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Linear viscoelasticity of unentangled corona blocks and star arms

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Abstract: ABA type triblock copolymers form micellar structures consisting of B-rich cores and A-rich coronas in A-selective solvents. The relaxation of A corona is known to be qualitatively similar to, but quantitatively different from that of a star-shaped A chain due to the geometric (spatial) constraint by the core and the thermodynamic (osmotic) constraint. The effect of the geometric constraint on the block dynamics can be modeled by a chain with one end grafted onto an impenetrable wall. We show that the impenetrable wall slightly accelerates the end-to-end vector relaxation in a direction normal to the wall, while it slightly decelerates the viscoelastic terminal relaxation. To test this prediction, we performed linear viscoelastic measurements for model systems: For polystyrene-polyisoprene-polystyrene (SIS) triblock copolymers in S-selective solvent (diethyl phthalate) forming micelles, the viscoelastic relaxation of unentangled S blocks (corona blocks) was found to be slower compared with star-branched S chains having the same molecular weight. This deceleration is partly attributable to the effect of the geometrical constraint. The analysis shows that the deceleration can also be caused by the deformation and rearrangement of micelles, and cooperative and heterogeneous dynamics of S blocks.

Keywords: Block copolymer · Tethered chain · Linear viscoelasticity · Relaxation time

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Introduction

Block copolymers form various micellar structures when dissolved into selective solvents. ABA type triblock copolymers form micelles consisting of the A-rich coronas and B-rich cores in A-selective solvents. (Hamley 2005) Micelles interact with each other and thus form the spatially higher order structures. The micelles exhibit rich dynamic behavior over wide length scales from chains to lattice.

The linear viscoelasticity (LVE) of the block copolymer micelles has been extensively studied. The relaxation of the corona A block is qualitatively similar to but quantitatively different from that of star-shaped A chains. The difference is considered to be due to the enthalpic (steric) repulsions between the A blocks and the core, and the low compressibility that suppresses the spatial variation of the segmental density. These *geometric and thermodynamic constraints* make the relaxation behavior of the corona blocks different from that of star arms. (Chen, et al. 2012, Hamley 2005, Matsumiya, et al. 2012, Watanabe, et al. 1999)

The geometric (spatial) constraint can be reasonably described by an impenetrable wall on which one end of a corona block is grafted. In this work, we examine the role of the geometric constraint on the dynamics of a corona block theoretically and experimentally. We limit ourselves to unentangled corona blocks, since the dynamics of entangled corona blocks have been extensively studied. (Sato, et al. 1996, Watanabe, et al. 1996) For entangled corona blocks, the arm-retraction type mechanism (Ball and Mcleish 1989, Doi and Kuzuu 1980, Pearson and Helfand 1984) becomes dominant. If corona chains are not entangled, the arm-retraction can be ignored and we expect the geometric constraint would play a big role.

This paper is organized as follows. In “Theory” section, we first consider the theoretical model for the statics and dynamics of corona blocks: We analyze the conformation and dynamics of an untangled Gaussian chain (Rouse chain) grafted onto an impenetrable wall. We show that the spatial constraint (due to the impenetrable wall) makes the chain stretched in the direction normal to the wall and moderately *accelerates* the end-to-end vector relaxation, as already pointed by Koch et al. (Koch, et al. 1997). We also show firstly that, on the contrary, the viscoelastic relaxation of the chain is *decelerated*. In “Experimental” and “Results” sections, we show the experimental results for the model polystyrene-polyisoprene-polystyrene (SIS) triblock copolymer solutions to examine this *deceleration effect*. We compare the viscoelastic relaxation behavior of the corona chains in the SIS triblock copolymer solutions with the linear and star polymer solutions. The comparison shows the deceleration of the viscoelastic relaxation of corona chains compared with that of the star arms. However, the deceleration is slightly stronger than the theoretical prediction of our model. In “discussion” section, we discuss possible origins of the stronger deceleration. Section “Concluding remarks” summarizes this work.

Theory

We consider an ideal Gaussian chain to examine the static and dynamics of the polymer chain in the coronas of micellar structures. In reality, the chain should feel the effective potential field such as the osmotic pressure field to behave differently from the ideal Gaussian chain. Nevertheless, the ideal Gaussian chain model allows us to conclude several dynamic aspects at least qualitatively, which is the focus of present study.

We express the number of segments of the ideal Gaussian chain as N , and the segment size as b . One chain end of the chain is grafted onto an impenetrable flat wall, whereas another end is free. We set the normal vector of the wall to the z -direction and the wall position as $z = 0$. As we mentioned, this wall is employed to express the impenetrable (geometric) constraint effect. The origin of the interaction between the micellar core and the corona chain is enthalpic, and thus strictly speaking, this effect is the “enthalpic repulsion” effect. In the followings, however, we express this effect as the conformational entropy loss, and call it as the “steric repulsion” effect which would be more intuitive.

The statistical properties of the chain can be calculated by solving the Edwards equation without the external potential field (Kawakatsu 2004, Müller and Schmid 2005),

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \frac{b^2}{6} \nabla^2 q(\mathbf{r}, s), \quad \frac{\partial q^*(\mathbf{r}, s)}{\partial s} = \frac{b^2}{6} \nabla^2 q^*(\mathbf{r}, s) \quad (1)$$

where s is the segment index along the chain, and $q(\mathbf{r}, s)$ and $q^*(\mathbf{r}, s)$ are the path integral fields at the position $\mathbf{r}$ and the segment index s . The initial and boundary conditions for the Edwards equation are

$$q(\mathbf{r}, 0) = \delta(\mathbf{r} - \boldsymbol{\varepsilon}) \quad q^*(\mathbf{r}, 0) = 1 \quad (2)$$

$$q(\mathbf{r}, s)|_{z=0} = q^*(\mathbf{r}, s)|_{z=0} = 0 \quad (3)$$

where $\boldsymbol{\varepsilon}$ represents the graft position ($\varepsilon_z > 0$), and we take the limit of $\boldsymbol{\varepsilon} \rightarrow 0$ at the end of the calculation. (Dimarzio 1965, Watanabe et al. 1999) The distribution of the free end is expressed as follows, by using the path integral fields.

$$\phi_e(\mathbf{r}) = \frac{q(\mathbf{r}, N) q^*(\mathbf{r}, 0)}{\int d\mathbf{r} q(\mathbf{r}, N) q^*(\mathbf{r}, 0)} \quad (4)$$

Eqs (1)-(3) can be solved analytically, and thus we have the following explicit expression for the free end distribution (after taking the limit of $\boldsymbol{\varepsilon} \rightarrow 0$). (Watanabe et al. 1999)

$$\phi_e(\mathbf{r}) = \frac{9}{2\pi N^2 b^4} z \exp\left(-\frac{3\mathbf{r}^2}{2Nb^2}\right) \quad (5)$$

From eq (5), we find that the free end distribution in the z -direction (the direction normal to the wall) is qualitatively different from one in the x - and y -directions (the directions parallel to the wall). The average square end-to-end sizes in the x -, y -, and z -directions are calculated to be $\langle x^2 \rangle = \langle y^2 \rangle = Nb^2/3$ and $\langle z^2 \rangle = 2Nb^2/3$ ($\langle \dots \rangle$ represents the statistical average). This means that the chain is *stretched* to the normal direction. We may interpret this result as that the free end feels the *effective repulsive potential* from the wall. From eq (5), the effective potential for the free end is formally expressed as

$$U_{\text{eff}}(\mathbf{r}) = -k_B T \ln \phi_e(\mathbf{r}) = \frac{3k_B T \mathbf{r}^2}{2Nb^2} - k_B T \ln z + (\text{const}) \quad (6)$$

with k_B and T being the Boltzmann constant and absolute temperature, respectively. The second term in the right hand side of eq (6) represents the effective repulsive potential due to the impenetrable wall.

Before we consider the dynamics, we briefly consider whether the interaction between chains can be reasonably ignored or not. The segmental density field can be slightly high near the interface. This situation is similar to the segmental density near the junction point of star polymers. The Daoud-Cotton model (Daoud and Cotton 1982, Likos 2001) allows us to estimate the segmental density profile of star polymers in dilute solutions. In the Daoud-Cotton model, star arms can be divided into so-called the Daoud-Cotton blobs, of which size depend on the distance from the junction r as $\xi_{\text{DC}}(r) \sim r f^{-1/2}$ (f is the functionality). This gives the segmental density profile as $\rho(r) \propto r^{-4/3}$. The segmental density profile of the corona chains becomes similar in the dilute solutions. As the concentration of micelles increases, the corona chain density approaches to the bulk density for large r . In the semi-dilute solutions, we can estimate the blob size in the bulk as $\xi_{\text{bulk}} \sim a \phi^{-3/4}$ (a is the segment size and ϕ is the segmental volume fraction of the corona) (de Gennes 1979). We expect that ξ_{bulk} is smaller than $\xi_{\text{DC}}(r)$, and the excluded-volume effect can be screened, unless r is very small or ϕ is very small. Thus we consider that the interaction between corona chains can be ignored without serious errors, if the concentration of micelles is not very low.

Dynamics

The dynamics of an unentangled polymer chain can be described well by the Rouse model. Thus, in the current case, we expect that the dynamical properties of the chain in the corona regions can be expressed by the Rouse model modified with respect to an impenetrable wall. However, such a modification is not analytically tractable. (Koch et al. 1997) Then, we employ some approximations to study the dynamics of the chain in the corona regions.

We consider only a single relaxation mode instead of all the Rouse modes (the dumbbell type model). (Kröger 2004) As a slow and characteristic dynamical variable, we employ the end-to-end vector of the chain, $\mathbf{R}$. Although these approximations make the situation simple, the model is still

not simple and is difficult to handle analytically. The friction (or the mobility) for the end-to-end vector is generally position-dependent and there is the memory effect. Because our purpose here is to study the dynamics of the corona chain, we introduce additional assumptions to make the analytical calculations. We ignore the memory effect and assume that the effective friction (mobility) of the end-to-end vector is isotropic. (These assumptions may be too rough and physically not plausible. Nevertheless our model can reproduce some interesting and physically plausible properties, and we believe our model can capture the essential nature of the corona chain dynamics.) The dynamics of the end-to-end vector is described by the following Langevin equation. (van Kampen 2007)

$$\frac{d\mathbf{R}(t)}{dt} = -\frac{1}{\zeta_{\text{eff}}} \frac{\partial U_{\text{eff}}(\mathbf{R})}{\partial \mathbf{R}} + \xi(t) \quad (7)$$

Here, ζ_{eff} is the effective friction coefficient, U_{eff} is the effective potential given by eq (6), and $\xi(t)$ is the Gaussian random noise which satisfies the fluctuation-dissipation relation of the second kind,

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(t') \rangle = \frac{2k_B T}{\zeta_{\text{eff}}} \delta(t - t') \mathbf{1} \quad (8)$$

with $\mathbf{1}$ being the unit tensor. It is still difficult to obtain the analytic solution of eq (7), due to the nonlinearity of force arises from eq (6). Thus we employ the harmonic approximation for the potential, in order to make the force linear in $\mathbf{R}$. The effective potential takes minimum at $\mathbf{R}^* = [0, 0, \sqrt{Nb^2/3}]^T$, and the expansion of eq (6) around $\mathbf{R} = \mathbf{R}^*$ gives the approximate harmonic potential, (Koch et al. 1997)

$$U_{\text{eff}}(\mathbf{r}) \approx \frac{3k_B T}{2Nb^2} [R_x^2 + R_y^2 + 2(R_z - \sqrt{Nb^2/3})^2] + (\text{const}) \quad (9)$$

By substituting eq (9) into eq (7), we have the following set of linear Langevin equations,

$$\frac{dR_\alpha(t)}{dt} = -\frac{1}{\tau} R_\alpha + \xi_\alpha(t) \quad (\alpha = x, y) \quad (10)$$

$$\frac{dR_z(t)}{dt} = -\frac{2}{\tau} (R_z - \sqrt{Nb^2/3}) + \xi_z(t) \quad (11)$$

where we have defined the characteristic relaxation time τ as $\tau = \zeta_{\text{eff}} Nb^2 / 3k_B T$. From eqs (10) and (11), we find that the relaxation in the z -direction is *accelerated* compared with the x - and y -directions. This is because the potential force in the z -direction is modulated by the repulsive potential by the wall, as clearly observed in eq (9). Such acceleration was reported earlier by Koch et al. (1997).

To calculate the linear viscoelasticity, we need the expression of the stress tensor (for a single chain). Because we have started from the Rouse chain, the stress tensor should be expressed in the usual Kramers form. However, we have introduced several approximations and assumptions and

only the end-to-end vector dynamics is considered here. The expression of the stress tensor for the end-to-end vector under the approximations and assumptions is not trivial. In this work, we simply employ the following expression based on the stress-optical rule, which is commonly used for the dumbbell type model. (Doi and Edwards 1986)

$$\hat{\mathbf{g}}(t) \approx \frac{3k_B T}{Nb^2} \mathbf{R}(t) \mathbf{R}(t) \quad (12)$$

The expression of the stress tensor is not obvious because the end-to-end vector feels the effective repulsive potential from the wall. One may prefer to employ the different stress tensor model. For example, the variational formalism will give a different expression that contains the derivative of the effective potential. (Doi and Edwards 1986, Kröger 2004) However, the resulting expression is not simple and difficult to handle with. We believe that the results shown below are *qualitatively* not affected by the specific choice of the stress tensor form, and do not consider other possible forms in this work. The equilibrium statistical average of the stress tensor is calculated as

$$\langle \hat{\mathbf{g}} \rangle = \frac{3k_B T}{Nb^2} \frac{\int d\mathbf{R} \mathbf{R} \mathbf{R} \exp(-U_{\text{eff}}(\mathbf{R})/k_B T)}{\int d\mathbf{R} \exp(-U_{\text{eff}}(\mathbf{R})/k_B T)} \approx k_B T \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 3/2 \end{bmatrix} \quad (13)$$

Thus we find that in our model, the normal stress is not isotropic even in equilibrium. We consider this is an artifact of the approximations in our model, and therefore we subtract the anisotropic parts if the anisotropic normal stress leads unphysical behavior.

The linear response theory gives the shear relaxation modulus as the correlation function of the stress fluctuation. If the flow and shear gradient directions are x - and y -directions, respectively, the shear relaxation modulus can be expressed by the following Green-Kubo form. (Evans and Morris 2008)

$$G(t) = \frac{\nu}{k_B T} \langle \hat{\sigma}_{xy}(t) \hat{\sigma}_{xy}(0) \rangle \quad (14)$$

Here ν is the number density of the chain. We should notice that eq (14) holds only when the flow and shear gradient directions are common for all the chains, but this is not a realistic situation. (Even if the micelles are perfectly ordered, the normal directions of corona chains are not common.) The shear relaxation modulus of a macroscopic sample should be the average of the shear relaxation modulus over various directions, instead. If we take the rotational average, the Green-Kubo form becomes (Likhtman 2012)

$$G(t) = \frac{\nu}{5k_B T} \left[\langle \hat{\sigma}_{xy}(t) \hat{\sigma}_{xy}(0) \rangle + \langle \hat{\sigma}_{yz}(t) \hat{\sigma}_{yz}(0) \rangle + \langle \hat{\sigma}_{zx}(t) \hat{\sigma}_{zx}(0) \rangle \right] \\ + \frac{\nu}{30k_B T} \left[\langle \hat{N}_{xy}(t) \hat{N}_{xy}(0) \rangle + \langle \hat{N}_{yz}(t) \hat{N}_{yz}(0) \rangle + \langle \hat{N}_{zx}(t) \hat{N}_{zx}(0) \rangle \right] \quad (15)$$

with $\hat{N}_{\alpha\beta}$ being the first normal stress difference in the α and β -directions (of a single chain). As we mentioned, our model gives artificial anisotropy for the equilibrium normal stress. Thus, to remove the artifact, we calculate the normal stress differences after subtracting the anisotropic part in eq (13).

$$\hat{N}_{xy}(t) = \frac{3k_B T}{Nb^2} [R_x^2(t) - R_y^2(t)] \quad (16)$$

$$\hat{N}_{yz}(t) = \frac{3k_B T}{Nb^2} [R_y^2(t) - R_z^2(t)] + \frac{k_B T}{2} \quad (17)$$

$$\hat{N}_{zx}(t) = \frac{3k_B T}{Nb^2} [R_z^2(t) - R_x^2(t)] - \frac{k_B T}{2} \quad (18)$$

Then, eq (15) can be rewritten as follows,

$$G(t) = \frac{\nu}{5k_B T} [C_x^{(2)}(t)C_y^{(2)}(t) + C_y^{(2)}(t)C_z^{(2)}(t) + C_z^{(2)}(t)C_x^{(2)}(t)] \\ + \frac{\nu}{15k_B T} \left[C_x^{(4)}(t) + C_y^{(4)}(t) + C_z^{(4)}(t) - \frac{17}{4} \right] \quad (19)$$

where $C_\alpha^{(2)}$ and $C_\alpha^{(4)}$ are the two-time two- and four-body correlation functions.

$$C_\alpha^{(2)}(t) = \frac{3}{Nb^2} \langle R_\alpha(t) R_\alpha(0) \rangle, \quad C_\alpha^{(4)}(t) = \frac{9}{N^2 b^4} \langle R_\alpha^2(t) R_\alpha^2(0) \rangle \quad (20)$$

By calculating the correlation functions from eqs (10)-(12) and substituting them into eq (19), finally we have the following explicit expression for the shear relaxation modulus.

$$G(t) = \nu k_B T \left[\frac{2}{5} e^{-t/\tau} + \frac{3}{5} e^{-2t/\tau} + \frac{1}{5} e^{-3t/\tau} + \frac{1}{30} e^{-4t/\tau} \right] \quad (21)$$

The detailed calculations are shown in Appendix.

From eq (21), the longest viscoelastic relaxation time of the chains in the corona regions is estimated to be τ . If there is no impenetrable wall, the viscoelastic relaxation time becomes half of the end-to-end vector relaxation, $\tau/2$. Thus our model predicts that the viscoelastic relaxation is *decelerated* by the impenetrable wall, while the end-to-end vector relaxation is rather *accelerated* by the wall. (If we employ the weight-averaged relaxation time determined from the terminal region of the storage and loss moduli is 0.74τ , which is still slower than $\tau/2$.) Similar deceleration effect is also reported for diblock copolymer melts which form lamellar microphase-separated structures. (Uneyama 2009)

It should be noted here that the deceleration comes from the property of the correlation function $C_z^{(2)}(t)$. Because the chain is stretched to the z -direction, $C_z^{(2)}(t)$ is non-zero even at the limit of $t \rightarrow \infty$ (as shown in Appendix). Such a non-relaxing component makes the relaxation time the same as the relaxation time of the end-to-end vector in x - and y -directions, τ . From eq (21), we also find

that the impenetrable wall makes the viscoelastic relaxation spectrum broader. This result seems to be consistent with the theoretical analysis of the dielectric relaxation of a type-A chain grafted onto an impenetrable flat wall by Koch et al. (1997).

The results in this section are based on rather rough approximations and thus they are not *quantitative*. Some approximations are not fully justified. Strictly speaking, we should also take into account the anisotropic friction, memory effect, and the osmotic pressure field. Nonetheless we consider that our model provides insight into the essential physics of a chain in corona structures. Namely, (1) The relaxation of z component of the end-to-end vector is accelerated due to a “squeezed” potential field in the z direction (Koch et al. 1997). (2) The viscoelastic relaxation in the xy plane is decelerated due to the non-relaxed component $C_z^{(2)}(t)$ in the function (i.e., part of the memory function in the z direction never decay due to the stretching effect), leading to coupling for decay of orientational anisotropy in the xy plane and that of memory function of the x and y components of the end-to-end vector. As a result, the viscoelastic terminal relaxation time and the relaxation time of the end-to-end vector become the same, and this feature is different from the usual Rouse chain for which the former is half of the later. (Doi and Edwards 1986)

Here, we note that our model predicts the dynamical behavior which is independent of the surface graft density or the functionality. In principle, the chain dynamics can also depends on the functionality. For unentangled star polymers with high functionality, van Ruymbeke, et al. (2011) reported the existence of some slow modes (colloidal modes). One may expect that these high-functional star chains would serve as a better analogue to block copolymer micelles having spherical core and large number of corona chains. However, the enthalpic (steric) interaction between core and corona, which is not present in star polymers, leads to different damping behavior (Watanabe, et al. 2005). Anyway, the slow modes for high functional star chains are out of the scope of the present study. Meanwhile, we will show later that the slower modes corresponding to SIS micelles are well separated from the fast corona modes. We consider that the fast modes are attributable to the corona chain relaxation, and the successful separation of modes enables us to study the corona chain relaxation.

Experimental

Two SIS triblock copolymer samples, S35-I13-S36 and S48-I26-S48, which were synthesized and characterized in our previous studies (Chen, et al. 2012, Matsumiya, et al. 2012) were used as model triblock copolymer samples. Two linear polystyrene (PS) samples, lin-S10 and lin-S38 (supplied from Tosoh Co.) and one 4-arm star-shaped PS sample, star-S39 were used as reference samples. The star-shaped PS sample was kindly provided by Prof. Yo Nakamura in Kyoto University, and details of this PS sample are described in references (Okumoto, et al. 1998, Okumoto, et al. 1997). The characteristics of these samples are summarized in Table 1. The

sample code number indicates the molecular weight of the corresponding block and arm, in unit of 1000.

Table 1. Characteristics of samples

code	$10^{-3}M_S$	$10^{-3}M_I$	$10^{-3}M_S$	M_w/M_n
S48-I26-S48	47.9	26.0	47.9	1.05
S35-I13-S36	35.1	13.1	36.3	1.07
lin-S10	9.5			1.02
lin-S38	37.9			1.03
star-S39	38.8 (for arm)			1.03

The polymers were dissolved into solvents to make the solution samples for linear viscoelasticity measurements. We used diethyl phthalate (DEP; Wako Co.) as the solvent. In particular, two testing samples were prepared: one is binary mixture of S35-I13-S36 and DEP and the other is ternary mixture of S48-I26-S48, lin-S10, and DEP with a small amount of lin-S10 added to ensure the same S/I/DEP composition for the two testing samples. For comparison, two reference samples, lin-S38/DEP and star-S39/DEP, with the same S/DEP composition as the two testing samples are also prepared.

To prepare those mixtures, predetermined amount of bulk sample(s) and DEP were dissolved in benzene in a weight fraction of 10wt% and cast slowly in a half-closed chamber at room temperature for 1 week, and latter in vacuum at $40^\circ\text{C} \leq T \leq 60^\circ\text{C}$ for nearly 3-5 days. During the evaporation process in vacuum, the samples were weighted every 5-10 hours so that all benzene and a small amount of DEP were evaporated. The final samples after the evaporation of benzene in vacuum were used for the measurements. The weight fractions of the S35-I13-S36/DEP and S48-I26-S48/lin-S10/DEP samples were the same, $w_S/w_I/w_{\text{DEP}} = 46\text{wt}/9\text{wt}/45\text{wt}$ (which corresponds to the volume fractions $\phi_S/\phi_I/\phi_{\text{DEP}} = 0.47/0.10/0.43$). The weight fractions of the reference lin-S38/DEP and star-S39/DEP samples were $w_S/w_{\text{DEP}} = 51\text{wt}/49\text{wt}$ ($\phi_S/\phi_{\text{DEP}} = 0.52/0.48$), the same S/DEP composition ratio as in the two testing samples. This S concentration is chosen to ensure all the PS blocks, arms, chains to be unentangled, i.e., $M_X < 2M_{e,\text{bulk}}/\phi_S = 64\text{K}$ ($X = \text{block, arm, and chain for copolymer samples, star and linear PS, respectively.}$), with $M_{e,\text{bulk}} = 16600$ being the entanglement molecular weight of PS in bulk.(Fetters, et al. 2007) The samples were subjected to differential scanning calorimetry (DSC), small angle X-ray scattering (SAXS), LVE experiments as explained in the followings. For convenience, the two testing copolymer mixtures are denoted as

SIS/DEP and SIS/lin-S/DEP, and the two reference samples are denoted as lin-S/DEP and star-S/DEP in the later discussion. (Both SIS/DEP and SIS/lin-S/DEP has rather high polymer concentration and we simply ignore the interaction between chains near the micellar cores, as mentioned in the “Theory” section.)

The DSC measurements were conducted with DSC Q20 calorimeter (TA Instrument). The samples of ca.20mg were rapidly quenched by liquid nitrogen to -125°C (by using the quench cooling accessory of DSC Q20), and then heated to 50°C at a speed of $10^{\circ}\text{C}/\text{min}$. This process was repeated once after the first measurement, and the DSC traces obtained from the second measurement were utilized.

The SAXS measurements were conducted with RINT-2000 X-ray diffraction goniometer (Rigaku) at room temperature. The samples were charged into a cell with two thin mica plates (windows) and subjected to Cu-K α X-ray having wavelength $\lambda = 0.154 \text{ nm}$. The scattering intensity $I(q)$ was measured as a function of the scattering wavenumber $q=(4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle.

The linear viscoelastic measurements were conducted with ARES rheometer (TA Instruments) at the temperature range $5^{\circ}\text{C} \leq T \leq 55^{\circ}\text{C}$. The highest temperature $T = 55^{\circ}\text{C}$ was chosen to ensure the high selectivity and negligible evaporation of DEP.(Lodge, et al. 2002) A parallel plate fixture with a diameter of 8mm was used. The oscillatory strain amplitude was kept small ($\leq 10\%$) to ensure the linearity of the storage and loss modulus, G' and G'' , measured as functions of angular frequency ω , at each temperature T . Then the G' and G'' data were shifted horizontally and vertically, by the shift factors a_T and b_T , respectively, to obtain the master curves.

Results

Structure

Figure 1 shows the SAXS intensity $I(q)$ of the SIS/DEP and SIS/lin-S/DEP samples. The scattering data of SIS/DEP have been shifted vertically to avoid overlapping with those of SIS/lin-S/DEP. The thick arrows in Figure 1 indicate the first peak wavenumbers, q_1 . From Figure 1, we observe that about 30-40 nm scale structures are formed in these solutions, and judging from the scale, these structures are formed by micelles. The ratio of the first, second, and third peak wavenumbers become $q_1:q_2:q_3 = 1:\sqrt{2}:\sqrt{3}$ if micelles form a body-centered cubic (BCC) lattice which is widely observed in block copolymer melts and solutions. Unfortunately, the second and third peaks are not clearly observed and broad shoulders are observed instead. This result means that the ordered BCC lattice is not present in these solutions. Instead, a liquid-like (amorphous) structure would be formed, where the lattice contains lots of defects thereby becoming highly disordered.

As a rough approximation, we may assume a BCC lattice to calculate the dimensions of the micelles. (The dimensions of micelles and lattices are not strongly affected by the specific choice of the lattice, and thus we consider the estimate here is sufficient for our purpose.) From q_1 ($= 0.24\text{nm}^{-1}$ for SIS/DEP and 0.18nm^{-1} for SIS/hS/DEP), we obtain the average distance between neighboring micelles $D = 2\pi\sqrt{3/2}q_1^{-1}$, the number density of micelles $v_{\text{core}} = 3\sqrt{3}D^{-3}/4$, and number of PI blocks per micelle, $n_1 = v_{\text{chain}}/v_{\text{core}}$, with v_{chain} being the number density of SIS chain. The core size can be further calculated as $d_{\text{core}} = 2(3Qn_1m_1/4\pi\rho_1)^{1/3}$, with m_1 being the weight per I block, Q the volumetric swelling ratio ($Q = 1$ if DEP is completely selective for PS and $Q = 1.7_5$ if DEP is common solvent). (Watanabe and Matsumiya 2005) The radius of the micelle is estimated as $R_{\text{micelle}} = 0.5d_{\text{core}} + 2^{1/2}R_s$, where $R_s = (4.37 \times 10^{-3}M_s)^{1/2}$ is the unperturbed S block size (Fetters, et al. 2007) and a factor of $2^{1/2}$ account for the expansion due to the geometric constraint (or the effective repulsive potential) which is explained in the previous section. The selectivity of DEP affects the effective volume fractions of S and I blocks. Here we consider two extreme cases: a completely selective solvent for S and a common solvent for S and I.

The estimate of the dimensional parameters is summarized in Table 2. (Both the completely selective solvent and the common solvent cases are considered.) From Table 2, we find that the average distance between micelles D is about 0.5 to 0.7 times the diameter of the micelles, $2R_{\text{micelle}}$, regardless of the selectivity of DEP (whether DEP is a completely selective solvent for S or a common solvent for S and I). This result indicates that the micelles are moderately overlapped in space. We expect that such moderate overlapping of S blocks do not exhibit the entanglement effect and thus the S blocks should exhibit the Rouse type dynamics.

Figure 1. Semilogarithmic plots of SAXS intensity $I(q)$ of SIS/DEP and SIS/lin-S/DEP samples. The data for the SIS/DEP sample is shifted vertically (by the factor A) to avoid heavy overlapping with those of the SIS/lin-S/DEP sample.

Table 2. Structural characteristics of SIS/DEP and SIS/lin-S/DEP under the assumption of the BCC type lattice. The superscripts (s) and (c) represent the completely selective solvent for S and the common solvent for S and I, respectively (see the main text).

	SIS/DEP	SIS/ <i>lin</i> -S/DEP
q_1 / nm^{-1}	0.24	0.18
D / nm	32. ₁	42. ₈
$v_{\text{core}} / 10^{22} \text{m}^{-3}$	3.9 ₄	1.6 ₆
n_{I}	10 ₆	12 ₇
R_{S} / nm	12. ₅	14. ₅
$d_{\text{core}}^{(\text{s})} / \text{nm}$	16. ₈	22. ₅
$d_{\text{core}}^{(\text{c})} / \text{nm}$	20. ₃	27. ₁
$R_{\text{micelle}}^{(\text{s})} / \text{nm}$	26. ₁	31. ₇
$R_{\text{micelle}}^{(\text{c})} / \text{nm}$	27. ₈	34. ₀

Thermal behavior.

Figure 2 shows the DSC traces obtained for the SIS/DEP, SIS/lin-S/DEP, lin-S/DEP and star-S/DEP samples. The heat flow was normalized by the weight of the sample. In Figure 2, at least two glass transitions are observed for all the samples. For lin-S/DEP and star-S/DEP, the low T process corresponds to the glass transition of super-cooled DEP while the high T transition reflects the glass transition of the S segment in DEP. SIS/DEP and SIS/lin-S/DEP samples contain I blocks that also exhibit the glass transition, and thus the glass transition at low temperature may also be contributed to glass transition of I blocks. As a clue, the low temperature glass transitions of SIS/DEP and SIS/lin-S/DEP samples are clearer and sharper than ones in lin-S/DEP and star-S/DEP. The glass transition of I block in bulk is $T_{\text{g,bulk}}^{\text{PI}} = -65^\circ\text{C}$, which is close to $T_{\text{g}}^{\text{DEP}}$ (low T transition). (If DEP behave as common solvent, the glass transition temperature of I block would be closer to $T_{\text{g}}^{\text{DEP}}$.) Thus we consider that the glass transitions of DEP and I block would not be distinguishable.

Figure 2. DSC traces of SIS/DEP, SIS/*lin-S*/DEP, and *star-S*/DEP and *lin-S*/DEP reference samples during the heating. Arrows show T_g of the S block, chain, or arm estimated from the WLF analysis.

Linear Viscoelasticity (LVE).

Overview

Since the application of time-temperature superposition (tTs) to microphase separated systems is usually questionable, here we discuss the applicability of the tTs for our systems briefly. (Alig, et al. 1997) To construct the apparent master curve, we shift the data to achieve the best superposition of the data corresponding to the position a G'' peak is observed. This superposition leads to failure of tTs at both higher and lower frequency, where the physical origins of the moduli are different. This failure can be clearly seen in $\tan\delta$ plotted against ω , as shown in Figure 3.

In general, the origins of the viscoelasticity are not single, and combination of several different dynamical (relaxational) modes contributes. If all of these modes have the same temperature dependence, tTs should work for whole the temperate and frequency ranges. Even if there are several relaxational modes which have different physical origins, tTs works in a limited frequency range when a single dynamical mode is dominant. This is the case of our experimental systems, and a good superposition can be achieved near the G'' peak where the relaxation of corona chains is the dominant dynamical mode. The tTs fails moderately at a transition region where different modes contribute comparably to the moduli, which is the case at high and low ω regions in the master curves. Thus, we should stress that the apparent master curves constructed here are meaningful only for the relaxation behavior of corona chains, and the high and low ω regions have no physical meaning.

Figure 3: Test of time temperature superposition for $\tan \delta$, $G'(\omega)$, and $G''(\omega)$ of SIS/DEP, SIS/lin-S/DEP in a temperature range of $T = 5$ to 55°C . $\tan \delta$ are shifted by a horizontal factor a_T to achieve the best superposition in a logarithmic frequency range of 0 to 2, where the relaxation of corona is expected. G' and G'' are multiplied by a factor of T_r/T and shifted horizontally by the same factor a_T .

Figure 4 shows master curves of $G'(\omega)$ and $G''(\omega)$ for the SIS/DEP, SIS/lin-S/DEP, and lin-S/DEP and star-S/DEP samples reduced at reference $T_r = 45^\circ\text{C}$. To construct the master curves, $G'(\omega)$ and $G''(\omega)$ of these samples were multiplied by the vertical shift factor $b_T = T_r/T$, and then the horizontal shift factor a_T was determined to achieve the best superposition. (Strictly speaking, the vertical shift factor should be expressed as $b_T = \rho(T_r)T_r/\rho(T)T$, where $\rho(T)$ represents the density at

the temperature T . However, the change of the density at the experimental range is sufficiently small and we simply ignore the density factor.)

The solid curves for reference samples in Figure 4 are fits to the experimental data to the Rouse-Ham model. (Ham 1957, Rouse 1953)

$$G'(\omega) + iG''(\omega) = \frac{\rho\phi_s RT}{M} \left[(f-1) \sum_{p \text{ odd}} \frac{i\omega\tau_R / p^2}{1 + i\omega\tau_R / p^2} + \sum_{p \text{ even}} \frac{i\omega\tau_R / p^2}{1 + i\omega\tau_R / p^2} \right] \quad (22)$$

where M is the molecular weight of chain, f is the functionality ($f = 2$ and 4 for lin-S and star-S, respectively), R is the gas constant, and τ_R is the Rouse time. In eq (22), only the Rouse time τ_R is the fitting parameter. We set $\tau_R = 1.2 \times 10^{-3}$ and 6.0×10^{-3} s for lin-S/DEP and star-S/DEP, respectively, to fit the experimental data. The ratio of 5.0 for τ_R of these two times is very close to the theoretically expected value, $(2M_{\text{arm}}^{\text{star}} / M^{\text{linear}})^2 = 4.2$, from molecular weights of these two samples. The agreement between the experimental result and the prediction of the Rouse model supports that these chains are not entangled. The dashed curves represent the estimate of the contribution of the lin-S in the SIS/lin-S/DEP sample from viscoelastic modulus of lin-S/DEP. The contribution of the lin-S is much lower than the experimental data and thus we consider its contribution to LVE is negligible. This means that the LVE data of SIS/lin-S/DEP shown in Figure 4 can be practically regarded as ones of the SIS samples.

The LVE of the copolymer samples show at least two relaxation processes. The high- ω relaxation is similar in amplitude to ones of the reference samples, but the relaxation time is considerably slower than reference samples. The low- ω plateau can be attributed to the elasticity of the lattice formed by micelles. In a very long time scale (very low frequency region) the lattice can completely rearrange and very slow relaxation behavior might be observed, while it is not observable in the experimental time scale.

Figure 4: Master curves of **(a)** $G'(\omega)$ and **(b)** $G''(\omega)$ of SIS/DEP, SIS/lin-S/DEP, lin-S/DEP, and star-S/DEP with the reference temperature $T_r = 45^\circ\text{C}$. The thick solid curves represent the fitting to the Rouse-Ham model. The dashed lines represent the estimates of the contribution of the lin-S10 chain in the SIS/lin-S/DEP sample.

The shift factors a_T are plotted against $T - T_r$ in Figure 5(a). The solid curve represents Williams–Landel–Ferry (WLF) curve (Williams et al. 1955) expected for PS bulk with reference $T_{r,\text{bulk}} = 174^\circ\text{C}$. (Watanabe, et al. 1985) The plots of reference S/DEP samples with $T_r = 45^\circ\text{C}$ agree with the WLF curve, meaning that the DEP shows the simple plasticization effect and reduced the Vogel temperature by $T_{r,\text{bulk}} - T_r = 129^\circ\text{C}$. From this difference, we can estimate the effective glass transition temperature of S in reference S/DEP samples as $T_g = T_{g,\text{bulk}} - T_{r,\text{bulk}} + T_r = -29^\circ\text{C}$, with $T_{g,\text{bulk}} = 100^\circ\text{C}$ being the glass transition temperature of PS in bulk. The glass transition temperatures obtained in this way for the reference samples are shown by arrows in Figure 2.

The shift factors of the SIS triblock copolymers show slightly stronger temperature dependence than that of the reference samples. There are several possible mechanisms causing such a difference. For example, the slow relaxation (plateau) of the low frequency region may affect the relaxation mode distribution of the high frequency region. One plausible mechanism is that the DEP is not completely selective solvent for S block and thus the effective concentration of S block in DEP of SIS triblock samples is lower than one of reference samples. If this is true, the difference can be absorbed into the Vogel temperature. Actually, we found that to choose a new iso-frictional reference temperature of $T_{\text{iso}} = 50^\circ\text{C}$ for the copolymer samples enables a good superposition. The shift factors thus obtained are shown in Figure 5(b). This result means that DEP is not completely selective and the slight loss of DEP in the S-rich region increases the glass transition temperature by 5°C . We should notice that this difference in the glass transition temperature is not large, and is negligible in the structural analysis. (5°C is small compared with the 129°C difference between the glass transition temperatures of PS in DEP and that in bulk due to a strong plasticizing effect as mentioned earlier.)

The effective T_g of S in corona is thus estimated to be $T_g = T_{g,\text{bulk}} - T_{r,\text{bulk}} + T_{\text{iso}} = -24^\circ\text{C}$. We show this estimate by arrows in Figure 2. The estimated effective T_g is located around the high T glass transition process, confirming our previous assignment of the glass transition of the S blocks plasticized by DEP.

One may worry that the DEP concentration in the S corona (or I core) changes with the temperature and shift factor does not obey the WLF type T dependence. Nevertheless, we found that the WLF type T dependence holds at least apparently, and thus our analysis can be utilized without serious problems. The good selectivity of DEP for S in SI copolymer have been reported earlier by Lodge and coworkers (2002): The DEP solution of SI diblock copolymer ($M_S=11\times 10^3$ and $M_I=32\times 10^3$) exhibits the order-disorder transition (ODT) at $T_{\text{ODT}} \approx 150^\circ\text{C}$ for $\phi_S/\phi_{\text{DEP}} \approx 1$. Thus we consider that for current SIS, the effect of the selectivity of DEP is negligibly small at the testing temperature $T \leq 55^\circ\text{C}$.

Figure 5: **(a)** Shift factors for master curves of $G'(\omega)$ and $G''(\omega)$ of SIS/DEP, SIS/*lin*-S/DEP, *lin*-S/DEP, and *star*-S/DEP with the reference temperature $T_r = 45^\circ\text{C}$. The solid curve represents the WLF equation of bulk PS with the reference temperature $T_r = 174^\circ\text{C}$. **(b)** The same shift factor data to (a) with new reference temperature (the iso-frictional temperature) T_{iso} . The reference temperature is set to $T_{iso} = 50^\circ\text{C}$ for SIS/DEP, SIS/*lin*-S/DEP, $T_{iso} = 45^\circ\text{C}$ for the reference samples (*lin*-S/DEP and *star*-S/DEP). The solid curve represents the WLF equation for bulk PS ($T_r = 174^\circ\text{C}$.)

Relaxation of corona blocks

The WLF analysis above suggests that the iso-frictional temperature S block of the SIS triblock samples is different from one of the reference samples. Thus we should compare the LVE data of the SIS triblock samples at $T_{\text{iso}} = 50^\circ\text{C}$ with the data of the reference samples at $T_{\text{iso}} = 45^\circ\text{C}$. In Figures 6 and 7, we show master curves of SIS/DEP, SIS/*lin*-S/DEP, and reference samples normalized by the characteristic modulus $\nu_X k_B T$ at T_{iso} (50°C for SIS/DEP and SIS/*lin*-S/DEP, and $T_{\text{iso}} = 45^\circ\text{C}$ for references). Here, ν_X means the number density of X, with $X = \text{S block, chain, and arm for copolymer, linear, and star PS, respectively}$. The time scale should be also normalized to correct the difference of molecular weights among the S blocks and the S arms/chains of the reference samples: The master curves of the reference *lin*-S/DEP and star-S/DEP are shifted horizontally by $\Delta_M = (2M_{\text{chain}}/M_{\text{block}})^2$ and $\Delta_M = (M_{\text{arm}}/M_{\text{block}})^2$, respectively. The factor of Δ_M is chosen based on the Rouse model, which may not fully account chain tethered at the impenetrable interface. As far as the authors know, there is no simple alternative choice, and we believe that this Δ_M factor is not unreasonable. The open symbols in Figures 6 and 7 represent thus obtained normalized master curves.

Figure 6: Master curves of **(a)** $G'(\omega)$ and **(b)** $G''(\omega)$ of the SIS/DEP, lin-S/DEP, and star-S/DEP at the iso-frictional temperature, normalized by the characteristic modulus $\nu_X kT$ and the correction factor Δ_M for the molecular weight differences. The filled sphere symbols is the data of star-S/DEP further shifted horizontally to be compared with data of SIS/DEP, the filled square symbols are obtained via subtracting a plateau modulus (the solid line in (a)) from G' of SIS/DEP.

After this normalization, we find that the terminal relaxation behavior of the two reference samples almost coincides. On the other hand, the relaxation of SIS triblock samples is clearly different from one of the reference samples. The relaxation of the S block is considerably *decelerated*, compared with the reference data. To quantify the difference, we further shifted the master curve of star-S/DEP horizontally so that the loss moduli of S block (corona) and S arm coincides. The filled symbols in Figures 6 and 7 represent the shifted reference data, with the extra horizontal shift factor $\Delta_{\text{ex}} = 0.3$. This shift factor characterizes the deceleration of the corona S block to the reference S chain/arm. The factor 0.3 is *slightly smaller* than a factor of 0.5 expected from our theoretical analysis, meaning the deceleration effect is stronger than the theoretical prediction. A similar deceleration of unentangled S block in the lamellar microphase separated diblock copolymers was recently reported by Takahashi and coworkers. (Fang, et al. 2013) They reported that the S block in the lamellar is decelerated by about 1 decade compared with linear S chains. This deceleration effect is stronger than ours but qualitatively similar to our result.

The final comment is on the plateau modulus, one may worry that the slower micelle modes would affect the faster relaxation mode of the corona chains. We examine this by subtracting the plateau modulus from the G' data in Figures 6 and 7. We subtract the plateau modulus G_N (shown in solid lines in Figures 6 and 7) from the SIS/DEP (Figure 6) and SIS/lin-S/DEP (Figure 7), and show $G' - G_N$. We find that for $\omega < 10^3$ rad/s, the $G' - G_N$ data are moderately different from the data before the subtraction. However, the differences are not so large and the shapes of the $G' - G_N$ data are quite similar to ones of the G' data before the subtraction. Thus we consider that the corona relaxation may be affected by the slower relaxation mode, but this does not lead us to misestimate the relaxation time for corona chains.

The plateau modulus contains some information on the spatially ordered structure of micelles. For example, the Zwanzig-Mountain theory (Zwanzig and Mountain 1965) relates the plateau modulus and the radial distribution function. Another interesting work is by Sebastian et al (Sebastian et al 2002), which relates the plateau modulus and the distance from the ODT temperature T_{ODT} . Sebastian et. al. reported that $G_N(2\pi/q_1)^3/kT$ decreases when T approaches to T_{ODT} . Here, q_1 is the first peak wavenumber in the SAXS, and $(2\pi/q_1)^3$ corresponds to the volume per one micelle. Thus $G_N(2\pi/q_1)^3/kT$ can be interpreted as the number of units which exerts the stress, and the value of $G_N(2\pi/q_1)^3/kT$ decreases as the temperature approaches to the ODT temperature. In current study that $G_N(2\pi/q_1)^3/kT = 27$ for SIS/DEP and 47 for SIIS/hS/DEP. This result is in good agreement with BCC lattice at $T/T_{\text{ODT}} < 0.8$. This result in turn suggests that T_{ODP}

> 100°C, in accordance with a discussion in Figure 5.

Figure 7: Master curves of **(a)** $G'(\omega)$ and **(b)** $G''(\omega)$ of the SIS/lin-S/DEP, lin-S/DEP, and star-S/DEP normalized by the characteristic modulus $\nu_X kT$ and the correction factor Δ_M for the molecular weight differences. The filled sphere symbols is the data of star-S/DEP further shifted horizontally to be compared with data of SIS/lin-S/DEP, the filled triangle symbols are obtained via subtracting a plateau modulus (the solid line in (a)) from G' of SIS/lin-S/DEP.

Although the relaxation times of S blocks cannot be clearly determined from the storage and loss moduli data, we may regard the viscoelastic relaxation time $\tau = [G'(\omega) / \omega G''(\omega)]_{\omega \rightarrow 0}$ of the shifted star-S/DEP in Figures 6 and 7 (filled sphere) as the terminal relaxation time of the S blocks of

SIS/DEP and SIS/lin-S/DEP samples, respectively. Figure 8 compares thus estimated terminal relaxation times of S blocks with those of reference samples, at the iso-frictional temperature T_{iso} . For comparison, we also show the terminal relaxation times of bulk S chain at $T_{\text{r,bulk}} = 174^\circ\text{C}$ (Chen, et al. 2010). To compare the terminal relaxation times, τ data are plotted against $2M_{\text{block}}$, $2M_{\text{arm}}$ (for star-S/DEP), or M (for lin-S/DEP and bulk). For bulk PS (plus symbols in Figure 8), the terminal relaxation time scales as $\tau \propto M^2$ for $M < M_c \approx 2M_{\text{e,bulk}} = 33200$ (see solid line), and scales as $\tau \propto M^{3.4}$ for $M > M_c$ where PS chains are entangled.(Fetters, et al. 1999). The τ data for two reference samples, lin-S/DEP and star-S/DEP, are on the extrapolated line (see dashed line) of unentangled PS bulk data, while the two reference samples, SIS/DEP and SIS/lin-S/DEP deviates from the extrapolated line. Thus we confirm that, the S blocks exhibit slower relaxation than unentangled PS.

Figure 8: Terminal relaxation time data of the S block, chain, and arm, at the iso-frictional temperature. To compare data for the different molecular architectures, the data for SIS/DEP and SIS/lin-S/DEP samples are plotted against $2M_{\text{block}}$, and the data for star-S/DEP reference are plotted against $2M_{\text{arm}}$. Data for linear samples (lin-S/DEP reference and bulk PS) are plotted against M .

Discussion

Although the deceleration effect for S blocks in the micellar coronas is observed in our experimental data, the detailed analysis in Figures 6 to 8 raises a question: why the deceleration effect is slightly stronger than the theoretical prediction? One possible explanation is that our theoretical model is too rough to capture such a factor *quantitatively*. However, there are other possible origins that cause the strong deceleration effect. In this section, we discuss possible mechanisms that cause the strong deceleration effect.

We firstly consider the effect of structures and ordering of micelles. In SIS/DEP and SIS/lin-S/DEP samples, I blocks form micellar cores and S blocks form micellar coronas, both of which are in the liquid state. Thus a micelle in these samples can be regarded as a soft and deformable particle. The micelles repel each other and thus form a higher order structure such as an amorphous-like or lattice structure. In both cases, the higher order structure formed by micelles exhibits the elasticity at the long time scale and thus we observe the plateau in the storage modulus. In the short time scale, the deformation and local rearrangement of micelles would occur. Such relaxation dynamics would decrease the plateau modulus when the frequency is decreased. This scenario seems to be consistent with our experimental data. The deformation and local rearrangement of micelles would also affect the relaxation of S blocks in corona regions. We expect that some cooperative behavior for the dynamics of S blocks, and this cooperative effect would decelerate the relaxation of S blocks.

Secondly we consider the effect of the interaction between segments (the osmotic pressure). In the mean-field approximation, segments feel the effective potential field which originates from the enthalpic interaction between segments. In spatially inhomogeneous polymer melts or solutions, polymer chains feeling the osmotic pressure field which would try to keep the total segmental density spatially homogeneous. We ignored the effect of the osmotic pressure field in the model in “Theory” section. Naively, the effect of the osmotic pressure field can be taken into account by introducing the mean field effective potential. It can be achieved by adding an extra potential to eq (6). This modification changes the expansion coefficient in eq (9) and thus the effective relaxation time in the direction normal to the wall is modulated. However, even if the relaxation time of the end-to-end vector in the normal direction is accelerated, the viscoelastic longest relaxation time is not modulated in our model. We expect that the osmotic pressure field may not largely affect the deceleration, although this point needs more concrete proof.

Thirdly we consider the effect of the inhomogeneous frictional field. In S corona region, segment density is not homogeneous. (Hamley 2005) Although we consider the interaction between chains near the micellar cores is *statically* not so important, the effect of the inhomogeneous density distribution to the *dynamics* cannot be simply ignored. We expect that the plasticization effect is spatially not homogeneous. Even if this plasticization effect is not large, there can be inhomogeneous frictional field. One end of a corona chain is graft onto a wall, and we expect that the graft point behave in a similar way to the junction point of star chains. The segments in a star arm feel larger friction near the junction point, and thus we consider a corona chain segment feel larger friction near the core-corona interface. Moreover, the dynamics of S blocks can be affected by the deformation and rearrangement of micelles and thus the environment for S blocks is spatially and temporally fluctuating. These arguments imply that the frictional environment for S block is rather heterogeneous. Such heterogeneity would broaden the relaxation mode distribution, and some S blocks would be decelerated whereas some S blocks would be accelerated. Although it is difficult to observe clear broadening in our experimental data, the loss moduli data of S blocks

seem to be slightly broader than one of the linear or star S chains, and we consider this scenario is plausible.

From these discussions, we conclude that the deceleration of the S block dynamics can be caused by several different mechanisms. We consider that the geometrical constraint by the impenetrable wall is primarily important mechanism, and the deformation and rearrangement of micelles, as well as the spatial heterogeneity of friction, may also enhance the deceleration. Unfortunately, it is difficult to quantify these contributions from our current theoretical model and experimental data. Further developments in the theoretical analysis as well as carefully designed experiments will be required.

Concluding Remarks

We studied the difference between the unentangled corona chains in micelles and star arms from the linear viscoelasticity data. By modelling a corona chain as the ideal Gaussian chain grafted onto an impenetrable wall, we showed that a corona chain feels the effective repulsive potential from the wall. As a result, the end-to-end vector relaxation of the corona chain in the direction normal to the wall is *accelerated* whereas the viscoelastic relaxation of a corona chain is *decelerated*, compared with a star arm.

To test the theoretical prediction, we performed linear viscoelasticity measurements for model systems (SIS triblock copolymer solutions and reference linear and star PS solutions). We analyzed the experimental data and showed that unentangled coronas exhibit *longer relaxation times* compared with star arms having the same M . The observed deceleration effect was *stronger* than the theoretical prediction. We discussed the possible origins of the stronger deceleration: deformation and rearrangement of micelles, and heterogeneous frictional environment were considered as candidate mechanisms. This work reveals two important mechanisms due to impenetrable interface, (1) the effective potential field in the normal direction (Koch et al. 1997) which “squeeze” the corona chain and accelerates the end-to-end fluctuation, and (2) a part of the orientational memory in the normal direction can never decay due to the stretching effect, and this leads the deceleration of the viscoelastic relaxation of the corona chain.

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Appendix

In this appendix, we show the detailed calculation of the correlation functions and the shear relaxation modulus for the model in “Theory” Section. We first consider the two and four body correlation functions defined by eq (20). Eqs (10) and (11) describe the Ornstein-Uhlenbeck processes and can be formally integrated as

$$R_\alpha(t) = e^{-t/\tau} R_\alpha(0) + \int_0^t dt' e^{-(t-t')/\tau} \xi_\alpha(t') \quad (\alpha = x, y) \quad (A1)$$

$$Q_z(t) = e^{-2t/\tau} Q_z(0) + \int_0^t dt' e^{-2(t-t')/\tau} \xi_z(t') \quad (A2)$$

where we have defined $Q_z(t) = R_z(t) - \sqrt{Nb^2/3}$. The two body correlation functions for $R_x(t)$, $R_y(t)$, and $Q_z(t)$ can be calculated straightforwardly.

$$\langle R_\alpha(t) R_\alpha(0) \rangle = \langle R_\alpha^2 \rangle e^{-t/\tau} = \frac{Nb^2}{3} e^{-t/\tau} \quad (\alpha = x, y) \quad (A3)$$

$$\langle Q_z(t) Q_z(0) \rangle = \langle Q_z^2 \rangle e^{-2t/\tau} = \frac{Nb^2}{6} e^{-2t/\tau} \quad (A4)$$

The two body correlation functions in eq (20) become

$$C_\alpha^{(2)}(t) = e^{-t/\tau} \quad (\alpha = x, y) \quad (A5)$$

$$C_z^{(2)}(t) = \frac{3}{Nb^2} \left[\langle Q_z(t) Q_z(0) \rangle + \frac{Nb^2}{3} \right] = 1 + \frac{1}{2} e^{-2t/\tau} \quad (A6)$$

Because $R_x(t)$, $R_y(t)$, and $Q_z(t)$ are the Gaussian processes, the higher order correlation functions can be calculated straightforwardly. Here we note that eq (A6) contains a non-relaxing component ($C_z^{(2)} \rightarrow 1$ at the limit of $t \rightarrow \infty$). The four body correlations can be factorized into the two body correlations. (van Kampen 2007) Thus we have

$$C_\alpha^{(4)}(t) = \frac{9}{N^2 b^4} \left[\langle R_\alpha^2 \rangle^2 + 2 \langle R_\alpha(t) R_\alpha(0) \rangle^2 \right] = 1 + 2e^{-2t/\tau} \quad (\alpha = x, y) \quad (A7)$$

$$\begin{aligned} C_z^{(4)}(t) &= \frac{9}{N^2 b^4} \left\langle (Q_z(t) + \sqrt{Nb^2/3})^2 (Q_z(0) + \sqrt{Nb^2/3})^2 \right\rangle \\ &= \frac{9}{N^2 b^4} \left[\langle Q_z^2 \rangle^2 + 2 \langle Q_z(t) Q_z(0) \rangle^2 + \frac{4Nb^2}{3} \langle Q_z(t) Q_z(0) \rangle + \frac{2Nb^2}{3} \langle Q_z^2 \rangle + \frac{N^2 b^4}{9} \right] \\ &= \frac{9}{4} + 2e^{-2t/\tau} + \frac{1}{4} e^{-4t/\tau} \end{aligned} \quad (A8)$$

By substituting eqs (A5)-(A8) into eq (19), we finally have

$$\begin{aligned}
G(t) &= \frac{1}{5} \nu k_B T \left[e^{-2t/\tau} + 2e^{-t/\tau} \left(1 + \frac{1}{2} e^{-2t/\tau} \right) \right] + \frac{1}{15} \nu k_B T \left[6e^{-2t/\tau} + \frac{1}{4} e^{-4t/\tau} \right] \\
&= \nu k_B T \left[\frac{2}{5} e^{-t/\tau} + \frac{3}{5} e^{-2t/\tau} + \frac{1}{5} e^{-3t/\tau} + \frac{1}{60} e^{-4t/\tau} \right]
\end{aligned} \tag{A8}$$

This gives eq (21).

The shear relaxation modulus calculated in the main text (and in this appendix) is for a non-interacting chain. In reality, the chains interact each other and a chain feels the osmotic pressure field. As we discussed in the main text, this modulates the effective potential for the chain end (eq (6)). We briefly consider how this affects the shear relaxation modulus. By the addition of the extra term, the position of the minimum of the effective potential and the expansion coefficient are changed. Then we may have the following harmonic approximation form instead of eq (9).

$$U_{\text{eff}}(\mathbf{r}) \approx \frac{3k_B T}{2Nb^2} [R_x^2 + R_y^2 + c(R_z - \bar{R}_{\text{mp}})^2] + (\text{const}) \tag{A9}$$

Here c is a positive constant and $\bar{R}_{\text{mp}}$ is the most probable bond length. The use of eq (A9) changes the relaxation time in the z -direction (from 2τ to $c\tau$) as well as the average end-to-end vector size in the z -direction (from $\sqrt{Nb^2/3}$ to $\bar{R}_{\text{mp}}$). These changes, however, do not affect the longest relaxation time of the shear relaxation modulus because the longest relaxation time arises from the coupling between the relaxation of the x - or y -direction and the time-independent component in the z -direction. (The weight average relaxation time can be affected, although we expect that the effect will not be large.)

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