺ g ⁺ tg ⁻ g ⁻	0.619	0.744	0.940
g ⁺ tg ⁺ g ⁺ tg ⁺	1.212	1.407	1.670	g ⁺ g ⁺ g ⁺ g ⁺ tt	1.030	1.186	1.303
g ⁺ tg ⁺ g ⁺ g ⁺ t	0.917	1.335	1.818	g ⁺ g ⁺ g ⁺ g ⁺ tg ⁺	1.139	1.245	1.425
g ⁺ tg ⁺ g ⁺ g ⁺ g ⁺	0.519	0.861	1.223	g ⁺ g ⁺ g ⁺ g ⁺ tg ⁻	1.075	1.227	1.345
g ⁺ tg ⁺ g ⁺ g ⁻ g ⁺	1.778	2.645	3.489	g ⁺ g ⁺ g ⁺ g ⁺ g ⁺ t	1.228	1.484	1.727
g ⁺ tg ⁺ g ⁺ g ⁻ g ⁻	2.178	2.802	3.475	g ⁺ g ⁺ g ⁺ g ⁺ g ⁺ g ⁺	0.943	1.171	1.420
g ⁺ tg ⁺ g ⁻ tt	2.086	2.448	2.813	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ t	1.229	1.725	2.346
g ⁺ tg ⁺ g ⁻ g ⁺ g ⁺	4.187	4.898	5.591	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ g ⁻	1.512	1.759	2.073
g ⁺ tg ⁺ g ⁻ g ⁻ t	1.582	2.115	2.702	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ g ⁻	2.020	2.303	2.622
g ⁺ tg ⁺ g ⁻ g ⁻ g ⁻	2.147	2.834	3.647	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ g ⁻	2.770	2.973	3.297
g ⁺ tg ⁻ ttt	0.831	0.973	1.176	g ⁺ g ⁺ g ⁺ g ⁺ g ⁺ t	2.951	3.430	4.030
g ⁺ tg ⁻ ttg ⁺	1.244	1.297	1.458	g ⁺ g ⁺ g ⁺ g ⁺ g ⁺ g ⁺	3.925	4.326	4.847
g ⁺ tg ⁻ tg ⁺ t	0.881	1.123	1.441	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ t	2.669	2.988	3.351
g ⁺ tg ⁻ tg ⁺ g ⁺	1.256	1.332	1.447	g ⁺ g ⁺ g ⁺ g ⁺ g ⁻ g ⁻	2.880	3.210	3.556
g ⁺ tg ⁻ tg ⁻ t	1.009	1.277	1.628	g ⁺ g ⁺ g ⁺ g ⁻ ttt	1.103	1.390	1.716
g ⁺ tg ⁻ tg ⁻ g ⁻	1.149	1.238	1.400	g ⁺ g ⁺ g ⁺ g ⁻ tg ⁺ t	1.093	1.404	1.732
g ⁺ tg ⁻ g ⁺ tt	2.815	2.964	3.147	g ⁺ g ⁺ g ⁺ g ⁻ tg ⁺ g ⁺	1.816	1.982	2.220
g ⁺ tg ⁻ g ⁺ g ⁺ t	2.679	2.989	3.358	g ⁺ g ⁺ g ⁺ g ⁻ tg ⁻ t	0.867	1.191	1.528
g ⁺ tg ⁻ g ⁺ g ⁺ g ⁺	3.195	3.549	4.027	g ⁺ g ⁺ g ⁺ g ⁻ tg ⁻ g ⁻	0.873	1.000	1.177
g ⁺ tg ⁻ g ⁺ g ⁻ t	3.509	3.907	4.393	g ⁺ g ⁺ g ⁺ g ⁻ g ⁺ tt	2.931	3.581	4.295
g ⁺ tg ⁻ g ⁻ tt	1.631	1.782	1.941	g ⁺ g ⁺ g ⁺ g ⁻ g ⁺ tg ⁺	3.201	3.539	3.966
g ⁺ tg ⁻ g ⁻ tg ⁻	1.848	1.924	2.105	g ⁺ g ⁺ g ⁺ g ⁻ g ⁺ g ⁺ t	3.134	3.504	3.872
g ⁺ tg ⁻ g ⁻ g ⁺ t	1.090	1.500	2.026	g ⁺ g ⁺ g ⁺ g ⁻ g ⁺ g ⁺ g ⁺	3.472	4.004	4.620
g ⁺ tg ⁻ g ⁻ g ⁺ g ⁺	1.721	1.977	2.356	g ⁺ g ⁺ g ⁺ g ⁻ g ⁻ tg ⁺	1.040	1.666	2.413
g ⁺ tg ⁻ g ⁻ g ⁻ t	1.280	1.515	1.756	g ⁺ g ⁺ g ⁺ g ⁻ g ⁻ tg ⁻	1.411	1.733	2.143
g ⁺ tg ⁻ g ⁻ g ⁻ g ⁻	1.684	1.844	2.055	g ⁺ g ⁺ g ⁺ g ⁻ g ⁻ g ⁺ t	1.954	2.923	4.001
g ⁺ g ⁺ tttt	0.116	0.255	0.354	g ⁺ g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ t	1.316	1.637	1.976
g ⁺ g ⁺ ttg ⁺ t	-0.409	-0.144	0.215	g ⁺ g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ g ⁻	1.145	1.387	1.594
g ⁺ g ⁺ ttg ⁺ g ⁺	0.569	0.660	0.801	g ⁺ g ⁺ g ⁻ ttg ⁺ t	-0.290	-0.038	0.273
g ⁺ g ⁺ ttg ⁻ t	0.010	0.267	0.551	g ⁺ g ⁺ g ⁻ tg ⁻ g ⁺ g ⁻	0.980	1.241	1.583
g ⁺ g ⁺ ttg ⁻ g ⁻	0.202	0.280	0.387	g ⁺ g ⁺ g ⁻ tg ⁻ g ⁻ g ⁻	1.132	1.390	1.630
g ⁺ g ⁺ tg ⁺ tt	0.464	0.615	0.780	g ⁺ g ⁺ g ⁻ g ⁺ tg ⁺ g ⁻	0.720	1.210	1.774
g ⁺ g ⁺ tg ⁺ g ⁺ t	0.677	0.910	1.157	g ⁺ g ⁺ g ⁻ g ⁻ ttt	0.436	0.734	1.048
g ⁺ g ⁺ tg ⁺ g ⁺ g ⁺	0.577	1.110	1.659	g ⁺ g ⁺ g ⁻ g ⁻ ttg ⁻	1.039	1.217	1.362
g ⁺ g ⁺ tg ⁺ g ⁻ t	0.685	0.999	1.377	g ⁺ g ⁺ g ⁻ g ⁻ tg ⁺ t	0.208	0.683	1.276
g ⁺ g ⁺ tg ⁺ g ⁻ g ⁻	1.326	2.235	3.209	g ⁺ g ⁺ g ⁻ g ⁻ tg ⁺ g ⁺	0.753	1.052	1.464
g ⁺ g ⁺ tg ⁻ tt	0.708	0.857	0.994	g ⁺ g ⁺ g ⁻ g ⁻ tg ⁻ g ⁺	1.662	2.028	2.226
g ⁺ g ⁺ tg ⁻ g ⁺ t	1.224	1.470	1.680	g ⁺ g ⁺ g ⁻ g ⁻ tg ⁻ g ⁻	0.264	1.068	1.903
g ⁺ g ⁺ tg ⁻ g ⁺ g ⁺	1.446	1.690	2.055	g ⁺ g ⁺ g ⁻ g ⁻ g ⁺ tt	2.962	3.363	3.778
g ⁺ g ⁺ tg ⁻ g ⁻ t	0.811	1.067	1.341	g ⁺ g ⁺ g ⁻ g ⁻ g ⁺ tg ⁻	3.028	3.278	3.649
g ⁺ g ⁺ tg ⁻ g ⁻ g ⁻	0.190	0.485	0.901	g ⁺ g ⁺ g ⁻ g ⁻ g ⁺ g ⁺ t	2.858	3.695	4.642
g ⁺ g ⁺ g ⁺ ttt	0.417	0.598	0.843	g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ tg ⁺	1.418	1.592	1.789
g ⁺ g ⁺ g ⁺ tg ⁺ t	-0.153	0.050	0.163	g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ g ⁺ t	1.531	2.095	2.602
g ⁺ g ⁺ g ⁺ tg ⁺ g ⁺	0.826	0.938	1.106	g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ g ⁺ g ⁺	1.172	1.493	1.847
g ⁺ g ⁺ g ⁺ tg ⁻ t	0.119	0.412	0.769	g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ g ⁻ t	1.204	1.561	1.941
				g ⁺ g ⁺ g ⁻ g ⁻ g ⁻ g ⁻ g ⁻	1.248	1.671	2.204

^aUnder the rotational isomeric state approximation, 729 (=3⁶) conformers are conceivable for MAH, and the molecular symmetry decreases the number of irreducible conformers to 365. As a result of the geometrical optimization at the B3LYP/6-311++G(2d,p) level for all the 365 conformers, 181 remained. From left to right, the conformations of bonds 3–6 are written.

Table S2 Geometrical parameters of PCL, used in the RIS calculations ^a

Conformation						Bond d					
<i>j</i> - 1	<i>j</i>	<i>j</i> + 1	<i>l_j</i> ^b	$\angle j \wedge (j + 1)$ ^c	ϕ_j ^d	t	t	t	1.531	112.8	0.0
Bond a						t	t	t	1.535	114.5	112.2
t	t	t	1.350	116.2	0.0	t	g ⁺	t	1.535	114.5	-112.2
g ⁺	t	t	1.352	115.7	0.6	t	g ⁻	t	1.531	112.7	0.7
g ⁻	t	t	1.352	115.7	-0.6	g ⁺	t	t	1.535	114.4	113.3
t	t	g ⁺	1.351	117.0	0.2	g ⁺	g ⁺	t	1.536	115.6	-109.8
g ⁺	t	g ⁺	1.351	117.0	0.2	g ⁻	t	t	1.531	112.7	-0.7
g ⁻	t	g ⁺	1.351	117.0	0.2	g ⁻	g ⁺	t	1.536	115.6	109.8
t	t	g ⁻	1.351	117.0	-0.2	g ⁻	g ⁻	t	1.535	114.4	-113.3
g ⁺	t	g ⁻	1.351	117.0	-0.2	t	t	g ⁺	1.533	114.5	3.7
g ⁻	t	g ⁻	1.351	117.0	-0.2	t	g ⁺	g ⁺	1.536	116.4	114.9
Bond b						t	g ⁻	g ⁺	1.537	116.5	-114.5
t	t	t	1.447	107.9	0.0	g ⁺	t	g ⁺	1.532	114.6	4.2
t	g ⁺	t	1.448	111.5	91.3	g ⁺	g ⁺	g ⁺	1.537	116.2	117.8
t	g ⁻	t	1.448	111.5	-91.3	g ⁺	g ⁻	g ⁺	1.562	117.8	-106.8
t	t	g ⁺	1.449	108.3	0.3	g ⁻	t	g ⁺	1.533	114.5	2.7
t	g ⁺	g ⁺	1.450	112.0	89.8	g ⁻	g ⁺	g ⁺	1.538	117.1	119.9
t	g ⁻	g ⁺	0.000	0.0	0.0	g ⁻	g ⁻	g ⁺	1.537	116.2	-117.5
t	t	g ⁻	1.449	108.3	-0.3	t	t	g ⁻	1.533	114.5	-3.7
t	g ⁺	g ⁺	0.000	0.0	0.0	t	g ⁺	g ⁻	1.537	116.5	114.5
t	g ⁻	g ⁻	1.450	112.0	-89.8	t	g ⁻	g ⁻	1.536	116.4	-114.9
Bond c						g ⁺	t	g ⁻	1.533	114.5	-2.7
t	t	t	1.517	112.0	0.0	g ⁺	g ⁺	g ⁻	1.537	116.2	117.5
t	g ⁺	t	1.517	114.2	114.6	g ⁺	g ⁻	g ⁻	1.538	117.1	-119.9
t	g ⁻	t	1.517	114.2	-114.6	g ⁻	t	g ⁻	1.532	114.6	-4.2
g ⁺	t	t	1.521	111.9	3.4	g ⁻	g ⁺	g ⁻	1.562	117.8	106.8
g ⁺	g ⁺	t	1.521	114.1	118.1	g ⁻	g ⁻	g ⁻	1.537	116.2	-117.8
g ⁺	g ⁻	t	1.521	114.2	-111.9	Bond e					
g ⁻	t	t	1.521	111.9	-3.4	t	t	t	1.530	112.5	0.0
g ⁻	g ⁺	t	1.521	114.2	111.9	t	g ⁺	t	1.534	113.8	113.7
g ⁻	g ⁻	t	1.521	114.1	-118.1	t	g ⁻	t	1.534	113.8	-113.7
t	t	g ⁺	1.518	113.3	3.2	g ⁺	t	t	1.532	112.2	3.1
t	g ⁺	g ⁺	1.518	115.4	117.0	g ⁺	g ⁺	t	1.536	113.7	116.1
t	g ⁻	g ⁺	1.519	116.3	-105.5	g ⁺	g ⁻	t	1.541	114.6	-90.3
g ⁺	t	g ⁺	1.523	113.4	9.1	g ⁻	t	t	1.532	112.2	-3.1
g ⁺	g ⁺	g ⁺	1.523	115.3	120.6	g ⁻	g ⁺	t	1.541	114.6	90.3
g ⁺	g ⁻	g ⁺	1.519	114.0	-115.7	g ⁻	g ⁻	t	1.536	113.7	-116.1
g ⁺	t	g ⁺	1.523	113.3	0.9	t	t	g ⁺	1.531	113.6	-0.1
g ⁺	g ⁺	g ⁺	1.523	115.5	111.1	t	g ⁺	g ⁺	1.535	115.1	113.4
g ⁺	g ⁻	g ⁺	1.523	116.2	-111.9	t	g ⁻	g ⁺	1.535	114.9	-116.5
g ⁺	g ⁻	g ⁺	1.524	116.2	-111.9	g ⁺	t	g ⁺	1.533	113.4	4.7
t	t	g ⁻	1.518	113.3	-3.2	g ⁺	g ⁺	g ⁺	1.537	114.9	117.0
t	g ⁺	g ⁻	1.519	116.3	105.5	g ⁺	g ⁻	g ⁺	1.539	117.0	-109.8
t	g ⁻	g ⁻	1.518	115.4	-117	g ⁻	t	g ⁺	1.533	113.2	-4.4
g ⁺	t	g ⁻	1.523	113.3	-0.9	g ⁻	g ⁺	g ⁺	1.537	116.2	118.3
g ⁺	g ⁺	g ⁻	1.524	116.2	111.9	g ⁻	g ⁻	g ⁺	1.537	114.9	-114
g ⁺	g ⁻	g ⁻	1.523	115.5	-111.1	t	t	g ⁻	1.531	113.6	0.1
g ⁺	t	g ⁻	1.523	113.4	-9.1	t	g ⁺	g ⁻	1.535	114.9	116.5
g ⁺	g ⁺	g ⁻	1.519	114.0	115.7	t	g ⁻	g ⁻	1.535	115.1	-113.4
g ⁺	g ⁻	g ⁻	1.523	115.3	-120.6	g ⁺	t	g ⁻	1.533	113.2	4.4
						g ⁺	g ⁺	g ⁻	1.537	114.9	114.0
						g ⁺	g ⁻	g ⁻	1.537	116.2	-118.3
						g ⁻	t	g ⁻	1.533	113.4	-4.7
						g ⁻	g ⁺	g ⁻	1.539	117.0	109.8
						g ⁻	g ⁻	g ⁻	1.537	114.9	-117

Bond f					
t	t	t	1.526	113.6	0.0
t	g ⁺	t	1.529	113.7	108.7
t	g ⁻	t	1.529	113.7	-108.7
g ⁺	t	t	1.528	113.3	3.8
g ⁺	g ⁺	t	1.531	113.7	111.2
g ⁺	g ⁻	t	1.534	114.3	-95.8
g ⁻	t	t	1.528	113.3	-3.8
g ⁻	g ⁺	t	1.534	114.3	95.8
g ⁻	g ⁻	t	1.531	113.7	-111.2
t	t	g ⁺	1.540	111.3	2.9
t	g ⁺	g ⁺	1.537	114.2	117.2
t	g ⁻	g ⁺	1.544	112.5	-100.3
g ⁺	t	g ⁺	1.540	112.0	6.8
g ⁺	g ⁺	g ⁺	1.542	113.0	121.0
g ⁺	g ⁻	g ⁺	1.532	113.8	-112.3
g ⁻	t	g ⁺	1.541	111.8	0.8
g ⁻	g ⁺	g ⁺	1.539	116.6	105.6
g ⁻	g ⁻	g ⁺	1.532	113.8	-112.3
t	t	g ⁻	1.540	111.3	-2.9
t	g ⁺	g ⁻	1.544	112.5	100.3
t	g ⁻	g ⁻	1.537	114.2	-117.2
g ⁺	t	g ⁻	1.541	111.8	-0.8
g ⁺	g ⁺	g ⁻	1.532	113.8	112.3
g ⁺	g ⁻	g ⁻	1.539	116.6	-105.6
g ⁻	t	g ⁻	1.540	112.0	-6.8
g ⁻	g ⁺	g ⁻	1.532	113.8	112.3
g ⁻	g ⁻	g ⁻	1.542	113.0	-121
Bond g					
t	t	t	1.512	110.9	0.0
t	g ⁺	t	1.511	111.6	121.1
t	g ⁻	t	1.511	111.6	-121.1
g ⁺	t	t	1.514	111.1	-19.2
g ⁺	g ⁺	t	1.513	111.5	121.4
g ⁺	g ⁻	t	1.512	112.2	-93.7
g ⁻	t	t	1.514	111.1	19.2
g ⁻	g ⁺	t	1.512	112.2	93.7
g ⁻	g ⁻	t	1.513	111.5	-121.4

^aOptimized at the B3LYP/6-311++G(2d,p) level. *j* denotes the current bond. ^bLength of bond *j*. ^cAngle formed between bonds *j* and *j* + 1. ^dDihedral angle of bond *j*, defined according to the convention in polymer science: t, $\phi_j \approx 0^\circ$; g[±], $\phi_j \approx \pm 120^\circ$.

Table S3 Optimized and experimental crystal structures of PES^a

	Optimized ^b			Experimental ^c		
	Lattice Constant (Å)					
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
	7.42	10.08	8.48	7.60	10.75	8.33
	$\Delta_{\text{LC}} = 2.3\%$ ^d					
	Fractional Coordinates					
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C	0.721	-0.027	0.664	0.719	-0.013	0.663
C	0.806	0.083	0.569	0.787	0.094	0.571
C	0.799	0.201	0.328	0.798	0.198	0.331
O	0.731	0.094	0.425	0.724	0.099	0.422
O	0.929	0.153	0.614	0.903	0.161	0.615
H	0.760	-0.122	0.609	0.760	-0.097	0.600
H	0.575	-0.021	0.651	0.575	-0.013	0.665
H	0.944	0.191	0.311	0.939	0.190	0.316
H	0.772	0.295	0.386	0.765	0.282	0.396
	$\Delta_{\text{CHO}} = 0.016$ ^e					

^aOrthorhombic, space group *Pbnb*. ^bAt 0 K. ^cUeda, A. S.; Chatani, Y.; Tadokoro, H. *Polym. J.* **1971**, *2*, 387–397. At room temperature.

$${}^d \Delta_{\text{LC}} = \frac{1}{3} \left[\left(\frac{a_{\text{calc}} - a_{\text{expt}}}{a_{\text{expt}}} \right)^2 + \left(\frac{b_{\text{calc}} - b_{\text{expt}}}{b_{\text{expt}}} \right)^2 + \left(\frac{c_{\text{calc}} - c_{\text{expt}}}{c_{\text{expt}}} \right)^2 \right]^{1/2} \times 100 (\%)$$

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

which was calculated for carbon, oxygen, and hydrogen atoms.

Table S4 Optimized and experimental crystal structures of α form of PBS^a

	Optimized ^b				Experimental ^c			
	Lattice Constant (Å, °)							
	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>a</i>	<i>b</i>	<i>c</i>	β
	5.21	8.71	10.88	125.7	5.23	9.12	10.90	123.9
	$\Delta_{LC} = 1.2\%$ ^d							
	Fractional Coordinates							
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	
C	0.1351	0.0571	0.5489		0.0839	0.0711	0.5389	
C	0.0890	0.1524	0.6513		-0.0117	0.1387	0.6360	
C	0.0074	0.0964	0.8420		-0.0195	0.0832	0.8352	
C	0.0634	-0.0237	0.9551		0.0690	-0.0216	0.9564	
O	0.1262	0.0508	0.7670		0.0696	0.0351	0.7495	
O	-0.1270	0.2189	0.8202		-0.1536	0.1964	0.8164	
H	0.1556	0.1359	0.4765		0.0392	0.1534	0.4566	
H	0.3600	-0.0048	0.6175		0.3308	0.0504	0.6104	
H	0.2639	0.2440	0.7082		0.1104	0.2419	0.6821	
H	-0.1473	0.2021	0.5889		-0.2591	0.1590	0.5696	
H	0.3171	-0.0467	1.0308		0.3190	-0.0237	1.0322	
H	-0.0486	-0.1293	0.8911		-0.0138	-0.1308	0.9106	
	$\Delta_{CHO} = 0.068$ ^e							

^aMonoclinic, space group $P2_1/n$. ^bAt 0 K. ^cIchikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. *Polymer* **2000**, *41*, 4719–4727; **2001**, *42*, 847–847.

$${}^d \Delta_{LC} = \frac{1}{4} \left[\left(\frac{a_{\text{calc}} - a_{\text{expt}}}{a_{\text{expt}}} \right)^2 + \left(\frac{b_{\text{calc}} - b_{\text{expt}}}{b_{\text{expt}}} \right)^2 + \left(\frac{c_{\text{calc}} - c_{\text{expt}}}{c_{\text{expt}}} \right)^2 + \left(\frac{\beta_{\text{calc}} - \beta_{\text{expt}}}{\beta_{\text{expt}}} \right)^2 \right]^{1/2} \times 100 (\%)$$

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

which was calculated for carbon, oxygen, and hydrogen atoms.

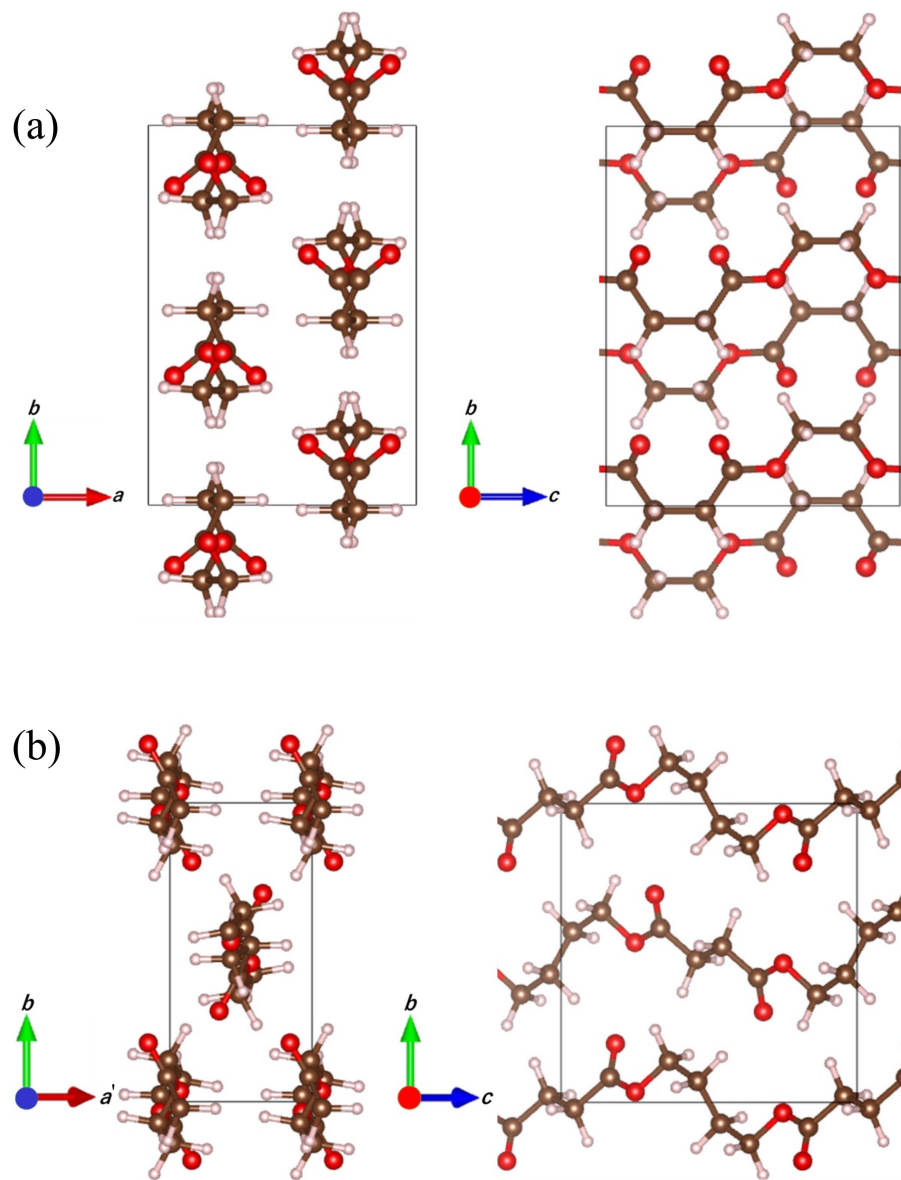


Fig. S1 Crystal structure optimized by the periodic DFT at the B3LYP-D/6-31G(d,p) level: (a) PES; (b) α -form of PBS.

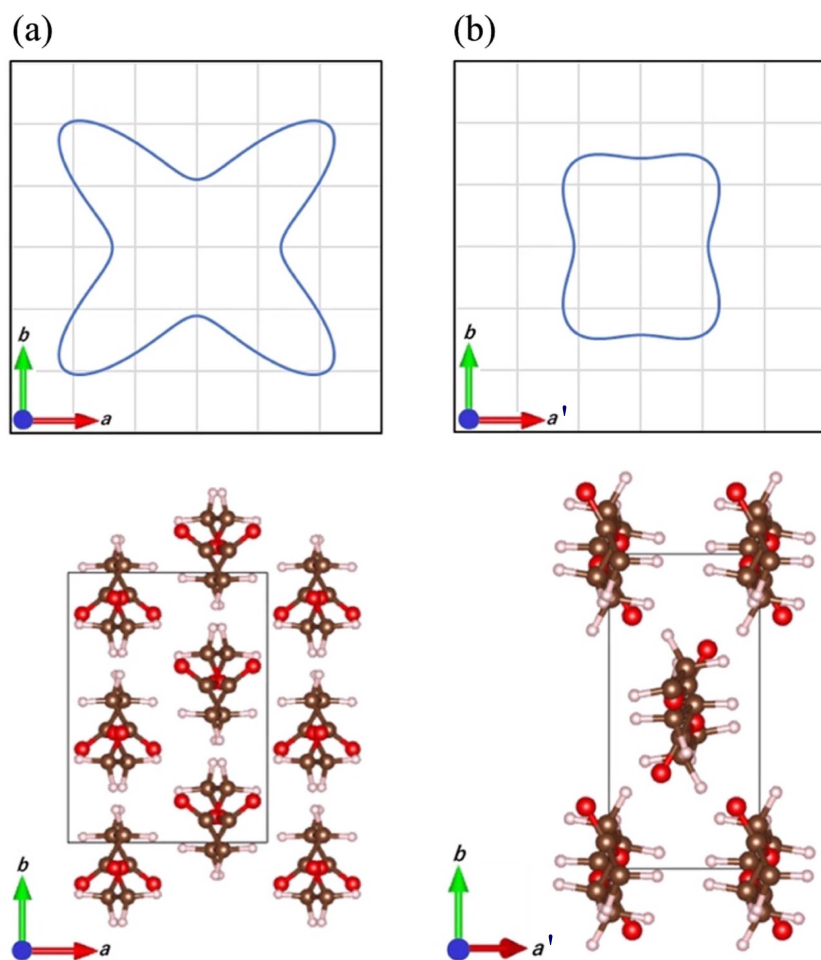


Fig. S2 Young's modulus distributions on the plane perpendicular to the fiber axis: (a) PES; (b) α -form of PBS. The grid spacing corresponds to 10 GPa.