Electronic Supplementary Information

How specific ion effects influence the mechanical behaviors of amide macromolecules? A cross-scale study

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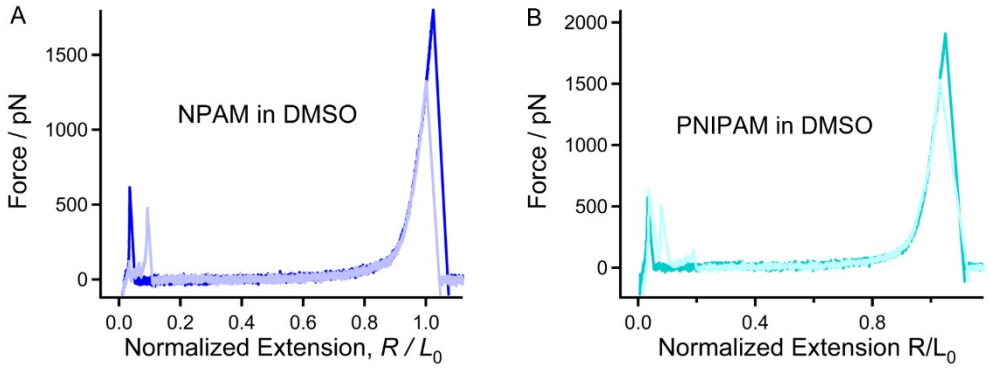

Figure S1. Normalized F-E curves of NPAM and PNIPAM obtained in DMSO.

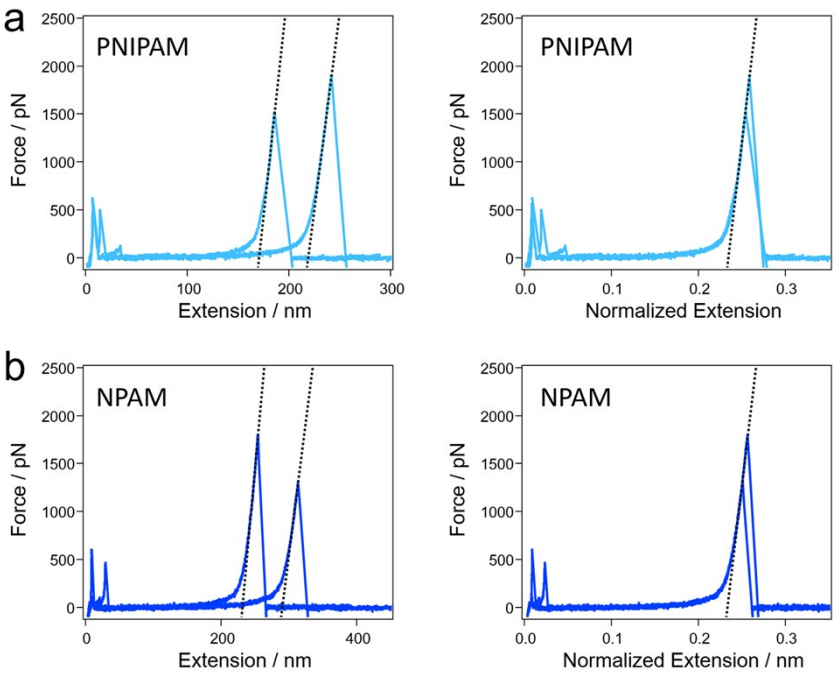

Figure S2 (**a**) Left: the original F-E curves of PNIPAM obtained in DMSO and their respective linear fitting curves to the high forces. Right: the normalized F-E curves of PNIPAM to a contour length of its segment (0.25 nm), and the linear fitting curve. (**b**) The curves of NPAM the same to (a). From the fitting, we obtain the segment elasticity of 76.2 ± 0.3 and 77.6 ± 0.3 nN/nm for PNIPAM and NPAM respectively, which are almost the same each other since they share the same backbone.

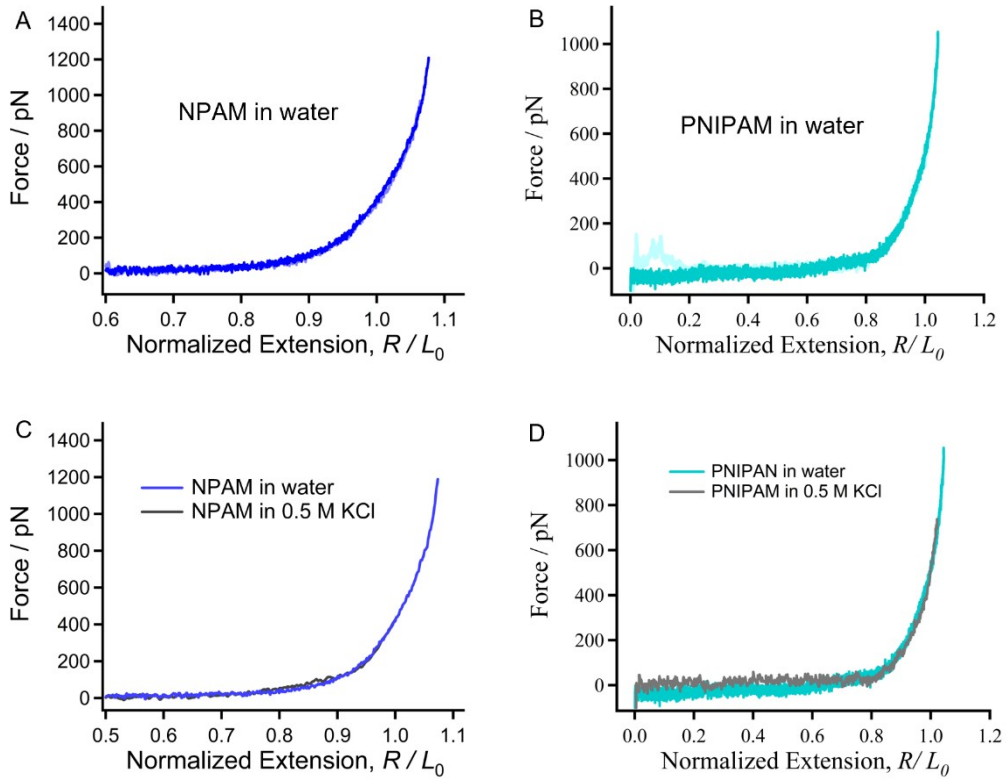

Figure S3. Normalized F-E curves of PNIPAM and NPAM obtained in ultrapure water and 0.5 M KCl.

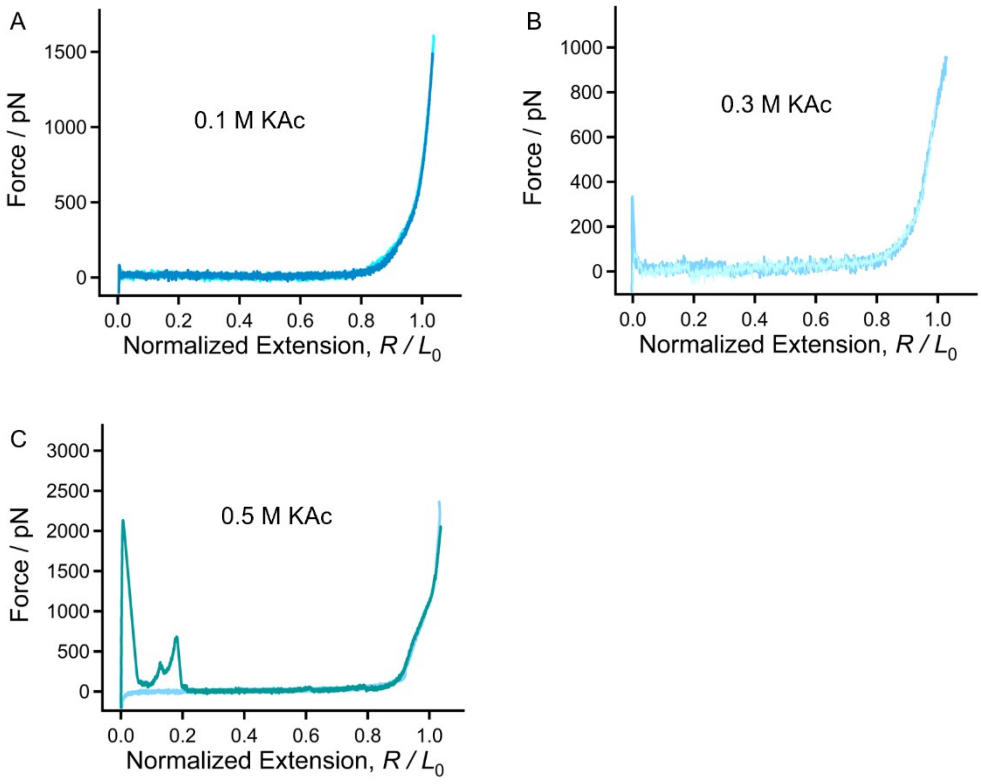

Figure S4. Normalized F-E curves of PNIPAM obtained in KAc solutions with concentration gradient.

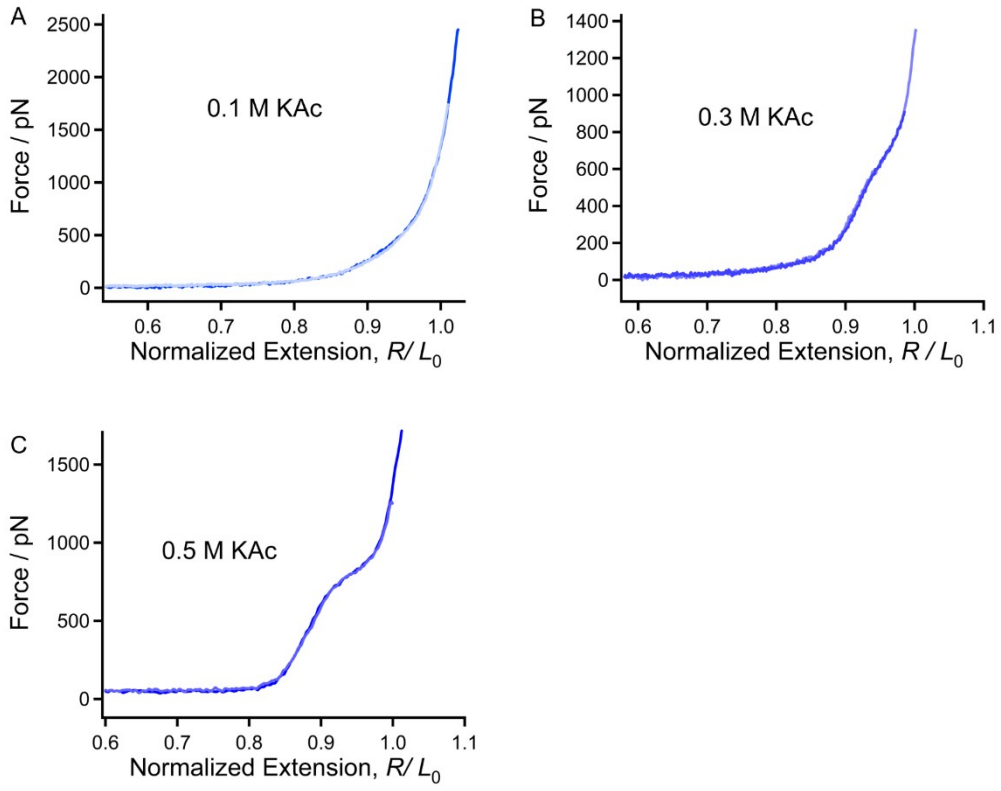

Figure S5. Normalized F-E curves of NPAM obtained in KAc solutions with concentration gradient.

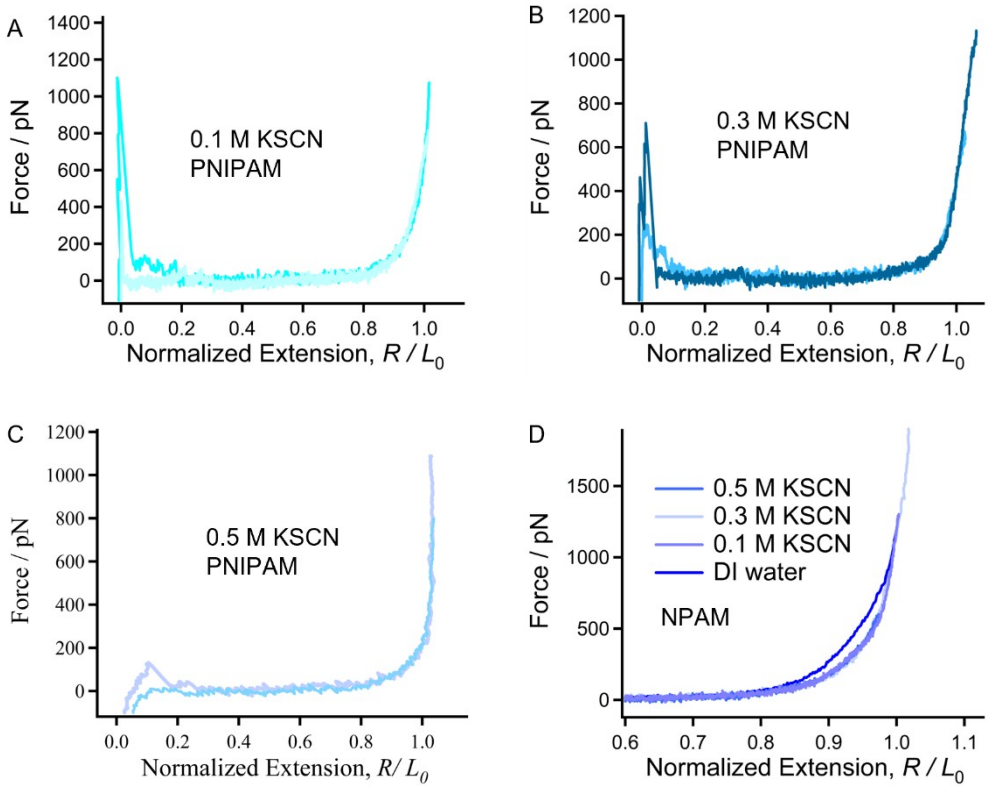

Figure S6. Normalized F-E curves of PNIPAM and NPAM obtained in KSCN solutions with concentration gradient.

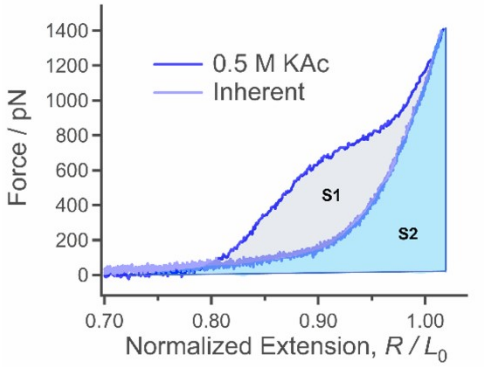

Figure S7. Stretching energy of NPAM in 0.5 M KAc (S1+S2) comparing to its inherent stretching energy (S2). The upper force is 1400 pN, which corresponds to the strength of most covalent bonds.

Theoretical Background of Cui method.

The original models. The entropic elasticity of a polymer chain can be described well by FRC, FJC or WLC model, depending on the flexibility of the backbone. In general, FRC model is suitable for flexible polymers, for example, these with a C-C backbone. FJC model shows respectable applicability for semi-rigid chains. WLC model is appropriate for rigid chains. The forms of FRC, FJC and WLC model are shown in Eqs S1-S3 in turn:

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

$$R = L[F]\cdot \{\coth \left[\left(F\cdot l_k\right)\right]/(k_B T)] - (k_B T)/(F\cdot l_k)\} \quad \text{(S2)}$$

$$F\cdot\frac{l_p}{k_B T} = \frac{R}{L[F]}\cdot + \frac{1}{4(1 - R/L[F])^2} - \frac{1}{4} \quad \text{(S3)}$$

In these equations, R is the end-to-end distance of a polymer chain at given stretching force F, $L[F]$ is the contour length of the polymer chain being stretched, k_B is the Boltzmann constant, T isthe temperature, l_b , l_k and l_p are the rotating unit length, Kuhn length and the persistence length the polymer chain, respectively. the original models have two free parameters. One is the contour length of the polymer and another is l_b for FRC, l_K for FJC and l_p for WLC. It must be pointed out that the three basic models are all entropic models based on the conformational change of the chain despite the deformation of the backbone itself. Therefore, these models failed to describe the enthalpic elasticity of a polymer at high forces, where the bond length and angle are largely deformed.

Quantum-mechanical (QM) calculation. The deformation of the polymer backbone can be calculated precisely via QM calculations, which provides the relationship between extension and the stretching energy of the bond (the scatter plots in Figure S7). The elastic modulus ($\gamma_i, i = 1,2,3\cdots$) of the chain can then be estimated by performing a polynomial fitting on the scatter plots (the solid line in Figure S7):

$$E = E_0 - a_0 \sum_{n=2}^{4} \gamma_{n-1} (a[E]/a_0 - 1)^n / n \tag{S4}$$

where a_0 is the length of the oligomer chain at zero force, $a[E]$ is the length at a given extension with energy *E*. The derivative of Eq S5 thus gives the relationship between the stretching force *F* and the countour length $a[F]$ in the calculations:

$$F = \frac{\partial E}{\partial a} = \sum_{n=1}^{m} \gamma_n \left(a[F]/a_0 - 1\right)^n \tag{S5}$$

or the countour length *L[F]* in a more general format:

$$F = \sum_{i=1}^{n} \gamma_i \left(\frac{L[F]}{L_0} - 1\right)^i \tag{S6}$$

The QM modified models. As described in Eqs S1-S3, each original model has two free parameters. One is the contour length of the polymer, *L[F]*. Another is l_b for FRC, l_k for FJC and l_p for WLC, respectively. By integrating the QM results into these original models, we then obtain the QM models as Eqs S(7)-(9), respectively.

$$\frac{R}{L_0} = \left(\frac{L[F]}{L_0}\right) \cdot \left[1 - \frac{k_B T}{2F \cdot l_b}\right] \tag{7}$$

$$\frac{R}{L_0} = \left(\frac{L[F]}{L_0}\right) \cdot \left\{\left[\left(F \cdot l_k\right)\right]/(k_B T)] - (k_B T)/(F \cdot l_k)\right\} \tag{8}$$

$$F\frac{l_p}{k_B T} = \frac{R/l_0}{L[F]/L_0} + \frac{1}{4(1 - (R/L_0)/(L[F]/L_0))^2} - \frac{1}{4} \tag{9}$$

In these models, both the entropic contribution in the chain conformational change and the enthalpic contribution in the chain backbone deformation are all taken into account. Therefore, these QM series models are an update of the original models, which can describe the chain elasticity in a much broad range from low to high forces.[1-2]

References

1. Y. Bao, Z. Luo and S. Cui, Environment-dependent single-chain mechanics of synthetic polymers and biomacromolecules by atomic force microscopy-based single-molecule force spectroscopy and the implications for advanced polymer materials. *Chem. Soc. Rev.* 2020, 49, 2799-2827.
2. W. Cai, S. Lu, J. Wei and S. Cui, Single-chain polymer models incorporating the effects of side groups: An approach to general polymer models. *Macromolecules* 2019, **52**, 7324-7330