Single-molecule studies reveal the mechanism of strong and weak polyelectrolytes in aqueous solution

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1. The details of the QM-FRC model fitting.

In the FRC model,[1,2] the relationship between the stretching force (F) and the extension (R) of the chain can be written as

$$R = L[F]\left[1 - k_B T/(2Fl_b)\right] \quad \text{S1}$$

In Eq S1, k_B is the Boltzmann constant, T is temperature, l_b is the length of the rotating unit, F is the stretching force acted on the polymer chain, $L[F]$ is the contour length of the chain at a given F, and R represents the extension of the polymer chain (end-to-end distance).

Note that $L[F]$ increases with the increasing of force. Considering that the bond angles and bond lengths are increased upon elongation, the quantum mechanical (QM) calculations are used to obtain the theoretical elasticity of the polymers with a C-C backbone.[3] In the QM calculations, the polymer chain only has H atoms as 'side chains'. These results have been used successfully to describe the single-molecule elasticity of the polymers with C-C backbones (PDEAm, PAAm and PS).[4] This result suggests that the influence of the side chains on the polymer single-chain enthalpic elasticity (SCEE) of these polymers can be ignored. Therefore, for most polymers with a C-C backbone, we hypothesize that the SCEE will not be influenced by the side chains. Thus, we can use the same elastic modulus below:

$$F = \sum_{n\,=\,1}^{3} \gamma_n \left({}^{L[F]}/_{L_0} - 1 \right)^n$$

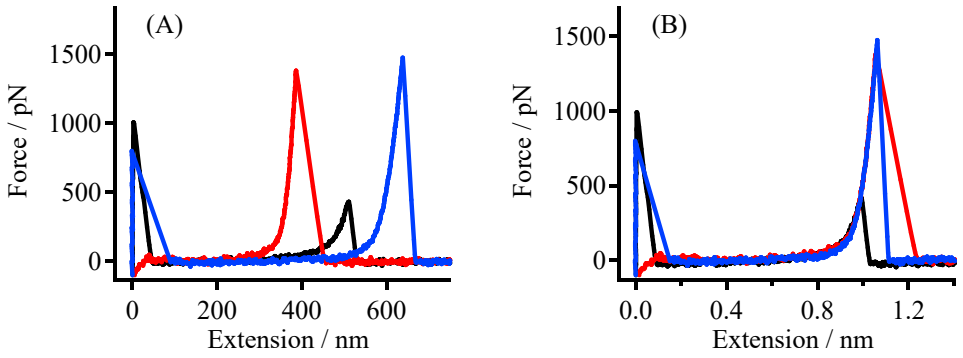
$$\gamma_1 = 28.7\ nN,\ \gamma_2 = -42.0\ nN,\ \gamma_3 = 16.9\ nN \qquad \text{SE 2}$$

where L_0 is the contour length of the polymer chain at zero force. Therefore, if we normalize the end-to-end distance by L_0, the model can be modified as

$$ {}^{R}/_{L_0} = \left({}^{L[F]}/_{L_0} \right) \cdot \left[1 - {}^{k_B T}/_{(2Fl_b)} \right] \qquad \text{S3}$$

where R/L_0 is the normalized extension of a polymer chain. The details of this model can be found in the reference.[1-4] In brief, ${}^{L[F]}/_{L_0}$ increases with increasing F (F can be calculated by Eq S2) until the breakage of the polymer bridge. Thus, the model has only one parameter (^{l_b}) left. The modified FRC model (Eq S3), which is integrated with the QM results, is called the QM-FRC model. Taking into account that the molecular structure of PSSNa has the same C-C backbone with the previously studied polymers,[2] we also use the result (${}^{l_b} = 0.154\ nm$) to obtain the fitting curve, because the C−C bond length is represented by the value of ^{l_b}. Thus, a QM-FRC fitting curve can be generated, see Fig. 2.

2. Supporting Figueres



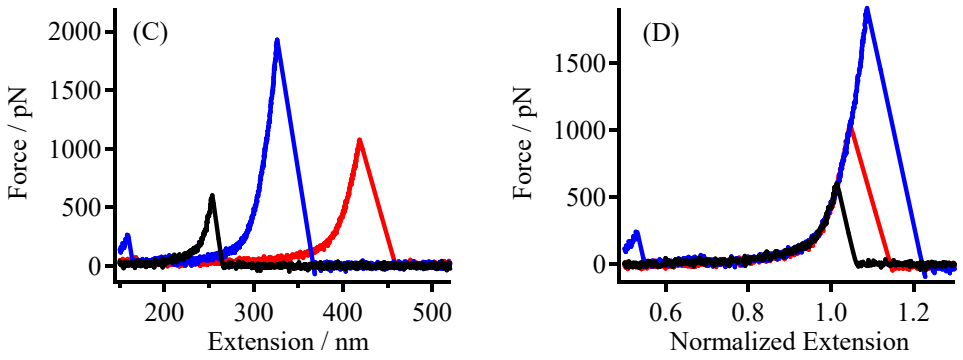


Fig. S1 The single-chain F-E curves of PSSNa (a) Original curves (b) Normalized curves; and PAA (c) Original curves (d) Normalized curves obtained in octylbenzene.

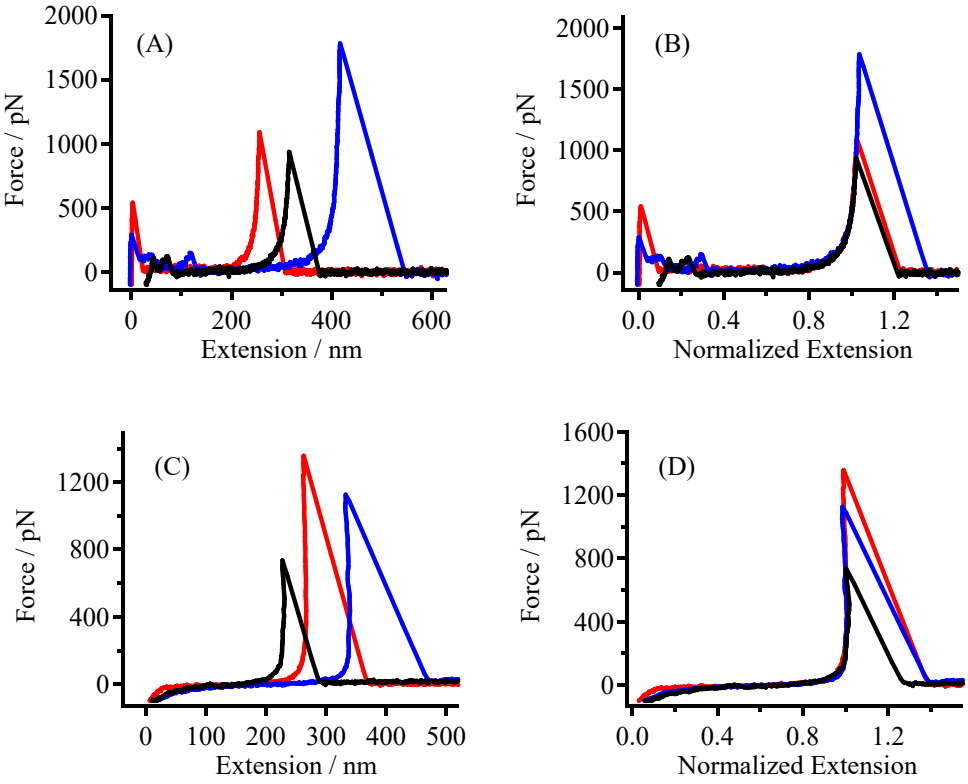


Fig. S2 The single-chain F-E curves of PSSNa (a) Original curves (b) Normalized curves; and PAA (c) Original curves (d) Normalized curves obtained in DI water.

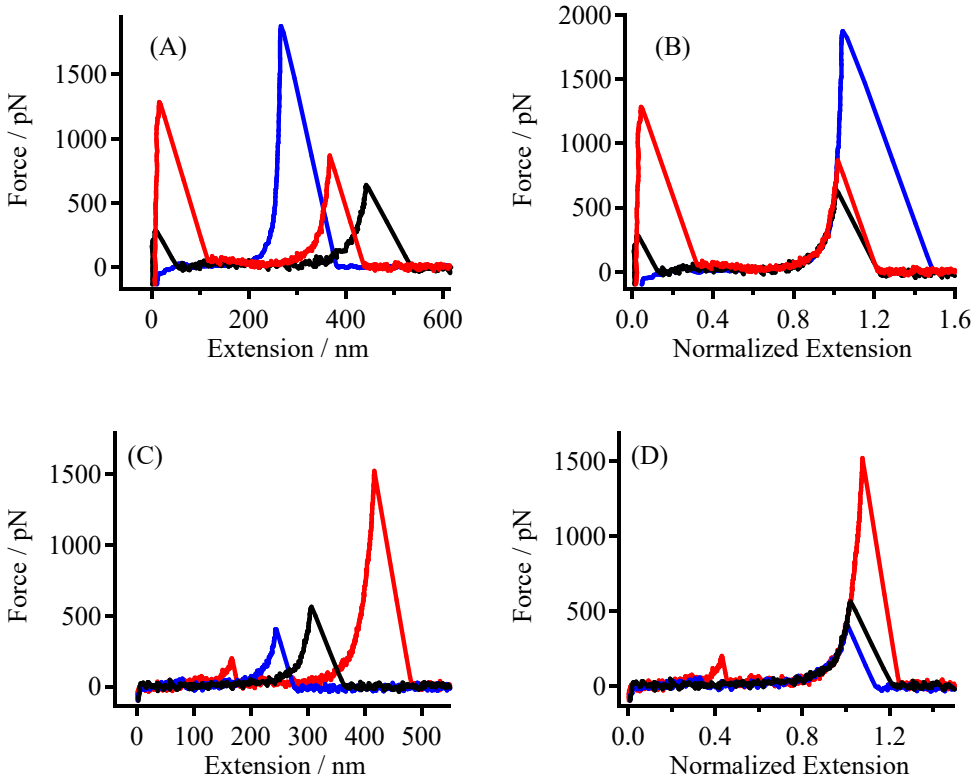


Fig. S3 The single-chain F-E curves of PSSNa (a) Original curves (b) Normalized curves; and PAA (c) Original curves (d) Normalized curves obtained in disodium hydrogen phosphate-citrate buffer (pH = 8).

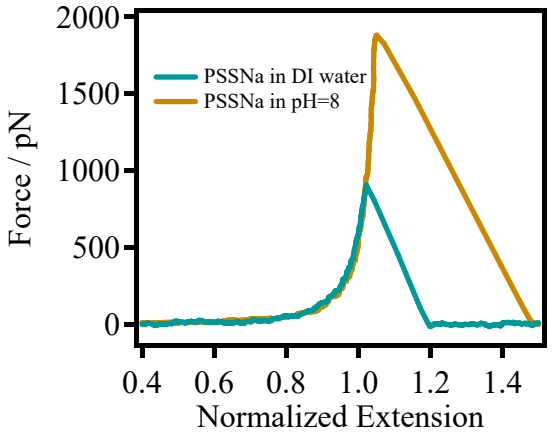


Fig. S4 The single-chain F-E curves of PSSNa in DI water and disodium hydrogen phosphate-citrate buffer (pH = 8).

References

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