

Short-chain Length Dependence of Equilibrium Dynamics and Nonlinear Rheology in Unentangled Long-chain/Short-chain Polymer Blends

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Electronic Supplementary Information

Abstract The equilibrium dynamics and nonlinear rheology of unentangled polymer blends remain inadequately understood, especially regarding the influence of short-chain matrix length N_s on the structure and rheological behavior of dispersed long chains. Using molecular dynamics simulations based on the Kremer-Grest model, we systematically explore the N_s -dependence of static conformations, equilibrium dynamics, and nonlinear shear responses in unentangled long-chain/short-chain polymer blends. Our results demonstrate a decoupling between the static and dynamic sensitivity to N_s : while the static chain size, R_g , follows Flory theory with slight swelling at small N_s due to incomplete excluded volume screening, the diffusion coefficient, D , and the relaxation time, τ_0 , exhibit a strong, non-monotonic N_s -dependence, transitioning from monomeric friction dominance at small N_s to collective segmental rearrangement at large N_s . Additionally, we observe partial decoupling between the viscous and normal stress responses: while the zero-shear viscosity, η , is strongly N_s -dependent, the first and second normal stress coefficients, Ψ_1 and Ψ_2 , collapse onto universal curves when scaled by the dimensionless shear rate, $\dot{\gamma}\tau_0$, suggesting a common mechanism of orientation and stretching. Under shear, long chains compress in the vorticity direction $\lambda_z \sim Wi^{-0.2}$, which reduces collision frequency and contributes to shear thinning, while the scaling of weaker orientation resistance $m_G \sim Wi^{0.35}$ reflects hydrodynamic screening by the short-chain matrix. These findings highlight the limitations of single-chain models and emphasize the necessity of considering N_s -dependent matrix dynamics and flow-induced structural changes in understanding the rheology of unentangled polymer blends.

Keywords Unentangled polymer blend; Nonlinear rheology; Equilibrium dynamics; Hydrodynamic interaction screening; Molecular dynamics simulation

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INTRODUCTION

Understanding the molecular mechanisms underlying shear thinning in polymer melts and solutions is fundamental to developing predictive constitutive relations that govern their flow behavior in polymer physics and soft matter science.^[1–5] In entangled polymer systems, the pronounced reduction in viscosity (η) under shear arises from the coupled effects of chain disentanglement, stretching, and orientation—an intricate interaction that has long posed a significant challenge in polymer rheology.^[6–9] In contrast, unentangled polymer systems offer a simplified model, where the elimination of entanglement effects enables the precise decoupling of key physical quantities,

such as molecular orientation and friction coefficients.^[10] This reductionist approach provides an ideal framework for elucidating the intrinsic origins of shear thinning and for establishing quantitative relationships between viscosity and shear rate. As a result, advancing our understanding of shear-thinning mechanisms in unentangled polymers serves as a critical theoretical foundation for unraveling the nonlinear rheology of polymer melts and solutions more broadly, offering both fundamental insights and practical utility in materials design and processing.^[11–14]

Under shear, the steady-state viscosity of unentangled polymer fluids exhibits a pronounced dependence on shear rate $\dot{\gamma}$, which is a nonlinear response arising from the dynamic interplay between multi-scale relaxation processes and conformational entropy.^[15] Based on the scaling relationship ($\eta \sim \dot{\gamma}^\delta$), theoretical models of shear thinning in unentangled polymers can be broadly classified into two categories (Fig. 1).

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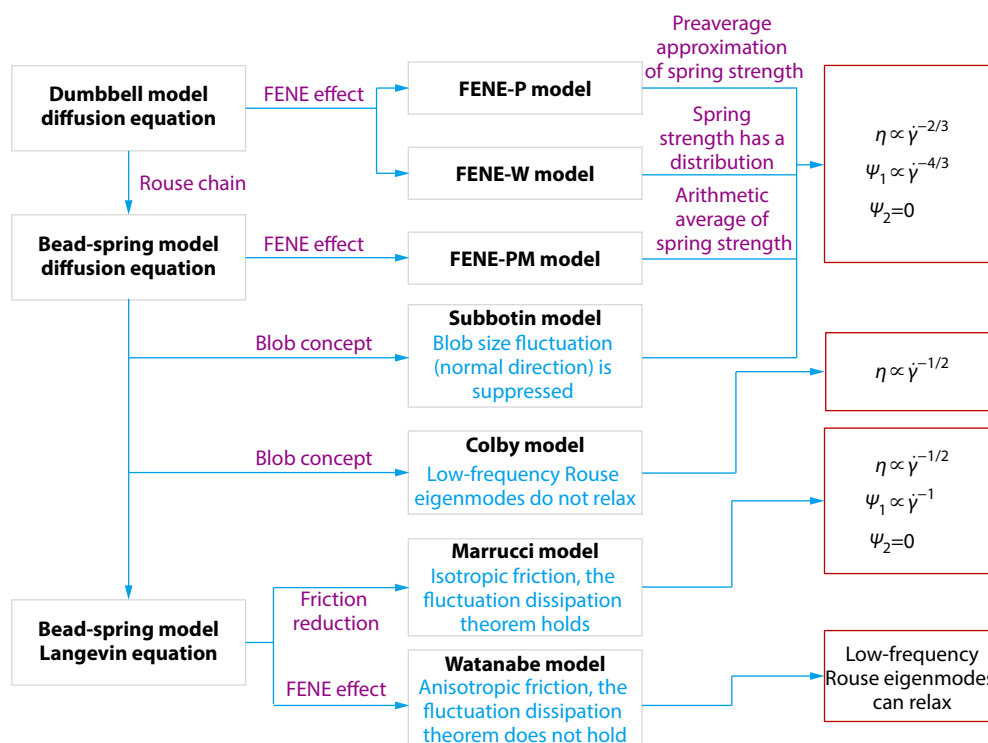


Fig. 1 Theoretical framework for shear thinning in unentangled polymers, illustrating competing models and scaling predictions.

The first category emphasizes analytical tractability, aiming to derive exact solutions for stress constitutive equations,^[16,17] and predicts a scaling exponent $\delta = -2/3$. The second category, which focuses on rigorous scaling derivations and experimental data fitting,^[15,18] yields $\delta = -1/2$. This dichotomy in scaling behavior highlights the ongoing debate over the molecular mechanisms driving shear thinning in these systems.

In the first category of models (with $\delta = -2/3$), the Dumbbell model,^[19] which coarsens polymer chains into a spring-connected bead pair, serves as a classical framework for describing chain behavior under shear. To capture chain behavior, this model incorporates finite extensible nonlinear elasticity (FENE), leading to variants such as the FENE-P and FENE-W models. The FENE-P model^[20] uses a pre-averaging approximation for spring strength, while the FENE-W model^[21] assumes a specific distribution of spring strengths. Both models predict $\eta \sim \dot{\gamma}^{-2/3}$ and $\psi_1 \sim \dot{\gamma}^{-4/3}$, where ψ_1 is the first normal stress difference coefficient. However, the Dumbbell model's inability to describe internal chain modes led Wedge-wood *et al.*^[16,17] to extend the Rouse model with FENE-PM nonlinear springs, deriving analytical solutions for stress under steady shear, which also yield $\eta \sim \dot{\gamma}^{-2/3}$. In contrast, Watanabe *et al.*^[22–25] challenged the Rouse model's assumption of constant friction and spring strength under rapid flow, proposing anisotropic bead friction coefficient and mean-square Brownian force intensity that modify nonequilibrium moduli. Their work suggests that all eigenmodes contribute to viscosity, with magnitudes determined by friction and elasticity. More recently, Subbotin *et al.*^[26] attributed viscosity reduction to suppressed chain size fluctuations in the gradient direction above a critical shear rate, also predicting $\eta \sim \dot{\gamma}^{-2/3}$

and $\psi_1 \sim \dot{\gamma}^{-4/3}$. Collectively, these models converge on $\delta = -2/3$ but diverge in their microscopic justifications, ranging from mode suppression to anisotropic friction.

In the second category of models (with $\delta = -1/2$), the focus is on scaling derivations and experimental validation rather than analytical exactness. Colby *et al.*^[15] combined the Rouse model with blob theory, proposing that low-frequency Rouse modes fail to relax under shear and thus do not contribute to energy dissipation; viscosity is instead dominated by high-frequency modes, leading to $\psi_1 \sim \dot{\gamma}^{-1/2}$. Marrucci *et al.*^[18] further supported this framework by assuming that the fluctuation-dissipation theorem remains valid under rapid flow, incorporating FENE elasticity and isotropic friction to recover $\eta \sim \dot{\gamma}^{-1/2}$. Notably, Marrucci *et al.* predict $\psi_1 \sim \dot{\gamma}^{-1}$, conflicting with the prediction of Subbotin *et al.*, $\psi_1 \sim \dot{\gamma}^{-4/3}$.^[26] These discrepancies highlight unresolved questions in the field: what are the correct scalings of η and ψ_1 with $\dot{\gamma}$? Resolving these debates necessitates direct observation of chain dynamics under shear at the molecular level.

To address these critical gaps, molecular dynamics (MD) simulations offer a powerful tool to directly visualize and quantitatively characterize the microscopic processes—such as chain stretching, orientational ordering, and friction evolution—that govern macroscopic rheological responses.^[27–30] However, most MD studies to date have been limited to monodisperse, unentangled systems,^[18,31–33] leaving unresolved the question of how polymer chains, together with the surrounding background chains, influence the mechanisms that modulate shear-thinning behavior. This issue becomes even more complex in blends of long and short unentangled chains, a scenario frequently encountered in industrial formulations. In these blends, short chains may serve as a “solvent,”

altering the friction and relaxation dynamics of the long chains. Despite its potential importance, the impact of such mixed-chain architectures on nonlinear rheological scaling relationships remains largely unexplored.

In this work, we investigated unentangled long-chain/short-chain polymer blends, where long chains are dispersed in a matrix of short chains, to dissect the role of short-chain length in modulating equilibrium dynamics and nonlinear rheology. By systematically varying the short-chain length (N_s), we first characterized the equilibrium size and diffusion of long chains, thereby establishing how matrix chain length affects interchain friction and conformational statistics. We then subjected these blends to rapid large-deformation shear, quantifying nonlinear responses such as viscosity scaling, first normal stress difference, and chain orientation dynamics. By bridging equilibrium dynamics and nonlinear rheology in blends, this study aims to reconcile conflicting theoretical predictions—the scalings of η and Ψ_1 with $\dot{\gamma}$ —and provide a unified molecular picture of shear thinning in compositionally heterogeneous unentangled systems. Ultimately, our findings aim to clarify how matrix chain length modulates the interplay between orientation, stretching, and friction, potentially offering new insights for the rational design of polymer melts and solutions with tailored flow properties.

SIMULATION DETAILS

To investigate the equilibrium dynamics and nonlinear rheology in unentangled long-chain/short-chain polymer blends, we employed the Kremer-Grest (KG) bead-spring model,^[34,35] a widely validated coarse-grained framework for simulating polymer dynamics. In this model, each monomer is represented as a spherical bead, and inter-monomer interactions are governed by two distinct potentials: non-bonded interactions and bonded interactions. Non-bonded interactions between monomers are described by a truncated and shifted Lennard-Jones (LJ) potential,

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] \Theta(r_c - r) \quad (1)$$

where r is the distance between two monomers, ϵ and σ are the energy and length units, respectively, and $\Theta(x)$ is the Heaviside step function; $\Theta(x) = 0$, for $x < 0$; $\Theta(x) = 1$, for $x \geq 0$. The cutoff radius r_c is set to $2^{1/6}\sigma$ to ensure computational efficiency while capturing inter-monomer interactions. Bonded interactions between consecutive monomers on the same chain are modeled using the finitely extensible nonlinear elastic (FENE) potential to account for chain connectivity and finite extensibility:

$$U_{FENE} = -\frac{\kappa}{2} R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], r < R_0 \quad (2)$$

where $\kappa = 30\epsilon/\sigma^2$ is the spring constant and $R_0 = 1.5\sigma$ is the maximum allowable bond length, consistent with standard KG model parameters.^[34,35] All simulations were performed in dimensionless reduced units, where the monomer mass $m=1$, temperature $T = \epsilon/k_B$ with (k_B as Boltzmann constant, $k_B T = 1$), and time unit $\tau = (m\sigma^2/\epsilon)^{0.5}$. The integration time step Δt was set to 0.01τ for equilibrium simulations to ensure energy conservation; for non-equilibrium simulations involving rapid large deformations, Δt was reduced to 0.005τ to simulate nonequilibrium

dynamics.

To isolate the effect of short-chain length (N_s) on long-chain dynamics while eliminating entanglement effects, we constructed unentangled binary blend systems consisting of a single long chain of length N_L dispersed in a matrix of short chains of length N_s . The long-chain lengths were fixed at $N_L=100$ and 200 . The short-chain matrix lengths were varied over $N_s=2, 3, 5, 10, 15, 20, 25, 40, 60, 100$ to span the oligomeric to polymeric matrix regimes. For clarity, systems are denoted as $N_L X/N_s Y$, where $X = N_L$ and $Y = N_s$, e.g., $N_L 100/N_s 2$ for $N_L=100$ and $N_s=2$. It is important to note that, for the long-chain/short-chain blends with $N_L=100$ and $N_L=200$, the volume fractions of long chains ϕ are 8.84% and 6.97%, respectively. These compositions ensure the systems remain unentangled, consistent with the focus of this study.

System density was fixed at $\rho = 0.85\sigma^{-3}$, a standard value for polymer melts in the KG model.^[34,35] To avoid finite-size effects, the simulation box dimensions were set to $8R_{g0} \times 8R_{g0} \times 4R_{g0}$, where R_{g0} is the equilibrium root-mean-square radius of gyration. All simulations were executed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).^[36] System temperature was controlled via the dissipative particle dynamics (DPD) thermostat,^[37] which efficiently maintains thermal equilibrium. The simulation protocol comprised three stages. (i) Equilibration: systems were first subjected to $10^6\tau$ of simulations to reach equilibrium; (ii) Equilibrium dynamics: following equilibration, $10^7\tau$ of simulations were performed to compute equilibrium properties; (iii) Nonlinear rheology: for shear deformation, shear was imposed using the *Fix deform* command equivalent to the Lees–Edwards periodic boundary condition^[38] at strain rates $\dot{\gamma}\tau_0=0.2\text{--}600$. To ensure statistical reliability, all measurements were averaged over 10 independent parallel samples, with each sample initialized from distinct random configurations.

RESULTS AND DISCUSSION

Effects of Short-chain Length on the Equilibrium Size and Dynamics of Long Chains

The equilibrium behavior of long chains in a matrix of short, unentangled chains is a crucial starting point for understanding their nonlinear rheological behavior under shear. Here, we systematically investigate the influence of short-chain length (N_s) on the conformational properties and dynamics of long chains ($N_L=100, 200$), focusing on deviations from classical polymer dynamics theories. Our findings provide new insights into how the short-chain matrix affects both the static and dynamic properties of long chains, advancing the understanding of polymer blend systems.

Equilibrium conformational statistics: validation of Flory's screening theory

The size of long chains in a matrix of shorter chains is primarily determined by the balance between excluded volume interactions and the screening effects provided by the matrix. According to Flory's theory for polymer blends and semidilute solutions, for a long probe chain with N_L monomers of size b in a melt of unentangled shorter chains with N_s monomers, the measure of excluded volume *i.e.*, two-body interactions is giv-

en by $\nu = (1/N_S - 2\chi)b^3$, where χ is the Flory interaction parameter, which is a dimensionless measure of the difference in the strength of pairwise interaction energies between monomers in the mixture. For chemically identical polymer chains in the blend melt, $\chi=0$, so the excluded volume interaction between long chains is dominated by the short-chain matrix. Consequently, the excluded volume interactions for long chains can be expressed as: $\nu = b^3/N_S$, which describes how long chains interact with themselves in the presence of the short-chain matrix. Below the thermal blob size (ξ), excluded volume interactions are negligible, and the long-chain conformation follows Gaussian statistics: $\xi \approx bg^{1/2}$. g is the number of monomers in a thermal blob. The thermal energy (of order $k_B T$) can be written as $k_B T \nu g^2 / \xi^3 \approx k_B T$. Then, we have $g \approx N_S^2$, $\xi \approx bN_S$. The size of long chain R_L can be estimated as a self-avoiding walk of thermal blobs:

$$R_L \approx \xi \left(\frac{N_L}{g} \right)^\nu \approx bN_S \left(\frac{N_L}{N_S^2} \right)^\nu \approx bN_L^\nu N_S^{1-2\nu} \quad (3)$$

with $\nu=0.5$ for θ conditions (ideal chains), ν of approximately 0.588 for good solvents.^[39] In the scenario where $N_S^2 > N_L$, short chains effectively screen the excluded volume interactions of long chains, leading to ideal random-walk conformations where the long-chain size becomes independent of N_S . Under these conditions, $R_L \approx bN_L^{1/2}$,^[39] and the conformational behavior is consistent with the ideal chain behavior described by Flory.

Conversely, when $N_S^2 < N_L$, screening is incomplete, leading to chain swelling due to unscreened excluded volume interactions. This results in a size dependence on N_S , where $R_L \sim bN_L^{0.588} N_S^{-0.176}$. To test this prediction, we computed the root-mean-square radius of gyration (R_g) and the root-mean-square end-to-end distance (R_e) for long chains with $N_L=100$ and $N_L=200$ as a function of N_S ranging from 2 to 100. As shown in Figs. 2(a) and 2(b), we observe two distinct regimes: (i) strong screening ($N_S^2 \geq N_L$): for $N_S \geq 10$ for $N_L=100$ and $N_S \geq 14$ for $N_L=200$, the values of R_g and R_e plateau, consistent with the ideal chain behavior. This confirms that the long chains adopt ideal random-walk conformations, and the size of the long chain becomes independent of N_S , in agreement with Flory's screening theory.^[39] (ii) Incomplete screening ($N_S^2 < N_L$): for smaller N_S , R_g and R_e exhibit significant increases with decreasing N_S , indicating pronounced chain swelling. For example, for $N_L=100$ and $N_S=2$, the radius of gyration R_g is approximately 17% larger than the ideal chain value. This result suggests that the short chains cannot effectively screen the long-range excluded volume interactions, leading to swollen chain conformations in the absence of sufficient screening.^[39] These findings strongly support the validity of Flory's screening theory for static chain conformations, confirming that the short-chain length N_S acts as a tunable parameter to switch between ideal and swollen states for long chains. Notably, the fitted exponent of -0.1 is significantly larger than the Flory

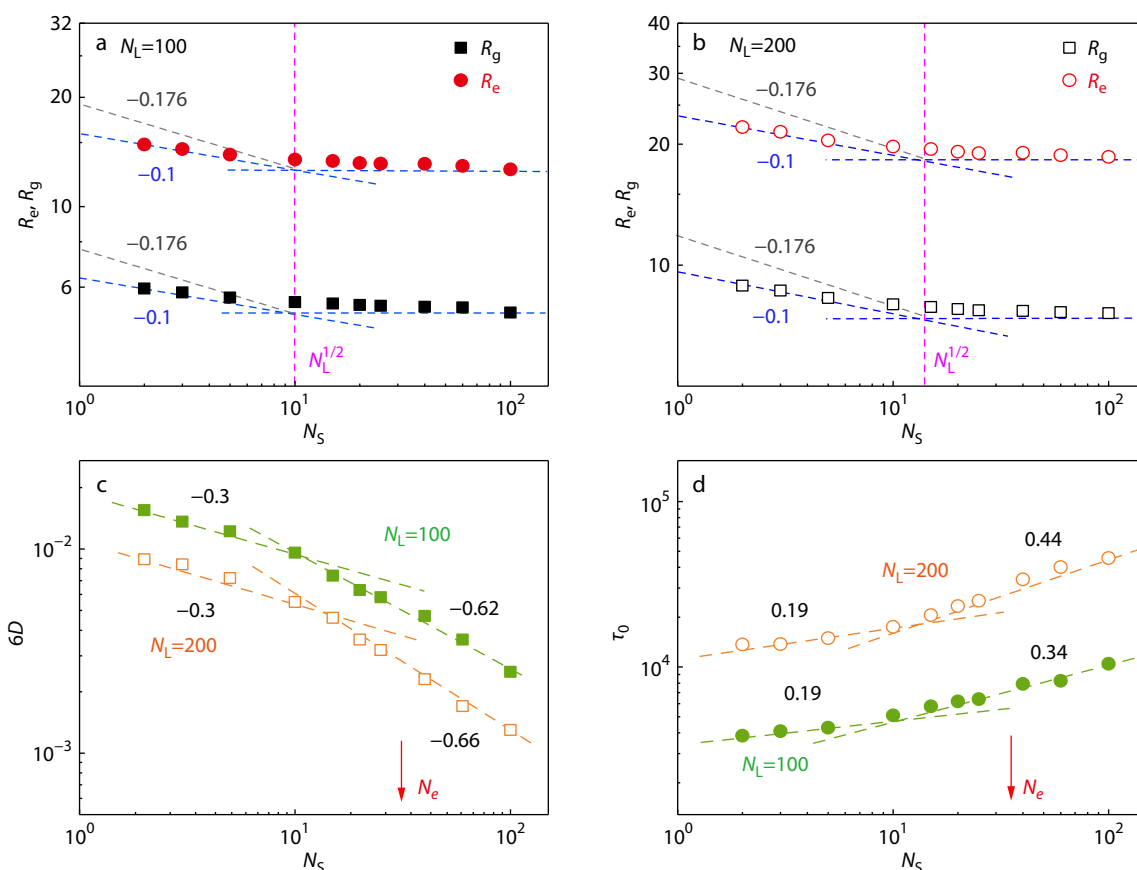


Fig. 2 Effects of short-chain length (N_S) on size and dynamics of long-chain under equilibrium conditions. (a, b) Long-chain size (R_g , R_e) versus N_S ; (c, d) Diffusion coefficient (D) and relaxation time (τ_0) versus N_S . Magenta dashed lines: critical N_S for chain swelling onset. Red arrow: N_S at entanglement onset.

theory prediction of -0.176 for good solvent (ν of approximately 0.588), indicating ν of approximately 0.55 for our blends. This discrepancy implies the short-chain matrix does not act as a simple swelling solvent; instead, short chains partially screen long-chain interactions at intermediate scales, weakening the swelling effect.

Equilibrium dynamics: deviations from Rouse to Zimm crossover predictions

While the static behavior of long chains is well-explained by Flory's theory, their dynamics—characterized by the diffusion coefficient (D) and relaxation time (τ_0)—reveal unexpected deviations from classical polymer dynamics models, such as the Rouse and Zimm frameworks. Here, τ_0 denotes the relaxation time of long chains in the short-chain matrix, calculated by fitting the end-to-end vector autocorrelation function $C(t)$ to the time corresponding to $C(t) = 1/e$. According to these models, the dynamic behavior is governed by the ratio (N_L/N_S^2).

Rouse regime ($N_S^2 \geq N_L$): in this regime, the short chains behave as a “solvent” phase, where the solvent viscosity η_s scales as N_S . For unentangled melts, the friction coefficient experienced by the long chains is expected to be independent of N_S , leading to diffusion coefficients and relaxation times that are independent of N_S . Consequently, the diffusion coefficient follows Rouse scaling as $D \sim k_B T / N_L$ and the characteristic relaxation time as $\tau_0 \sim R_L^2 / D \sim N_L^2$, with neither quantity exhibiting dependence on N_S .

Zimm regime ($N_S^2 < N_L$): hydrodynamic interactions (HI) dominate, resulting in Zimm scaling for diffusion and relaxation times, where $D \sim k_B T / (\eta_s R_L) \sim N_L^{-\nu} N_S^{2\nu-2}$ and $\tau_0 \sim R_L^2 / D \sim N_L^{3\nu} N_S^{4-6\nu}$ with ν of approximately 0.588 for good solvents, $\nu=0.5$ for θ conditions.^[39,40] Here, D and τ_0 inherit dependence on N_S through the solvent viscosity $\eta_s \sim N_S$.^[39]

However, our simulations indicate a more complex behavior. As shown in Figs. 2(c) and 2(d), both D and τ_0 exhibit strong, non-monotonic dependence on N_S across all N_S regimes, contradicting the classical predictions of N_S -independence in both the Rouse and Zimm regimes.^[39] Specifically, for:

(1) $N_L=100$: (i) Swollen regime ($N_S < 10$): $D \sim N_S^{-0.3}$ and $\tau_0 \sim N_S^{0.19}$, deviating from Zimm scaling. (ii) ideal regime ($N_S \geq 10$): D continues to decrease weakly with N_S , with $D \sim N_S^{-0.62}$, while τ_0 increases as $\tau_0 \sim N_S^{0.34}$, contradicting the assumption of N_S -independent friction in the Rouse model.

(2) $N_L=200$: (i) Swollen regime ($N_S < 14$): Similar behavior to the $N_L = 100$ case, with $D \sim N_S^{-0.3}$ and $\tau_0 \sim N_S^{0.19}$, showing clear deviation from Zimm predictions. (ii) Ideal regime ($N_S \geq 14$): again, D weakly decreases with N_S as $D \sim N_S^{-0.66}$, and τ_0 increases as $\tau_0 \sim N_S^{0.44}$, not consistent with classical predictions.

This discrepancy suggests that the classical Rouse and Zimm models, which assume either pure Rouse or pure Zimm behavior, fail to accurately describe the dynamics of long chains in unentangled short-chain matrices. Even when the long chains adopt ideal conformations *i.e.*, $N_S^2 \geq N_L$, their dynamics remain sensitive to N_S , indicating that the short-chain matrix does not act as a simple solvent but instead modulates the local friction experienced by the long chains. This could be due to enhanced packing constraints or interchain entanglement-like correlations in the short-chain matrix, which are not captured by classical models. The observed

scaling behavior likely reflects a crossover between monomeric friction dominant for small N_S and collective segmental rearrangement dominant for large N_S .

Key insight: static-dynamic decoupling

An important observation from Figs. 2(a)–2(d) is the decoupling of static and dynamic responses to changes in N_S . While static properties *e.g.*, R_g , R_e , exhibit a sharp crossover at $N_S^2 \approx N_L$, consistent with Flory's screening theory, the dynamic properties (D , τ_0) show a more gradual and continuous evolution with N_S across this threshold. This decoupling implies that the mechanisms governing static conformations and dynamics are distinct. As a result, the dynamic response of long chains cannot be described by a single critical N_S value, but instead depends on the interplay between monomeric friction, collective segmental dynamics, and matrix relaxation processes.

For instance, even when the long chains adopt ideal conformations *i.e.*, ($N_S^2 \geq N_L$), their dynamics remain sensitive to N_S due to the increasing relaxation time $\tau_s \sim N_S^2$ of the short-chain matrix. When $\tau_s \ll \tau_0$, the matrix behaves as a fast solvent, and friction is dominated by monomeric interactions. In contrast, when $\tau_s \sim \tau_0$, collective segment rearrangements in the matrix enhance intermolecular friction, leading to slower diffusion and longer relaxation times. This dynamic coupling, absent from classical models, offers a more nuanced understanding of the N_S -dependence of the dynamics in ideal polymer blends.

Nonlinear Rheological Response

The equilibrium dynamics characterized herein bear significant implications for elucidating the nonlinear rheological response of long-chain systems under shear deformation. The observed dependence of both D and τ_0 on N_S strongly suggests that the effective monomeric friction coefficient—and consequently, the extent of shear-induced chain orientation and stretching—exhibits a non-trivial dependence on N_S . For instance, matrices with shorter N_S may hinder chain orientation, reducing shear thinning, while longer N_S matrices could promote orientation. Additionally, swollen long-chain conformations in small N_S matrices might amplify extensional nonlinearities. Below, we validate these hypotheses by analyzing steady-state viscosity and normal stress differences, linking equilibrium dynamics to flow-induced nonlinearities.

Shear rate dependence of viscosity

Steady-state viscosity η quantifies the resistance of a fluid to flow under shear and is defined as the ratio of shear stress σ_{xy} to shear rate $\dot{\gamma}$ for simple shear:

$$\eta = -\frac{\sigma_{xy}(\dot{\gamma})}{\dot{\gamma}} \quad (4)$$

Shear stress was computed using the virial stress tensor formula:^[41]

$$\sigma = \frac{1}{V} \left\langle \sum_i m \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{i \neq j} \mathbf{r}_{ij} \mathbf{F}_{ij} \right\rangle \quad (5)$$

where V is the system volume, m and $\mathbf{v}_i$ are the monomer mass and velocity, respectively, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the position difference between monomers i and j , $\mathbf{F}_{ij}$ is the force between monomers i and j , and $\langle \cdot \rangle$ denotes ensemble averaging. The first term accounts for kinetic contributions, while the second term includes both intra- and intermolecular interactions.

For entangled polymers, viscosity exhibits Newtonian behavior ($\eta \sim \dot{\gamma}^0$) at low shear rates ($\dot{\gamma} < \dot{\gamma}_c$) and shear thinning ($\eta \sim \dot{\gamma}^{-a}$, $a > 0$) at high $\dot{\gamma}$ ($\dot{\gamma} > \dot{\gamma}_c$), where $\dot{\gamma}_c \sim 1/\tau_0$ is the critical shear rate. While our unentangled blends qualitatively follow a distinct trend, the scaling of η with $\dot{\gamma}$ shows pronounced N_S -dependence (Fig. 3). The strong N_S -dependence of $\eta(\dot{\gamma})$ contradicts classical Rouse predictions for unentangled melts, where $\eta \sim N_L^2$ (no N_S dependence). For the Newtonian Plateau region where the shear rate $\dot{\gamma} \ll \dot{\gamma}_c$, the viscosity η is independent of $\dot{\gamma}$ for all N_S . Here, the zero-shear viscosity η_0 increases with N_S , consistent with equilibrium dynamics: matrices with higher N_S exhibit a longer characteristic relaxation time τ_0 (Fig. 2d), thereby enhancing viscous drag. For shear-thinning regime where the shear rate $\dot{\gamma} \gg \dot{\gamma}_c$, the onset of shear thinning ($\dot{\gamma}_c$) and thinning exponent a depend strongly on N_S . Notably, at $N_S=5$, where swollen long chains and dominant hydrodynamic interactions prevail, a is about 0.1, which is significantly smaller than that observed at $N_S=25$ (a is about 0.5). For high shear rates ($\dot{\gamma} > 0.005 \text{ s}^{-1}$, red shaded region), a second apparent thinning regime with $a \approx 1.8$ emerges, but

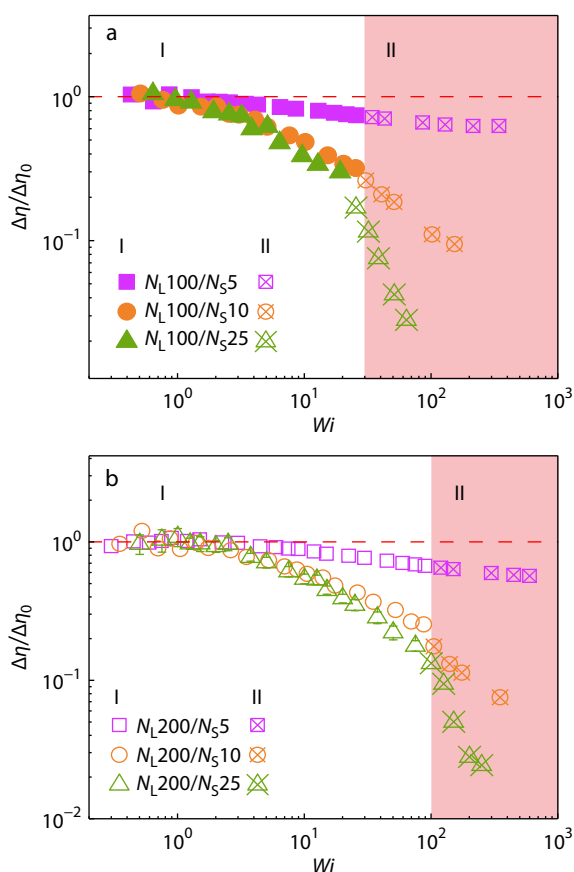


Fig. 3 Shear viscosity contribution of long chains ($\Delta\eta$) versus Weissenberg number (Wi) for (a) $N_L=100$ and (b) $N_L=200$ in short-chain matrices of varying N_S . $\Delta\eta$ denotes the difference between the total steady-state viscosity of the blend and that of the pure short-chain matrix at the same shear rate, isolating the long-chain contribution to bulk viscosity. $\Delta\eta_0$ is the normalized zero-shear viscosity difference (linear regime data). Non-collapse of $\Delta\eta/\Delta\eta_0$ across N_S indicates nonlinear long-short chain coupling. Red shaded region (Region II): ineffective temperature control under the given shear rates.

this arises from thermal runaway (Fig. S1 in the electronic supplementary information) rather than a new physical mechanism. Uncontrolled heating reduces monomer friction, artificially lowering η ; thus, this regime is not discussed further.

Normal stress differences: controversies in scaling and N_S -independence

Normal stress differences ($N_1 = \sigma_{xx} - \sigma_{yy}$, $N_2 = \sigma_{yy} - \sigma_{zz}$) characterize elastic nonlinearities. Their coefficients are defined as:

$$\psi_1 = -\frac{N_1}{\dot{\gamma}^2} \quad (6)$$

$$\psi_2 = -\frac{N_2}{\dot{\gamma}^2} \quad (7)$$

The first normal stress difference coefficient (ψ_1) reflects shear-induced chain stretching/orientation. For unentangled monodisperse polymer melts, computational studies have reported conflicting scaling behaviors: Jiang *et al.*^[31] observed $\psi_1 \sim \dot{\gamma}^{-5/4}$, whereas Xu *et al.*^[32] identified $\psi_1 \sim \dot{\gamma}^{-4/3}$ which they attributed to finite extensible nonlinear elastic (FENE) effects. Our simulation results, presented in Fig. 4, resolve these discrepancies in the literature. Within the controlled temperature regime ($\dot{\gamma} < 0.005 \text{ s}^{-1}$), the first normal stress difference ex-

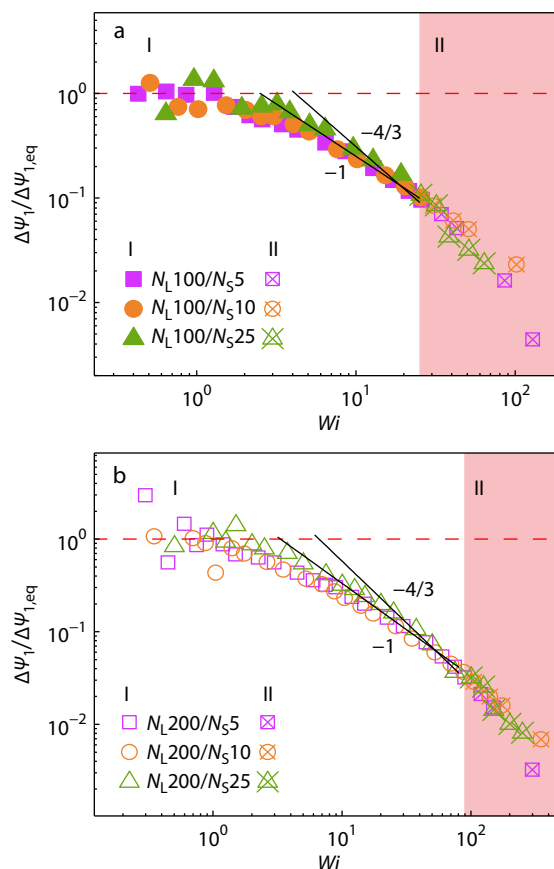


Fig. 4 First normal stress difference coefficient contribution ($\Delta\psi_1$) of long chains versus Wi for (a) $N_L=100$ and (b) $N_L=200$ in short-chain matrices of varying N_S . $\Delta\psi_1$ represents the difference between the total first normal stress difference coefficient of the system and that of the pure short-chain matrix at identical shear rates, normalized by nearly equilibrium data. Red shaded region (Region II): ineffective temperature control under the given shear rates.

hibits universal scaling behavior $\Psi_1 \sim \dot{\gamma}^{-1}$ across all N_s . This observation aligns with prediction from Marrucci Model.^[26] Notably, unlike the zero-shear viscosity η_0 , Ψ_1 shows no significant dependence on N_s in this regime. This N_s -independence suggests that the primary determinant of shear-induced chain orientation is the dimensionless product $\dot{\gamma}\tau_0$, i.e., the ratio of the flow time scale ($1/\dot{\gamma}$) to the characteristic relaxation time τ_0 , rather than the absolute magnitude of τ_0 itself. In contrast, for the uncontrolled temperature regime where $\dot{\gamma} > 0.005 \text{ s}^{-1}$, the scaling exponent deviates to $\Psi_1 \sim \dot{\gamma}^{-4/3}$, indicating a transition to non-equilibrium dynamics dominated by shear-induced heating.

The second normal stress difference coefficient (Ψ_2) is smaller in magnitude than Ψ_1 and theoretically predicted to be zero for Gaussian chains.^[16,17,19–21,26] However, our simulations show $-\Delta\Psi_2 \sim -\dot{\gamma}^{-1.2}$ for both $N_L=100$ and 200 (Fig. 5). This non-zero Ψ_2 arises from flow-induced anisotropy in intermolecular forces, not hydrodynamic interactions, as N_s dependence is extremely weak. However, due to poor signal-to-noise ratios, simulated data for Ψ_2 exhibit significant variance.

A critical finding is the partial decoupling between the vis-

cosity and normal stress responses to N_s : viscosity (η) exhibits strong N_s -dependence, arising from equilibrium dynamics specifically (τ_0 , hydrodynamic interactions HI, and matrix friction). In contrast, the normal stress coefficients (Ψ_1 , Ψ_2) are N_s -independent and governed by the dimensionless shear rate ($\dot{\gamma}\tau_0$). This decoupling implies that while N_s modulates the magnitude of viscous resistance, the nonlinear orientation/stretching mechanism is universal across N_s , dictated by the ratio of flow to relaxation times. These results provide new insight into the debate over nonlinear rheology in unentangled blends and highlight the necessity of incorporating matrix relaxation where $\tau_s \sim N_s^2$ into dynamic modeling frameworks.

Shear-induced Structural Evolution

The nonlinear rheological response of polymer blends is inherently linked to flow-induced changes in chain conformation and orientation. Here, we quantify these structural rearrangements using the radius of gyration tensor and orientation parameters, revealing how short-chain length (N_s) and HI modulate the interplay between stretching, orientation, and anisotropic fluctuations under shear.

Shear-induced stretching

The radius of gyration tensor $\mathbf{G}_{\alpha\beta}$ describes the spatial distribution of a polymer chain and is defined as:^[42–45]

$$\mathbf{G}_{\alpha\beta} = \frac{1}{N_L} \sum_{i=1}^{N_L} \Delta \mathbf{r}_{i,\alpha} \Delta \mathbf{r}_{i,\beta} \quad (8)$$

where $\Delta \mathbf{r}_{i,\alpha} = \mathbf{r}_{i,\alpha} - \langle \mathbf{r}_a \rangle$ is the position of monomer i relative to the chain's center of mass, and $\alpha, \beta \in x, y, z$, denote flow, gradient, vorticity directions. At equilibrium, the tensor is isotropic, with diagonal components $G_{xx} = G_{yy} = G_{zz} = \langle R_{g0}^2 \rangle / 3$. Under shear, anisotropy emerges, with components evolving differently with shear rate $\dot{\gamma}$.

To quantify shear-induced conformational changes, we computed the total stretch ratio ($\lambda = R_g^2(\dot{\gamma})/R_{g0}^2$) and its components ($\lambda_a = \mathbf{G}_{aa}/R_{g,a0}^2$, $a = x, y, z$, denotes the flow, gradient, and vorticity directions, respectively) for long chains with $N_L=100$ and 200 embedded in matrices of $N_s=5, 10$, and 25 (Fig. 6). These data reveal two distinct dynamical regimes governed by the Weissenberg number $Wi = \dot{\gamma}\tau_0$. In the Newtonian regime ($Wi < 1$), the shear rate is sufficiently low that chains relax to equilibrium between flow perturbations, resulting in λ of about 1 and no measurable anisotropy in the directional components (Figs. 6a and 6b). Above the critical Weissenberg number ($Wi > 1$), the system enters the shear-thinning regime, where conformational anisotropy develops with three key characteristics.

Total stretch ratio (λ) and flow-direction component (λ_x): Both quantities increase with Wi , scaling as $\lambda \sim Wi^{0.51}$ and $\lambda_x \sim Wi^{0.76}$ for $N_L = 100$ and $\lambda \sim Wi^{0.66}$ and $\lambda_x \sim Wi^{0.88}$ for $N_L = 200$. The stronger dependence on Wi for longer chains reflects enhanced FENE effects, where increased chain length amplifies entropic resistance to stretching at high Wi .

Gradient-direction component (λ_y): Compression dominates, with $\lambda_y \sim Wi^{-0.5}$ (Fig. 6c), consistent with experimental and theoretical results (see Fig. S2 in ESI). Teixeira *et al.*^[46] reported $\lambda_y \sim Wi^{-0.52}$ for dilute DNA solutions, which they attributed to HI; however, Hur *et al.*^[47] theoretically predicted the identical scaling ($\lambda_y \sim Wi^{-0.5}$) for Rouse chains without HI,

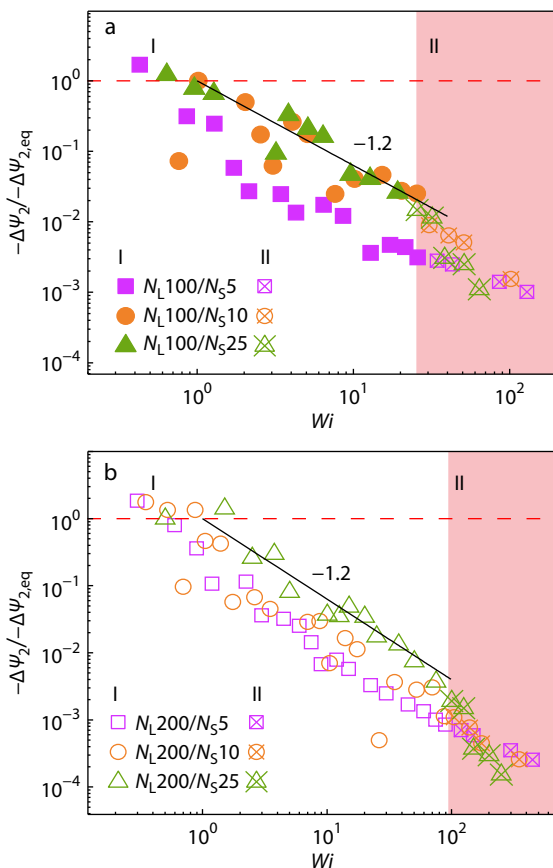


Fig. 5 Second normal stress difference coefficient contribution ($\Delta\Psi_2$) of long chains versus Wi for (a) $N_L=100$ and (b) $N_L=200$ in short-chain matrices of varying N_s . $\Delta\Psi_2$ represents the difference between the system's total second normal stress difference coefficient and that of the pure short-chain matrix at identical shear rates, normalized by nearly equilibrium data. Red shaded region (Region II): ineffective temperature control under the given shear rates.

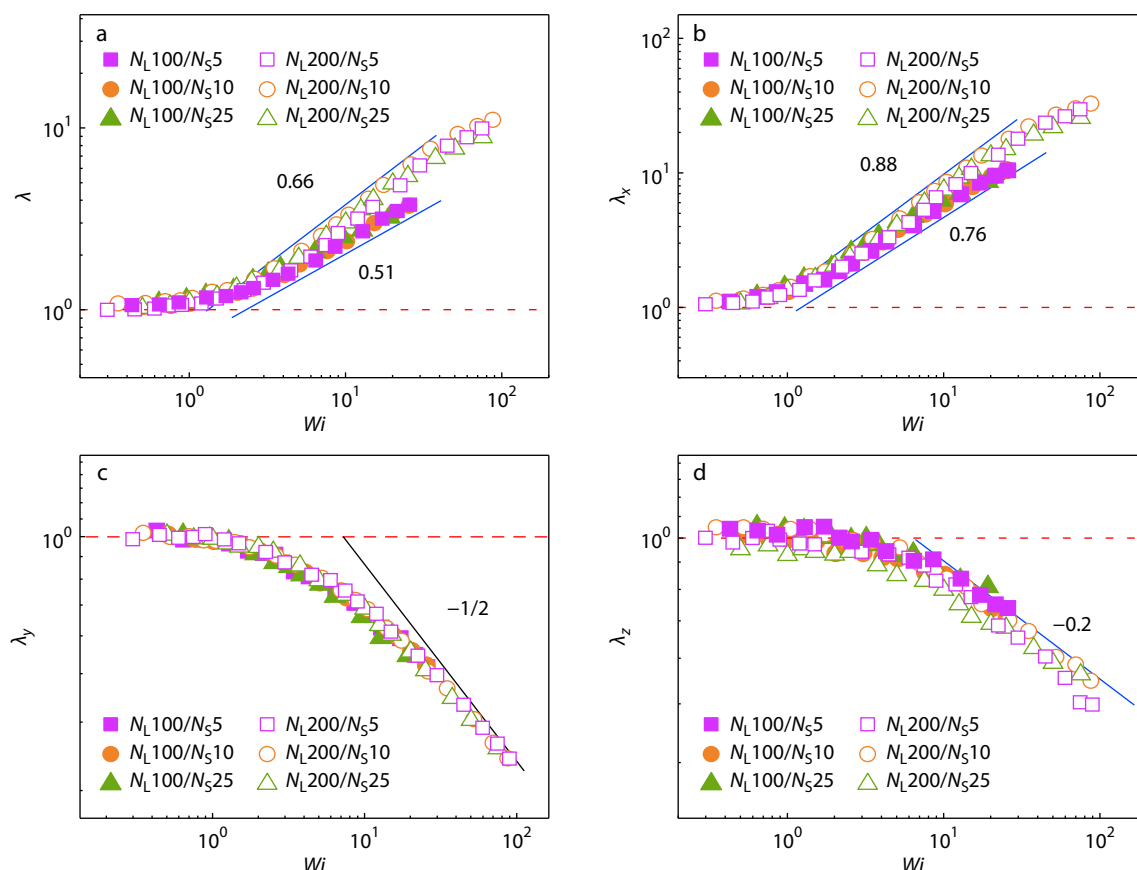


Fig. 6 Radius of gyration stretch ratio ($\lambda = \langle R_g^2 \rangle / \langle R_{g0}^2 \rangle$) and components for $N_L=100$ and 200 in $N_S=5, 10, 25$ matrices versus Wi . (a) Total λ ; (b) Flow-direction component ($\lambda_x = \langle R_{g,x}^2 \rangle / \langle R_{g,x0}^2 \rangle$); (c) Gradient-direction component ($\lambda_y = \langle R_{g,y}^2 \rangle / \langle R_{g,y0}^2 \rangle$); (d) Vorticity-direction component ($\lambda_z = \langle R_{g,z}^2 \rangle / \langle R_{g,z0}^2 \rangle$).

arising purely from entropic compression perpendicular to the flow gradient. Our results resolve this apparent contradiction: in unentangled blends, the short-chain matrix screens long-range HI, reducing their influence on conformational dynamics. Thus, the observed $\lambda_y \sim Wi^{-0.5}$ scaling confirms that gradient-direction compression is an entropic effect, dominated by Rouse-like dynamics rather than hydrodynamic drag.

Vorticity-direction component (λ_z): unexpectedly, λ_z decreases with Wi , following $\lambda_z \sim Wi^{-0.2}$ (Fig. 6d). This behavior is consistent with FENE effects: as chains stretch along the flow direction, their conformational entropy decreases, and the resulting anisotropic fluctuations amplify compression in the vorticity direction. This directly contradicts classical rheological models,^[48,49] which predict $\lambda_z=1$ under the assumption that vorticity-direction fluctuations remain unaffected by shear flow.

Notably, λ and its components show no significant dependence on N_S (Fig. 6). This aligns with the analysis of Babcock *et al.*^[1] who demonstrated that chain stretching is governed by Wi . Since Wi absorbs the N_S -dependence of τ_0 , the stretching behavior collapses onto a universal curve when plotted against Wi , regardless of matrix chain length.

Orientation resistance: N_S -dependent barriers to alignment

To characterize the flow-induced orientation of long chains, we

computed two key metrics: the orientation resistance parameter (m_G) and the orientation angle, which quantifies the average misalignment of chains from the flow direction,^[32,42–44,50]

$$m_G = \dot{\gamma} \tan(2\phi) = \frac{2\dot{\gamma} \langle G_{xy} \rangle}{\langle G_{xx} \rangle - \langle G_{yy} \rangle} \quad (9)$$

where, ϕ represents the angle between the principal axis of the polymer chain and the flow direction. m_G quantifies the difficulty of chain orientation. m_G scales with Wi as $m_G \sim Wi^{0.35}$ for both $N_L=100$ and 200 (Fig. 7), a weaker dependence than the $m_G \sim Wi^{0.54}$ observed in dilute polymer solutions.^[42,51] This discrepancy arises from the screening of HI by the short-chain matrix in blends. In dilute solutions, strong HI amplify drag forces, increasing the energy barrier to orientation and thus steepening the m_G - Wi scaling. In blends, however, the short-chain matrix disrupts long-range HI, reducing effective hydrodynamic drag and weakening the Wi -dependence of m_G . Notably, m_G exhibits a clear N_S -dependence at fixed Wi : smaller N_S increases m_G e.g., $m_G(N_S=5) > m_G(N_S=25)$.

Our findings address two longstanding controversies in polymer rheology, while also highlighting opportunities for model refinement: (1) vorticity-direction compression challenges classical assumptions: the observation of $\lambda_z \sim Wi^{-0.2}$ directly contradicts the classical assumption that vorticity-direction fluctuations are flow-insensitive ($\lambda_z = 1$).^[48,49] This has crit-

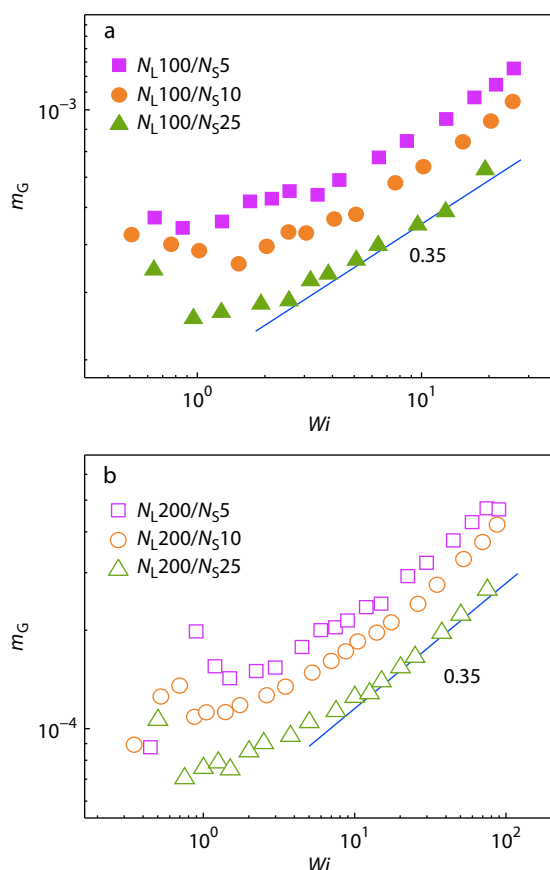


Fig. 7 Orientation resistance parameter of long chains versus Wi for (a) $N_L=100$ and (b) $N_L=200$ in short-chain matrices of varying N_S .

ical implications for shear-thinning models: vorticity compression reduces the effective volume occupied by chains, lowering interchain collision frequency and thus contributing to viscosity reduction in addition to the well-established orientation-induced decrease in stress. (2) Hydrodynamic Interaction screening in blends: the weaker scaling of orientation resistance ($m_G \sim Wi^{0.35}$) compared to dilute solutions ($m_G \sim Wi^{0.54}$)^[42,51] provides direct evidence that the short-chain matrix screens long-range HI. This screening simplifies the dynamics of unentangled blends relative to dilute solutions, where HI dominate conformational and orientational behavior.

The orientation angle ϕ decreases with Wi , scaling as $\phi \sim Wi^{-\omega} = Wi^{-0.6}$ for $N_L = 100$ and $\phi \sim Wi^{-0.7}$ for $N_L = 200$ (Fig. 8). The steeper slope for longer chains ($N_L=200$) indicates stronger alignment with the flow direction, a consequence of enhanced FENE effects: longer chains experience greater entropic resistance to stretching, favoring conformations aligned with the flow to minimize extensional deformation. For comparison, Teixeira *et al.*^[46] reported $\phi \sim Wi^{-0.46}$ for dilute DNA solutions, a significantly shallower slope than observed in our blend simulations. This difference arises from the stronger HI in dilute solutions, where hydrodynamic drag opposes chain rotation and orientation, whereas HI are screened in our blend system, allowing more efficient alignment at equivalent Wi .

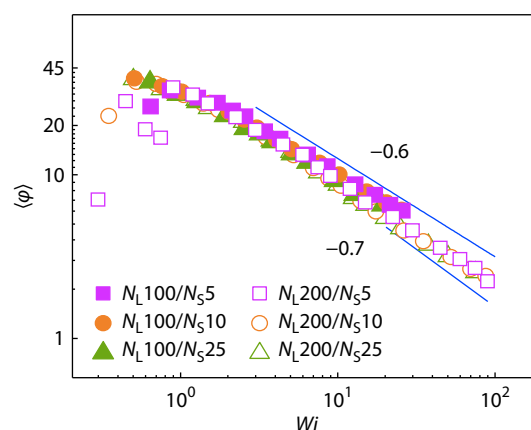


Fig. 8 Average orientation angle of long chains versus Wi for $N_L=100$ and 200 in short-chain matrices of varying N_S .

CONCLUSIONS AND OUTLOOK

The equilibrium dynamics and nonlinear rheology of unentangled long-chain/short-chain polymer blends are strongly modulated by the short-chain matrix length N_S , as revealed by Kremer-Grest model molecular dynamics simulations. Our findings highlight critical limitations of classical single-chain theories and underscore the need for frameworks incorporating N_S -dependent matrix effects. (1) Static and dynamic properties exhibit striking decoupling: while the radius of gyration, R_g , follows Flory theory—with minor swelling at small N_S due to incomplete excluded volume screening—the diffusion coefficient, D , and relaxation time, τ_0 , display non-monotonic N_S -dependence, transitioning from monomeric friction dominance at small N_S to collective segmental rearrangement at large N_S . This dynamic crossover invalidates Rouse/Zimm predictions of N_S -independence and emphasizes the interplay of monomeric friction, matrix dynamics, and hydrodynamic interactions (HI). (2) Viscous and normal stress responses are partially decoupled: zero-shear viscosity, η , depends strongly on N_S via modifications to τ_0 , HI, and matrix friction, yet the first and second normal stress coefficients, Ψ_1 and Ψ_2 , collapse onto universal curves when scaled by $\dot{\gamma}\tau_0$, indicating a universal orientation/stretching mechanism. (3) Under shear, long chains compress in the vorticity direction $\lambda_z \sim Wi^{-0.2}$, contradicting the classical assumption of flow-insensitive vorticity fluctuations $\lambda_z=1$. This compression reduces interchain collisions, contributing to shear thinning alongside orientation-induced stress reduction. Additionally, weaker orientation resistance scaling $m_G \sim Wi^{0.35}$ versus $m_G \sim Wi^{0.54}$ in dilute solutions indicates HI screening by the short-chain matrix, simplifying dynamics relative to HI-dominated dilute systems.

These results motivate four key directions for future work: (1) Isolating the molecular origin of N_S -dependent friction via targeted simulations *e.g.*, bead-spring models with/without HI and segmental relaxation measurements; (2) Direct measurement of monomeric friction ζ and its shear dependence is challenging in our KG model, as existing frameworks^[18,24] rely on monodisperse melts or inextensible chains, respectively. This will be explored in future work via friction-sensitive observables *e.g.*, diffusion anisotropy. (3) Generalizing beyond the dilute limit and fixed long-chain length N_L by varying N_L and long-chain volume fraction to test the universality of stat-

ic-dynamic decoupling; and (4) developing constitutive models incorporating vorticity compression and anisotropic conformational fluctuations to enable accurate prediction of stress and viscosity in non-dilute, multi-chain systems. Addressing these gaps will bridge molecular insights with macroscale modeling, advancing the design of polymer blends with tailored rheological properties.

Conflict of Interests

Yu-Yuan Lu is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. 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/s10118-025-3514-4>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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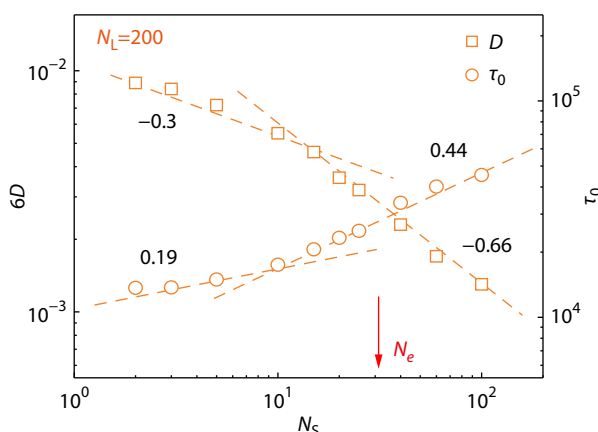
Graphical Abstract

Short-chain Length Dependence of Equilibrium Dynamics and Nonlinear Rheology in Unentangled Long-chain/Short-chain Polymer Blends

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Molecular dynamics simulations reveal that the diffusion coefficient D , and the relaxation time τ_0 , exhibit a strong, non-monotonic N_S -dependence, transitioning from monomeric friction dominance at small N_S to collective segmental rearrangement at large N_S .



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