Supporting Information

Single-chain Level Decoding of the Conformational Distribution in Bisphenol A Polycarbonate

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Details of the QM-based models

The worm-like chain (WLC) model has been used to describe the theoretical single-chain elasticity of a semi-rigid or rigid polymer chain.[1-3] In the WLC model, the relationship between the end-to-end distance R of a polymer chain and stretching force F can be written as follows:

$$F\frac{l_{\mathrm{p}}}{k_{\mathrm{B}}T}=\frac{R}{L[F]}+\frac{1}{4(1-R/L[F])^{2}}-\frac{1}{4} \tag{S1}$$

where l_{p} is the persistence length, $L[F]$ is the contour length of a polymer chain upon stretching with force F, k_{B} is the Boltzmann constant, and T is the temperature in Kelvin scale. As shown in Eq. S1, there are two free parameters in the WLC model. One is the contour length of the single polymer, $L[F]$. The other one is the persistence length, l_{p}.

To integrate the QM-derived theoretical elasticity into the WLC model, L_0 is introduced as follows:

$$\frac{Fl_{\mathrm{p}}}{k_{\mathrm{B}}T}=\frac{R/L_0}{\mathrm{L}[F]/L_0}+1/[4\left(1-\frac{R/L_0}{L[F]/L_0}\right)^{2}]-\frac{1}{4} \tag{S2}$$

The modified WLC model (Eq. S2, Eq. 3 in the main text), which is integrated with the QM results, is called the QM-WLC model.

The theoretical elasticity of *cis-cis*-PC was also integrated into the FJC and FRC models, resulting in the QM-FRC and QM-FJC models.[4-8] Eqs. S3-4 are given as follows:

$$z_{\mathrm{FRC}}=R/L_0=(L[F]/L_0)\,[1-k_{\mathrm{B}}T/(2Fl_{\mathrm{b}})] \tag{S3}$$

$$z_{\mathrm{FJC}}=R/L_0=(L[F]/L_0)\,[coth\frac{Fl_{\mathrm{k}}}{k_{\mathrm{B}}T}-\frac{k_{\mathrm{B}}T}{Fl_{\mathrm{k}}}] \tag{S4}$$

Details of the area-deviation calculation

The optimal l_{p} can be determined by calculating the area difference between the Type 1 experimental curve and the QM-WLC theoretical curves. The area (S) enclosed by the experimental or theoretical curve within this interval was calculated using the trapezoidal integration method, as follows:

$$S=\sum_{i-1}^{n}\frac{F_i+F_{i-1}}{2}\cdot(R_i-R_{i-1}) \tag{S5}$$

where F_{i} and $F_{\mathrm{i-1}}$ are the forces at two adjacent data points, while R_{i} and $R_{\mathrm{i-1}}$ are the corresponding normalized extensions, which serve as the two parallel sides (bases) and the height of the trapezoid, respectively.

The normalized area deviation (ΔS) is defined as the area difference obtained by integrating the experimental and theoretical *F-E* curves over the normalized extension (R/L_0). The corresponding expression is given as follows:

$$\Delta S = |S_e - S_s| \tag{S6}$$

where S_e is the area enclosed by the experimental curve and the horizontal axis (*R*-axis) within the specified interval, and S_s is the area enclosed by the theoretical curve and the horizontal axis within the same interval.

The optimal QM-WLC fitting parameters for the experimental curve can be determined by identifying the minimum area difference. As shown in Fig. S13b, the best fit for the Type 1 curve is obtained at l_p = 0.41 nm, with a mean deviation close to 0 pN·(R/L_0). In contrast, the minimum deviation for the Type 2 curve is ~1.5 pN·(R/L_0), indicating that the QM-WLC model cannot adequately describe its behavior.

Details of the TSQM-WLC model

The TSQM-WLC model is used to quantify the effects of the *trans* conformation on the single-chain mechanics of PC. It is assumed that the PC single chain consists of many modules. Under the action of an external force, each module can undergo a transition between two energetically distinct states: the folded (*trans*) state and the unfolded (*cis*) state. The lengths of the modules in the *trans* and *cis* states are denoted as l_f and l_u, respectively. The transition from *trans* to *cis* leads to an extension of the module. At the free state ($F = 0$), the rates of unfolding α_0 and folding β_0 can be determined by the following equations:

$$\alpha_0 = \omega e^{-\Delta G_u^*/k_B T} \tag{S7}$$

$$\beta_0 = \omega e^{-\Delta G_f^*/k_B T} \tag{S8}$$

where ΔG_u^* is the activation barrier for unfolding, ΔG_f^* is the activation barrier for folding, ω is the reciprocal of the diffusive relaxation time.

According to the Bell-Evans model,[9, 10] when the module is stretched by an external force, the altered unfolding and folding rate can be calculated by the following equations, respectively:

$$\alpha_1 = \omega e^{-(\Delta G_u^* - F x_u)/k_B T} = \alpha_0 e^{F x_u/k_B T} \tag{S9}$$

$$\beta_1 = \omega e^{-(\Delta G_f^* + F x_f)/k_B T} = \beta_0 e^{-F x_f/k_B T} \tag{S10}$$

where F is the external force, x_u and x_f are the widths of the activation barrier for unfolding and folding, respectively.

At equilibrium, the number of folding and unfolding modules follow the relationship below:

$$\alpha_1 N_f = \beta_1 N_u = \beta_1(N - N_f) \tag{S11}$$

where N is the number of all the modules in the chain, N_f and N_u are the number of the folded and unfolded modules in the chain under an external force at equilibrium, respectively.

Thus, N_f and N_u under a given force can be calculated by the following equations, respectively:

$$N_f = \frac{\beta_1}{\alpha_1+\beta_1} N = \frac{1}{e^{(-\Delta G+F\Delta L)/k_B T}+1} N \tag{S12}$$

$$N_u = \frac{\alpha_1}{\alpha_1+\beta_1} N = \frac{1}{e^{(\Delta G-F\Delta L)/k_B T}+1} N \tag{S13}$$

where ΔG is the free energy difference of the module between two states, ΔL is the length difference of the module between two states ($\Delta L = l_u - l_f$).

For a PC chain consisting of a large number of modules, the polymer contour length (L_{TS}) at a given force without the elastic contribution can be calculated by:

$$L_{TS} = N_f l_f + N_u l_u = N\left[\frac{l_f}{e^{(-\Delta G+F\Delta L)/k_B T}+1} + \frac{l_u}{e^{(\Delta G-F\Delta L)/k_B T}+1}\right] \tag{S14}$$

The L_{TS} and the polymer chain extension R_{TS} follow the relationship described in the QM-WLC model, in which both entropic and enthalpic elasticity are considered:

$$R_{TS}/L_{TS} = z_{WLC} = R/L_0 \tag{S15}$$

Hence, the value of R_{TS} can be calculated using the equation: $R_{TS}=L_{TS}\cdot z_{WLC}$. In the TSQM-WLC model, the normalized extension of PC is:

$$Z_{TS} = R_{TS}/L_0 = z_{WLC}L_{TS}/Nl_u = \left[\frac{l_f}{e^{(-\Delta G+F\Delta L)/k_B T}+1} + \frac{l_u}{e^{(\Delta G-F\Delta L)/k_B T}+1}\right] \cdot z_{WLC}/l_u \tag{S16}$$

where z_{WLC} is the normalized extension of a polymer chain in the QM-WLC model, Nl_u is the contour length of *cis-cis*-PC at zero force.

In the TSQM-WLC model, the value of $L[F]/L_0$ is force-dependent and is used to evaluate the deformation of the bond length and angle of the backbone during stretching. Additionally, the value of $\left[\frac{l_f}{e^{(-\Delta G+F\Delta L)/k_B T}+1} + \frac{l_u}{e^{(\Delta G-F\Delta L)/k_B T}+1}\right]$ is used to assess the deformation of the bond lengths and angles of the backbone influenced by the *trans* conformation during stretching. Therefore, both components are used to measure the enthalpy contributions to the single-chain mechanics of PC. The remaining parts of the TSQM-WLC model are used to evaluate the entropy contributions.

In the TSQM-WLC model, the three variables are ΔG, l_f, and l_u, whereas $\Delta L = l_\mathrm{u} - l_\mathrm{f}$, is not an independent variable. In the two-state model used in this work, the parameter l_u corresponds to the persistence length of the unfolded state (*cis* conformation). According to the QM-WLC fitting of Type 1, the persistence length of the *cis* conformational module was determined to be 0.41 nm; therefore, l_u was fixed at 0.41 nm. The model thus retains only two free parameters, ΔG and l_f.

The two-state model was established by incorporating the difference between the *cis* and *trans* states into the QM-WLC framework. Therefore, in the absence of any distinction between the two states, the TSQM-WLC model reduces to the QM-WLC model, corresponding to the initial condition $l_\mathrm{u} = l_\mathrm{f} = 0.41$ nm and $\Delta G = 0$ $k_\mathrm{B}T$ module^{-1}. Based on this, since the folded state is more compact than the extended state, l_f was scanned downward from 0.41 nm; because the stretching process requires additional energy input, ΔG was scanned upward from 0 $k_\mathrm{B}T$ module^{-1}.

To determine the optimal parameters, we first fixed $\Delta G = 0$ and evaluated l_f by comparing the area deviation between the theoretical and experimental curves. The results show that as l_f decreases, the area deviation initially decreases (Fig. S16a), reaches a minimum at $l_\mathrm{f} = 0.38$ nm, and then increases again. Subsequently, based on this result, l_f was fixed at 0.38 nm, and it was found that the area deviation decreases with increasing ΔG (Fig. S16b), reaching a minimum (approaching zero) at $\Delta G = 0.45$ $k_\mathrm{B}T$ module^{-1}, after which it increases again. Therefore, the optimal fitting parameters were determined to be $l_\mathrm{f} = 0.38$ nm and $\Delta G = 0.45$ $k_\mathrm{B}T$ module^{-1}.

Supporting figures and table

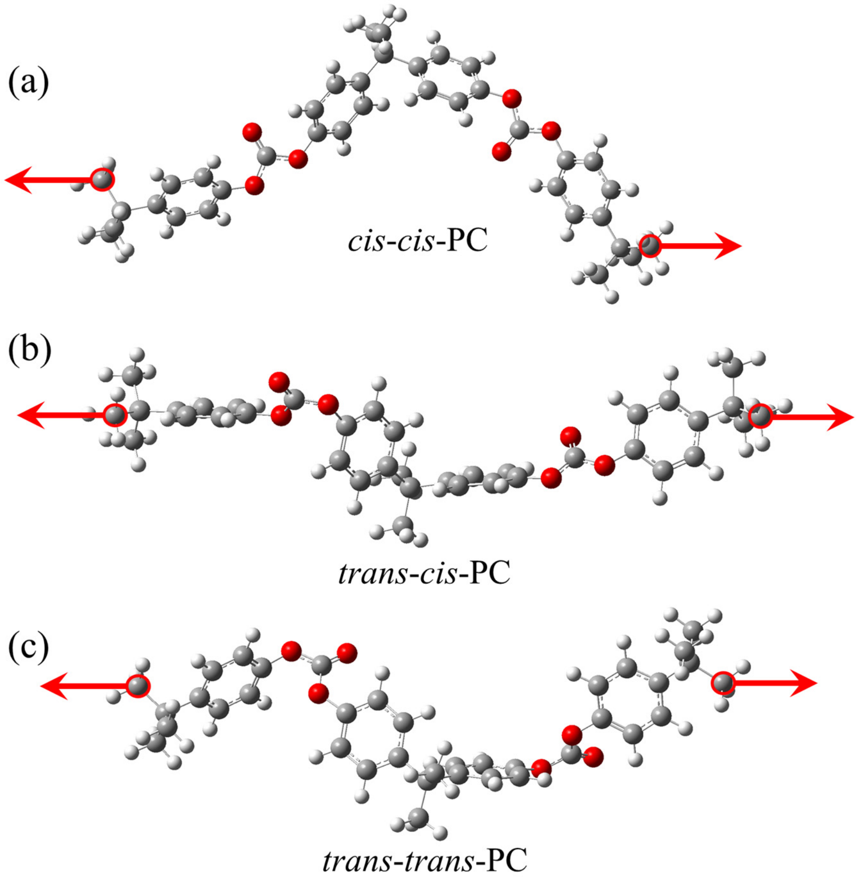

Figure S1. PC dimer structures with (a) *cis*-*cis*, (b) *trans*-*cis*, and (c) *trans*-*trans* conformation used for QM calculations. Atomic color scheme: white = hydrogen (H), gray = carbon (C), blue = nitrogen (N), red = oxygen (O). Red arrows indicate terminal C atoms.

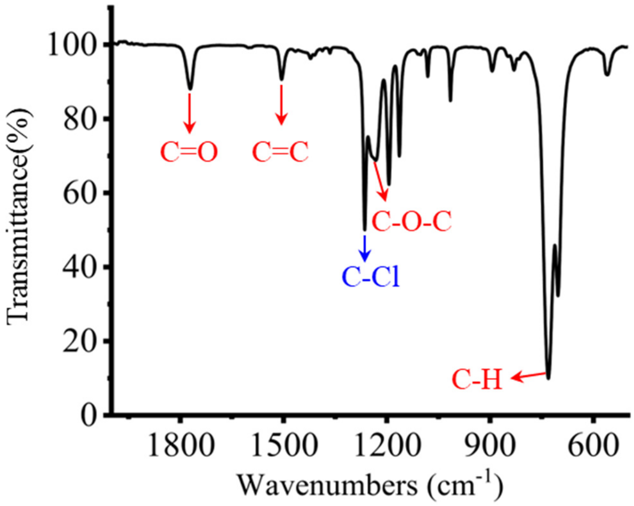

Figure S2. Full-range FTIR spectra of the PC sample in the 2000–550 cm^{-1} region.

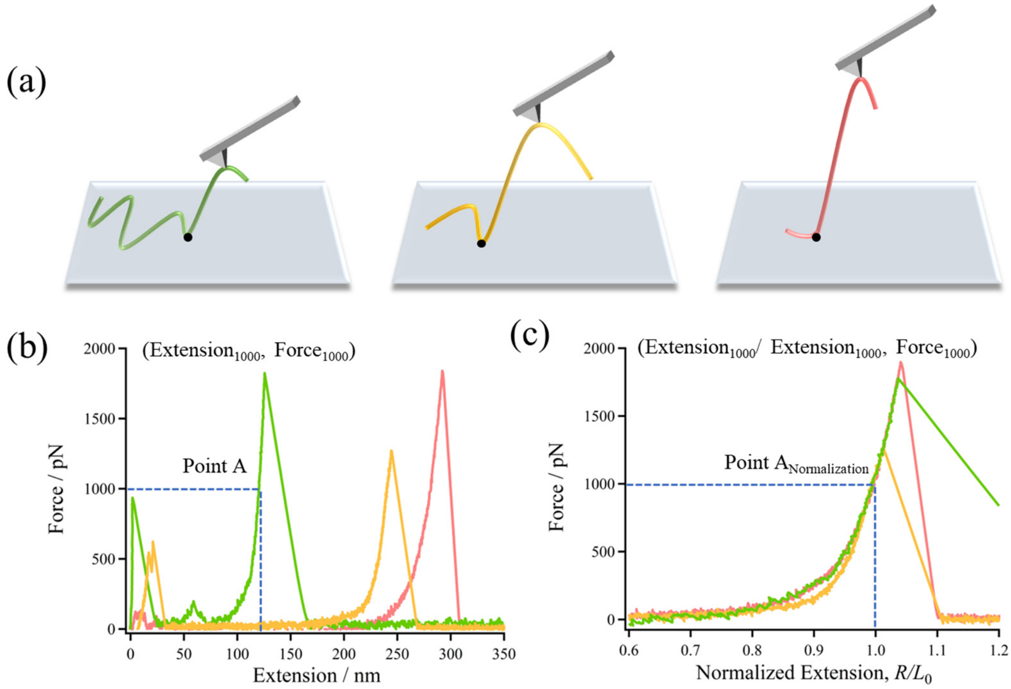

Figure S3. (a) Several conditions of the PC being stretched in nonane. The black dot indicates the attachment point of the PC to the substrate. (b) Several *F*-*E* curves of PC acquired in nonane. The coordinate of point A on the green *F*-*E* curve can be expressed as (Extension_{1000}, Force_{1000}). (c) Normalized *F*-*E* curves derived from (b). The coordinate of point $\text{A}_{\text{Normalization}}$ in the green *F*-*E* curve can be expressed as ($\text{Extension}_{1000}/\text{Extension}_{1000}$, Force_{1000}).

Table S1. Type 1/Type 2 population ratio in different environments or solvents.

	Specific Condition	**Type 1: Type 2 Raw ratio**	**Type 1: Type 2 Normalized ratio**
Solvents	PC/DCM	12:13	1:1.08
	PC/DMF	7:6	1:0.85
	PC/DMSO	5:6	1:1.22
Environments	Nonane	12:14	1:1.17
	DMF	7:6	1:0.86
	n-pentanol	6:5	1:0.83

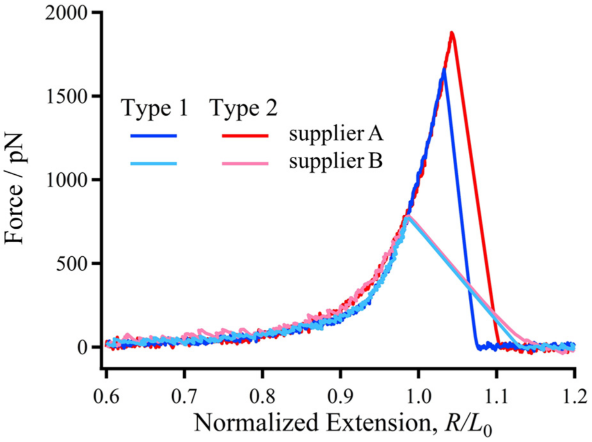

Figure S4. Comparison of the normalized *F-E* curves of PC from different suppliers obtained in nonane.

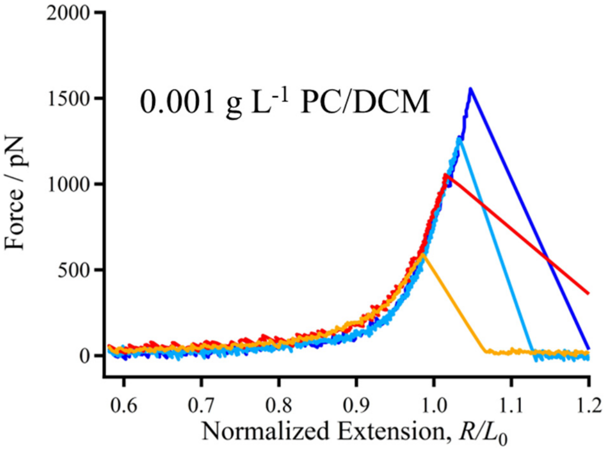

Figure S5. The normalized *F*-*E* curves of PC from a 0.001 g L^{-1} PC/DCM solution obtained in nonane.

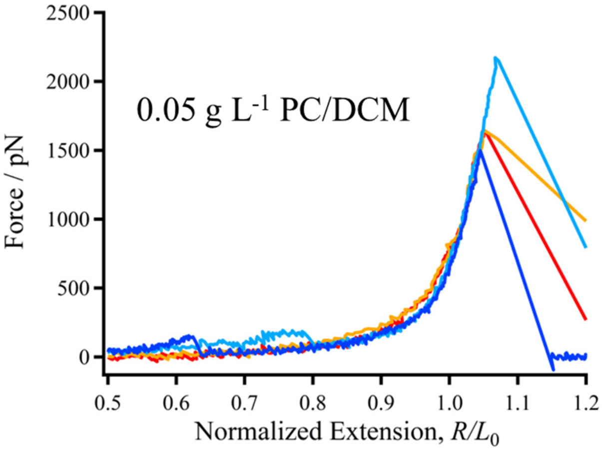

Figure S6. The normalized *F*-*E* curves of PC from a 0.05 g L^{-1} PC/DCM solution obtained in nonane.

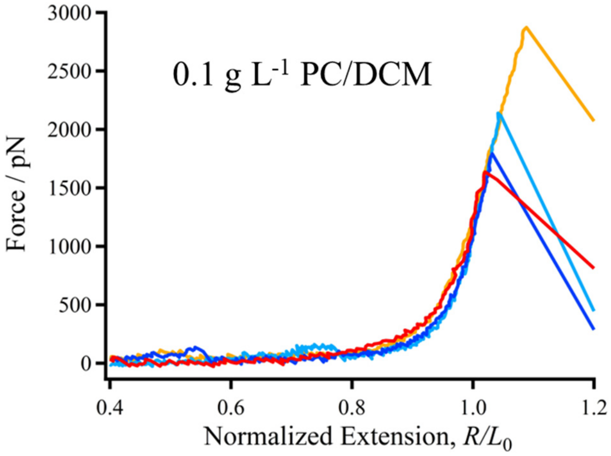

Figure S7. The normalized *F*-*E* curves of PC from a 0.1 g L^{-1} PC/DCM solution obtained in nonane.

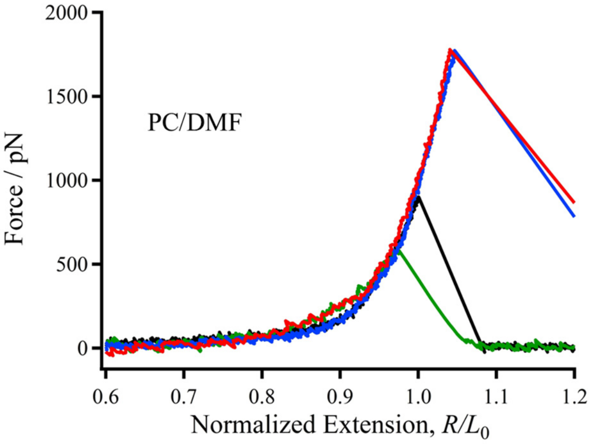

Figure S8. The normalized *F-E* curves of PC from a PC/DMF solution obtained in nonane.

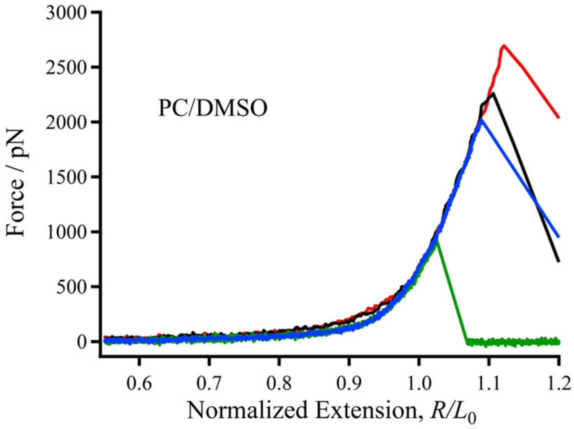

Figure S9. The normalized *F-E* curves of PC from a PC/DMSO solution obtained in nonane.

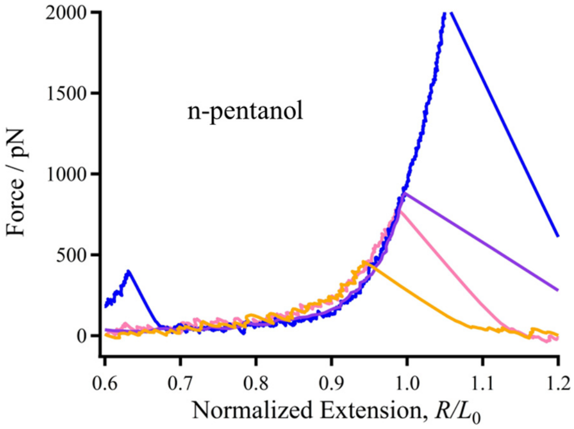

Figure S10. The normalized *F*-*E* curves of PC from a PC/DCM solution acquired in n-pentanol.

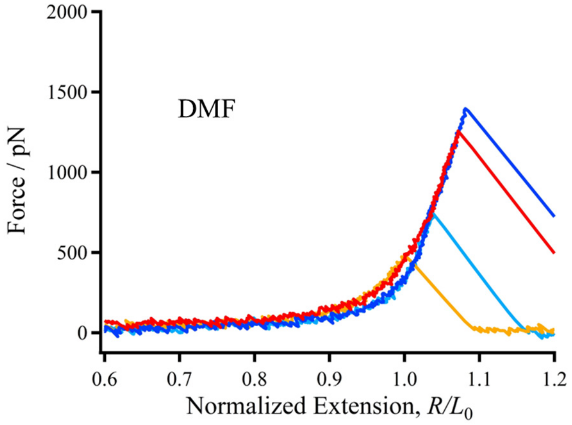

Figure S11. The normalized *F-E* curves of PC from a PC/DCM solution acquired in DMF.

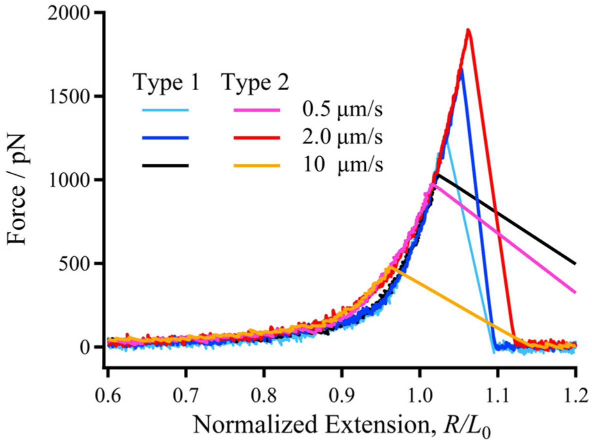

Figure S12. The normalized single-chain *F*-*E* curves of PC from a 0.01 g/L PC/DCM solution obtained in nonane at different stretching velocities (0.5, 2.0, and 10 μm/s).

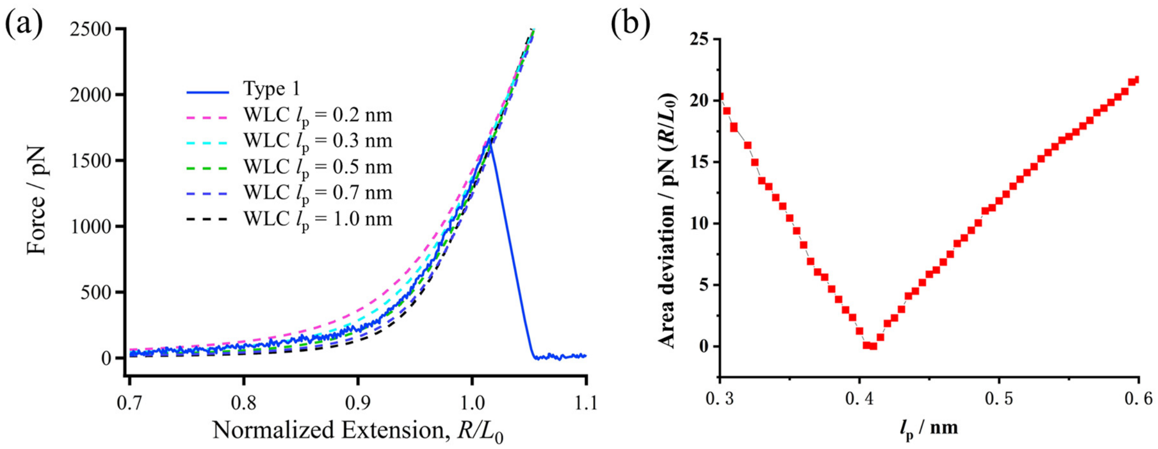

Figure S13. (a) Comparison between the Type 1 curve of PC (solid blue line) and the QM-WLC fitting curves with different l_p values: l_p = 0.2 nm (dashed pink line), l_p = 0.3 nm (dashed cyan line), l_p = 0.5 nm (dashed green line), l_p = 0.7 nm (dashed purple line), and l_p = 1.0 nm (dashed black line). (b) The area deviation between the Type 1 curve of PC obtained in nonane and the corresponding QM-WLC fitting curves plotted as a function of l_p, showing a minimum approaching zero at l_p = 0.41 nm.

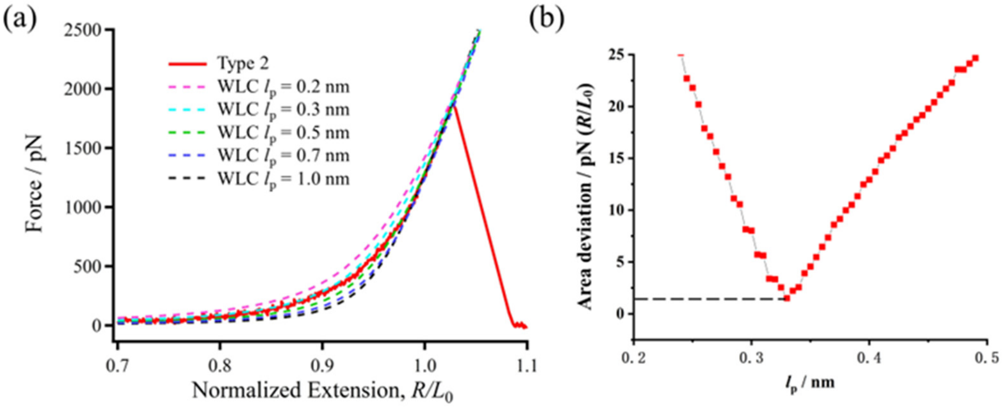

Figure S14. Comparison between the Type 2 curve of PC (solid red line) and the QM-WLC model with different l_p values: l_p = 0.2 nm (dashed pink line), l_p = 0.3 nm (dashed cyan line), l_p = 0.5 nm (dashed green line), l_p = 0.7 nm (dashed purple line), and l_p = 1.0 nm (dashed black line). (b) The area deviation between the Type 2 curve of PC obtained in nonane and the QM-WLC fitting curves with varying l_p values reached a minimum of 1.51 pN·(R/L_0).

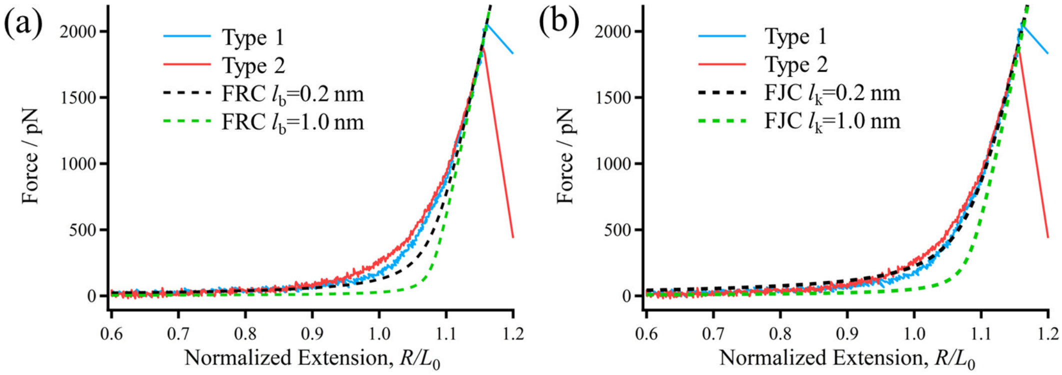

Figure S15. Comparison of Type 1 (solid blue line) and Type 2 (solid red line) curves with (a) QM-FRC model fits using l_b = 0.2 nm (dashed black line) and 1.0 nm (dashed green line), and (b) QM-FJC model fits using l_k = 0.2 nm (dashed black line) and 1.0 nm (dashed green line).

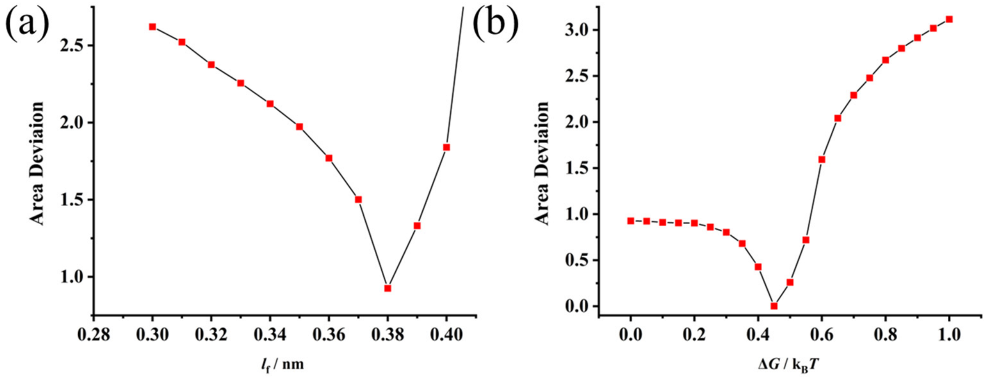

Figure S16. The area deviation between the Type 2 curve of PC obtained in nonane and the TSQM-WLC fitting curves, (a) with $\Delta G = 0$ k_BT module^{-1} and $l_f = 0.3$-0.41 nm; (b) with $l_f = 0.38$ nm and $\Delta G = 0$-1 k_BT module^{-1}.

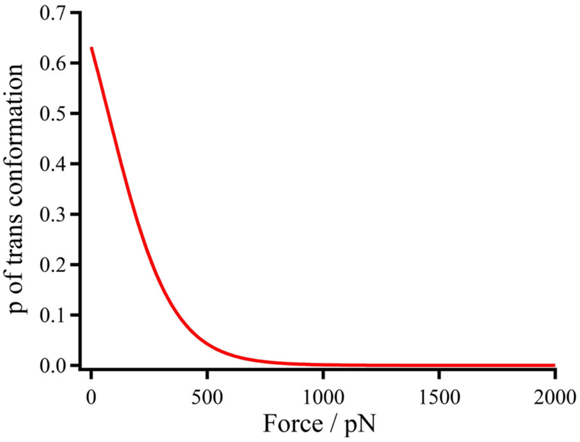

Figure S17. Proportion of *trans* conformation of PC under different forces.

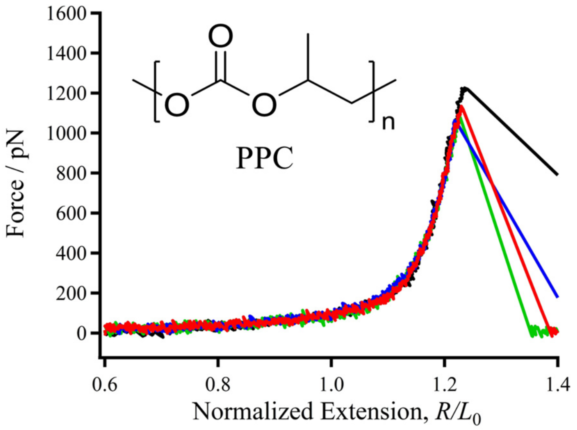

Figure S18. Normalized single-chain *F-E* curves of PPC from a 0.01 g L^{-1} PPC/DCM solution in nonane. Inset: the primary structure of PPC.

References

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