Supporting Information

Exploring the glass transition region: crowding effect, nonergodicity and thermorheological complexity

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Figure S1: Time dependences of the first normal stress difference, $N_1(t)$ (open circles), $4(<b_x(t)^2> - <b_y(t)^2>)$ (red curve) and $4(<u_x(t)^2> - <u_y(t)^2>)$ (blue curve), obtained from the simulation of the 16 chains × 20 beads system, using $\sigma = 0.36$ and $\varepsilon^* = 0.15$ (corresponding to $\Delta T = 10^0$ C of the monodisperse polystyrene sample), for a step-shear deformation $\dot{\lambda} = 0.2$. Here, $b_x(t)$ is the $x$-component of the bond segment vector and $u_x(t)$ is the corresponding unit vector component. The important feature of these results is that the first normal stress difference is proportional to the
corresponding orientation components in the slow mode region, by a factor of 4. This confirms the entropic nature of the slow mode (see text, Section 3.6).

Figure S2: Time dependences of the second normal stress difference, $|N_2(t)|$ (open circles), $4(<b_y(t)^2> - <b_z(t)^2>)$ (red curve) and $4(<u_y(t)^2> - <u_z(t)^2>)$ (blue curve), obtained from the simulation of the 16 chains × 20 beads system, using $\sigma = 0.36$ and $\epsilon^* = 0.15$ (corresponding to $\Delta T = 10^0 \text{C}$ of the monodisperse polystyrene sample), for a step-shear deformation $\lambda = 0.2$. Here, $b_y(t)$ is the $y$-component of the bond segment vector and $u_y(t)$ is the corresponding unit vector component. The vertical line indicates the time step where $N_2(t)$ changes the sign. The important features of these results are: (1) the second normal stress difference is about 1/3 to 1/10 of the first normal stress difference (Figure S1), (2) $|N_2(t)|$ is proportional to the corresponding orientation components in the slow mode region, by a factor of 4, and (3) Negative values of the functions, $4(<b_y(t)^2> - <b_z(t)^2>)$ and $4(<u_y(t)^2> - <u_z(t)^2>)$ indicate that the $z$-components of the bond segment vector and unit vector are larger in magnitudes. This confirms that the orientation in the $y$-direction is depleted of polymer orientations relative to the $z$-direction.