Supporting Information

Viscoelastic Properties of Tightly Entangled Semiflexible Polymer Solutions

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S1. Determination of molar mass of CTC

The absolute molar mass of CTC was estimated using a GPC system composed of a pump (Viscotek VE 1122, Malvern Panalytical), two polystyrene gel columns [TSKgel GMHHR-M × 2, Tosoh Bioscience (exclusion limit molar mass = 4×10^5 g mol^{-1}; bead size = 5 μm; column size =300 mm; Inner diameter= 7.8 mm); flow rate = 0.7 mL min^{-1}], and a multidetector of refractive index (RI), with laser light scattering (λ = 670 nm, scattering angles = 90° and 7°), and a differential pressure viscometer (Viscotek TDA 305, Malvern Panalytical). The elution solvent was tetrahydrofuran. Monodisperse linear polystyrene (M_w = 105k g mol^{-1}) with a known dn/dc (= 0.185) value purchased from Malvern Panalytical was utilized for calibration of the GPC equipment. The dn/dc value of CTC was determined as 0.1715 via analysis of the RI signal. The data were analyzed using the OmniSec software program (Malvern Panalytical).

S2. Shift factor of time–temperature superposition principle for CTC solution in TCP

Figure S1 shows the temperature dependence of shift factors, a_T, for CTC110k with c= 0.01 and 0.23 gcm^{-3} and neat TCP. The reference temperature is –10ºC. The shift factor for the dilute solution with c = 0.01 gcm^{-3} is very close to that of neat TCP, while that for the solution with c = 0.23 gcm^{-3} shows a stronger temperature dependence, reflecting the increase in the glass transition temperature of the solution.
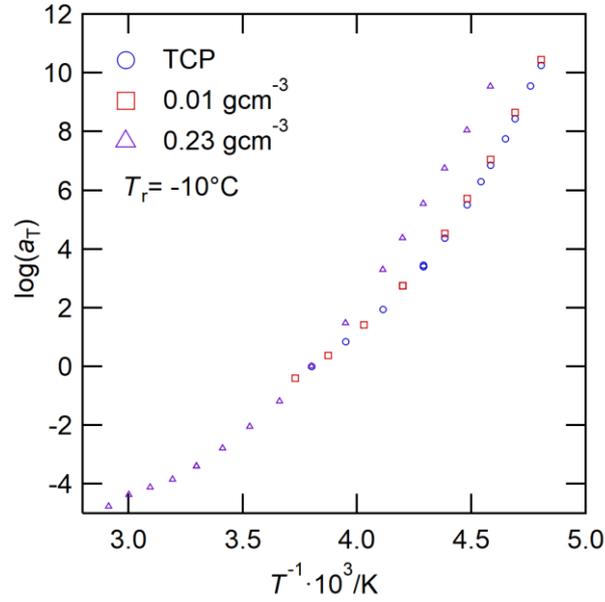
Figure S1 Temperature-dependent shift factor, a_T, for CTC110k with $c = 0.01$ and 0.23 gcm^{-3} and for neat TCP. Reference temperature, T_r, is -10ºC.

S3. Estimation of the tension mode from the complex modulus

Figure S2 shows $G'-G'_{link}$ and $G''-G''_{link}$ of the CTC/TCP solution with $c = 0.01$gcm^{-3}. Here, G'_{link} and G''_{link} were calculated as K'_{link}/C and K''_{link}/C, respectively. In the frequency regions of $\log(\omega a_T/s^{-1}) < 6$, $G'-G'_{link}$ was regarded as G'_{ten} and showed power law behavior with an exponent of 3/4. Therefore, G'_{tens} was approximated with a power-law-type function, given in Eq. (S-1).

$$G'(\omega) = G_0 \sum_{i=1}^{N(\infty)} \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad , G''(\omega) = G_0 \sum_{i=1}^{N(\infty)} \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \qquad \text{S-1}$$

$$\tau_i = \frac{\tau_0}{i^a} \qquad \text{S-2}$$

Here, G_0, τ, and a are the fitting parameters. We set $G_0 = 1100$ Pa $\sim cRT/M_s$, $\tau_0 / s = \tau_{tens} / s = 2.5 \times 10^{-3}$, and $a = 4/3$. The result is presented in Figure S2 as the green solid line.

The theoretical storage modulus of the tension mode, $G'_{\text{Morse,Lp}}$, given by the Morse theory[1] was calculated and is indicated by the red broken line in Figure S2. For calculation, we used the following equation, which is valid for $L \gg L_P$ and $t \gg \tau_p$ (the relaxation time of undulation mode for the contour wavelength approaching L_p).

$$G^*_{tens}(\omega) \cong \frac{2^{3/4}}{15} \frac{\rho k_B T}{L_p} \left(i\omega \frac{\zeta_\perp L_p^3}{k_B T} \right)^{3/4}$$

S-3

Here, ρ and d respectively represent the concentration of the contour length ($\rho = vL$; v: number density of the polymer) and the steric diameter of the chain. $\zeta_\perp$ is the effective friction coefficient for the rigid transverse motion of a rod.[1] Following Morse et al, we ignored the effects of long range hydrodynamic interactions and therefore.[2]

$$\zeta_\perp \cong 4\pi\eta_s$$

S-4

The parameters used for this calculation are summarized in Table S1. The value of η_s was determined using the viscoelastic data for TCP; $\eta_s = G''(\omega)/\omega$ ($\omega \to 0$). The theoretical prediction is qualitatively consistent with the experimental result ($G'_{\text{tens}} \propto \omega^{3/4}$), but it gives an approximately three times lower modulus or $3^{3/4}$ times faster relaxation. To determine the origin of this disagreement, we calculated $\tau_{rod}(\lambda^{-1})$,[1, 2] which corresponds to the shortest Rouse relaxation time. We found that the calculated theoretical value of $\tau_{rod}(\lambda^{-1}) \sim 1\text{x}10^{-4}$ s was lower than the experimental value (see Figure 2 and also Figure S4). Therefore, we tentatively attributed the disagreement to the smaller estimated value of $\zeta_\perp$. In a glass-forming solvent, there exists some cooperativity between the polymer and solvent dynamics; this means that the effective viscosity of the solvent around the polymer would be enhanced. This aspect should be examined in future studies on different polymer–solvent combinations.
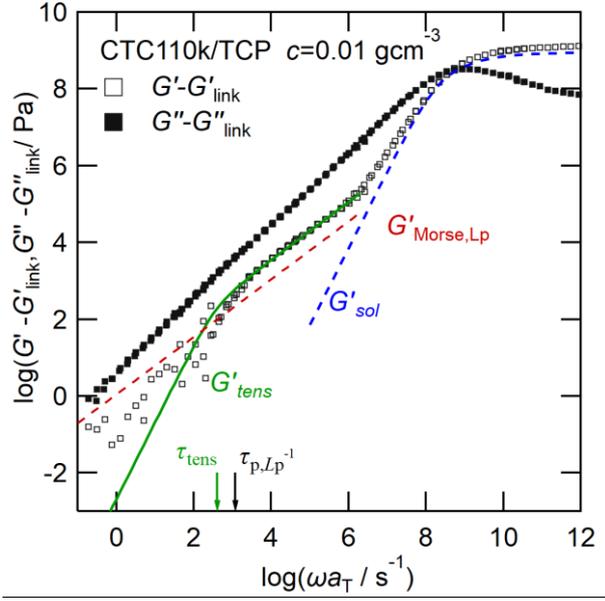
Figure S2. G'–G'_{link} and G''–G''_{link} of CTC/TCP solution with $c = 0.01$ gcm^{-3}. Green solid line represents the fitting result obtained using Eq.(S-4) and red broken line represents the fitting result obtained using Eq.(S-3). Characteristic relaxation times are also presented. τ_{tens} is the fitting parameter.

Table S1. Parameters for calculating $G'_{Morse,Ls}$, $G'_{Morse,Lp}$, and $\tau_{p,Lp}$.

L_p/nm	L_s/nm	ρ /nm^2	d/nm	η_s/Pas	T/K
5.75	14.4	6.02×10^3	1.0	1.7	263

S4. Determination of the viscoelastic segment size, M_s

$G^*_{link}(\omega)$ represents the reorientation process of the viscoelastic segments and it can be described using the Rouse–Zimm model. Thus, the limiting modulus of $G^*_{link}(\omega)$ can be related to the viscoelastic segment (the Rouse segment).

$$M_s = \frac{cRT}{G'_{link}(\infty)} \qquad \text{S-6}$$

Here, c, R, and T represent the concentration, gas constant, and temperature, respectively. According to Eq. (10), G'_{link} is equal to $K'_{link}C^{-1}$. Therefore, Eq. S-6 can be rewritten as follows.

$$M_s = \frac{cRT}{C^{-1}K'_{link}(\infty)} \qquad \text{S-7}$$

This method has been used for various polymers, and the relationship between the viscoelastic segment and Kuhn segment is discussed elsewhere.[3-6]

S5. Estimation of G^*_{tens} and G^*_{bend} for tightly entangled system

Figure S3 shows $G'–G'_{link}$ of the CTC/TCP solution with c = 0.23 gcm^{-3} and the estimated values of G'_{bend} and G'_{tens}. We first calculated G'_{tens} using Eqs.(S-1) and (S-2). Here, τ_0 for the tension mode is estimated from $G'_{tens}(1/\tau_{tens}) = cRT/M_s$. The resultant modulus, $G'–G'_{link} –G'_{tens}$ is regarded as G'_{bend} and fitted to Eqs.(S-1) and (S-2). The obtained fitting parameters are summarized in Table 2.
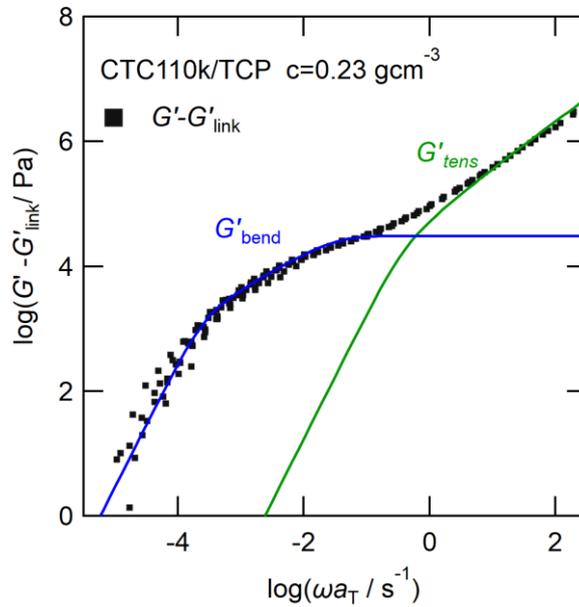
Figure S3. $G'-G'_{link}$ of CTC/TCP solution with c = 0.23 gcm^{-3}. Blue and green solid lines represent the fitting results of G'_{bend} and G'_{tens}, respectively.

Table S2. Fitting parameters for G'_{tens} and G'_{bend}

	G_0/Pa	τ_0/s	a
G'_{tens}	28000	1.95	1.33
G'_{bend}	2800	3200	2

S6. Complex modulus and strain-optical coefficient for short CTC in TCP

Figure S4 displays the real and imaginary components of G^* and K^* for a 0.015 gcm^{-3} solution of CTC25k in TCP. The Kuhn segment number for this sample is 2.2. The results are similar to the 0.01 gcm^{-3} solution of CTC110k, except for the narrower relaxation mode distribution for K^* at lower frequencies, $\log(\omega a_T/s^{-1}) < 6$, where K' is negative. A negative K' can be attributed to the orientation mode of CTC and is rather close to a rod-like single Maxwellian relaxation. This result indicates that the contribution of bending and tension modes to birefringence is negligibly small, supporting our assumption $C_{bend} \sim C_{tens} \sim 0$ in this study.
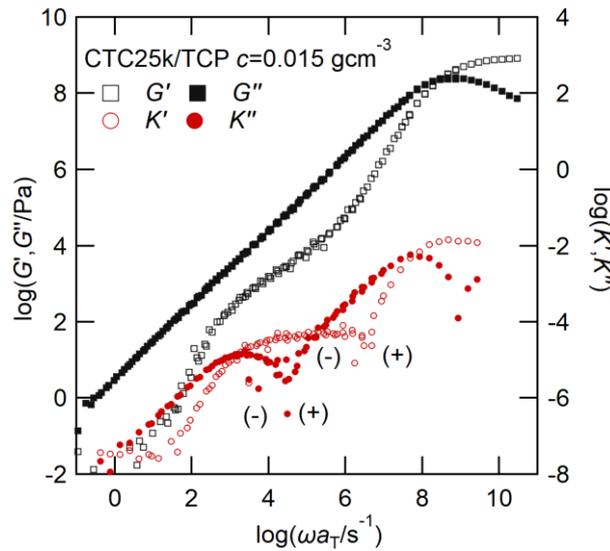
Figure S4. Real and imaginary components of G^* and K^* for a 0.01 gcm^{-3} solution of CTC25k in TCP. Reference temperature is −10°C.

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