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Stretching Elasticity and Flexibility of Single Polyformaldehyde Chain

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Electronic Supplementary Information

Abstract In this work, the single-chain elasticity of polyformaldehyde (POM) is studied, for the first time, by employing atomic force microscopy (AFM)-based single molecule force spectroscopy (SMFS). We find that the single-chain elasticity of POM in a nonpolar organic solvent (nonane) can be described well by a theoretical model (QM-FRC model), when the rotating unit length is 0.144 nm (C—O bond length). After comparison, POM is more flexible than polystyrene (a typical polymer with C—C backbone) at the single-chain level, which is reasonable since the C—O bond has a lower rotation barrier than C—C bond. This result indicates that the flexibility of a polymer chain can be tuned by the C—O bond proportion in backbone, which casts new light on the rational design of new synthetic polymers in the future.

Keywords Polyformaldehyde; Single molecule force spectroscopy; Inherent elasticity; Flexibility; QM-FRC model

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INTRODUCTION

Polyoxymethylene (POM), a linear polymer with high crystallinity, is very important in both polymer research history and applications.[1−3] As an engineering plastic, POM is used in a huge number of applications ranging from big functional parts in industry to tiny precision objects in electronics. The excellent mechanical properties of POM are closely related to its dense crystal structure formed by chain folding. During the past decades, studies of POM were focused on characterization by ensemble methods, such as crystal structures[1,4,5] and mechanical properties.[6,7] However, properties of single POM chain were rarely reported. One of the reasons is that the dispersion of a POM crystal into single chains is difficult due to the lack of good solvents at room temperature.[8,9] Although several solvents like the phenols are available for dissolving POM at elevated temperatures (>100°C), thermal instability of POM in this case discouraged the study of its single-chain properties.[10] Moreover, the traditional methods (such as light scattering, infrared spectroscopy and viscometry measurements) for the ensemble properties of polymer aggregates often failed in reflecting the nature of a single polymer chain, especially when the entanglement of chains occurs.

Here, we utilized atomic force microscopy (AFM)-based single molecule force spectroscopy (SMFS) to investigate single-chain mechanics of POM. To date, the elastic behaviors of many polymers, from synthetic polymers to biomacromolecules, have been successfully measured at the molecular scale by means of SMFS.[11−27] One of the advantages of SMFS is that an individual polymer chain can be directly manipulated and detected. In addition, an extremely low concentration (~2 mg/L) polymer solution is usually used in the SMFS experiment, in which the entanglement among polymer chains can be eliminated. The very dilute solution of POM can be easily obtained at a lower temperature, which minimizes the degradation of POM. The fundamental research will be helpful to understand the nature of this important polymer.

EXPERIMENTAL

Materials and Sample Preparation

POM (M_w=2.0×10^4) with a melting point of 165–180 °C was purchased from Dupont Corp. Poly(ethylene glycol) (PEG, M_w=3.5×10^4) and polystyrene (PS, M_w=2.0×10^5) were purchased from Sigma-Aldrich Inc. Deionized (DI) water (>18 MΩ·cm) was used when water was involved. The solvents, *i.e.*, nonane, tetrahydrofuran and *p*-chlorophenol (analytically pure, Sigma-Aldrich) were used without further treatment.

PEG was dissolved in DI water to a concentration of 2 mg/L. POM was dissolved in *p*-chlorophenol by stirring the mixture (400 r/min, 60 °C) to a concentration of 2 mg/L. PS was dissolved in tetrahydrofuran to a concentration of 50 mg/L. The quartz substrates were immersed in a hot piranha solution (a mixture of 98% H_2SO_4 and 35% H_2O_2, V/V=7/3) for 30 min, followed by washing with sufficient DI water and dried by air flow. A few drops of the prepared polymer solution were de-

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posited onto a clean substrate for 20 min. Then the excess polymer chains on the substrate surface were removed by pure solvent rinsing. The prepared sample was immediately used in the SMFS experiment.

Force Measurements

All force measurements were performed on an AFM (Nano Wizard II, JPK Instruments, Germany) at room temperature. Liquid was injected between the V-shaped Si_3N_4 AFM cantilever (Bruker Corp., CA) and the sample substrate before measurements. Force measurements were performed while force-extension (F-E) curves were recorded at the same time. The spring constant (~40 pN/nm) of each AFM cantilever was calibrated by the thermal fluctuation method. The details of the AFM-SMFS instrumentation can be found in literature.[11,28–30] Force measurements were repeated on multiple samples (at least three) to ensure the reproducibility of experimental results.

Quantum Mechanics Calculations

Theoretical single-chain elasticity of POM was obtained by quantum mechanics (QM) calculations with Gaussian 09 program. The molecule model used for QM calculations is dimethoxymethane (DMM, $CH_3O\text{-}CH_2\text{-}OCH_3$), see Fig. S1 (in the electronic supplementary information, ESI). The details of calculations are shown in ESI.

RESULTS AND DISCUSSION

Elastic Behaviors of Single POM Chain in Nonpolar Organic Solvents

Noncovalent interactions in polymer solution, such as hydrophobic effect and H-bonds, may affect the behaviors of the polymer chain remarkably.[28,31,32] Therefore, it is necessary to obtain the inherent elasticity of POM chain in a quasi-undisturbed environment. In nonpolar organic solvents, only weak van der Waals forces exist between solute and solvent molecules. Considering the molecular structure of POM, it is expected that the effect of vdW forces on the single chain elasticity is negligible.[33] Here, nonane was selected as the liquid environment for force measurements. The typical F-E curves of POM with different contour lengths obtained in nonane were displayed in Fig. 1. After the beginning part, the F-E curve increases monotonously with stretching distance until the maximum force is reached. With further elongation, the molecular bridge ruptures while the force returns to noise level shortly (Fig. 1a). All F-E curves generated from individual polymer chains with the same structure but varied contour length should have identical performance when they are scaled to the same length (*i.e.*, normalization).[30] The F-E curves can be superposed well after being normalized (Fig. 1b), meaning that each curve corresponds to a stretching event of single POM chain.

Theoretical Model and the Inherent Elasticity of Single POM Chain

The theoretical models are important to understand the single chain elasticity of polymers.[30,34] Classical models include the freely-jointed chain (FJC) model, freely rotating chain (FRC) model and worm-like chain (WLC) model. FJC and FRC models are often used to describe the elasticity of a flexible polymer chain, such as C—C backbone polymers and PEG.[30] Considering that the C—O bond of POM chain can rotate around its neighboring bond, FRC model is used to describe the elasticity of single POM chain. In this model, the relationship between the end-to-end distance R and the force F is described as follows:

$$R = L[F]\left[1 - \frac{k_BT}{(2Fl_b)}\right] \tag{1}$$

where k_B is Boltzmann constant, T is the temperature in the Kelvin scale, l_b is the length of rotating unit, *i.e.*, the length of a single bond (C—O bond for the case of POM) of polymer backbone, $L[F]$ is the contour length of polymer chain at a given force. The FRC model for POM is shown in Fig 2(a).

However, the deformations of bond length and angle are ignored in the FRC model, namely, the effect of enthalpic elasticity on the chain contour length is not considered.[35] Therefore, it is necessary to introduce the enthalpic elasticity by QM calculations to improve the FRC model. The enthalpic nonlinear elasticity of POM is expressed as follows:[36]

$$F = \sum_{n=1}^{3} \gamma_n \left(\frac{L[F]}{L_0} - 1\right)^n \tag{2}$$

where L_0 is the original contour length of the polymer chain, γ_1, γ_2 and γ_3 are the elastic coefficients of POM (γ_1=32870 pN, γ_2=−67425 pN, γ_3=3520 pN). By introducing QM calculation results into FRC model, the QM-FRC model is obtained:

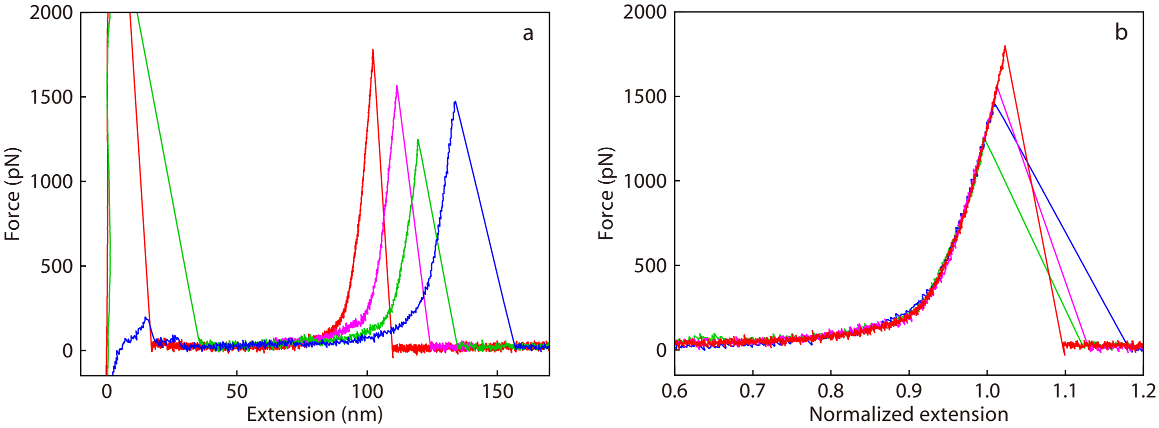

Fig. 1 (a) Typical single-chain F-E curves of POM obtained in nonane; (b) The normalized F-E curves of those shown in (a). (The online version is colorful.)

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$$R/L_0 = \left(L\left[F\right]/L_0\right)\cdot\left[1-\frac{k_BT}{2Fl_b}\right] \qquad (3)$$

where R/L_0 is the normalized extension of a polymer chain. Now, l_b is the only free parameter in the model.

During the elongation of the polymer chain, the value of $L\left[F\right]/L_0$ is increased from 1 with the increase of stretching force. In this study, the rupture force corresponding to the maximum of $L\left[F\right]/L_0$ is set to a typical value of covalent bond (2000 pN). According to Eq. (3), the maximum of $L\left[F\right]/L_0$ is 1.07. A fitting curve corresponding to each l_b can be obtained when $L\left[F\right]/L_0$ is increased from 1.00 to 1.07. For different l_b, the fitting curves differ in the lower force regime[35] (Fig. 2b). For a given contour length of polymer, the lower value of l_b, the higher entropic elasticity of the polymer chain. The l_b was analyzed in the scope of 0.1–0.5 nm with an increment of 0.001 nm. For a given value of l_b, the averaged deviation of force between the experimental and fitting curve of QM-FRC for all points, according to $\left(\sum_{i=1}^{n}\left|F_{\exp}-F_{\mathrm{fit}}\right|\right)/n$, can be obtained. The minimum deviation is obtained when l_b=0.144±0.001 nm (Fig. 2c and Fig. S3 in ESI), revealing that the value of l_b is suitable for POM.

It can be clearly observed that the fitting curve of QM-FRC can be superposed well with the F-E curve in nonane in the entire force regime (Fig. S4 in ESI) when l_b is set to 0.144 nm, indicating that POM shows its inherent single-chain elasticity in nonane,[37] *i.e.*, this nonpolar organic solvent (nonane) can be considered as the quasi-undisturbed environment of POM chain. Interestingly, this value for l_b exactly equals to the length of a C—O bond, showing that the QM-FRC model is a structure relevant model for POM.

Comparison of Inherent Elasticity of Chains with Different C—O Bond Proportions

It was reported that the flexibility of POM and PS is virtually the same.[9] However, it can be inferred that the polymer of C—O backbone should be more flexible than that of C—C backbone, since the C—O bond has a lower rotation barrier than that of C—C bond.[38]

To prove this conjecture, the single chain inherent elasticity F-E curves of three polymers (POM, PEG[39] and PS[36]) with different C—O bond proportions in the backbone were compared. PS is a C—C backbone polymer with a phenyl side group. Wang *et al.* reported that the side group of PS in a nonpolar organic solvent has no significant effect on its chain elasticity.[36] Thus, PS can be used as a representative of C—C backbone polymer here. With modified-freely jointed chain (M-FJC) model, the flexibility of these polymers can be distinguished by comparing the elastic modulus (K_0) from the curve fitting.[40] The smaller K_0, the more flexible of the polymer chain (see ESI for detail). It can be found that the modulus K_0 decreased in an order from PS (~ 0% C—O bonds in the back-

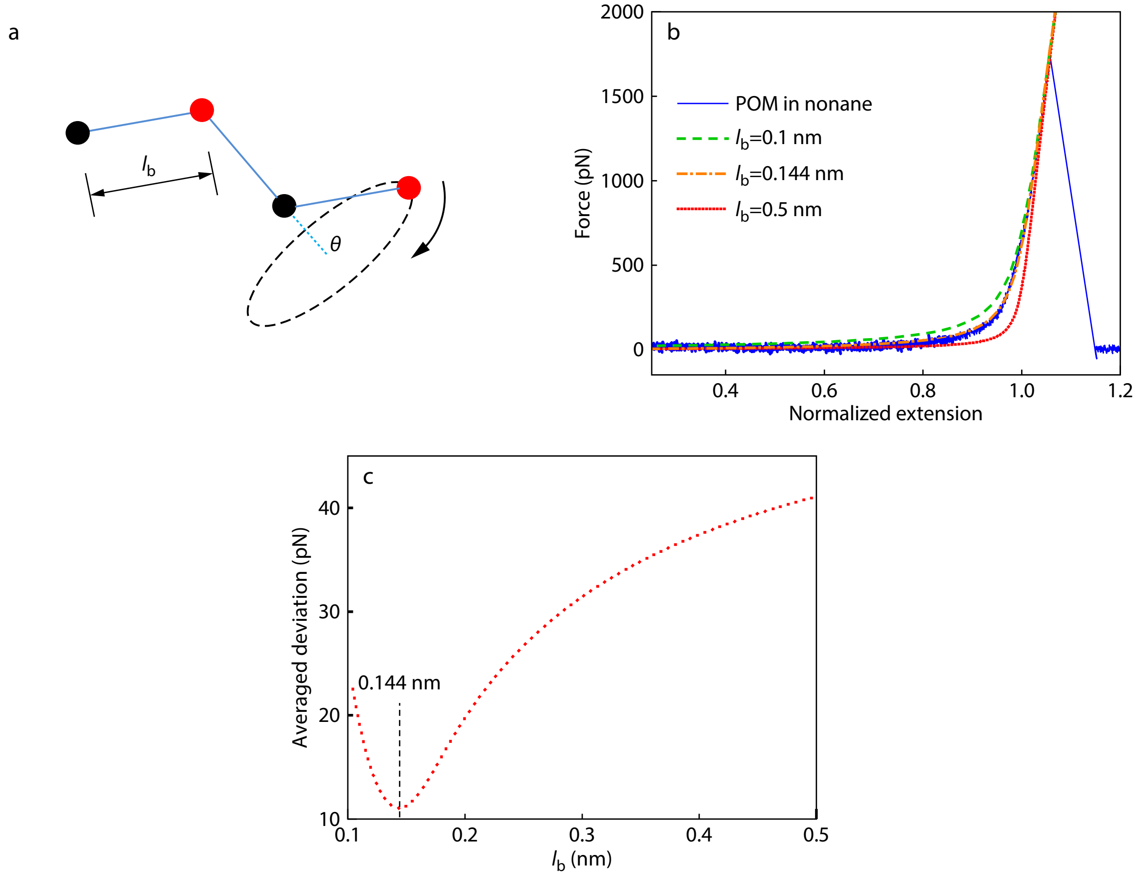

Fig. 2 (a) Diagram of FRC model for POM. Black and red balls represent C and O atoms, respectively. The bond angles of POM chain are fixed to a constant value, but each C—O bond is allowed to rotate freely; (b) QM-FRC fitting curves with different l_b values versus POM F-E curve in nonane; (c) Average deviation of force between POM curve in nonane and the QM-FRC fitting curve. The minimum value is obtained at l_b=0.144 nm.

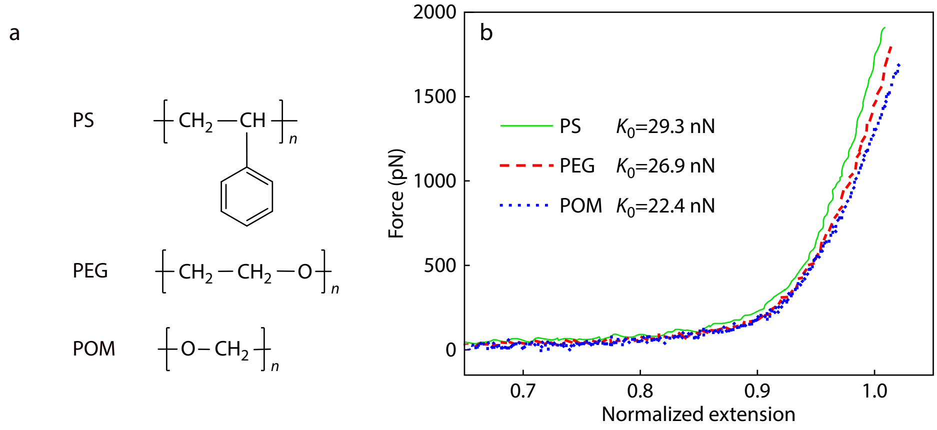

Fig. 3 (a) The chemical structures of PS, PEG and POM; (b) Comparison of the single-chain flexibility of these polymers.

bone, K_0=29.3 nN), PEG (~50% C—O bonds in the backbone, K_0=26.9 nN) to POM (~100% C—O bonds in the backbone, K_0=22.1 nN), indicating that the chain flexibility increased in the same order (Fig. 3b). The results show that the flexibility of a polymer chain can be tuned by the C—O bond proportion in backbone and the POM chain (C—O backbone) is the most flexible one in the three polymers.

CONCLUSIONS

In this study, the elastic behaviors of POM at single chain level were detected by SMFS for the first time. Nonane was selected as the quasi-undisturbed environment of POM chain. The elastic stretching event of single POM chain in nonane was observed. The QM-FRC model is established by introducing the enthalpic elasticity of POM into the FRC model. We find that the single chain elasticity of POM in nonane can be described well by the QM-FRC model, meaning that inherent elasticity of single POM chain was achieved. The value of l_b (0.144 nm) in model fitting exactly equals to the length of a single C—O bond, indicating that the new model is relevant to the structure of POM. In the future, the nature of interactions between the POM chain and solvent molecules can be revealed by exploring single chain mechanics of POM in various solvents.

A comparison of elastic modulus (K_0) of single polymer chains showed a decreased tendency in the order of PS (~0% C—O bonds), PEG (~50% C—O bonds) and POM (~100% C—O bonds). This result indicates that POM is a very flexible polymer although its bulk material shows very high rigidity. It also suggests that the flexibility of a polymer chain can be tuned by the C—O bond proportion in the backbone, which may cast a new light on the rational design of new synthetic polymers.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-022-2679-3.

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