

## Supporting Information for:

# Rheological Properties of Blends of Isotactic Polystyrene – Isotactic Poly(*para*-methylstyrene) Films Derived from a Comparative Dewetting Study

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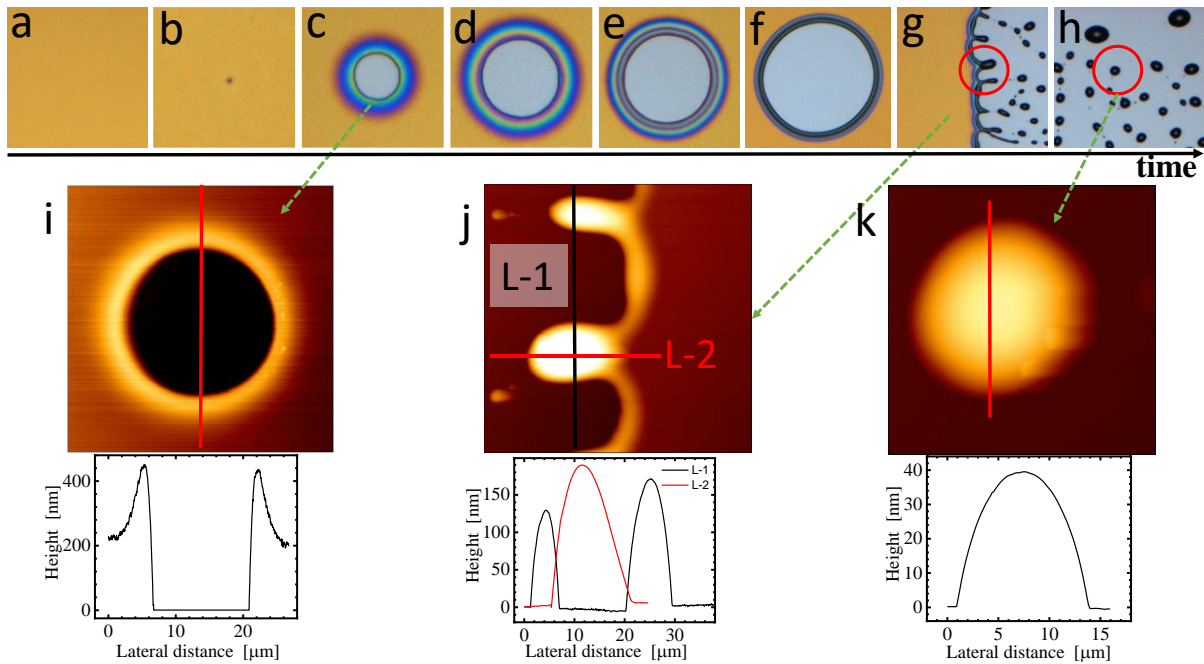
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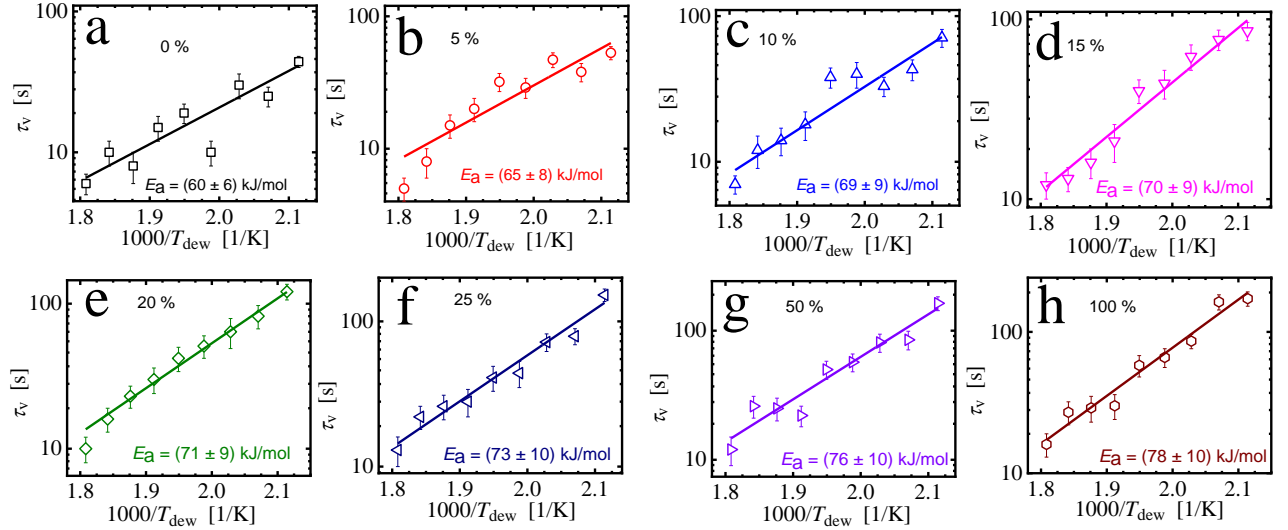
## 1. Optical microscopy (OM) and atomic force microscopy (AFM) images



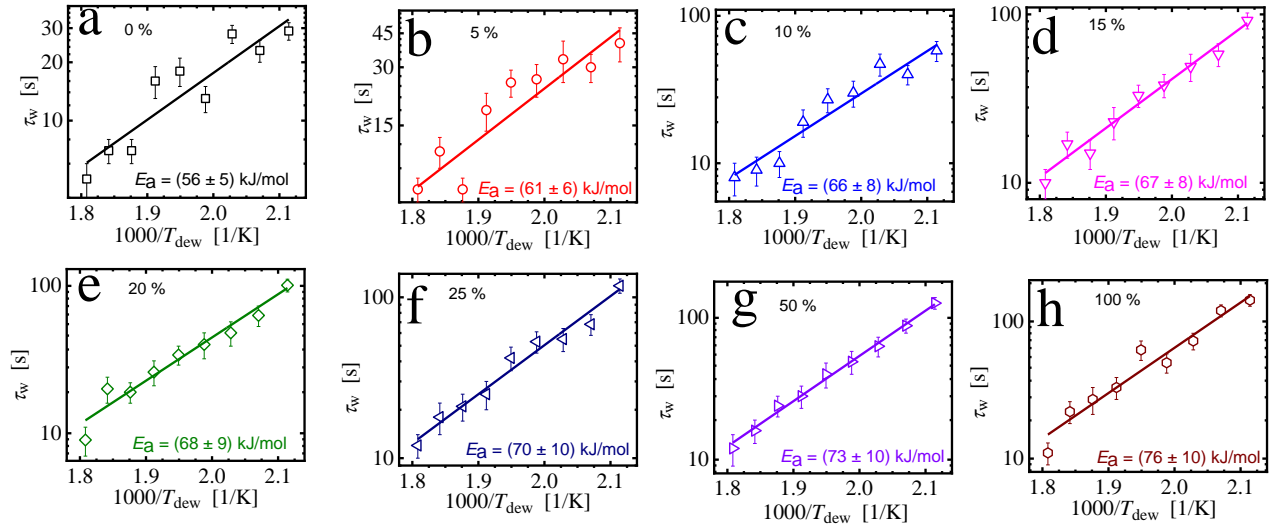
**Figure S1:** Optical micrographs and atomic force microscopy (AFM) images for the 95 % iPpMS – 5 % iPS binary system dewetted at  $T_{\text{dew}} = 240 \text{ }^\circ\text{C}$  and at different incubation times. (a) shows a 200 nm film before the dewetting experiment. (b) – (d) show the dewetting process for shorter incubation times and (e) – (h) show dewetting process at longer incubation times. (i) - (k) (2D) are the AFM images of (c), the circled section in (g) and circled droplet in (h), respectively. The graphical representation of the cross-sectional profiles for the lines indicated in (i), (j) and (k) are given beneath. The scales for (a) – (d) and for (e) – (h) are  $110 \times 110 \text{ } \mu\text{m}^2$  and  $225 \times 225 \text{ } \mu\text{m}^2$ , respectively.

## 2. Determination of activation energy based on relaxation times $\tau_r \in \{\tau_v, \tau_w\}$ : Graphical analysis

For  $\tau_v$  :



For  $\tau_w$  :



**Figure S2:** Semi-logarithmic plots of relaxation time  $\tau_r \in \{\tau_v, \tau_w\}$  against  $1000/T_{\text{dew}}$  for different iPS content, indicated in the graphs.

The activation energies for both cases were deduced from  $\ln \tau_r = \ln \tau_0 + E_{\eta}/k_B T_{\text{dew}}$ .

We set  $\tau_r \in \{\tau_v, \tau_w\}$ ,  $k_B T_{\text{dew}} \equiv \frac{R}{N_A} T_{\text{dew}}$ , with  $R = \frac{8.314 \text{ kJ}}{\text{mol}\cdot\text{K}}$  and  $N_A = 6.02214076 \cdot$

$10^{23} \frac{1}{\text{mol}}$ .

### 3. Stress calculations

To calculate the stress acting in the as-prepared films, we require the surface energies of both isotactic polystyrene (iPS) and isotactic poly(*para*-methylstyrene) (iPpMS) polymers. Based on the literature, rheological properties of both *isotactic* polymers have not been established completely. Thus, we have used the surface energies of their respective atactic counterparts, aPS and aPpMS, respectively. According to reference,<sup>1</sup> the surface tension  $\gamma_L$  of atactic poly(*para*-methylstyrene) is  $\gamma_L = 25.8 \text{ mJ/m}^2$  at 20°C and that of atactic polystyrene is  $\gamma_L = 28.3 \text{ mJ/m}^2$  at 20°C. For polymers,  $\gamma_L$  decreases with increasing temperature by ca.  $-0.08 \text{ mJm}^{-2}\text{K}^{-1}$ .<sup>1,2,3</sup> For simplicity and as we do not know the exact value of  $\gamma_L$  for iPpMS, we used  $\gamma_L = 25.8 \text{ mJ/m}^2$  and  $\gamma_L = 28.3 \text{ mJ/m}^2$  as a minimum value for iPS for the purpose of estimating the capillary stresses. Using the experimentally determined values of contact angles (in radians) for holes dewetting at 240 °C at different iPS content, Table S1 gives the calculated stresses.

$$\sigma_{\text{cap}} = |S|/h_0, |S| = \gamma_L(1 - \cos \theta_{\text{equ}})$$

$$\sigma_{\text{res}} = \sigma_{\text{cap}}(\overline{B}_v - 1)$$

$$\sigma_{\text{tot}} = (\sigma_{\text{cap}} + \sigma_{\text{res}}).$$

iPS %	$\theta_{\text{dyn}}$	$\sigma_{\text{cap}}$ kPa	$\overline{B}_v - 1$	$\sigma_{\text{res}}$ kPa	$\sigma_{\text{tot}}$ kPa
<b>0</b>	0.37	17.5	1.6	28.0	45.5
<b>5</b>	0.40	22.1	4.0	88.4	110.5
<b>10</b>	0.41	23.1	5.0	115.5	138.6
<b>15</b>	0.42	24.2	6.0	145.2	169.4
<b>20</b>	0.41	23.1	7.1	164.0	187.1
<b>25</b>	0.44	26.5	8.1	214.7	241.2
<b>50</b>	0.43	25.4	9.0	228.6	254.0
<b>100</b>	0.42	24.2	10.1	244.4	268.2

**Table S1:** Calculated values of  $\sigma_{\text{cap}}$ ,  $\sigma_{\text{res}}$ , and  $\sigma_{\text{tot}} = \sigma_{\text{cap}} + \sigma_{\text{res}}$  in iPpMS and the corresponding blends at  $T_{\text{dew}} = 240 \text{ }^\circ\text{C}$ . The  $\overline{B}_v$  values were taken from Table 1 of the main text.

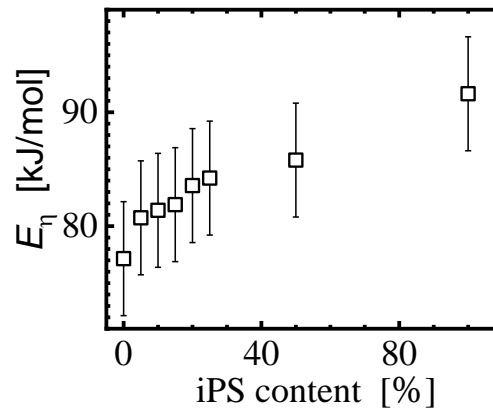
4. **Activation energy based on viscosity,  $E_\eta$ , ( $\eta(T_{\text{dew}}) = \eta_0 \cdot \exp(E_\eta/k_B T_{\text{dew}})$ )**

Table S2 gives the activation energy (which we can refer to as activation energy for flow), deduced from the data shown in Figure 9 (c) of the main text.

iPS %	$E_\eta$ kJ/mol
0	77.15
5	80.73
10	81.39
15	81.89
20	83.56
25	84.22
50	85.80
100	91.62

**Table S2:** Obtained values of  $E_\eta$ , based on  $\eta(T_{\text{dew}}) = \eta_0 \cdot \exp(E_\eta/k_B T_{\text{dew}})$

The tabulated values from **Table S2** were plotted in Figure S3.



**Figure S3:** Linear plot of activation energy from Table S2 against iPS content.

## References

- (1) Augsburg, A.; Grundke, K.; Pöschel, K.; Jacobascii, H. J.; Neumann, A. W. Determination of Contact Angles and Solid Surface Tensions of Poly(4-X-Styrene) Films. *Acta Polym.* **1998**, 49, 417 - 426.
- (2) Kempf, M.; Barroso, V. C.; Wilhelm, M. Anionic Synthesis and Rheological Characterization of Poly(*p*-methylstyrene) Model Comb Architectures with a Defined and Very Low Degree of Long Chain Branching. *Macromol. Rapid Commun.* **2010**, 31, 2140 – 2145.
- (3) Kempf, M.; Ahirwal, D.; Cziep, M.; Wilhelm, M. Synthesis and Linear and Nonlinear Melt Rheology of Well-Defined Comb Architectures of PS and P*p*MS with a Low and Controlled Degree of Long-Chain Branching. *Macromolecules* **2013**, 46, 4978– 4994.