

Unexpectedly Robust N–H...N Hydrogen Bonds in an Individual Polyallylamine Chain

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Electronic Supplementary Information

Abstract Quantifying the hydrogen bond (H-bond) strength of polymers is essential for rational design of advanced materials. However, direct measurement remains challenging because of the structural complexity of polymers and the weak nature of H-bonds. Vacuum-based single-molecule force spectroscopy (Vac-SMFS) offers a new and precise approach for such measurements. Using polyallylamine (PAAm) as a model polymer, the intrinsic strength (*i.e.*, strength without external influences) of representative N–H...N H-bonds was quantified to be about 5.25 kJ·mol^{−1}. Comparative Vac-SMFS analysis across different polymer systems revealed that the N–H...N H-bonds in PAAm are unexpectedly stronger than the N–H...O H-bonds in poly(*N*-isopropylacrylamide) (PNIPAM) and the O–H...O H-bonds in poly(hydroxyethyl methacrylate) (PHEMA). This trend contrasts with that of established small-molecule systems. These results highlight how side-chain length and spatial configuration dictate polymer H-bond strengths, expanding the fundamental knowledge of polymer interactions and enabling the rational design of next-generation functional materials.

Keywords Hydrogen bond; Polyallylamine; Intrinsic strength; Side-chain structure; Vacuum-based single-molecule force spectroscopy

Citation: Wang, Y. C.; Hu, M. H.; Ding, D.; Yuan, W. T.; Bao, Y.; Cui, S. X. Unexpectedly robust N–H...N hydrogen bonds in an individual polyallylamine chain. *Chinese J. Polym. Sci.* 2026, 44, 398–406.

INTRODUCTION

Hydrogen bonds (H-bonds), one of the most important noncovalent interactions, are essential for the structure and function of both living systems and man-made materials.^[1–3] In polymers such as polyamides, poly(vinyl alcohol), and poly(*N*-isopropylacrylamide) (PNIPAM), H-bonds play a crucial role in enhancing the mechanical strength, improving the thermal stability, enabling self-healing, and other functional properties, thereby broadening the scope of their applications.^[4–8] It is worth emphasizing that the strength of the H-bond is a critical factor in determining the functional performance of these materials.^[9–12] For instance, stronger H-bonds can enhance material rigidity and structural stability, whereas weaker H-bonds impart greater flexibility and promote dynamic transition.^[13–15] Thus, quantitative analysis of H-bond strength is crucial for revealing their fundamental roles and enabling precise tuning of the physicochemical properties of polymers, ultimately driving the rational design and development of polymer materials.

An H-bond typically forms when a hydrogen atom covalently bound to one electronegative atom interacts with an-

other lone-pair-bearing electronegative atom.^[16] Because potential partners include N, O, and F, H-bonds span a wide strength range and influence polymer systems in distinct ways. With the growing demand for tailoring the properties of polymers with H-bonds, there is an increasing need for the precise quantification of the strengths of various H-bond types within polymer systems.^[17] However, this task remains highly challenging because of the complexity of polymer systems, which involve both intra- and inter-molecular H-bonds and a wide range of structural variables. In most cases, the experimental samples are macroscopic aggregates comprising multiple types of H-bonds and are sensitive to environmental conditions.^[18] Consequently, conventional ensemble methods often fail to quantify the strengths of individual H-bond types. Although theoretical calculations and simulations can provide quantitative insights, their accuracy is limited by uncertainties and arbitrariness in model parameter selection.^[19,20] Additionally, these methods are time-consuming and inefficient when applied to complex polymer systems. To overcome these limitations, new strategies are required to simplify the system composition and minimize external interference, thereby enabling the precise measurement of specific H-bond types.

In recent decades, atomic force microscope-based single-molecule force spectroscopy (AFM-SMFS) has become a powerful technique for probing the single-chain properties of

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Received October 9, 2025; Accepted November 6, 2025; Published online January 15, 2026

polymers and their associated non-covalent interactions.^[21–36] More recently, the advancement of vacuum-based SMFS (Vac-SMFS) has enabled quantitative investigation of intramolecular interaction strengths within individual polymer chains.^[37–39] Previous studies have shown that, in the absence of environmental interference, the mechanical response of a single polymer chain is governed by the inherent elasticity of its backbone and side-chain interactions, such as π - π stacking and H-bonds.^[37–40] Since the inherent elasticity of a polymer remains unaffected by other experimental conditions at a given temperature, it provides a reliable internal standard for quantifying side-chain interactions. This approach has already been applied to determine the strengths of specific H-bonds, such as N—H...O and O—H...O H-bonds, in polymer systems.^[38,39,41] Despite these advances, current progress remains insufficient to achieve a comprehensive understanding of polymers with H-bonds. Further quantitative investigations of diverse H-bond types are essential to expand the database of H-bond strengths and deepen our understanding of how these interactions influence the properties and functionalities of polymers.

As a representative H-bond type, N—H...N H-bonds have been extensively studied in small-molecule systems.^[42,43] However, its characteristics, particularly strength, remain poorly understood in macromolecular systems.^[44] Herein, polyallylamine (PAAm, inset of Fig. 1a), a polymer featuring a C—C backbone and amine-containing side chains, was chosen as a model system capable of forming intramolecular N—H...N H-bonds. By utilizing Vac-SMFS combined with complementary techniques, the intrinsic strength (*i.e.*, the H-bond strength without external interferences) of N—H...N H-bonds within a single PAAm chain was quantified to be about 5.25 kJ·mol⁻¹, which is unexpectedly higher than those of other H-bonds reported in single polymer systems.^[38,39]

EXPERIMENTAL

Materials and Chemicals

PAAm (MW=65 kDa, 10 wt% aqueous solution) was purchased from Sigma-Aldrich. All other chemicals were of analytical grade. When water was required, deionized (DI) water with a resistance greater than 18 M Ω ·cm was used.

Sample Preparation

To meet the requirements of the force measurements, the PAAm aqueous solution was diluted to a concentration of 0.5 g/L. For substrate cleaning, a quartz substrate was cleaned using a mixture of (NH₄)₂S₂O₈/H₂O₂ in a solution of 0.75 g/mL at roughly 90 °C for 4 h. The substrate was then rinsed with water and dried under airflow. For sample preparation, approximately 100 μ L of the polymer solution was applied to the surface of the quartz substrate and allowed to adsorb for approximately 30 min. Prior to the SMFS experiment, the substrate was flushed with water to eliminate any loosely adsorbed polymers, and then dried by airflow.

Force Measurements

SMFS experiments in vacuum were conducted using high-vacuum AFM (5300E, Hitachi). Prior to vacuuming, the AFM was grounded, and both the tip and substrate were subjected to high-vacuum conditions for 2 h before conducting force measurements. The temperature was maintained constant (± 0.2 K) throughout the force measurement. Data were noted and transformed into curves using Igor Pro V6.05 with customized programs. The spring constant (about 300 pN/nm) of the Si₃N₄ AFM cantilever (SNL-10 model, Bruker Corp., CA, USA) was measured using the thermal excitation method.^[45]

For the SMFS experiments in liquids, another AFM (JPK NanoWizard II) was used. Before conducting the force measurements, an appropriate amount of ambient liquid was injected between the Si₃N₄ AFM cantilever (MSCT model, Bruker Corp., CA, USA) and the substrate. The spring constant is approximately 120 pN/nm. The tensile speed was 2.0 μ m/s unless stated otherwise.

RESULTS AND DISCUSSION

Because the accurate quantification of the intrinsic strength of N—H...N H-bonds in PAAm depends on its inherent elasticity, this property must be determined in advance. It has been demonstrated that polymers display inherent elasticity under conditions in which the effects of polymer-solvent and side-chain interactions (*e.g.*, van der Waals forces) are negligible.^[46,47] As a strong H-bond disruptor, dimethyl sulfoxide (DMSO) eliminates nearly all intramolecular H-bonds within the polymers.^[48]

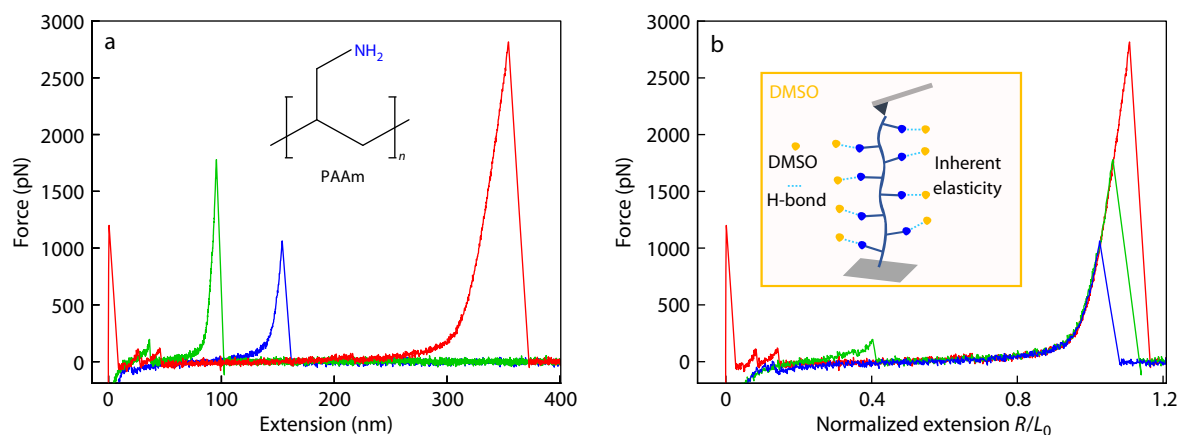


Fig. 1 (a) Experimental curves of PAAm obtained in DMSO. Inset: the primary structure of PAAm. (b) Normalized results of the curves shown in (a). Inset: schematic illustration of SMFS measurements on a single PAAm chain in DMSO.

Thus, PAAm is expected to adopt a conformation with virtually no intramolecular H-bonds when dissolved in DMSO. In this context, each DMSO molecule can be considered part of the side chain of PAAm (inset of Fig. 1b) with negligible impact on its inherent elasticity.^[39] Therefore, force measurements were conducted in DMSO to determine the inherent elasticity of PAAm. 24 valid force-extension curves were obtained from 13452 single-molecule events, yielding a capture probability of about 0.17% (Table S1 in the electronic supplementary information, ESI). Fig. 1(a) presents several force-extension curves of PAAm obtained in DMSO, showing that the polymer chain is stretched under increasing tensile force as the tip detaches from the substrate surface. Owing to polymer polydispersity and the random positions of chains captured by AFM tips, different contour lengths of the stretched chains were observed under identical conditions. For comparative analysis, all the experimental curves were normalized to 500 pN (Fig. 1b). The resulting excellent overlap indicated that the elastic response of a single PAAm chain in DMSO was effectively characterized.

Because inherent elasticity reflects the pure elastic response of a polymer backbone, PAAm and polyethylene (PE), both with C—C backbones, should exhibit identical elasticity. The theoretical enthalpic elasticity of PE, obtained from quantum mechanical calculations,^[49] was integrated into the freely rotating chain model of entropic elasticity, yielding an entropy-enthalpy coupled quantum mechanical-freely rotating chain (QM-FRC) model for describing the elasticity of polymer chains with C—C backbones (see Note 1 in ESI for details):

$$z = R/L_0 = (L[F]/L_0) \cdot [1 - k_B T / (2Fl_b)] \quad (1)$$

where R is the extension of the polymer chain, L_0 is the zero-force contour length, $L[F]$ is the contour length under force F , z (R/L_0) is the normalized extension, T is the temperature in Kelvin, l_b is the length of a freely rotating unit, and k_B is the Boltzmann constant.

Because $L[F]/L_0$ is an ergodic variable within a reasonable range (see Note 1 in ESI for details), the QM-FRC model at a given temperature is governed by a single parameter l_b . To confirm that PAAm exhibits inherent elasticity in DMSO, the experimental curve obtained in this case was fitted using the QM-FRC model across a series of l_b values. The average force

deviation between the experimental and fitting curves is plotted as a function of l_b (Fig. 2a), showing a minimum at $l_b = (0.146 \pm 0.030)$ nm, which is consistent with the typical C—C bond length. At this point, the average deviation (about 12 pN) fell within the experimental noise level (about 15 pN), and the theoretical curve closely matched the experimental data (Fig. 2b). These results confirm that the inherent elasticity of PAAm was achieved under ambient conditions in DMSO. Accordingly, the corresponding QM-FRC curve at $l_b = 0.146$ nm served as the internal standard for studying the intrinsic strength of the H-bonds in individual PAAm chains.

In a high vacuum, robust N—H...N H-bonds can be formed between the side chains of PAAm owing to the absence of environmental interference (inset of Fig. 3a). This minimal disturbance renders the vacuum environment particularly well suited for probing the intrinsic strength of H-bonds within a single polymer chain.^[38,41] Therefore, Vac-SMFS experiments were performed on PAAm to study the intrinsic strength of the N—H...N H-bonds (the number of valid curves and capture probability are summarized in Table S1 in ESI). The resulting experimental curves overlap excellently after normalization (Fig. 3a), suggesting the effective characterization of the mechanical response of the single PAAm chain in high vacuum. Notably, each experimental curve displays a long plateau at approximately 50 pN, which arises from the van der Waals forces between PAAm and the substrate in vacuum (see Fig. S1 and Note 2 in ESI).^[50] Because this desorption process did not affect the enthalpic elasticity of PAAm, the plateau region was excluded from further analysis. The experimental curve of PAAm obtained in high vacuum was compared with that obtained in DMSO, revealing a significant deviation in the 100–1300 pN force range (Fig. 3b). The absence of environmental interference indicates that the observed deviation resulted from the disruption of the N—H...N H-bonds within the PAAm chain. The overlap of the curves at forces exceeding 1300 pN implies that most of the H-bonds are disrupted under strong stretching, allowing the single-chain elasticity of PAAm to recover its inherent state.

Previous studies have demonstrated that the mechanical response of single polymer chains exhibiting side chain effects, such as π – π interactions and H-bonds, can be effectively described using the two-state QM-FRC (TSQM-FRC)

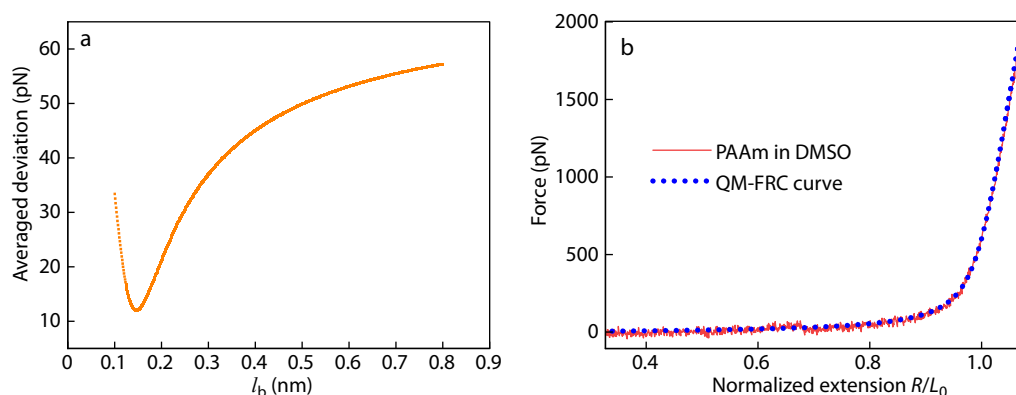


Fig. 2 (a) Averaged force deviation between the experimental and fitting curves, defined as $(\sum_1^n |F_{\text{exp}} - F_{\text{fit}}|)/n$, as a function of l_b . (b) Comparison between the experimental curve of PAAm obtained in DMSO (red line) and the QM-FRC curve at $l_b = 0.146$ nm (blue dot).

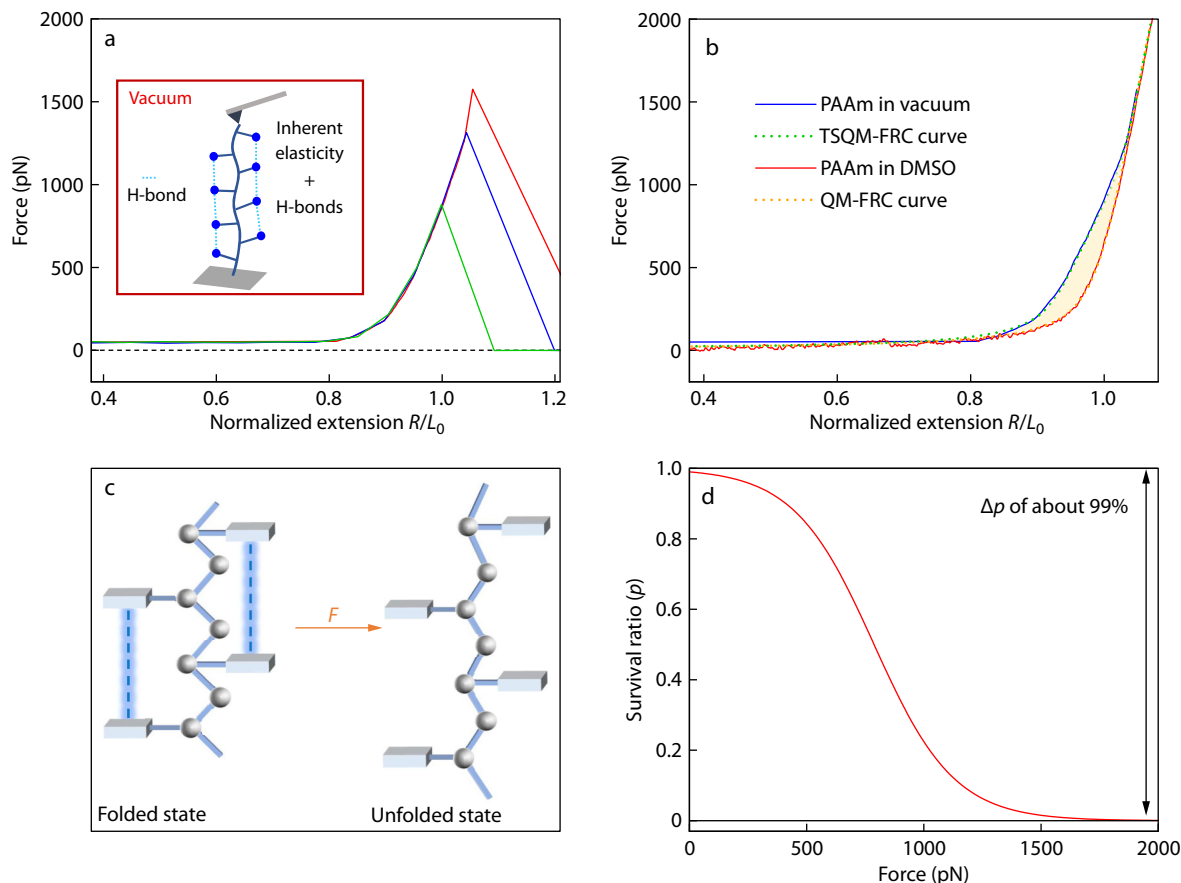


Fig. 3 (a) Normalized experimental curves of PAAm acquired in vacuum. Inset: schematic illustration of Vac-SMFS measurements on a single PAAm chain. (b) Comparison of PAAm curves obtained in vacuum (blue) and DMSO (red), along with the TSQM-FRC curve (green) and the QM-FRC curve (orange). The area difference between the two types of curves is highlighted in light gold. (c) Schematic illustration of the force-induced transition of a single module from the folded to the unfolded state. (d) Variation in the survival ratio of H-bonds as a function of external force.

model.^[37] In this framework, a two-state model^[51] is incorporated into the QM-FRC model to account for the conformational transitions between two distinct states (see Note 3 for details in ESI). The TSQM-FRC model was formulated as follows:

$$Z_{TS} = \left[\frac{l_f}{e^{(-\Delta G + F\Delta L)/k_B T} + 1} + \frac{l_u}{e^{(\Delta G - F\Delta L)/k_B T} + 1} \right] \times z/l_u \quad (2)$$

where Z_{TS} represents the normalized extension accounting for side-chain effects, l_f and l_u are the folded and unfolded module lengths, respectively, e is the natural constant, z is the normalized extension, ΔL is the length difference between l_f and l_u , and ΔG is the free energy difference.

The TSQM-FRC model was then utilized to describe the mechanical response of the individual PAAm chains in vacuum. Given that a polymer chain consists of repeating identical units, it can be conceptualized as a system of interconnected modules. In the absence of an external force, each module adopts a folded state that is stabilized by intramolecular H-bonds. As the external force increased, the module underwent considerable extension, leading to the disruption of these H-bonds and a transition into an unfolded state (Fig. 3c). Accordingly, the PAAm chain experiences a force-

driven shift between the folded and unfolded states during extension. The TSQM-FRC model fits well with the experimental curve of PAAm acquired in vacuum when $\Delta G = (10.40 \pm 0.40)$ kJ·mol⁻¹·module⁻¹, $l_f = 0.500$ nm, $l_u = 0.524$ nm (the length of two repeating units, see Fig. S2 and Note 4 for details in ESI), and $\Delta L = 0.024$ nm (Fig. 3b). This result confirms the force-driven transition between the two states of PAAm and the rupture of the N—H...N H-bonds during elongation. Consequently, the value of ΔG is attributed to the dissociation of H-bonds in high vacuum. Because each module contained two H-bonds (Fig. S2 in ESI), ΔG can be converted to (5.20 ± 0.20) kJ·mol⁻¹ per H-bond.

Given that a single PAAm chain contains many H-bonds, the bond strength should be corrected based on the number of H-bonds broken upon stretching. The survival ratio p at each applied force was defined as the ratio of the folded modules to the total module count (see Note 5 for details in ESI). The values of p were calculated across the force range of 0 pN (force-free) to 2000 pN (highly stretched) and are plotted in Fig. 3(d). The change in the survival ratio, $\Delta p = p_0 - p_{2000}$, represents the fraction of H-bonds ruptured during elongation, and was determined to be about 99%. Accordingly, the corrected H-bond strength was obtained as $\Delta G^* =$

$$\Delta G/\Delta p = (5.25 \pm 0.20) \text{ kJ} \cdot \text{mol}^{-1}.$$

To support the value derived from theoretical modeling, the area difference between the TSQM-FRC and QM-FRC curves, which reflects the energetic contribution of H-bonds, was quantitatively assessed (Fig. 3b). The calculated energy for H-bond dissociation (ΔG_A) was calculated to be $(9.54 \pm 0.48) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{module}^{-1}$, corresponding to $(4.77 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$ per H-bond. Accordingly, the corrected H-bond strength can be determined as $\Delta G_A^* = \Delta G_A/\Delta p = (4.82 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$.

Because the area integration method involves both model fitting and comparison, the resulting value is slightly lower than that obtained from direct model fitting, likely because of potential systematic and random errors (see Table S2 and Note 6 for error analyses in ESI). Nonetheless, this result corroborates the applicability of the TSQM-FRC model. Consequently, the more robust estimate of $(5.25 \pm 0.20) \text{ kJ} \cdot \text{mol}^{-1}$ from the TSQM-FRC fitting is defined as the intrinsic strength of the N—H...N H-bond. Interestingly, this value is considerably lower than that reported for analogous H-bonds in small molecules such as ammonia ($15.15 \text{ kJ} \cdot \text{mol}^{-1}$).^[52] This difference originates from the restricted conformational adaptability of the PAAm side chains due to their backbone, which hinders the formation of optimal H-bond geometries. In comparison, the flexibility of small molecules allows more effective H-bond formation.

Nonpolar organic solvents, such as octane, nonane, and octylbenzene, are frequently employed as alternatives to vacuum. To validate the vacuum data, SMFS experiments on PAAm were also conducted in these solvents, with the normalized experimental curves showing good superimposition (Fig. 4a; the number of valid curves and capture probability in octane are summarized in Table S1 in ESI). The experimental curve obtained in octane was then compared with that obtained in DMSO (Fig. 4b), revealing a deviation similar to, but smaller than, that shown in Fig. 3(b). This consistency supports the validity of the vacuum data, with a smaller deviation, likely due to the weakened H-bond strength in the organic solvent.^[38,53] The TSQM-FRC model can fit the experimental curve acquired in octane with $\Delta G = (3.03 \pm 0.15)$

$\text{kJ} \cdot \text{mol}^{-1} \cdot \text{module}^{-1}$, $l_f = 0.500 \text{ nm}$, $l_u = 0.524 \text{ nm}$, and $\Delta L = 0.024 \text{ nm}$ (Fig. 4b). The Δp value during PAAm elongation in octane was 80.22% (Fig. S3), leading to a corrected H-bond strength of $(1.89 \pm 0.09) \text{ kJ} \cdot \text{mol}^{-1}$. This value is only about 36% of its intrinsic strength, indicating that the H-bond strength is reduced by more than half, even in nonpolar organic solvents. This weakening likely arises from two factors: (1) compared with the nearly negligible number of gas molecules in vacuum, nonpolar solvent molecules exhibit much stronger thermal motion and frequently collide with the PAAm chains.^[54] Such collisions can disrupt the stable conformations required for H-bond formation, thereby weakening or breaking a portion of H-bonds. (2) The solvent molecules surrounding the PAAm chain introduce dielectric screening effects, which can perturb the local electrostatic environment of the intrachain H-bonds and substantially reduce their strength.^[38,53] In summary, the combined effects of thermal fluctuations and dielectric screening from solvent molecules significantly weakened the intrachain H-bonds of PAAm in nonpolar solvents.^[38]

Additionally, the experimental curves obtained at various stretching velocities in high vacuum and nonane overlapped well after normalization (Figs. S4 and S5 in ESI), indicating that chain segment motion occurred much faster than the force measurements. This suggested that the SMFS experiments were conducted under quasi-thermodynamic equilibrium conditions.^[54]

Finally, the intrinsic strength of the N—H...N H-bonds was compared to those of the N—H...O H-bonds in PNIPAM and the O—H...O H-bonds in poly(hydroxyethyl methacrylate) (HEMA), as determined by Vac-SMFS (Table 1).^[38,39] Interestingly, the results show that the N—H...N H-bonds in PAAm exhibit the highest intrinsic strength among the three polymers studied. Moreover, this trend deviates from observations in small-molecule systems, where the intrinsic strength follows the order: N—H...O H-bond approximately equals to O—H...H H-bond > N—H...N H-bond (Table 1).^[52,55,56] This discrepancy may arise from differences in molecular constraints. In small-molecule systems, low steric hindrance allows H-bonds to form with geometries close to their energetic optimum, par-

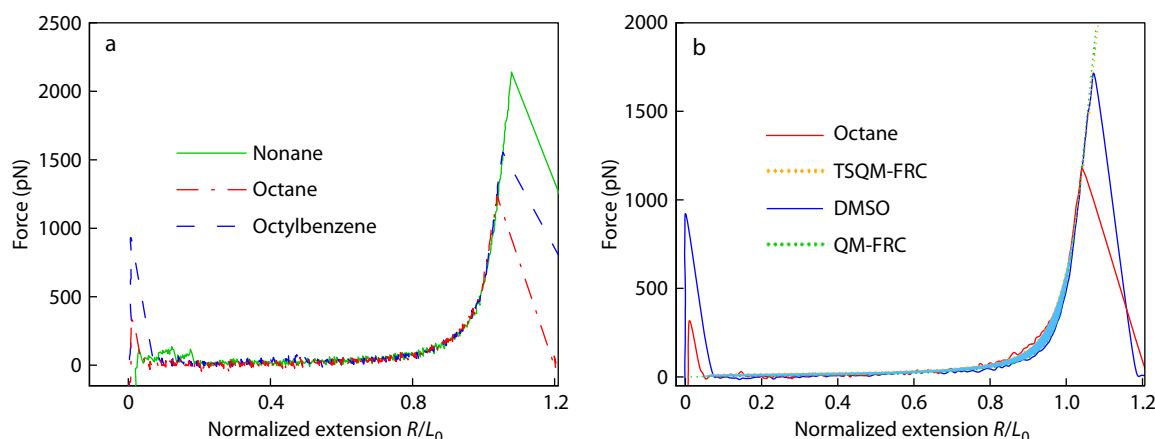
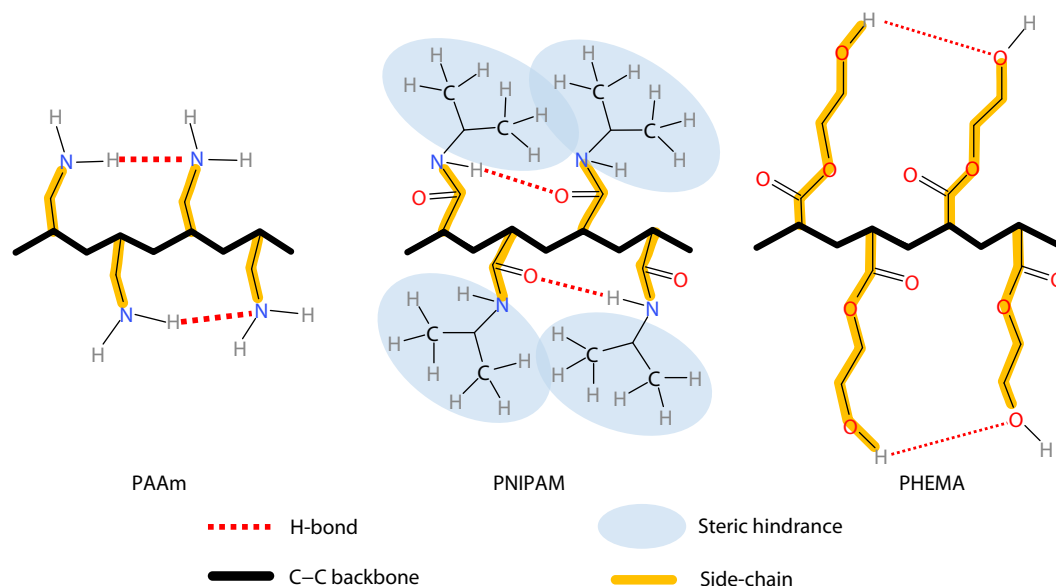


Fig. 4 (a) Normalized experimental curves of PAAm obtained in nonane (green), octane (red), and octylbenzene (blue). (b) Comparison of normalized curves of PAAm obtained in octane (red) and DMSO (blue), along with the TSQM-FRC curve (orange), and the QM-FRC curve (green). The area difference between the two types of curves is highlighted in cyan.

Table 1 Comparison of the intrinsic strength of various H-bond types.

H-bond type	Intrinsic strength (kJ·mol ⁻¹)			
	Polymer		Small molecule	
N—H...N	PAAm	5.25	ammonia ^[52]	15.15
N—H...O	PNIPAM ^[38]	4.65*	formamide ^[55]	21.21
O—H...O	PHEMA ^[39]	2.85	water ^[56]	21.00

*Determination based on literature data (see Note 7 for details in ESI).



Scheme 1 Schematic comparison of side-chain geometries of PAAm, PNIPAM, and PHEMA. H-bonds are marked in red dotted lines. C—C backbones are marked in black thick lines, and side-chains that contribute to the H-bonds are marked in orange thick lines. The steric hindrance of the side base is marked as blue areas.

ticularly in terms of bond length and angle. In this case, the H-bond strength was primarily determined by the electronegativity of the participating atoms. In contrast, polymer systems impose geometric and conformational constraints owing to backbone rigidity and side-chain steric effects, which hinder the formation of H-bonds with near-optimal geometries. Under such conditions, the influence of atomic electronegativity is no longer the dominant factor governing H-bond strength.

To rationalize the differences in the intrinsic H-bond strengths among the three polymers, the molecular architectures of PHEMA, PNIPAM, and PAAm were compared in terms of side-chain structure, length, and spatial accessibility (Scheme 1). In PHEMA, although the long side chains offer a certain degree of flexibility, the hydroxyl groups located at their termini may still struggle to achieve favorable H-bond lengths and angles, resulting in the weakest intrinsic strength of the O—H...O H-bonds. In PNIPAM, the amide group is positioned in the middle of the long side chain, which may facilitate the formation of H-bonds with favorable lengths and angles. However, this favorable tendency may be partially counteracted by the steric hindrance from the terminal isopropyl groups. Consequently, a geometric balance was achieved, leading to a moderate intrinsic strength of the N—H...O H-bond. In comparison, PAAm features amino groups linked to its main chain via a methylene bridge, offering both flexibility and spatial accessibility. This configuration likely facilitated the formation of N—H...N H-bonds with optimal lengths and

angles, resulting in the highest intrinsic strength among the three polymer systems. These findings highlight the critical role of polymer architecture, particularly side-chain length and spatial configuration, in the intrinsic strength of H-bonds in polymer systems. This insight may inspire the design of advanced polymer materials.

CONCLUSIONS

In summary, the intrinsic strength of the N—H...N H-bonds in a polymer chain was quantified for the first time using Vac-SMFS. The mechanical response of a single PAAm chain in high vacuum reflects both its inherent elasticity and the effect of H-bonds. Using the inherent elasticity as a benchmark, the intrinsic strength of the N—H...N H-bonds between the PAAm side chains was determined to be about 5.25 kJ·mol⁻¹. This value is significantly lower than that of analogous H-bonds in small molecules, likely due to steric and conformational constraints imposed by the polymer backbone, which hinder the optimal H-bond geometry. Comparative Vac-SMFS analysis across different polymer systems revealed that the N—H...N H-bonds in PAAm exhibit stronger intrinsic strength than the N—H...O H-bonds in PNIPAM and O—H...O H-bonds in PHEMA, which deviates from the trend typically observed in small-molecule systems. This enhancement is likely attributable to the optimal side-chain length and favorable spatial positioning of the amino group in PAAm, which allows the N—H...N H-bonds to adopt

more favorable geometries than those achievable in the other two systems. These findings highlight the critical role of the side-chain length and spatial configuration in determining the intrinsic strength of H-bonds in polymer systems. Moreover, this work advances the understanding of N—H...N H-bonds in polymer systems and contributes valuable data for the development of a comprehensive database of H-bond strengths in polymer systems. These insights can inform the rational design of next-generation polymer materials with tailored properties. In addition, the validated methodology presents a robust approach for exploring other types of H-bonds in similar systems.

Conflict of Interests

The authors declare no interest conflict.

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/s10118-025-3495-3>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding authors upon reasonable request. Contact information: baoyu@swjtu.edu.cn (Y.B.) and cuishuxun@neu.edu.cn (S.X.C.).

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 22273079) and Fundamental Research Funds for the Central Universities (No. 2682025ZTPY004).

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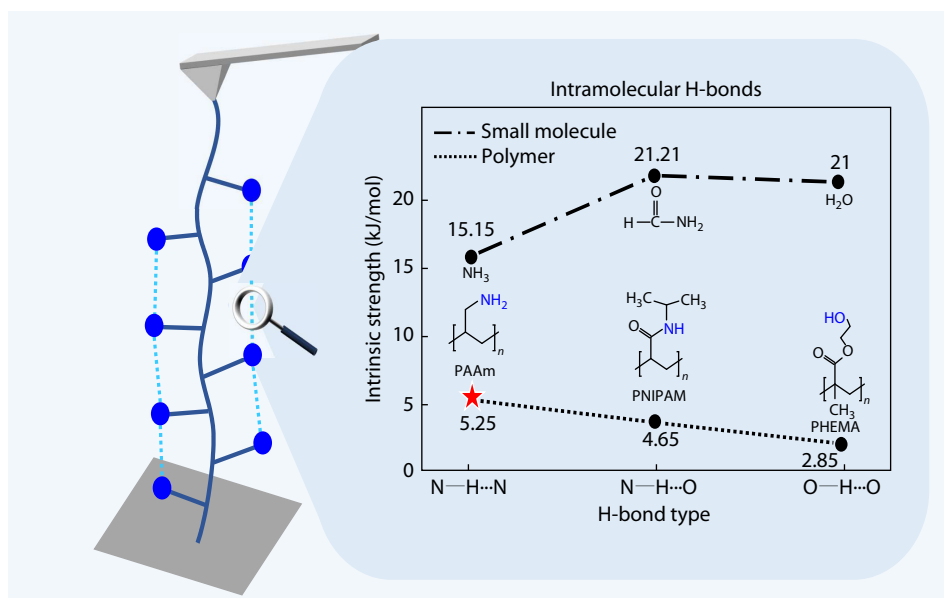
Graphical Abstract

Unexpectedly Robust N—H...N Hydrogen Bonds in An Individual Polyallylamine Chain

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The intrinsic strength of N—H...N H-bonds in polyallylamine, measured as about 5.25 kJ·mol⁻¹ by vacuum-based single-molecule force spectroscopy, exceeds those of N—H...O and O—H...O H-bonds in other polymers, contrasting with the trend in small-molecule systems and revealing how side-chain spatial configuration governs polymer H-bond strengths.



Chinese J. Polym. Sci. 2026, 44, 398–406

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