

**Nanofiller Induced Molecular Lubrication Strategy for Ultrathin Capacitor  
Films with High Energy Density and Minimal Thickness**

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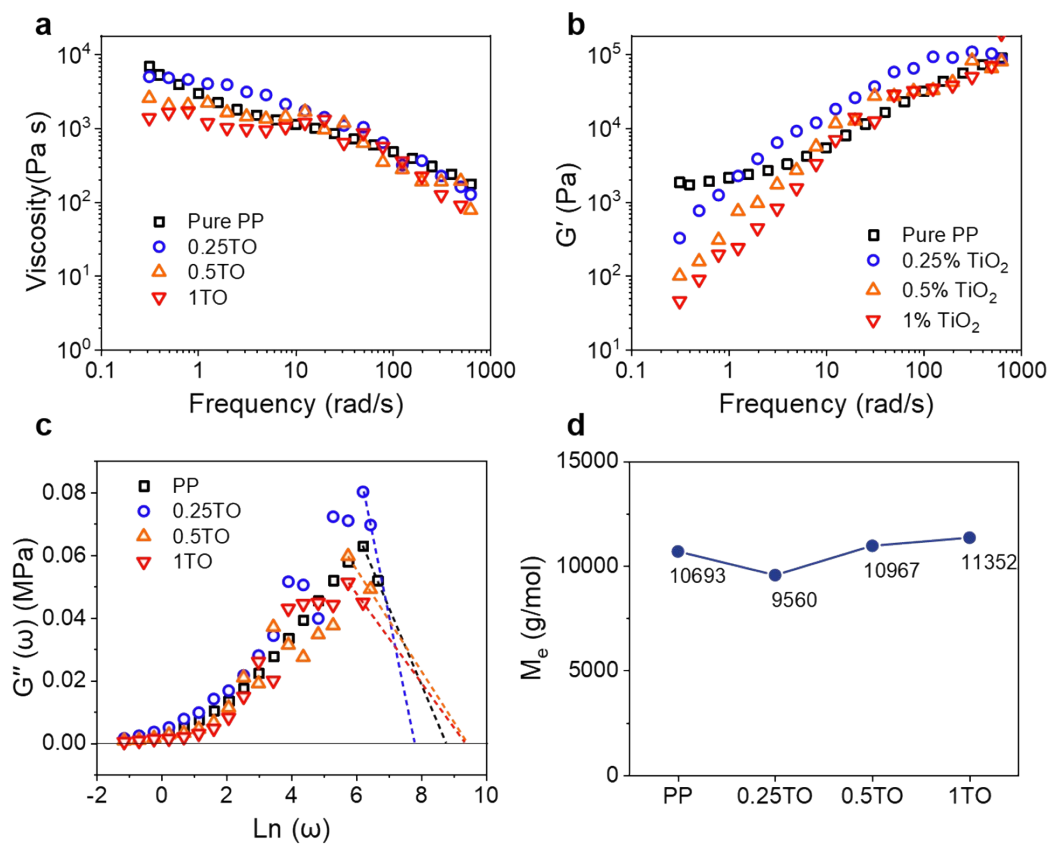
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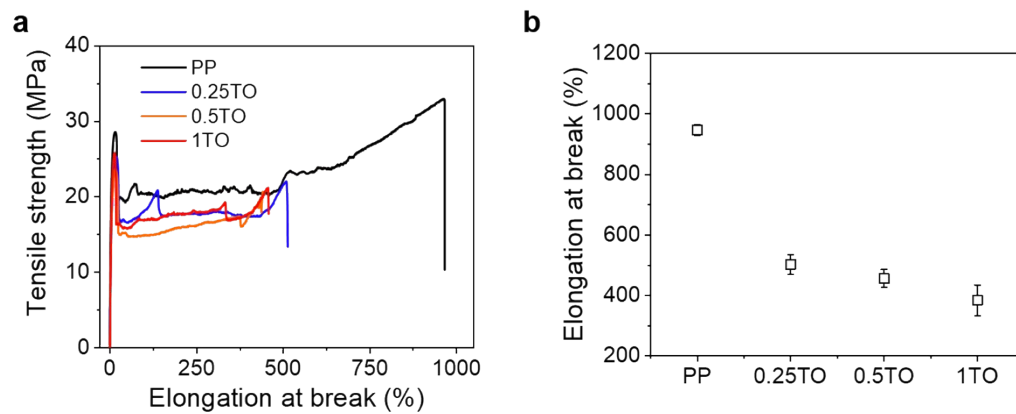
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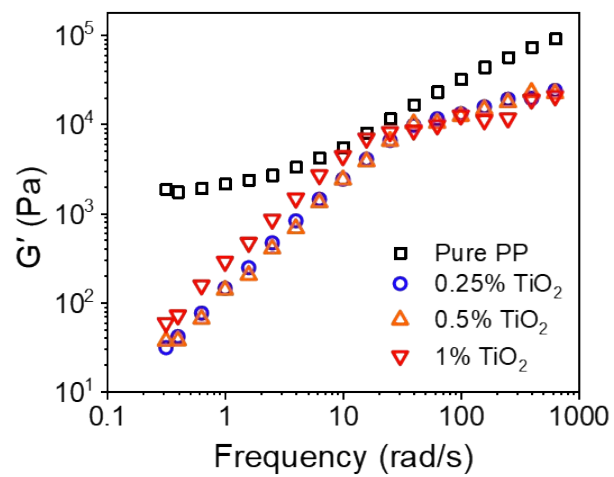
## Supplementary Figures



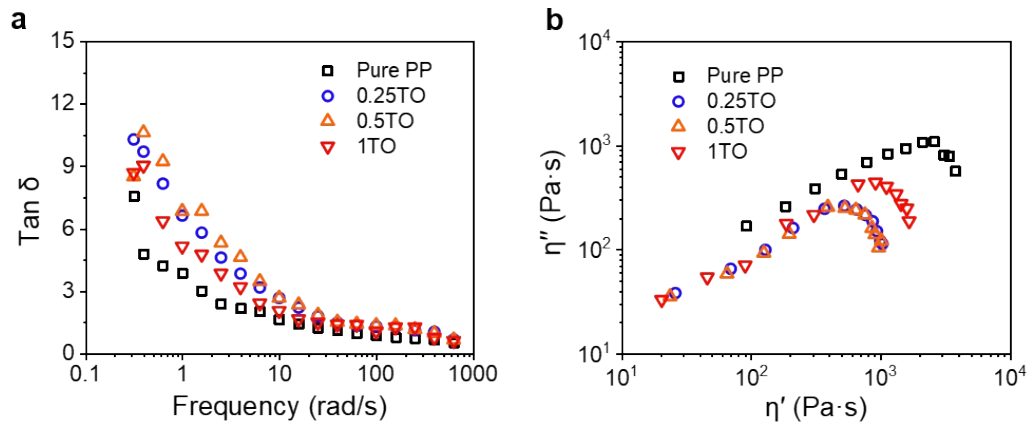
**Supplementary Fig. 1.** **a** Viscosity of PP/ $\text{TiO}_2$  composites with conventional large-particle  $\text{TiO}_2$ . **b** Modulus of PP/ $\text{TiO}_2$  composites with conventional large-particle  $\text{TiO}_2$ . **c** The plot of  $G''$  versus  $\text{Ln}(\omega)$  to calculate entanglement area associated with  $M_e$ . **d** The corresponding  $M_e$ .



**Supplementary Fig. 2. a** Stress-strain curves of PP/TiO<sub>2</sub> composites with conventional large-particle TiO<sub>2</sub>. **b** The corresponding elongation at break.

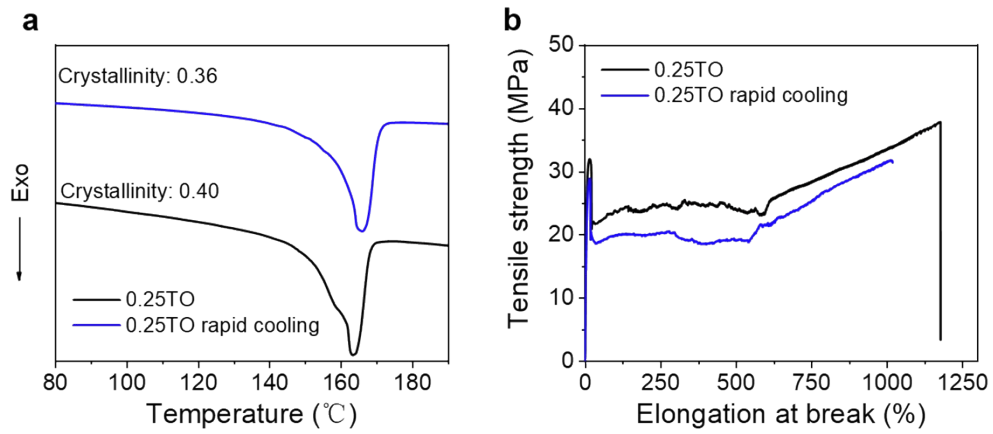


**Supplementary Fig. 3.** Modulus of PP/ $\text{TiO}_2$  composites with small-particle  $\text{TiO}_2$ .

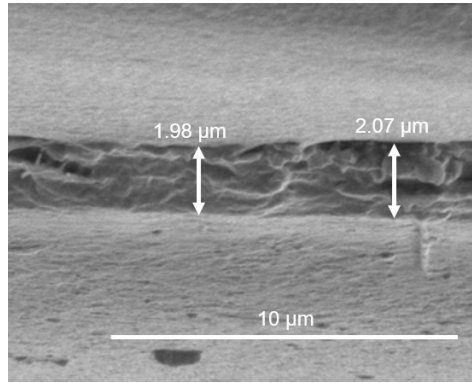


**Supplementary Fig. 4. a**  $\tan \delta$  of PP/TiO<sub>2</sub> composites with small-particle TiO<sub>2</sub>. **b**

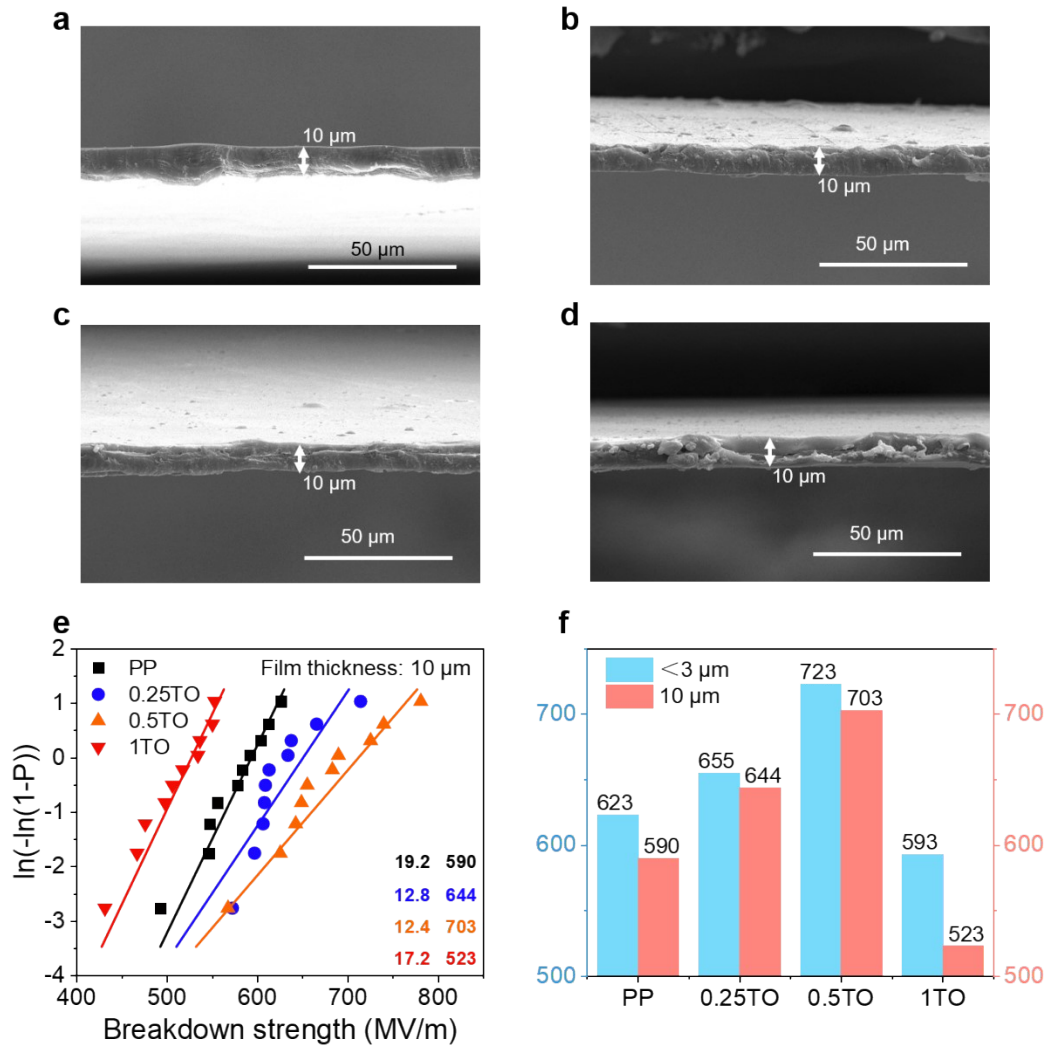
Cole-Cole plot of PP/TiO<sub>2</sub> composites with small-particle TiO<sub>2</sub>.



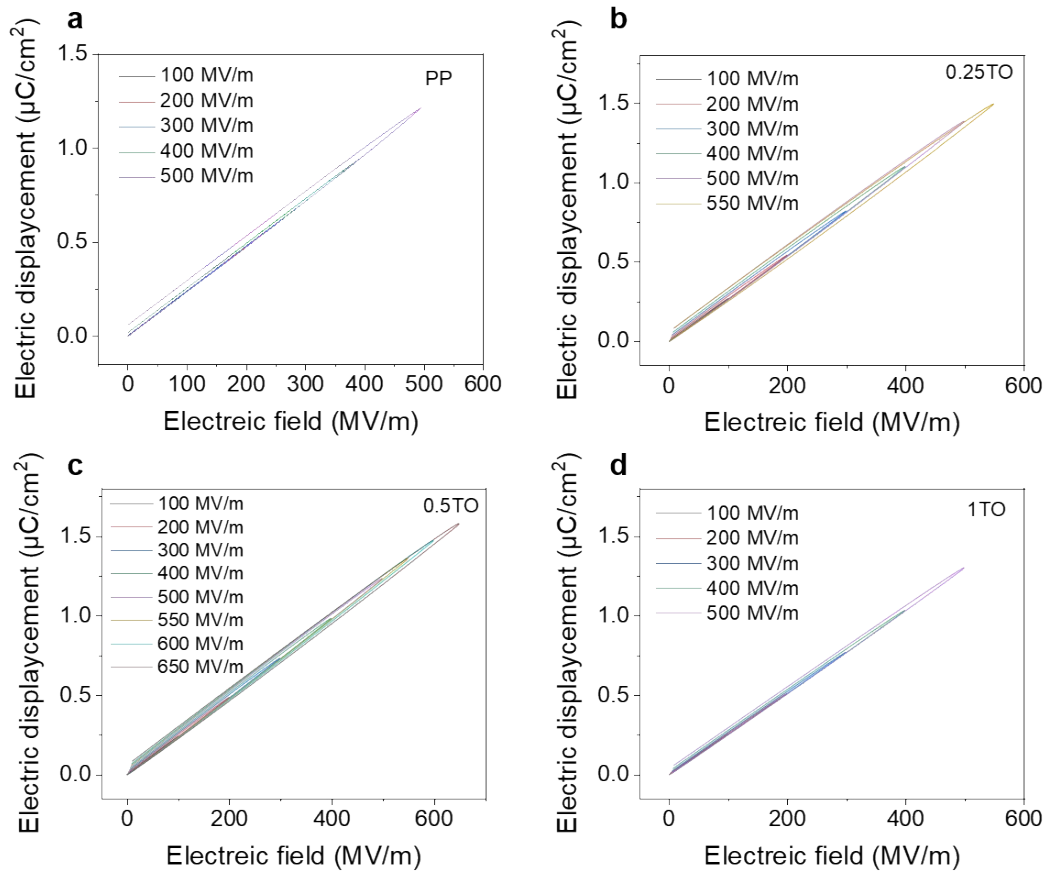
**Supplementary Fig. 5.** The DSC (a) and stress-strain curves (b) of 0.25TO and 0.25TO rapid cooling samples.



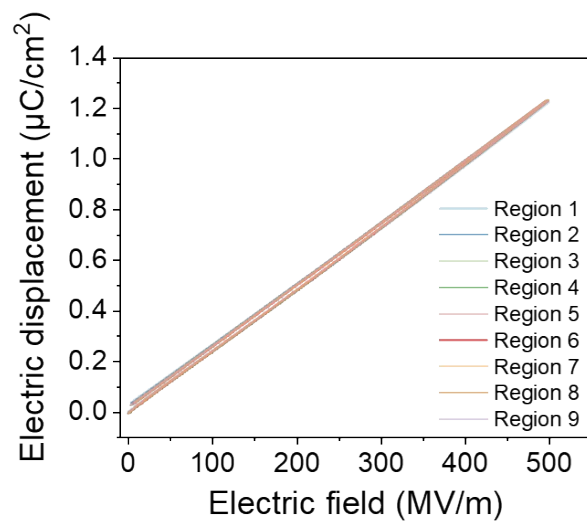
**Supplementary Fig. 6.** The cross-sectional SEM image of showing the thickness uniformity of 0.5TO ultrathin film.



**Supplementary Fig. 7.** The SEM images of film thickness (**a**: pure PP, **b**: 0.25TO, **c**: 0.5TO, **d**: 1TO). Weibull statistic of dielectric breakdown strength (**e**) and the corresponding breakdown strength (**f**).



**Supplementary Fig. 8.** D-E curves under different electric fields at 25 °C for PP (a), 0.25TO (b), 0.5TO (c) and 1TO (d) composite film.



**Supplementary Fig. 9.** D-E loops for 0.5TO ultrathin film under different electric fields at 25 °C.

## Supporting Notes

### Note S1. Molecular mass between entanglements ( $M_e$ )

$M_e$  are calculated by the plateau modulus  $G_N^\circ$  in rheological tests according to the INT method[1]:

$$G_N^\circ = \frac{g\rho RT}{M_e} \quad (S1)$$

where  $g$  represents a numerical factor (0.8),  $\rho$ ,  $R$  and  $T$  refer to density, gas constant and absolute temperature, respectively.

Since polypropylene does not exhibit a modulus plateau region, the  $M_e$  was calculated using a numerical integration method based on the terminal relaxation peak of  $G''(\omega)$ , according to the following equation[2]:

$$G_N^\circ = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega) d(\ln(\omega)) \quad (S2)$$

The plot of  $G''$  versus  $\ln(\omega)$  shows a maximum, followed by a linear decrease. Therefore, data at higher frequencies need to be linearly extrapolated before integration.

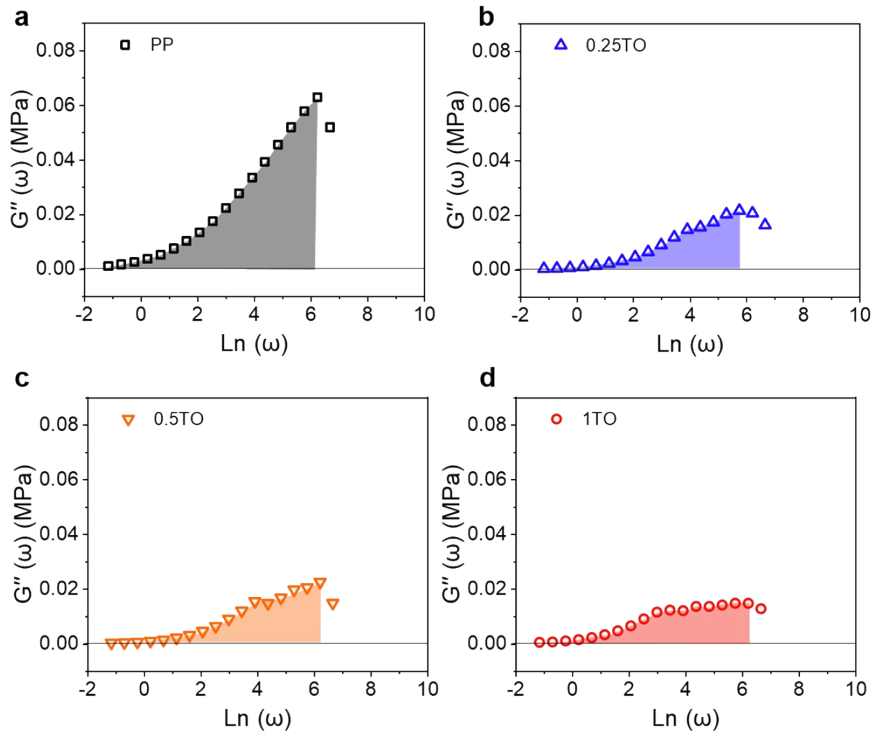
To ensure the reliability of the  $M_e$  values, two additional models were also employed to determine  $M_e$ .

The simplified INT method was proposed by Onogi S[3]. For polydisperse systems, the terminal relaxation spectrum is relatively broad, and some studies suggest that the loss modulus peak can be considered approximately symmetric. Therefore, the INT method may be simplified by taking twice the area under the peak prior to the peak frequency, thereby avoiding integration over the high-frequency

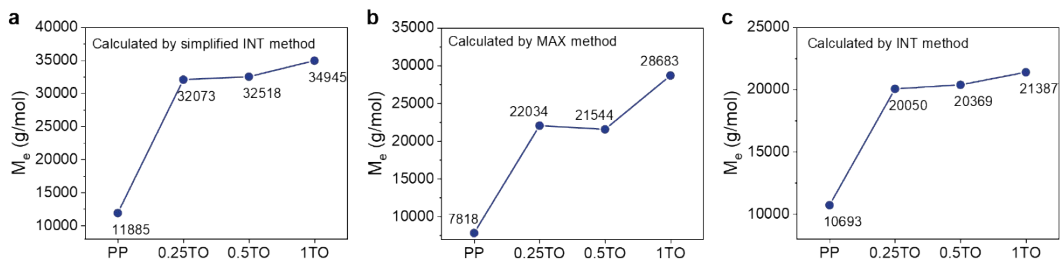
region where uncertainties are more pronounced:

$$G_N^\circ = \frac{4}{\pi} \int_{-\infty}^{\omega_{max}} G''(\omega) d(\ln(\omega)) \quad (S3)$$

Based on the equation (S1) and (S3), together with the loss modulus of PP/TiO<sub>2</sub> composites (**Supplementary Fig. 10**), the M<sub>e</sub> are calculated and shown in **Supplementary Fig. 11a**.



**Supplementary Fig. 10.** The loss modulus for PP (a), 0.25TO (b), 0.5TO (c) and 1TO (d) composites with small-particle TiO<sub>2</sub>.



**Supplementary Fig. 11.** The calculated  $M_e$  via simplified INT method **(a)**. The calculated  $M_e$  via MAX method **(b)**. The calculated  $M_e$  via INT method in this study **(c)**.

The MAX method has been proposed by Marvin Oser[4]:

$$G_N^\circ = 4.83G_{max}'' \quad (S4)$$

Based on the equation (S1) and (S4), together with the loss modulus of PP/TiO<sub>2</sub> composites (**Supplementary Fig. 10**), the  $M_e$  are calculated and shown in **Supplementary Fig. 11b**.

Although certain discrepancies in the calculated  $M_e$  values are observed among different models, all results consistently demonstrate a pronounced increase in  $M_e$  upon the incorporation of TiO<sub>2</sub>, thereby indicating that a trace amount of TiO<sub>2</sub> nanofillers is sufficient to effectively release the majority of disentangleable polymer chains.

## Note S2. Weibull statistics

Dielectric breakdown strengths are assessed by the Weibull distributions method according to the following equation[5]:

$$P(E) = 1 - \exp\left(-\frac{E}{E_b}\right)^\beta \quad (\text{S5})$$

where  $P(E)$  is the probability of electric failure,  $E$  and  $E_b$  represent tested breakdown strength and the characteristic breakdown strength at a 63.2% probability of electric failure, respectively, and the shape parameter  $\beta$  is employed to assess the data dispersion.

## Reference

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- [3] Onogi S, Masuda T, Kitagawa KJM. Rheological properties of anionic polystyrenes. I. Dynamic viscoelasticity of narrow-distribution polystyrenes. *Macromolecules*. 1970;3(2):109-16.
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- [5] Li X, Liu B, Wang J, Li S, Zhen X, Zhi J, et al. High-temperature capacitive energy storage in polymer nanocomposites through nanoconfinement. *Nat Commun*. 2024;15(1):6655.