Electronic Supplementary Information (ESI)

Effect of size of solvent molecule on the single-chain mechanics of poly(ethylene glycol): implications on a novel design of molecular motor

Zhonglong Luo[a], Bo Zhang[a], Hu-jun Qian[b], Zhong-yuan Lu[b], Shuxun Cui*[a]

[a]Key Laboratory of Advanced Technologies of Materials, Ministry of Education, Southwest Jiaotong University, Chengdu 610031, China

[b]State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

*E-mail: cuishuxun@swjtu.edu.cn (S.C.).

Table S1. The melting points of the organic solvents: n-octadecane, n-eicosane and n-docosane.

	melting point (°C)
n-octadecane ($C_{18}H_{38}$)	28.2
n-eicosane ($C_{20}H_{42}$)	36.8
n-docosane ($C_{22}H_{46}$)	44

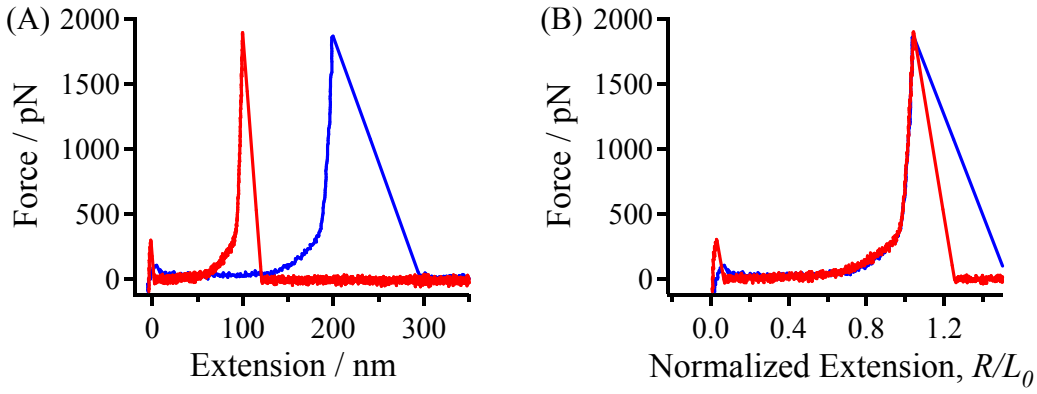

Fig. S1 (A) The typical single-chain F-E curves of PEG obtained in 1×PBS buffer. (B) The normalized single-chain F-E curves of those shown in (A). The good superposition of the force curves indicates that these F-E curves present the single-chain elasticity of PEG in water. This result implies that the PEG molecule assumes a helical conformation in water.

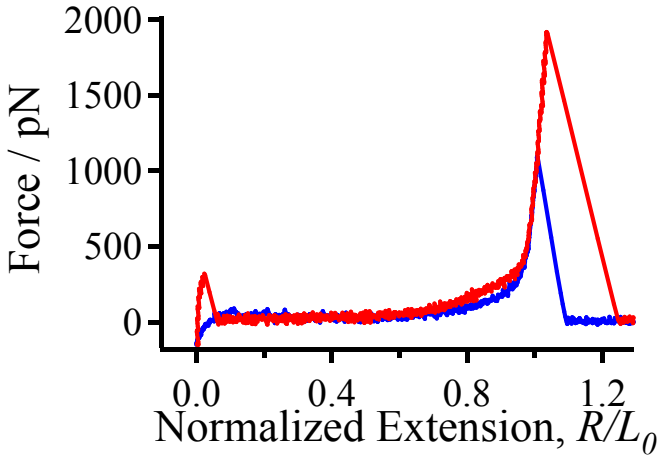

Fig. S2 The normalized single-chain F-E curve of PEG obtained in PBS (red) and TCE (blue). There is a marked difference between them.

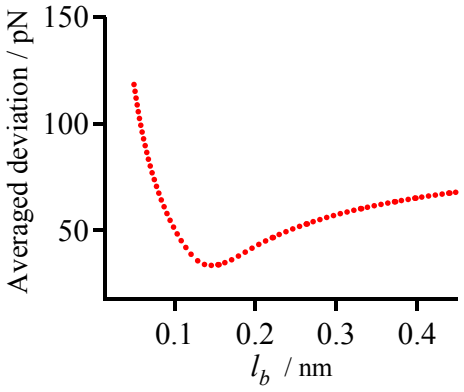

Fig. S3 Averaged deviation of force between an experimental F-E curve of PEG obtained in TCE and the QM-FRC fitting curves with various l_b values. The saddle point is determined to be the optimum value of l_b for the corresponding F-E curve.

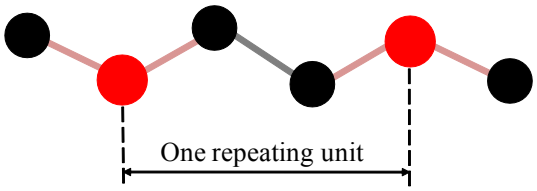

Fig. S4 The structure of PEG backbone. The lengths of the C-C bond and C-O bond are 0.154 nm and 0.143 nm, respectively. One can find that there are two C-O bond and one C-C bond in a repeating unit. Therefore, for a PEG chain, the average lengths of one C-C bond and two C-O bonds can be used as the rotating units, which is (0.154 + 2 × 0.143) nm / 3 = 0.147 nm. This value is very close to the the optimum value of l_b in the QM-FRC model.

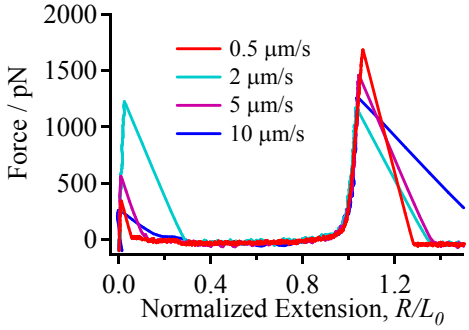

Fig. S5 The normalized F-E curves of PEG obtained in hexadecane under different pulling speed.

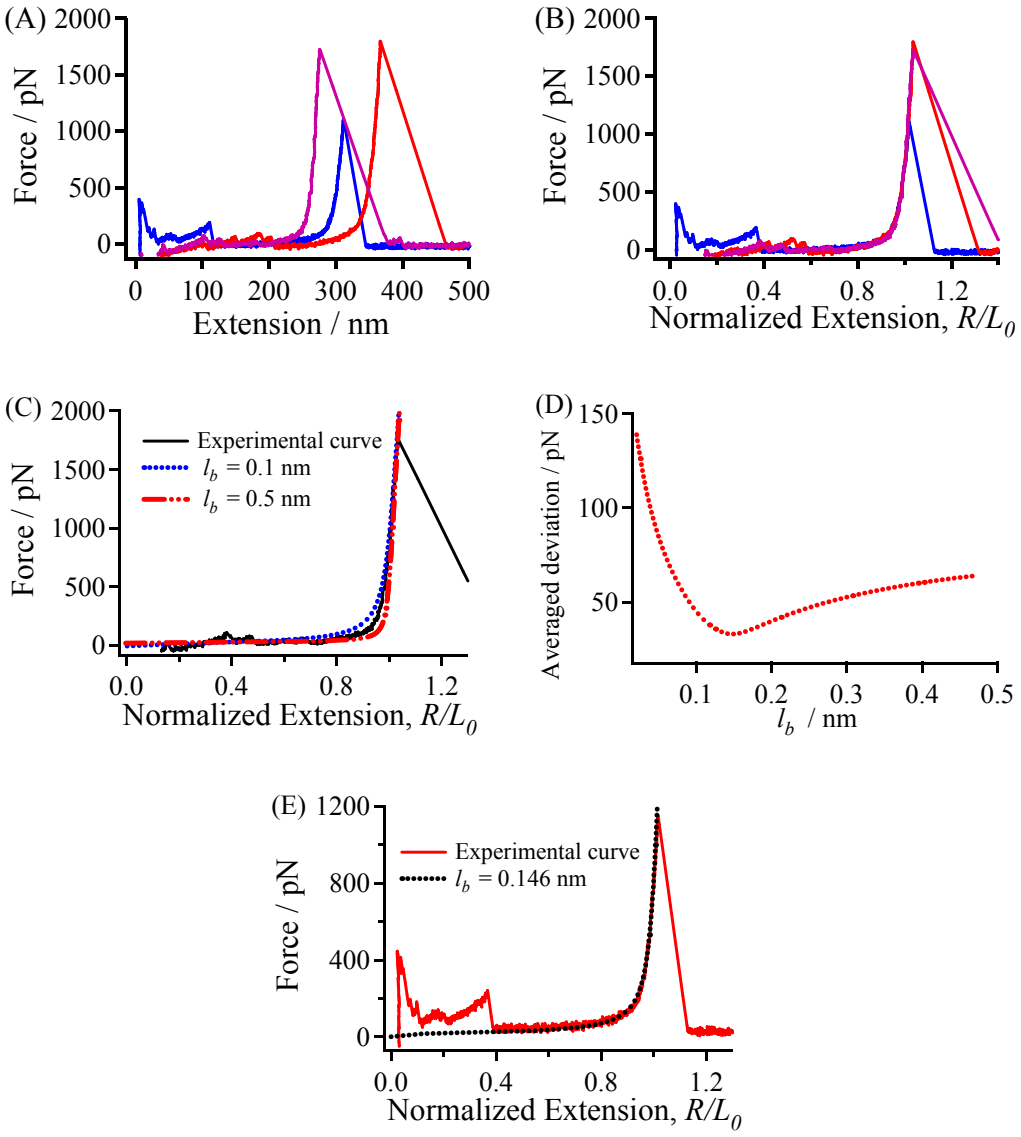

Fig. S6 (A) The F-E curves of PEG obtained in nonane. (B) The normalized F-E curves of those shown in (A). (C) Normalized F-E curves of PEG obtained in nonane vs QM-FRC fitting curves with various l_b values. (D) Averaged deviation of force between an experimental F-E curve of PEG in (C) and QM-FRC fitting curves with various l_b. The saddle point is determined to be the optimum value of l_b for the corresponding F-E curve in (C). (E) The F-E curves of PEG obtained in nonane can be superposed well by the QM-FRC fitting curve at $l_b = 0.146$ nm, (dotted line).

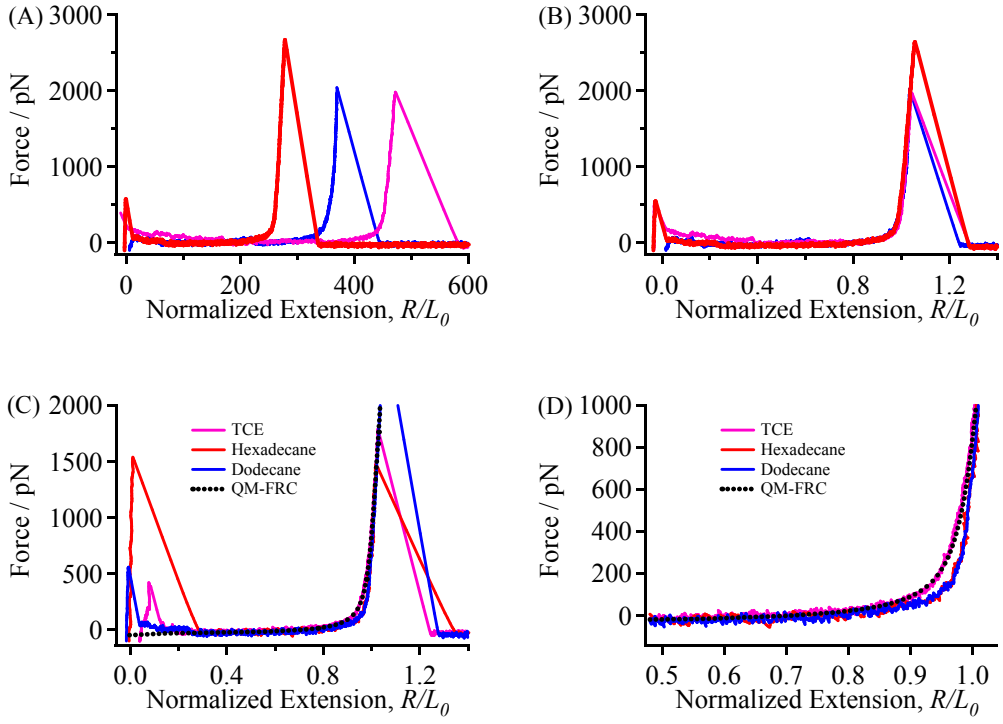

Fig. S7. (A) The F-E curves of PEG obtained in dodecane. (B) The normalized F-E curves of those shown in (A). (C) The normalized F-E curve of of PEG obtained in different nonpolar solvent. There is a marked difference between them. (D) To show a clearer difference between them, the F-E curves in (C) are enlarged.

The details of *ab*-initio calculations

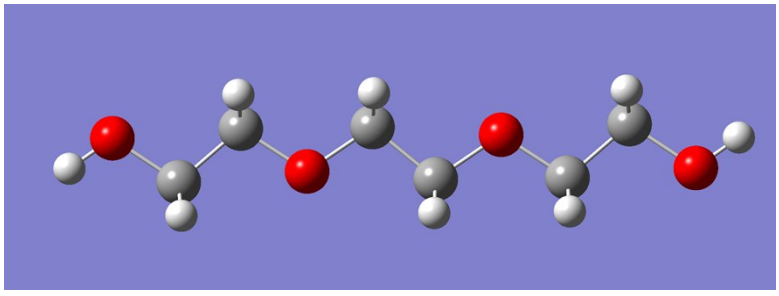

Fig. S8. PEG units used in the QM calculation. Ending oxygen atoms at both ends are kept at fixed distances.

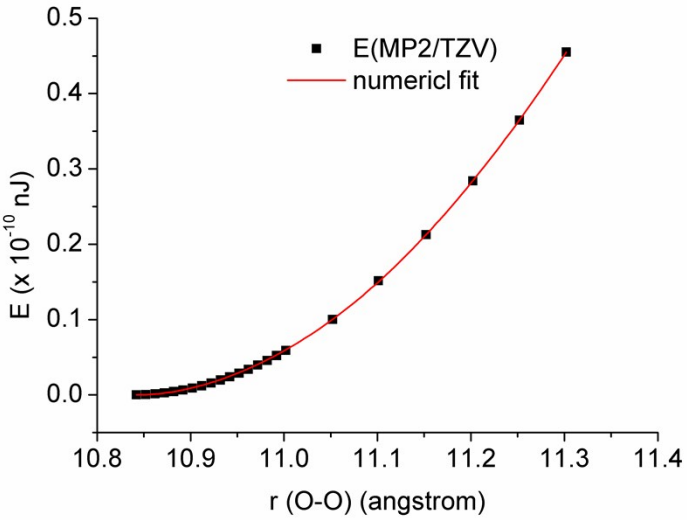

Fig. S9. The energies of stretched configurations at fixed distances between two ending oxygen atoms calculated at the MP2/TZV//B3LYP/TZV dual-level of theory. Solid line denotes the polynomial fit with eqn (S1).

All quantum mechanical (QM) calculations are carried out using the GAUSSIAN 09 program. A PEG trimer (as shown in Figure S8) terminated with –OH groups are used in our calculation. The distance between the two ending oxygen atoms is fixed at different values in our calculations, while the positions of all other atoms are optimized to minimize the total energy. The calculations are performed at the MP2/TZV//B3LYP/TZV dual-level of theory. Figure S9 presents the energy difference by stretching the model PEG trimer at fixed distances between two ending oxygen atoms, taking the unstreched ground state as the energy reference. The solid line in Figure S9 denotes polynomial fit according to

$$E = E_0 - L_0 \sum_{n=2}^{6} \gamma_{n-1} \left(L[E]/L_0 - 1 \right)^n / n \qquad \text{(S1)}$$

where L_0 is the length of the repeating unit at zero force, $L[E]$ is the length at a given extension with energy E. Fitting QM data to eqn (S1) gives γ_1 = 65.0 nN, γ_2 = -

2.65×10^3 nN, γ_3 = 1.44×10^5 nN, γ_4 = - 3.38×10^6 nN, and γ_5 = 2.82×10^7 nN. The derivative of this equation leads to the force expression, which is actually measurable experimentally,

$$F = \sum_{n=1}^{5} \gamma_n \left(L[F] / L_0 - 1 \right)^n \quad \text{(S2)}$$

where $L[F]$ is the length at the given force, F, as shown in eqn (2) in the main text.