

Electronic Supplementary Information (ESI)

Effect of Polymer-Nanoparticle Interactions on the Viscosity of Unentangled Polymers under Extreme Nanoconfinement during Capillary Rise Infiltration

Jyo Lyn Hor[†], Haonan Wang[‡], Zahra Fakhraai^{‡,*}, Daeyeon Lee^{†,*}

[†] Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

[‡] Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

*Corresponding author: Zahra Fakhraai (fakhraai@sas.upenn.edu); Daeyeon Lee (daeyeon@seas.upenn.edu)

Amplitude (ψ) and phase (Δ) data and model fit from *in situ* spectroscopic ellipsometry

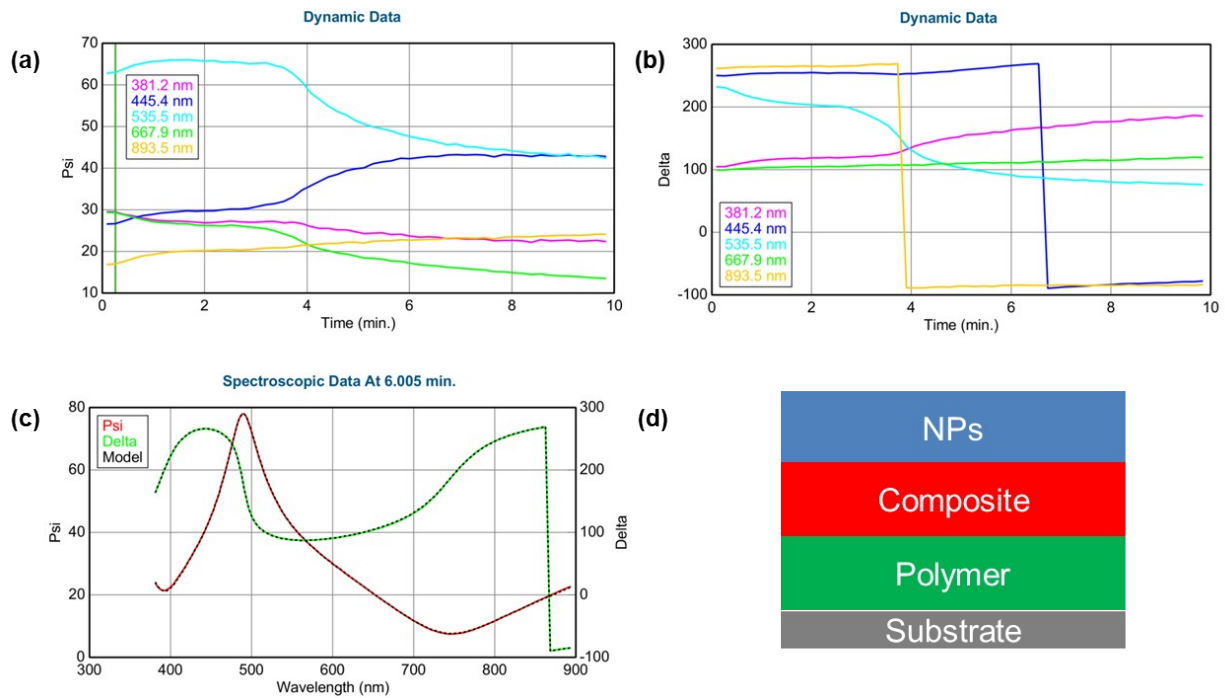


Figure S1. (a) Ψ and (b) Δ as a function of annealing time for P2VP-8k/ SiO₂ NP bilayer film annealed at 403 K. (c) A time slice ($t = 6.005$ min) of a ψ and δ data as a function of wavelength, where the dashed line indicates the (d) 3-layer Cauchy model fit to the data.

Thickness changes of NP, composite, and polymer layers during CaRI

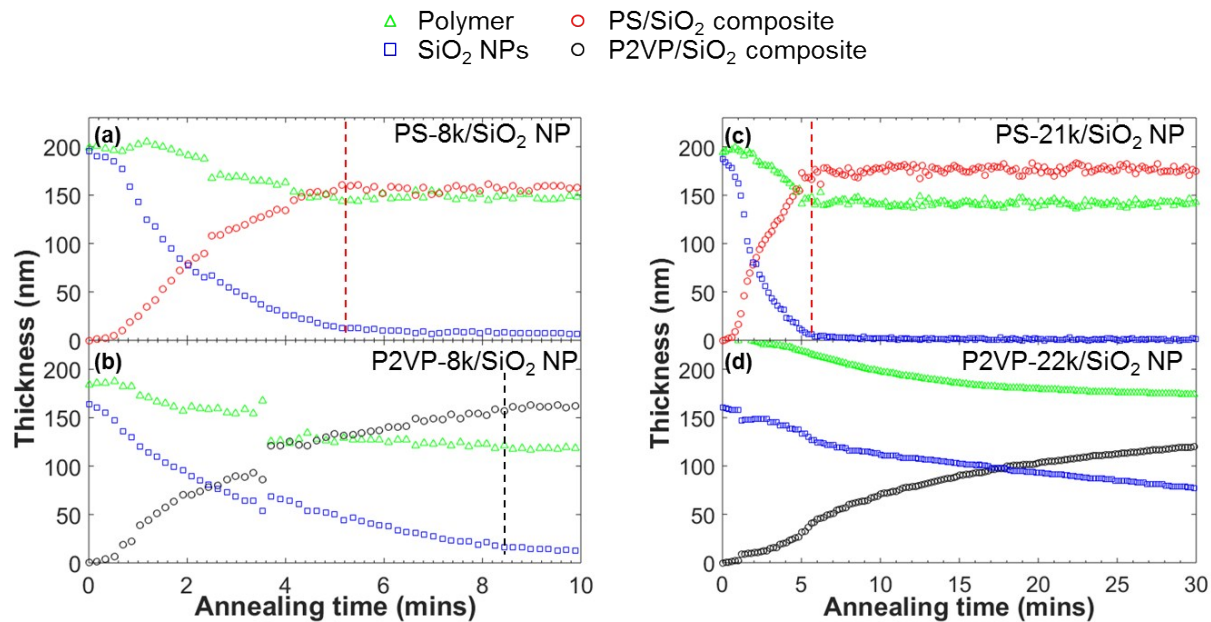


Figure S2. Thickness profile evolutions of NP, composite, and polymer layers of (a)PS-8k/ SiO_2 NP, (b) P2VP-22k/ SiO_2 NP, (c) PS-21k/ SiO_2 NP, and (d)P2VP-22k/ SiO_2 NP bilayer films at (a-b) 403 K and (c-d) 423 K, respectively.

Linear dependence of h^2 versus t for PS-21k/SiO₂ NP and P2VP/SiO₂ NP annealed at 423 K

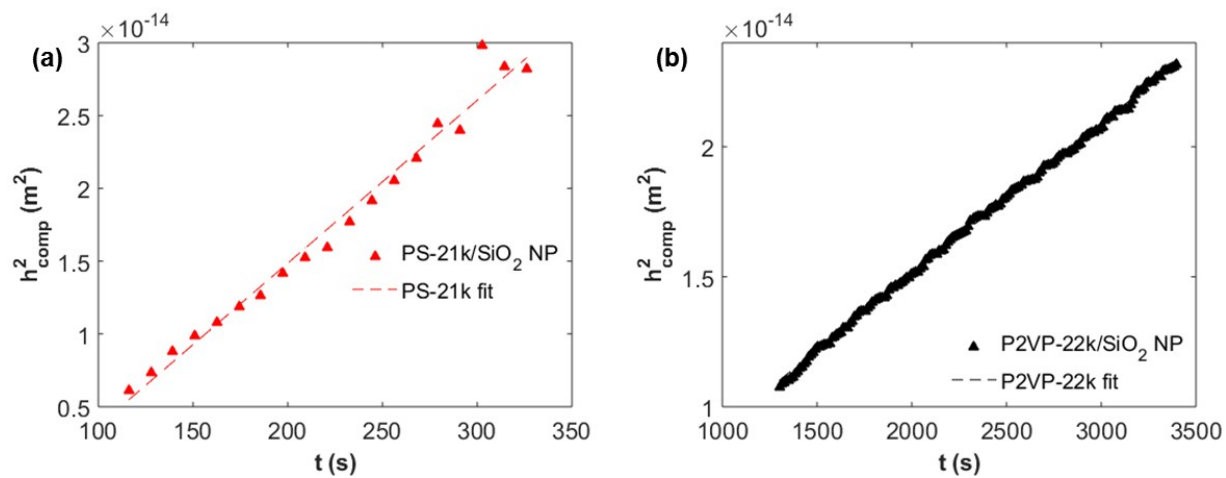


Figure S3. Plot of h^2 versus t for (a) PS-21k/SiO₂ NP and (b) P2VP-22k/SiO₂ NP annealed at 423K (150°C).

Sensitivity analysis on the viscosity calculation of PS-8k/SiO₂ NP based on polymer melt surface tension models and contact angle values

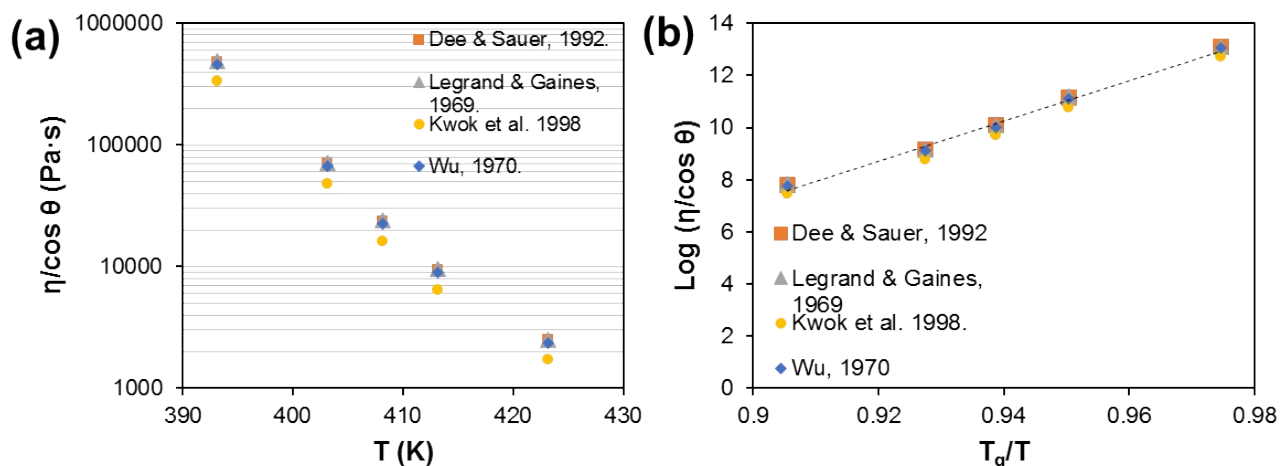


Figure S4. (a) Viscosity of confined PS-8k normalized by $\cos \theta$ extracted from CaRI of PS-8k/SiO₂ NP system and (b) the corresponding $\log(\eta/\cos \theta)$ versus T_g/T plot of confined PS-8k, based on various polymer melts surface tension models.¹⁻⁴

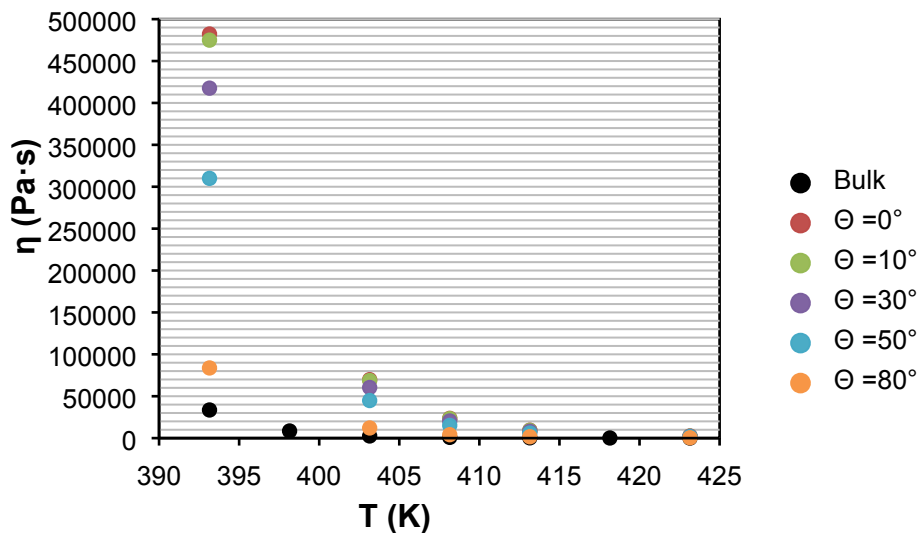


Figure S5. Viscosity of the bulk and confined PS-8k calculated using contact angle values $\theta = 0^\circ, 10^\circ, 30^\circ, 50^\circ,$ and 80° .

Bulk polymer viscosity value from literature

Poly(styrene)

The bulk polystyrene (PS) viscosity value is extracted from literature⁵ based on Figure 6 and Figure 10. Figure 6 shows the plot of $(\log(\eta_T/\eta_{217}))$ versus $1/T$, whereas Figure 10 plots \log viscosity versus $\bar{M}_w^{1/2}$ at $T = 217^\circ\text{C}$.

1. The normalized viscosity as a function of reciprocal temperature is extracted. These values are extracted from curve 1 (valid for $MW \sim 25,5000 - 134,000 \text{ gmol}^{-1}$) for 21k PS, whereas for 8k PS, the values are extracted from curve 2 ($MW \sim 11,000 - 13,5000 \text{ gmol}^{-1}$) and curve 3 ($MW \sim 7400 \text{ gmol}^{-1}$).
2. The viscosities of 8k and 21k PS at $T = 217^\circ\text{C}$ are extracted using the linear interpolation of the high slope region at low $\bar{M}_w^{1/2}$ values in Figure 10.
3. The viscosity values as a function of temperature can then be calculated for both 8k and 21k PS.
4. Since the normalized viscosity values extracted from step 1 is only valid at $T > 130^\circ\text{C}$, the viscosity values of PS at $T < 130^\circ\text{C}$ are obtained based on Williams-Landel-Ferry model of PS⁶⁻⁷:

$$\log(a_T) = \log\left(\frac{\tau}{1000}\right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g}$$

Where

Fitting parameters $C_1 = 13.35$, $C_2 = 42.00$

$a_T \equiv$ shift factor

$\tau \equiv$ relaxation time

$T \equiv$ experimental temperature

$T_g \equiv$ glass transition temperature

Viscosity and relaxation time are related through a vertical shift factor (b), that is determine by fitting the data to the data for bulk polymer in literature.

$$-\log \mu = -\log \tau - b$$

Poly(2-vinyl pyridine)

The bulk poly(2-vinyl pyridine) (P2VP) viscosity value is extracted from literature⁸ based on Figure 1 and Figure 4. Figure 1 shows the plot of $\log a_T$ versus T , whereas Figure 4 plots η versus M_w of bulk P2VP at $T = 160^\circ\text{C}$.

1. $\log a_T$ versus T is extracted using data from VPL8 (8,400 gmol⁻¹) for 8k P2VP and from VPK7 (17,000 gmol⁻¹) for 22k P2VP, from Figure 1.

2. The viscosities of 8k and 22k P2VP at $T = 160^{\circ}\text{C}$ are extracted from the linear interpolation of the low slope region at low M_w values ($M_w \sim 5,000 - 22,000 \text{ gmol}^{-1}$) in Figure 4.

The viscosity value as a function of temperature is obtained by solving for $a_T = \mu/\mu_{160}$, where μ_{160} refers to the viscosity at reference temperature $T = 160^{\circ}\text{C}$ obtained from step 2.

Determination of confined and bulk polymer glass transition temperature (T_g) using spectroscopic ellipsometry

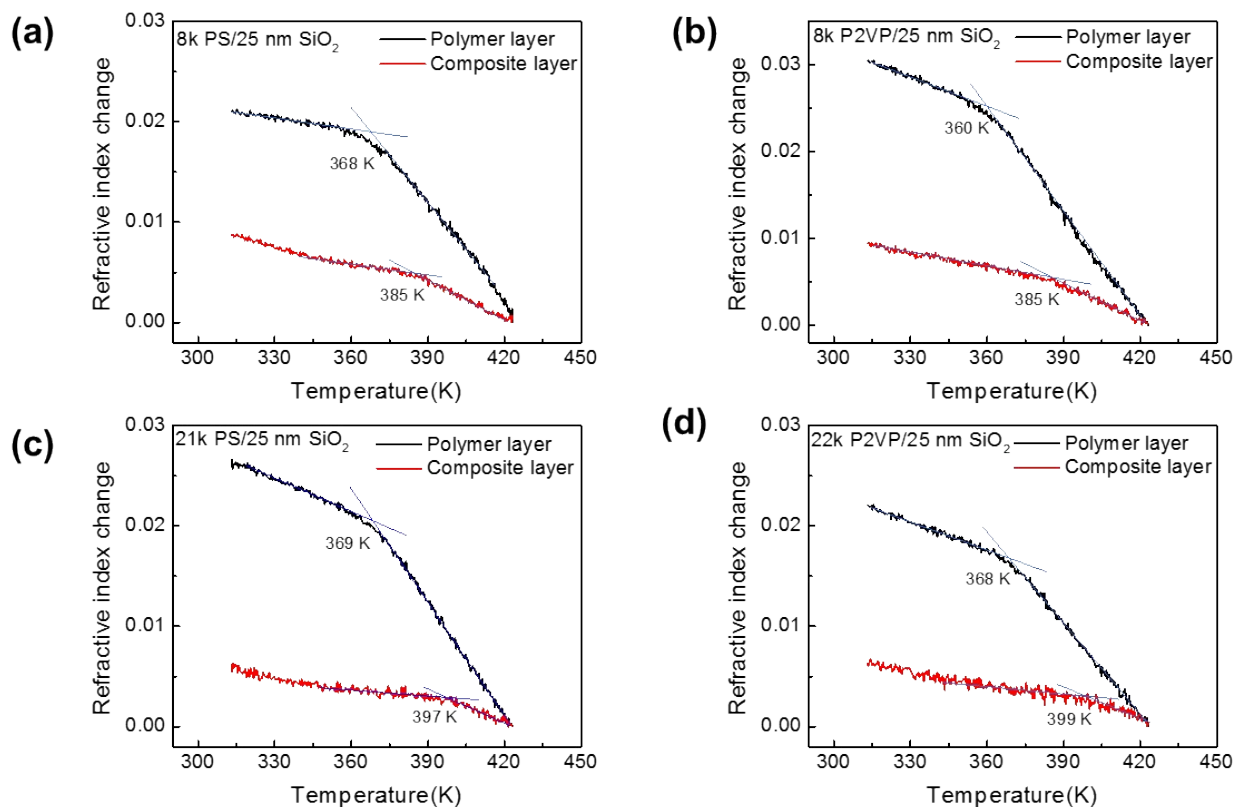


Figure S6. The glass transition temperatures (T_g) of bulk and confined (a)PS-8k, (b) P2VP-8k, (c) PS-21k, and (d) P2VP-22k are measured using spectroscopic ellipsometry, by determining the inflection point in the layer refractive indices with temperature at a cooling rate of 10K/min. The confined polymer T_g is determined from the composite layer, where polymer has fully filled the voids in the NP packing; whereas the bulk polymer T_g is determined from the residual polymer layer at the bottom.

Atomic force microscopy (AFM) topography and phase images of PS-8k/SiO₂ NP bilayer film surface before and after CaRI

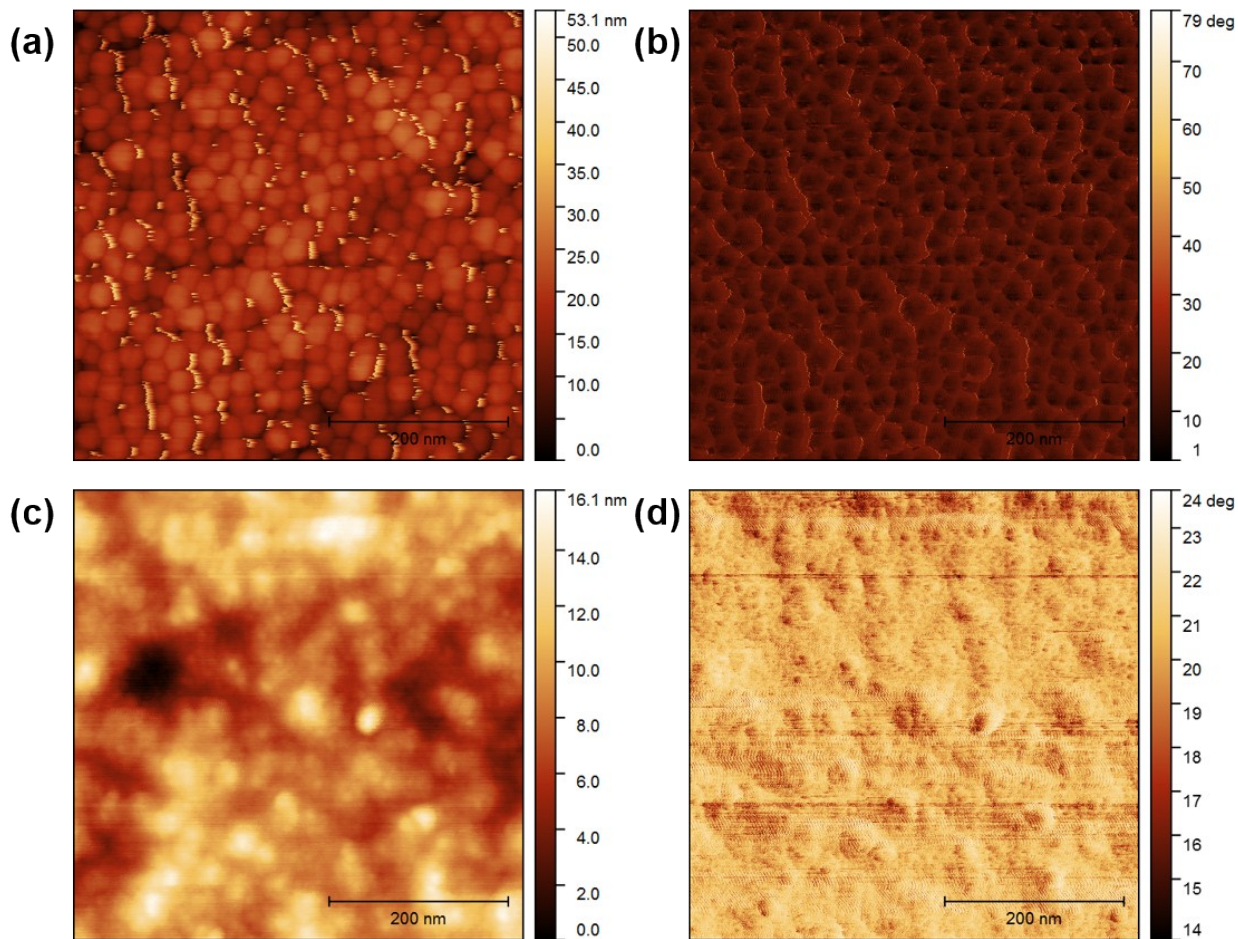


Figure S7. Topography (a,c) of the PS-8k/SiO₂ NP bilayer film taken using tapping-mode AFM (a) before and (c) after CaRI; phase image (b,d) of the film (b) before and (d) after CaRI. The scale bars are 200nm. The films are imaged using an Icon, Bruker AFM with a silicon tapping-mode probe.

Table T1. Glass transition temperature, T_g (K) measured using differential scanning calorimetry (DSC) and spectroscopic ellipsometry (SE) in the bulk and confined state.

Polymer	Glass transition temperature, T_g (K)		
	Bulk (DSC)	Bulk (SE)	Confined (SE)
P2VP-8k	342	360	385
P2VP-22k	355	368	399
PS-8k	356	368	385
PS-21k	366	369	397

References

1. Dee, G. T., Sauer, B. B. J. Colloid Interface Sci. 1992. **152**. 85-103.
2. Legrand, D. G., Gaines. G. L. J. Colloid Interface Sci. 1969. **31**. 162-167.
3. Kwok, D. Y., Cheung, L. K., Park, C. B., Neumann, A. W. Polym. Eng. Sci. 1998. **38**. 757-764.
4. Wu, S. J. Phys. Chem. 1970. **74**. 632-638.
5. Fox, P., Flory, T. G. J. Am. Chem. Soc. 1948. 70. 2384-2395.
6. Wang, J., McKenna, G. B. Macromolecules 2013, **46**, 2485-2495.
7. Glor, E. C., Fakhraai, Z. J. Chem. Phys. 2014. **141**, 194055.
8. Takahashi, Y., Ochiai, N., Matsushita, Y., Noda, I. Polym. J. 1996. 28. 1065-1070.