

Conformational and Dynamical Evolution of Block Copolymers in Shear Flow

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Abstract Conformation and dynamical evolution of block copolymers in shear flow is an important topic in polymer physics that underscores the forming process of various materials. We explored deformation and dynamics of copolymers composed of rigid or flexible blocks in simple shear flow by employing multiparticle collision dynamics integrated with molecular dynamics simulations. We found that compared with the proportion between rigid and flexible blocks, the type of the central blocks plays more important role in the conformational and dynamical evolution of copolymers. That is, if the central block is a coil, the copolymer chain takes end-over-end tumbling motion, while if the central block is a rod, the copolymer chain undergoes U-shape or S-shape deformation at mid shear rate. As the shear strength increases, all copolymers behave similar to flexible polymers at high shear rate. This can be attributed to the fact that shear flow is strong enough to overcome the buckling force of the rigid blocks. These results provide a deeper understanding of the roles played by rod and coil blocks in copolymers for phase interface during forming processing.

Keywords Block copolymer; Shear flow; Multiparticle collision dynamics; Molecular dynamics simulations; Conformation

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INTRODUCTION

Copolymers comprised of rigid and flexible blocks have been valuable ingredients in biomaterials,^[1,2] organic electronic^[3,4] and structure materials^[5–8] owing to the fact that they can maintain special nanostructures to improve interfacial compatibility or to bear deformation resistance. Besides, block copolymers can also regulate the micro phase separation in shear flow, which is crucial in the polymer process.^[9–11] Intensive studies have been made focusing on the impacts of copolymers on creep behaviors,^[12,13] processing kinetics and forming,^[14–17] and micro-fluidic separation.^[18–22] To decipher the roles of rigid or flexible block in the copolymers, their conformational and dynamical behaviors have been extensively studied under equilibrium,^[7,23–31] or in steady shear flow.^[14,32–36] However, the investigation in shear flow remains scarce.

Conformational evolutions for flexible polymers in shear flow have been studied both experimentally and theoretic-

ally. Dating back to 1974, de Gennes proposed that the coil-stretch conformational transition for flexible polymer chains occurs when the critical velocity gradient overwhelms the entropic retraction force.^[37] It was later validated by the ensemble averaged signals from birefringence and light scattering experiments.^[38–40] Later, Wirtz *et al.* traced the real-time dynamics of DNA molecules in simple shear flow with fluorescence labels and presented the dependence of stretching and collapse against shear rate.^[41] Chu and co-workers confirmed the end-over-end tumbling evolution including stretching, align, collapse and tumble motions *via* fluorescence microscopy and Brownian dynamics simulation.^[42,43] Recently, we revealed that flexible polymers follow a quasi-affine deformation in simple shear flow using molecular dynamics simulations and graph theory analysis.^[44]

Different from flexible polymers, rigid polymers may exhibit periodic Jeffery orbits when the persistence length L_p is much larger than the contour length L . As the L_p decreases from the scale $L_p \gg L$ for rigid chain to $L_p \sim L$, semiflexible polymers show diverse motion behaviors associated with deformation in shear flow.^[45] Winkler reported that semiflexible chains can turn to be flexible when the shear strength overwhelmed the energy barrier of conformational evolution.^[46]

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Liu *et al.* observed rod-like, elastic bulking then to snaking motions for semiflexible polymers.^[47] Munk *et al.* presented an empirical equation to describe the tumbling motion of actin filaments as a function of shear rate.^[48] Further supported by fluorescence microscopy, semiflexible polymers exhibit U-turn like motion and there is a scaling law for the critical end-to-end orientation angle ϕ_c against the shear rate: $\phi_c \sim \dot{\gamma}^{-1/3}$.^[47,49] Such scaling law for ensemble averaged parameters has been gradually recognized,^[50] whereas it is still elusive for local motions and the onset of motions for semiflexible polymer chains.

Alternatively, copolymers with rigid and flexible blocks have also been widely examined. For example, various morphologies like vesicles, spheres, onion-like structures, worm-like fivers assembled by BAB (A represent flexible and B is a rigid block) rigid-flexible copolymers have been observed at different concentrations in solutions.^[51] Lee and co-workers reported that ABA rigid-flexible copolymer exhibits assemble micelles or vesicles morphologies.^[52] Self-consistent field theory (SCFT) computation shows that rigid-coil diblock copolymers may produce the standing vertical structures more easily than coil-coil lamellae.^[53] A recent review also indicated that rigid-flexible copolymers have great potential to release assembly structure with bioactive cargos in the body upon stimuli.^[54] Behind these assembly structures and conformational changes, fundamental questions such as whether the conformational evolution of the copolymer is dependent on the fraction and the location of blocks, if the deformation has a conserved location, and what the case is for conformational evolution of the copolymer at high shear rate remain untouched.

In this work, a triblock copolymer with either rigid or flexible block in shear flow is studied using multiparticle collision dynamics (MPCD) integrated with molecular dynamics (MD) simulations, with the fraction and the location of rigid block as variables. We introduce the model and the hybrid MPCD/MD simulation method at first. Then local motions are analyzed using contact map and differential contact map. Finally, conformational and dynamical evolution of the whole chain and the contribution from each block are presented.

MODEL AND SIMULATION METHOD

Model for Triblock Copolymers in Shear Flow

The simulation system has a single triblock copolymer and solvents in a simple shear flow, and its schematic is presented in Fig. 1. The copolymers are composed of $N=60$ beads and each block has 20 beads. We consider 6 copolymers which include all combinations of flexible (labeled with A) and/or rigid (B) blocks accounting for the fraction and location of rigid blocks. Each spherical bead has a diameter of a and mass M ($M=10m$), with m the mass for a solvent bead. All beads have excluded volume, computed using truncated and shifted Lennard-Jones (LJ) potential U_{LJ} ,

$$U_{LJ} = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon, & r \leq r_{cut} \\ 0, & r > r_{cut} \end{cases} \quad (1)$$

where r is the distance between two beads, σ is the sum of the radius of two beads, r_{cut} is chosen as $2^{1/6}\sigma$ to account for the

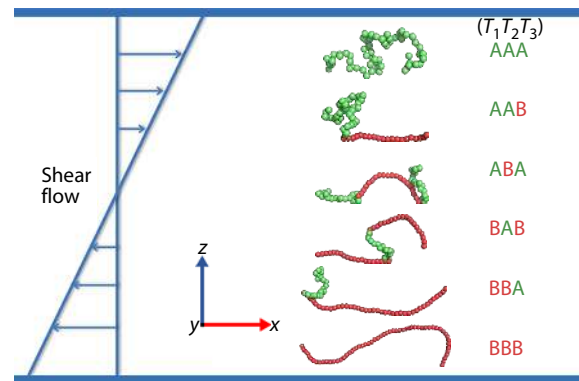


Fig. 1 Schematic for the simple shear flow and the copolymer with flexible (A, green) and rigid (B, red) blocks. Each block can be represented by T_1 , T_2 and T_3 for short. Here, x , y and z represent the flow, the vorticity and the gradient directions, respectively.

short-range repulsion, and the good depth ϵ equals $1.0k_B T$, with the temperature T and the Boltzmann constant k_B .

The bond potential U_b is defined by Hooke's law

$$U_b(r) = \frac{1}{2} k_b (r - r_0)^2 \quad (2)$$

where r_0 is the equilibrium bond length that equals the unit length σ , and the spring constant k_b is $10000\epsilon/\sigma^2$ to ensure that the extension of bond length is less than 0.2% at high shear rate.^[55,56] Beads in the rigid block B have one more interaction term, the bending potential U_ϕ , defined as

$$U_\phi = K_\phi (\cos \phi - \cos \phi_0)^2 \quad (3)$$

where ϕ is the bond angle and ϕ_0 equals 180° as the equilibrium bond angle. K_ϕ equals $300\epsilon/\sigma^2$ and the corresponding persistent length L_p is 50.

Simulation Method

The detail of the simulation method can be found in our recent reports.^[44,56–58] Briefly, the hybrid MPCD/MD simulation is in an NVT ensemble, the simulation box has a size of $60a \times 50a \times 50a$, and periodic boundary condition is applied in x and y directions. Besides the block copolymer, solvent beads also fill the space, where the average number of solvent beads per cell is $\rho=5$, the size of the cubic cell is $1a$ ($a = \sigma$) and the viscosity of solvent fluid is $8.7(\epsilon m)^{1/2}/\sigma^2$ according to Gompper's work.^[59] Constant temperature is maintained using a local Maxwellian thermostat.^[60] The collision time step is $0.1\tau_p$ and MD time step is $0.005\tau_p$, where the unit relaxation time $\tau_p = \sqrt{ma^2/k_B T}$.^[44,56,57] To further ensure large Schmidt numbers required for fluid-like behaviors, small collision time and large rotation angle are adopted according to the strategy proposed by Ripoll *et al.*^[61] To achieve the simple shear flow, we apply Lees-Edwards boundary condition, where the velocity field is given by $v_x = \dot{\gamma}z$, $v_y = 0$, $v_z = 0$ with $\dot{\gamma}$ representing the shear rate.

Each simulation trajectory has 4.8×10^7 MD simulation steps and 2.4×10^6 MPCD collision steps. In each trajectory, 1.2×10^5 conformation snapshots for copolymer in shear flow are captured in every 20 MPCD steps, and the last 10^5 snapshots are collected for analysis. Meanwhile, four parallel simulations with different initial conformations and velocities for a given shear rate and one of the six types of copolymers are also car-

ried out. The statistical parameters such as the radius of gyration (R_g) are averaged and the average gyration tensors (G_{xx} , G_{yy} , G_{zz}) are over 4×10^5 simulation snapshots. Such a large number of conformations make the error bar for statistical values normally smaller than the size of symbol, so the error bar will not be shown in the results unless specifically stated.

RESULTS AND DISCUSSION

Deformation

The radius of gyration (R_g) is an import quantity to estimate the conformational behaviors of copolymers in shear flow. The distributions of R_g^2 for the six types of copolymers at different shear rates are presented in Fig. 2. It can be observed that the distributions of R_g^2 for all copolymers transform from the unimodal distributions to the bimodal ones with the increase of shear rate. At very low shear rates, the unimodal distributions of R_g^2 are close to their equilibrium values. Generally, at $\dot{\gamma}=0$, the flexible block A is like a coil, while the rigid block extends as a rod. Intuitively, the peak position of the unimodal distributions obviously shifts toward right as the fraction of rod-like segments increases. However, we note that the peak position is more related to the type of the middle block at the low shear rate, i.e., the peak position is lower than 20 if the central block is a coil and is larger than 20 if the central block is a rod. The unimodal peak of all copolymers at the low shear rate decomposes into two peaks toward left and right at high shear rate, respectively. At the high shear rate, R_g^2 exhibits apparently bimodal distributions. This is mainly ascribed to the deformations of the stretching and collapse in the tumbling motions. For fully rod copolymers (BBB), the secondary peak is the collapse one, with the value of R_g^2 much larger than the collapse state of AAA due to the larger bending energy. The distribution of R_g^2 for BBA is between ABA and BBB due to the connection of the two rigid

blocks. In addition, we also find that the peak approaching large R_g^2 at high shear rate is sharper for copolymers with more rigid blocks as they are more stretched under high shear rate than flexible ones.^[62]

To further understand the deformations of polymer chains in shear flow, gyration tensors are characterized. The average gyration tensors $\langle G_{xx} \rangle$, $\langle G_{yy} \rangle$, and $\langle G_{zz} \rangle$ can also be determined by light scattering and fluorescence microscopy experiments. The eigenvalues of gyration tensor are denoted as G_1 , G_2 , and G_3 in the order from the largest to the smallest, $G_1 + G_2 + G_3$ is equal to R_g^2 . Fig. 3 and Fig. S1 (in the electronic supplementary information, ESI) display gyration tensor and their eigenvalues dependent on the shear rate, respectively. As observed in Fig. 3, in the lower shear regime ($\dot{\gamma} \leq 1 \times 10^{-4}$), the changes of all polymer chain conformations are negligible relative to the equilibrium ones. As shear rate increases ($\dot{\gamma} \leq 1 \times 10^{-3}$), the conformations are significantly extended if the mid-block is a coil (AAA, AAB, BAB) or the content of coil block is larger (ABA), as reflected from $\langle G_{xx} \rangle$ and $\langle G_1 \rangle$. In contrast, the block copolymers of BBB and BBA have no evident deformation with constant $\langle G_1 \rangle$, and only align along the shear flow direction. However, we note that their gyration tensor and eigenvalues present remarkable changes with the increase of shear rate, indicating that all polymers undergo deformation to relax the shear strength. The quick increase of $\langle G_{xx} \rangle$ and G_1 with the increase of shear rate for AAA, AAB, BAB and ABA suggests that they not only align along the flow direction, but also assume a stretched conformation. Interestingly, the triblock copolymers BAB present more deformation than ABA due to smaller change of G_1/G_3 for ABA. It means that the central blocks play a more important role than the fraction of the block. Furthermore, for BBB, the values of G_1 and R_g^2 show a dramatic decline, since the rigid polymer BBB undergoes the end-over-end tumbling motion when the

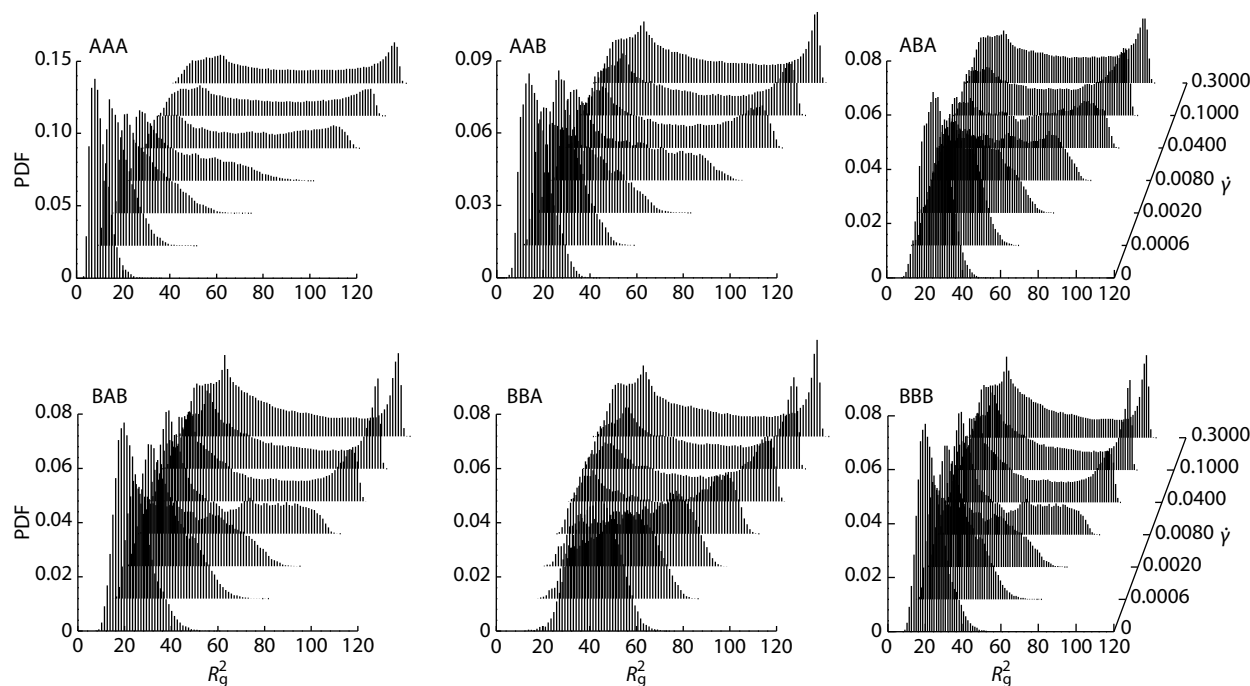


Fig. 2 Distribution of R_g^2 for six copolymers at the shear rates of 0, 0.0006, 0.002, 0.008, 0.04, 0.1 and 0.3. PDF, property density function.

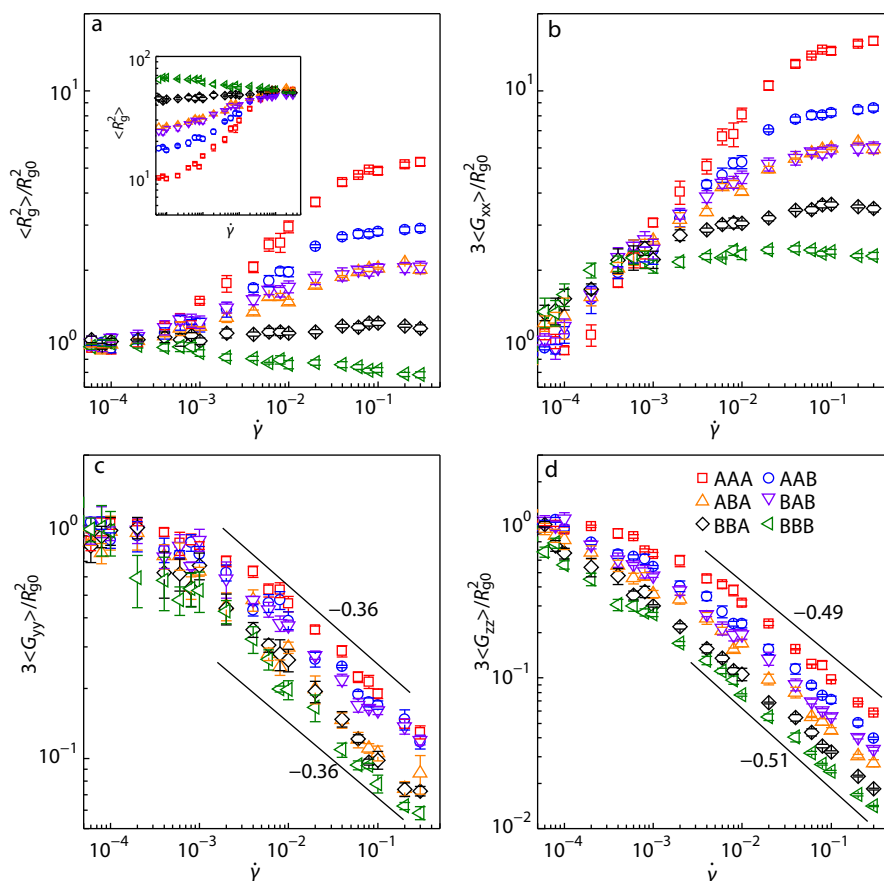


Fig. 3 (a) Mean-square radius of gyration $\langle R_g^2 \rangle$, (b) the flow component G_{xx} (c) the vorticity component G_{yy} and (d) the gradient component G_{zz} of the average gyration tensor as a function of shear rate $\dot{\gamma}$ for six copolymers, named AAA (red), AAB (blue), ABA (orange), BAB (purple), BBA (black) and BBB (green), respectively. R_{g0}^2 is the mean-square radius of gyration in the absence of shear flow.

shear flow is strong enough to overcome the buckling force.

In the gradient and vorticity directions (Figs. 3c and 3d), all polymer chains are compressed with the increase of shear rate. The scaling relationship of the contraction in the gradient direction follows $G_{zz} \sim \dot{\gamma}^{-0.51}$, consistent with experimental measurements for single double-stranded DNA under shear $G_{zz} \sim \dot{\gamma}^{-0.50}$.^[42] Compared with the compression in the gradient directions, the compression in the vorticity direction is more slowly and follows the scaling law $G_{yy} \sim \dot{\gamma}^{-0.36}$, slightly steeper than the observation of $G_{yy} \sim \dot{\gamma}^{-0.30}$ in semidilute solutions^[63] with interchain exclusion. We also note that the scaling exponents are independent of the type of block made of polymers. At last, as shown in the inset of Fig. 3(a), the $\langle R_g^2 \rangle$ of all polymers converge to the same values at high shear strength ($\dot{\gamma} > 0.1$), indicating that all copolymers exhibit the same character of flexible polymers.

Dynamics

To deeply decipher the conformational and dynamical evolution of six types of copolymers in shear flow, we calculate the contact maps and differential contact maps between particles at different shear rates, which are depicted in Figs. 4 and 5, Figs. S2, S3, S4 and S5 (in ESI), respectively. The contact map is defined as the ensemble average of all the adjacency matrixes for each copolymer in a given period in the collapse

or tumble process. As the adjacent matrix, represents the connected information of atoms in copolymer, the contact map can show us the density probability of connection for copolymer in the given process. The adjacent beads are defined by the spatial distance. Any two particles are regarded as in contact when they are closer than a cut-off distance, which is three times the equilibrium bond length $3r_0$. We have also changed the range of the cut-off distance from $2r_0$ to $4r_0$, and the results from graph theory analysis are qualitatively the same, as shown in Figs. S7 and S8 (in ESI). Moreover, the differential contact map is the ensemble average of the difference between two adjoined adjacent matrixes, which can represent the transformation of connection information for a given period.^[44] As reported in our previous investigation, flexible polymers will express end-to-end tumbling to relax shear strength and the semiflexible polymers are much likely to form the U-shape or S-shape when the shear strain overwhelms the deformation energy barrier. Compared with those homopolymers, copolymers composed of coil and rod blocks (AAB, ABA, BBA, BAB) will present tumbling motions with rich conformations such as U-shape, S-shape, dumbbell-shape, and half dumbbell-shape, depending on the block types. At a relatively low shear rate, the conformations of all the copolymers remain close to the equilibrium state. With the increase of the shear rate (shear rate from 0.001 to 0.1), all copolymers take end-over-end

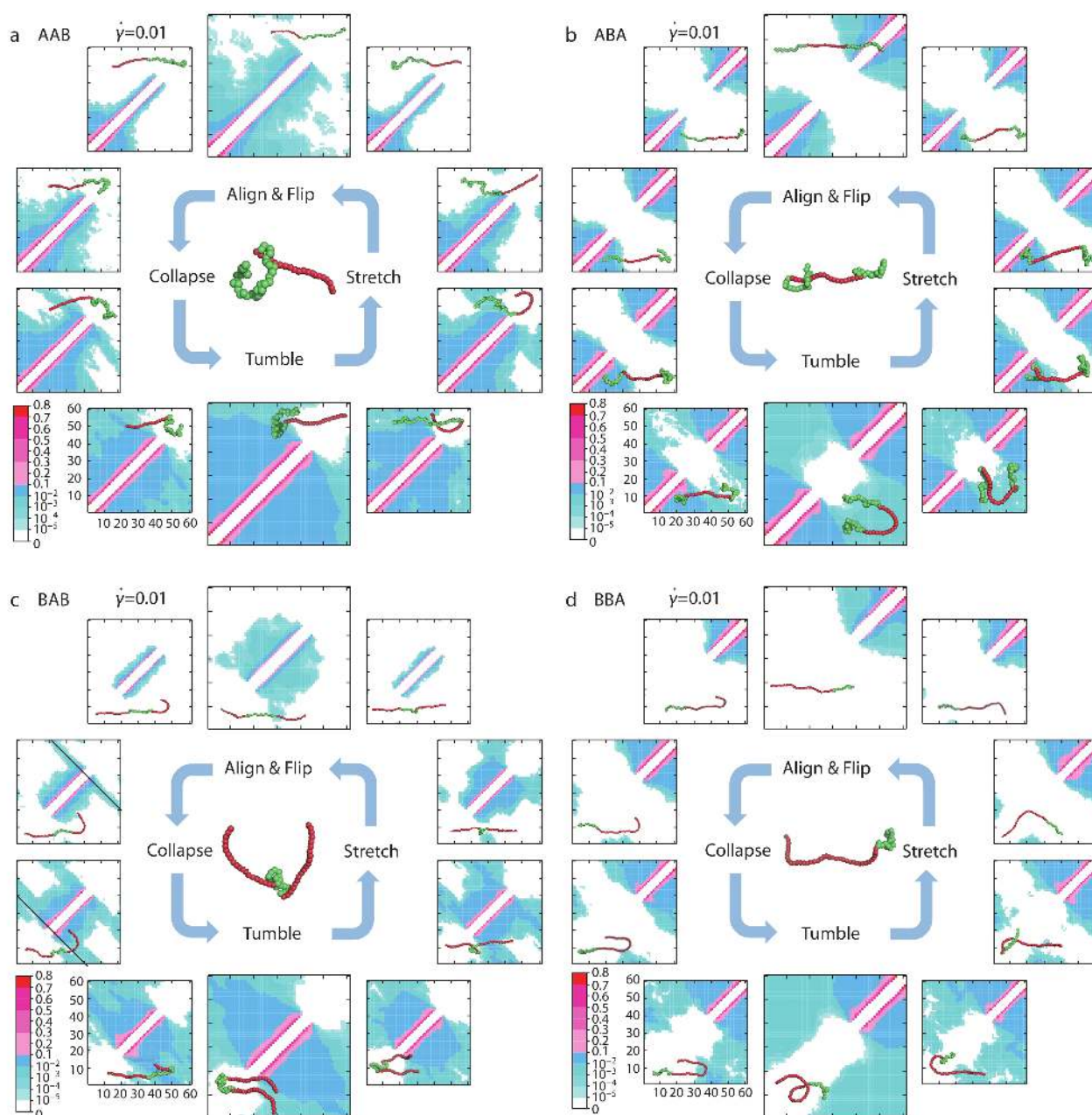


Fig. 4 The contact map and the conformational evolution for four copolymers (AAB, BAB, ABA and BBA) in shear flow with the shear rate equal to 0.01. The most probable equilibrium conformations are shown in the center of the figure.

tumbling motions and behave more like flexible polymers, as shown in Figs. S2 and S3 (in ESI). All copolymers will start to assume tumbling motion when the shear rate is larger than the relaxation frequency f ($f=1/\tau$, τ is the longest relaxation time). In the stretching process, all copolymers are extended along the flow direction, and compared with the flexible blocks, the rigid blocks show no obvious deformation due to the strong bending energy. Following the stretching, polymer chains generally align along the flow direction, with the small difference of the velocity across the chain. When the thermal disturbance changes the direction of the orientation angle, the polymer chains start to collapse. Then, the polymer chains start to tumble to avoid the large shear gradient. We note that if the mid-block of

copolymers (for AAB and BAB) is a coil, they take end-over-end tumbling behaviors, analogous to the completely flexible polymer (AAA), as shown in Figs. 4(a) and 4(c). However, when the mid-block (ABA and BBA) is a rod, the conformation behavior of copolymers is U-shape or J-shape, more like the semiflexible polymer (BBB), as shown in Figs. 4(b) and 4(d). Thus, the position of the blocks plays an important role in determining the deformation and dynamics of copolymers.

If the shear strength is strong enough ($\dot{\gamma}>0.1$) that can overcome the buckling force of rigid blocks, the copolymers all behave more and more like fully flexible polymer.^[46] We observe from Fig. 5 ($\dot{\gamma}>0.2$) that the contact maps present the distinct change of density probability for all copolymers, in-

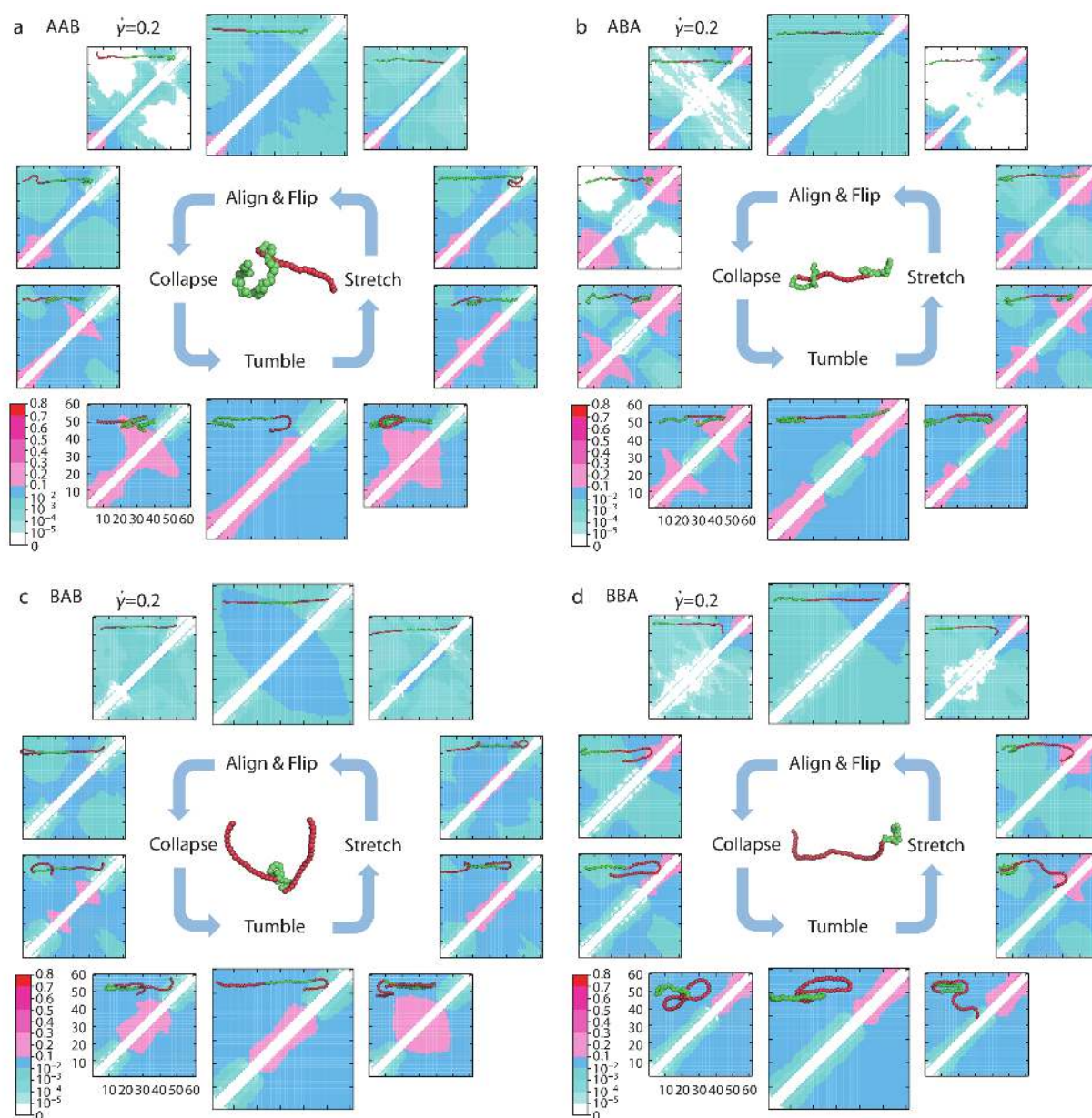


Fig. 5 The contact map and the conformational evolution for four copolymers (AAB, BAB, ABA and BBA) in shear flow where the shear rate equals 0.2. The most probable equilibrium conformations are shown in the center of the figure.

indicating that all copolymers show the end-over-end tumbling motions. The relax of copolymer chains is from the two flexible ends for ABA and AAA, while by one end for AAB, BAB, and BBA, as reflected by the differential contact maps of the collapse process for copolymers in Figs. S2 and S3 (in ESI). We also note that the peaks of all contact maps shift from the center to the ends in the stretching process. This suggests that all four copolymers are stretched from the center, followed by dumbbell-like (ABA and BAB with symmetrical structure) or half dumbbell-like (AAB and BBA) shape.

According to the analysis above, it is worth noting that the middle block (T_2) is intimately tied to deformations and dynamics of copolymers in shear rate. To further demonstrate this conclusion, we inspect the evolution of square radius of

gyrations R_g^2 of the whole copolymers and three blocks respectively against simulation time t , as shown in Fig. 6. With the increase of shear rate, all copolymers undergo the tumbling motion with the stretching and collapse processes. The profile of middle block T_2 exhibits a similar vibration with the whole copolymers T . We also find a bit of lag or lead of deformations of the blocks at the two ends T_1 and T_3 .

Moreover, the tumbling characteristic time τ_{tb} calculated by the cross-correlation function C_{xz} ^[44] is shown in Fig. 7. Under medium shear rate, the composition of copolymers has no obvious effect on the scaling relationship between the tumbling characteristic time and shear rate, where the scaling law is around $\tau_{tb} \sim \dot{\gamma}^{-0.68}$, in good agreement with both experimental^[42] and theoretical^[46] results. Compared with the

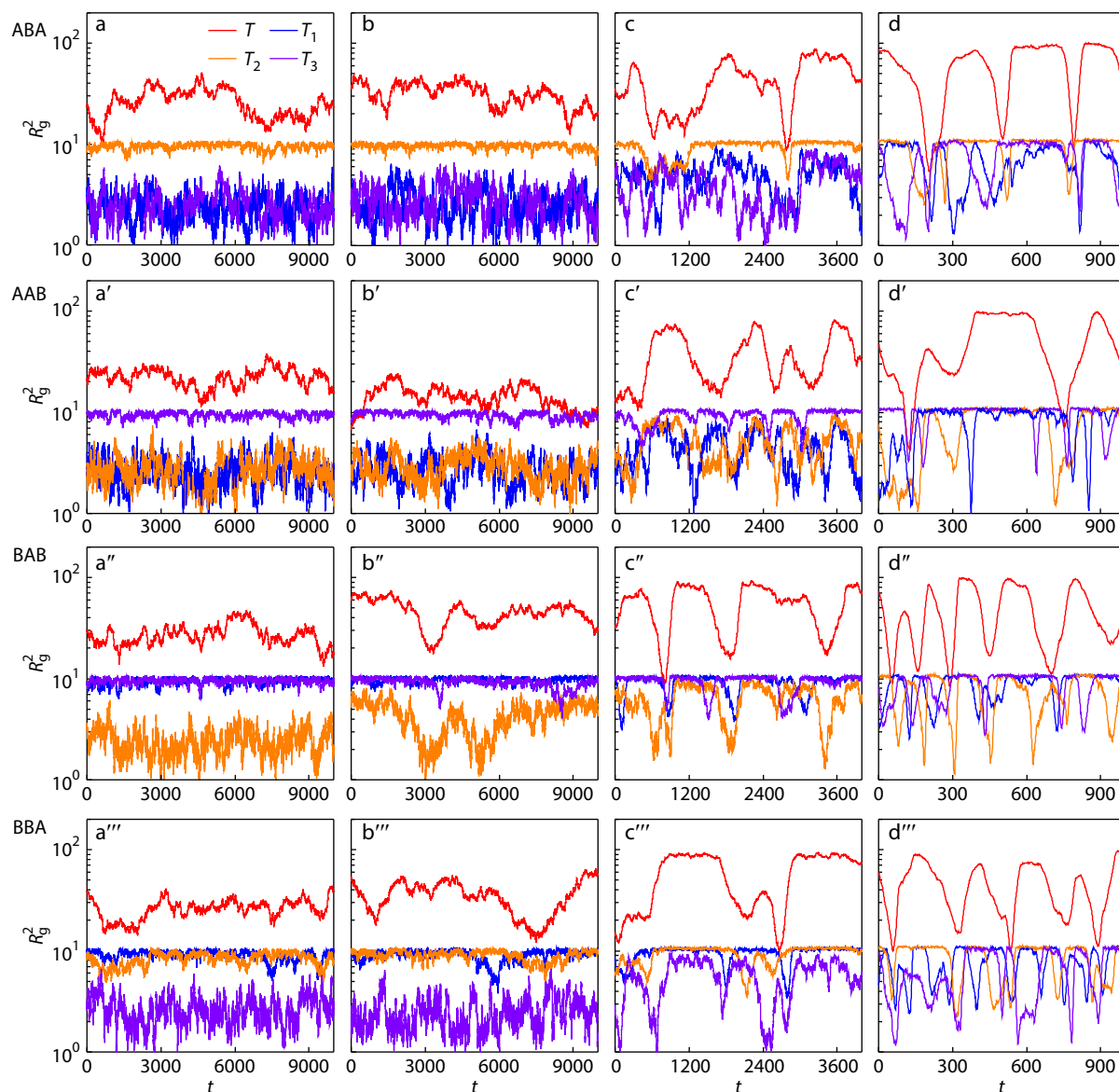


Fig. 6 The evolution of the square radius of gyration R_g^2 with the shear rate of (a–a'') 0.0002, (b–b'') 0.002, (c–c'') 0.02 and (d–d'') 0.2 for (a–d) ABA, (a'–d') AAB, (a''–d'') BAB, and (a'''–d''') BBA. All contains four curves which are the total T , the end block T_1 , the middle block T_2 , and the other end block T_3 part in red, blue, orange and purple, respectively.

flexible blocks, the rigid blocks take a longer tumbling characteristic time at small and mid shear rates, because the longest relaxation time of rigid blocks is much larger than the flexible blocks. With the shear strength increasing, the shear strength is strong enough to overcome the buckling force of the rigid blocks, all copolymers behave more and more like the flexible chain AAA, and the tumbling characteristic time of the whole chains τ_{tb} is almost identical for all copolymers.

Role of Each Block

To quantitatively examine the role of each block on the conformational and dynamical evolutions of copolymers, we calculate the Pearson correlation coefficient (P) of R_g^2 between three blocks versus the whole polymer chain as a function of shear rate. The Pearson correlation coefficient can estimate the degree of linear correlation between two random variables. As

seen from Fig. 8, R_g^2 of the middle block presents a relatively strong correlation with that of the whole polymers in shear flow, while the terminal blocks have a weak correlation. This indicates that mid-block dominates the conformational evolution of copolymers. The Pearson correlation coefficients at small shear rates are small for the insignificant deformations, while increase with the shear strength due to the obvious tumbling motions. As the shear rate increases, the Pearson correlation coefficients show a slight decline due to rapid deformations at the high shear rates.

Besides, the flow-induced alignment of copolymers is quantified by the angle ϕ , which is the angle between the gyration tensors within the flow field and the gradient direction (Fig. S6 in ESI), defined as:

$$\tan(2\phi) \sim 2\langle G_{xz} \rangle / (\langle G_{xx} \rangle - \langle G_{zz} \rangle) \quad (4)$$

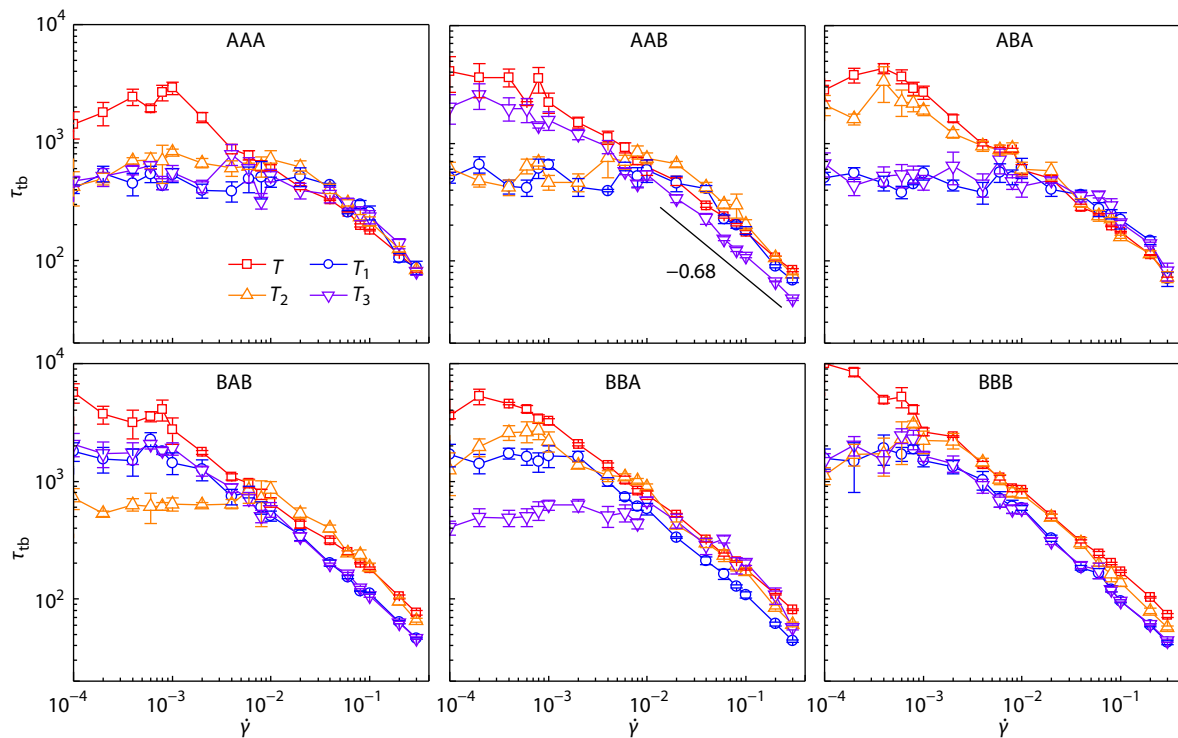


Fig. 7 The tumbling characteristic time of polymer chains as a function of shear rate $\dot{\gamma}$ with various compositions as indicated. The solid line shows that the scale index is $\tau_{tb} \sim \dot{\gamma}^{-0.68}$.

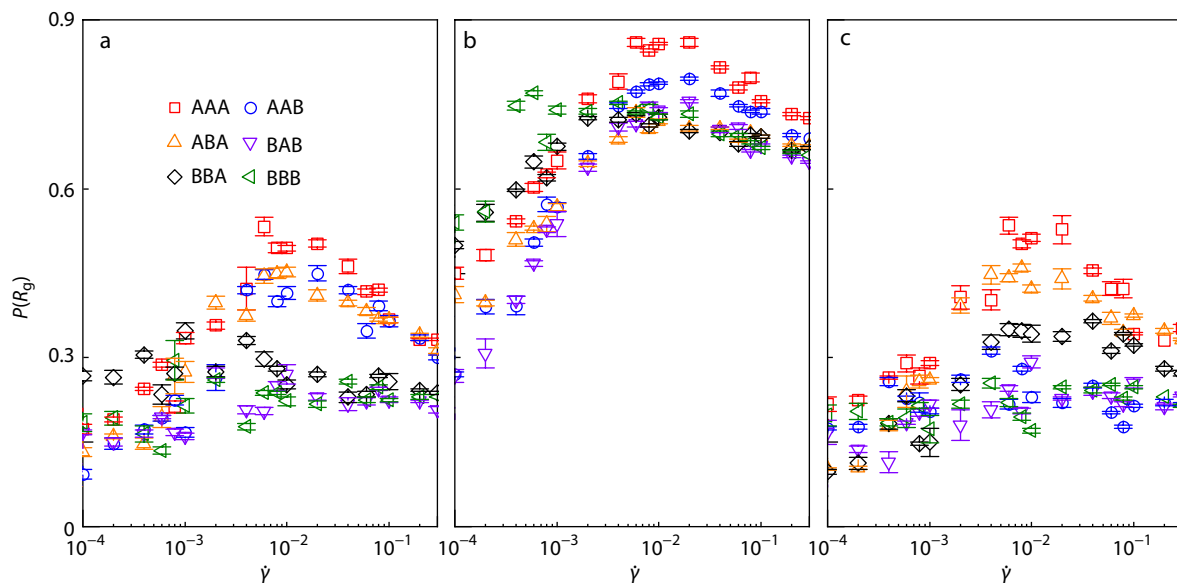


Fig. 8 The Pearson correlation coefficient (P) of R_g^2 between three blocks versus the whole polymer chain as a function of shear rate for six copolymers. (a) T_1 , (b) T_2 and (c) T_3 .

We also collected the critical orientation angle ϕ_c (Fig. 9), which is defined as the transition between the advection-driven process (collapse and stretching processes) and the diffusion process (align & flip). In this work, the critical angle is also extracted based on the definition of the four sub-process as we have reported before.^[44] When the drag force is dominant over the thermal fluctuations, the advective process is separated from the diffusive process with a critical orienta-

tion angle ϕ_c .^[49] It can be noticed that the critical orientation angle ϕ_c for the whole copolymers is much close to that of their mid-blocks at the mid and high shear rates, while ϕ_c is the same for the three blocks under low shear rates, because of no obvious deformations of the copolymers.

To clarify the orientation correlation between the three blocks and the whole chain, we calculate the coefficient of determination $\sqrt{\Delta\phi_c^2}$, as shown in Fig. 10. Similar to the Pear-

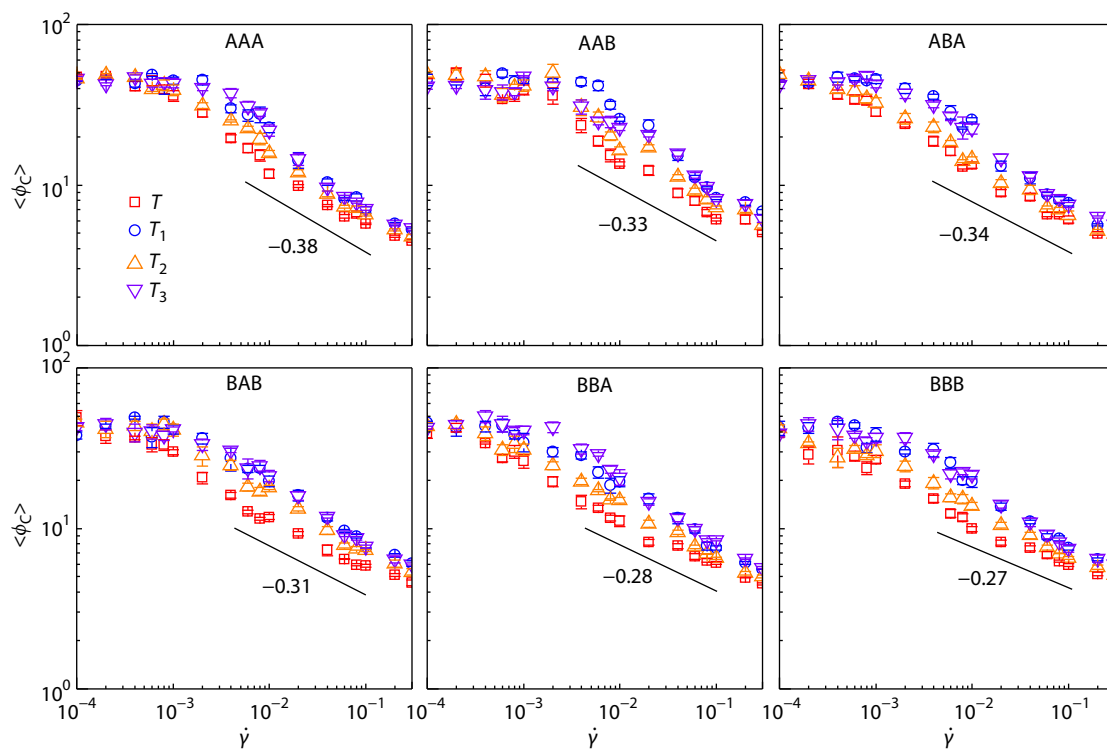


Fig. 9 The average critical orientation angle ϕ_c as a function of shear rate $\dot{\gamma}$.

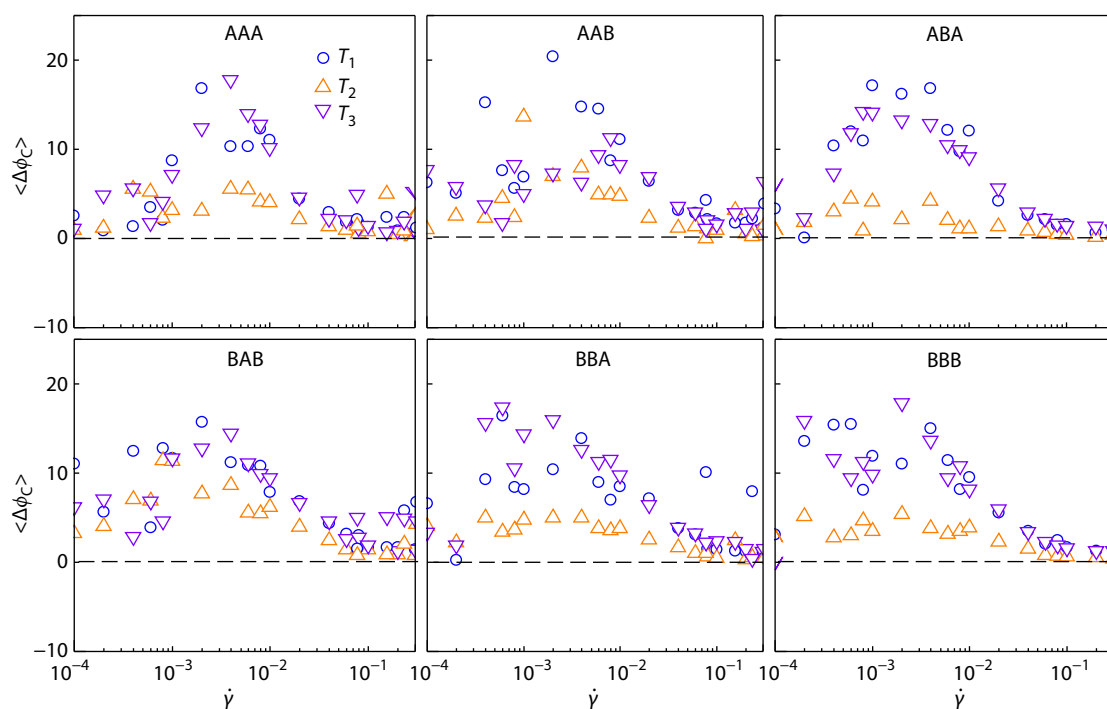


Fig. 10 The coefficient of determination $\sqrt{\Delta \phi_c^2}$ as a function of shear rate $\dot{\gamma}$.

son correlation coefficient (P) of R_g^2 , the orientation of the whole chain strongly correlates to the middle blocks. It means that the central block plays an important role in the deformation and orientation of the copolymer chains. The value of $\sqrt{\Delta \phi_c^2}$ decreases at the high shear rate, because of the chain

behaviors more and more like the flexible chain.

Besides, the flexible polymer AAA shows the scaling law of $\phi \sim \dot{\gamma}^{-0.40}$, the copolymers AAB, BAB and ABA obey the scaling law near $\phi \sim \dot{\gamma}^{-0.31}$, consistent with nonequilibrium molecular dynamics,^[64] and the other two copolymers follow the scal-

ing law like $\phi \sim \dot{\gamma}^{-0.24}$, larger than that from the fluorescence microscopy experiments^[43] and nonequilibrium molecular dynamics. This may be due to the short length of the rigid block with high potential energy and the statistic average of gyration tensor in the light scattering experiments and simulations. Moreover, the critical orientation angle follows a scaling law $\phi \sim \dot{\gamma}^{-0.38}$ for flexible polymer AAA, $\phi \sim \dot{\gamma}^{-0.33}$ for copolymers AAB, BAB, and ABA, and $\phi \sim \dot{\gamma}^{-0.28}$ for the other two copolymers, approximately consistent with the analytical predictions made by Harasim et al.^[49]

CONCLUSIONS

We studied the conformation fluctuation and transition for a triblock copolymer composed of rigid and flexible blocks in shear flow, employing multiparticle collision dynamics (MPCD) integrated with molecular dynamics (MD) simulations. The type of mid-block rather than the fraction dominates the conformational evolution and dynamics of block copolymer under this situation: for copolymers with a flexible mid-block, they will exhibit end-to-end tumbling motion like flexible polymer and if the mid-block is a rigid one, copolymers will have a U-shape or S-shape conformation change to relax the shear strength like semiflexible polymer. At high shear rate, as the shear strength is strong enough to overcome the buckling force of rigid blocks easily, all copolymers will behave much like flexible polymer. Our work will give a new insight to design the block copolymers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-021-2523-1>.

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