

## Electronic Supplementary Information

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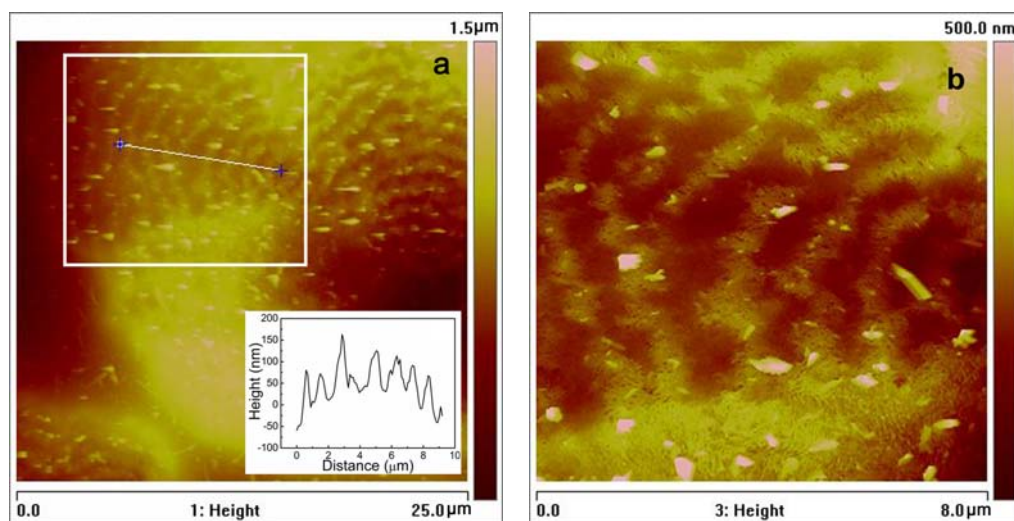
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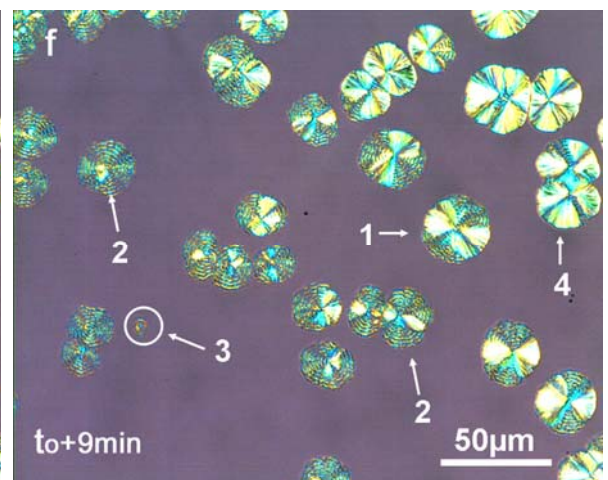
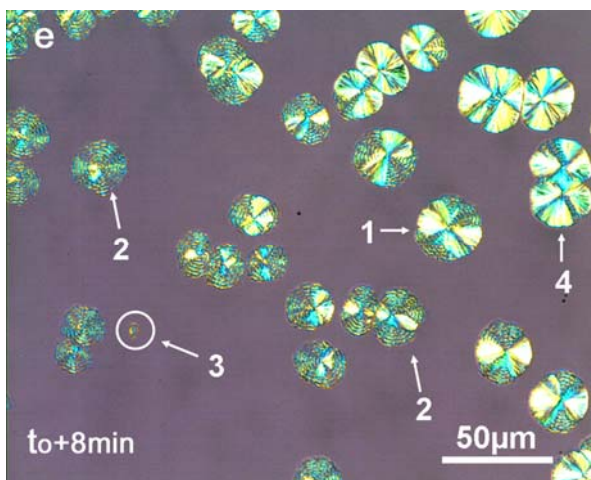
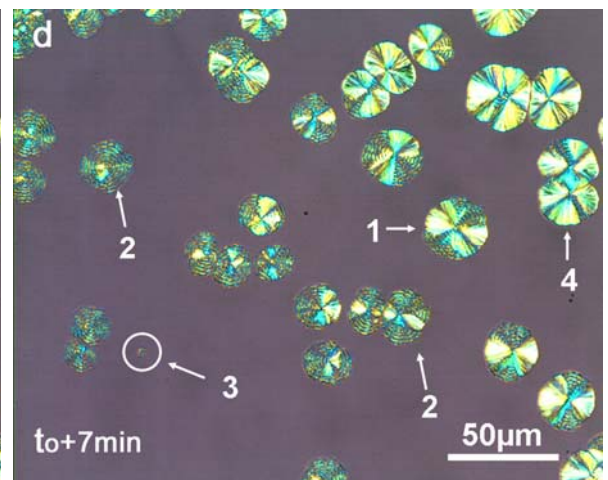
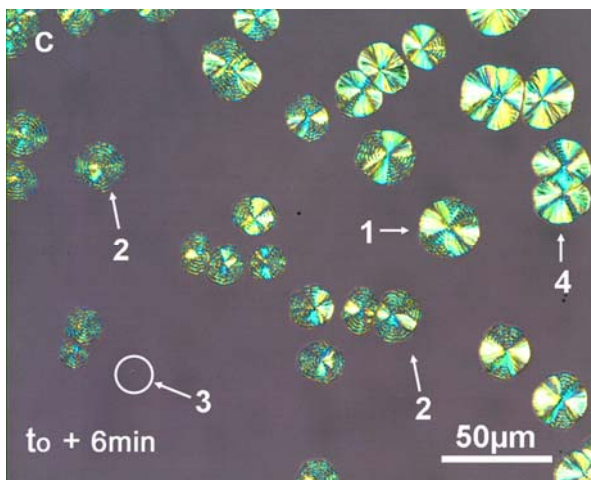
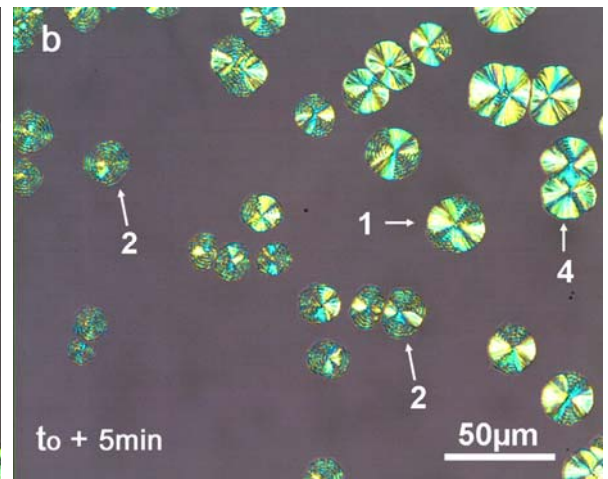
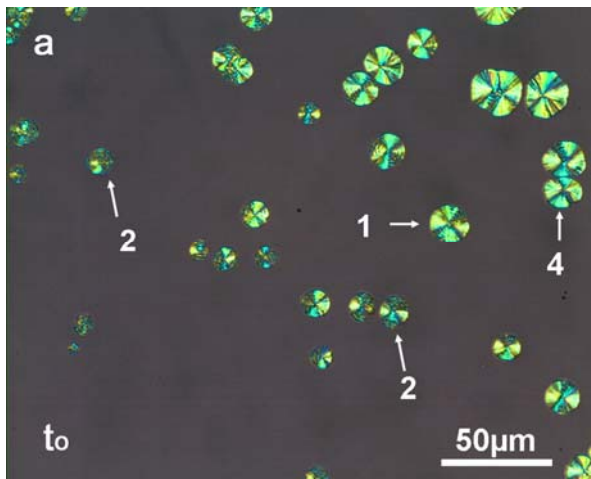
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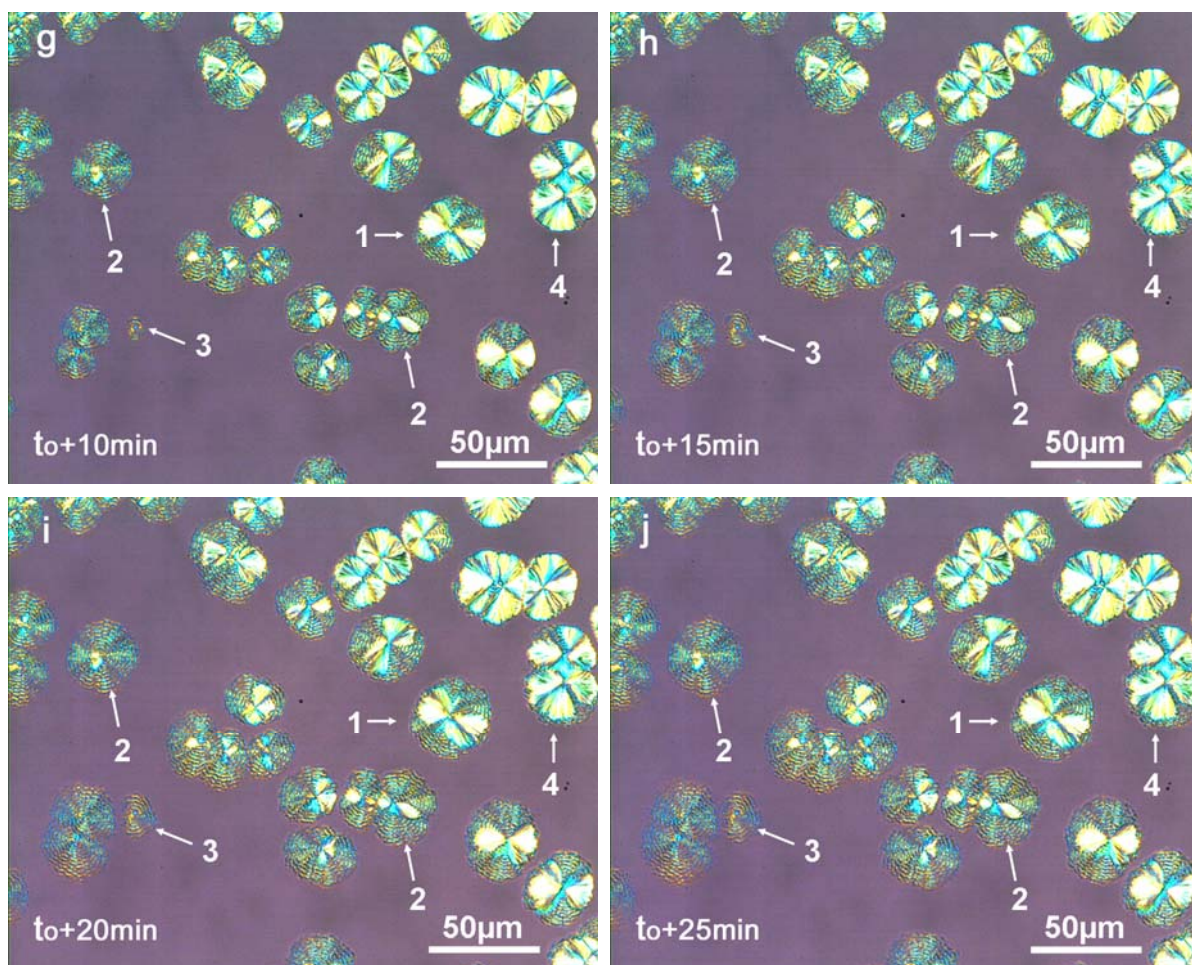
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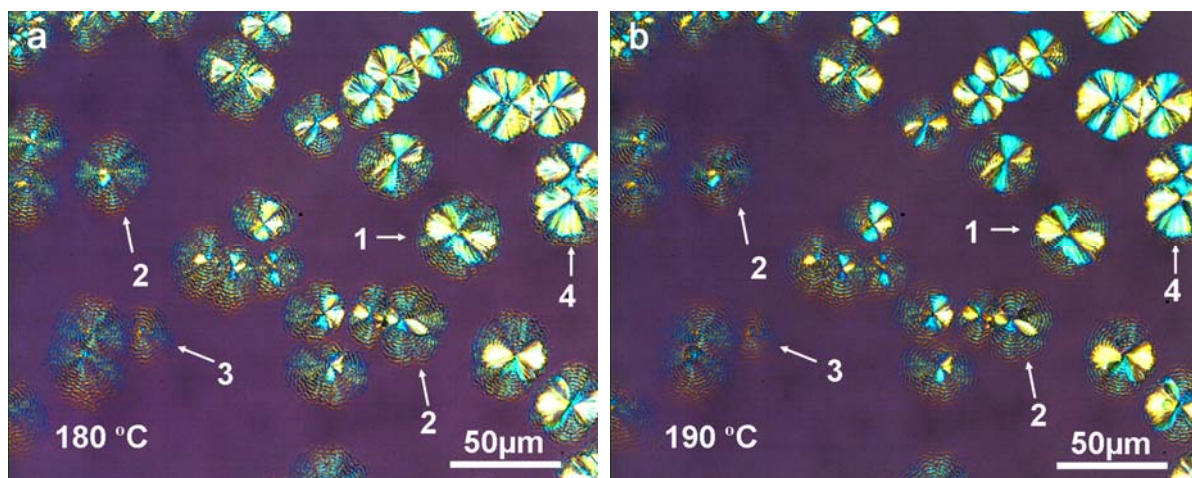
**Figure ESI 1.** AFM images. (a) Height image, inserted image represents height profile of the line; (b) Enlarged view of rectangular region in (a).

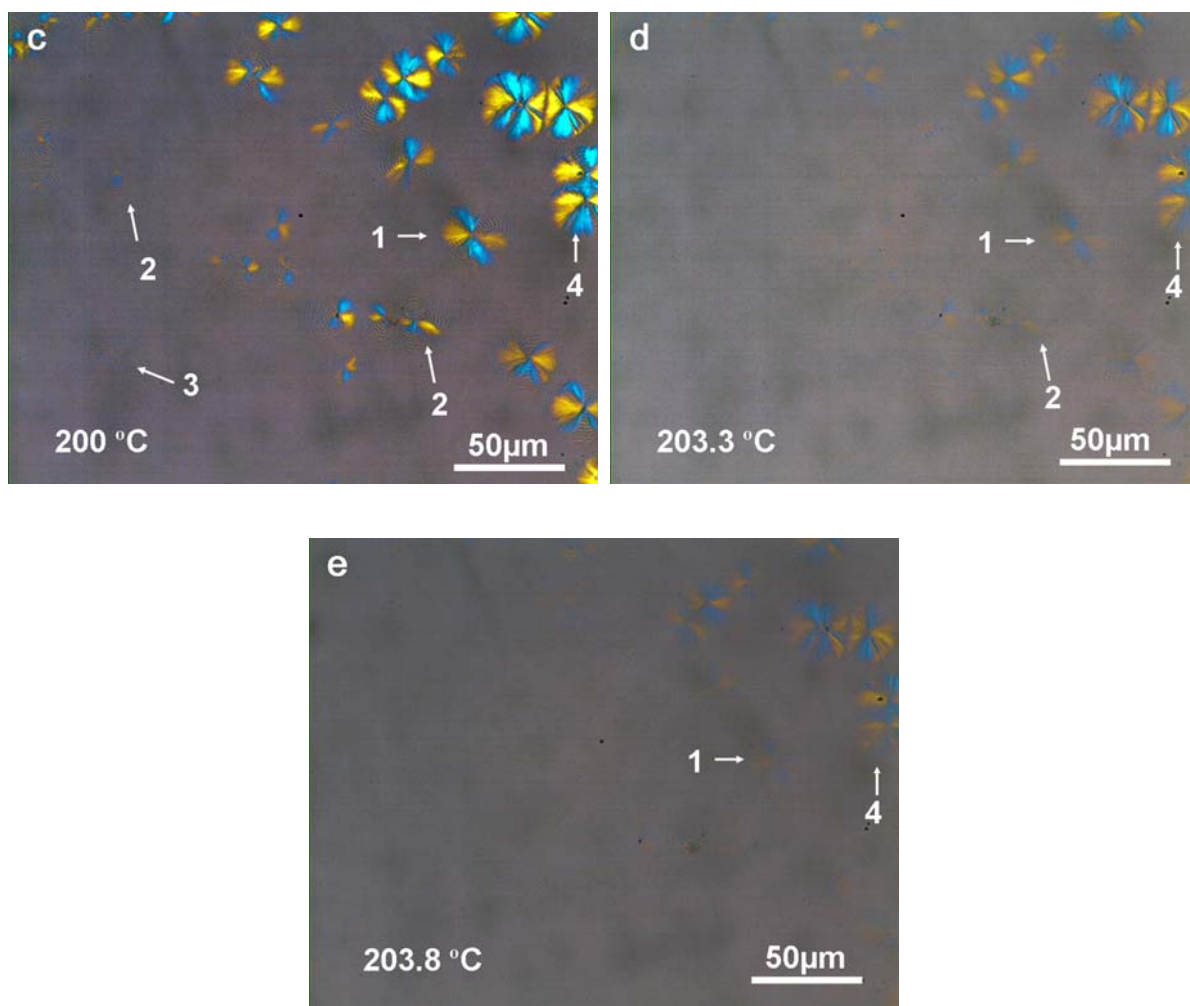
As shown in Figure ESI 1, some un-reacted cyclic butylene terephthalate oligomers (CBT) crystals disperse on the surface of polymerized cyclic butylene terephthalate (pCBT) spherulites which seriously impact the AFM scan and it has been intensively studied in our previous paper.<sup>1</sup>



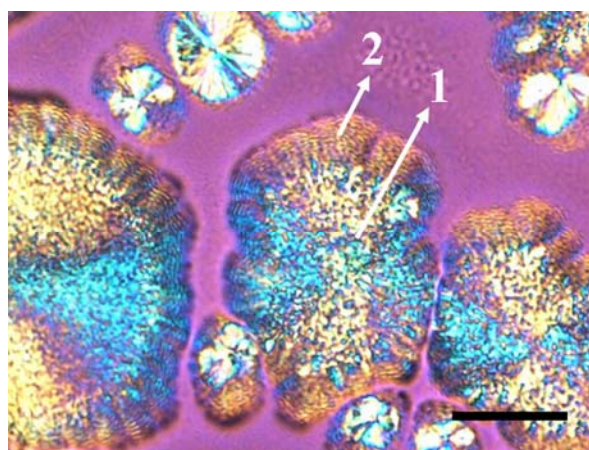


**Figure ESI 2.** In situ POM images of spherulites evolution at 170 °C for 30 min. Number 1, 2, 3 and 4 correspond to the spherulites in Figure 4a in manuscript. Circles indicate the evolution of normal ring-banded spherulite (number 3). Note that the contrast ratio of some images has been adjusted for better observation.





**Figure ESI 3.** In situ POM images during melting for number 1, 2, 3 and 4 spherulites in Figure 4a in manuscript. Note that the contrast ratio of some images has been adjusted for better observation.



**Figure ESI 4.** POM image of ring-bands enclosing pCBT spherulite. Scale bar: 20  $\mu\text{m}$ .

The crystallization of pCBT can take place during ROP of CBT at 190 °C.<sup>1,2</sup> In Figure ESI 4, it can be

found that pCBT spherulites (arrow 1) are enclosed by ring-banded pattern (arrow 2). Here, the pCBT spherulites obtained from 190 °C by crystallization during ROP, and the ring-banded shells formed by isothermal crystallization at 170 °C which was quenched from ROP temperature (190 °C) directly. Based on the molecular segregation mechanism,<sup>3</sup> low molecular weight pCBT cannot crystallize at 190 °C and only crystallize at lower crystallization temperature ( $T_C$ , 170 °C). This further reinforces the results in manuscript, in which the ring-banded pattern was achieved by ROP of CBT at 190 ~ 230 °C, erased heat history at 250 °C, followed by quenching to  $T_C$  (160 ~ 185 °C) to finish isothermal crystallization.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \times \frac{2}{P_n} \quad \text{--- Equation ESI 1}^{4,5}$$

$T_m$  : Melting point of crystal, (°C);

$T_m^0$  : Equilibrium melting point of lamellar crystal, (°C) ;

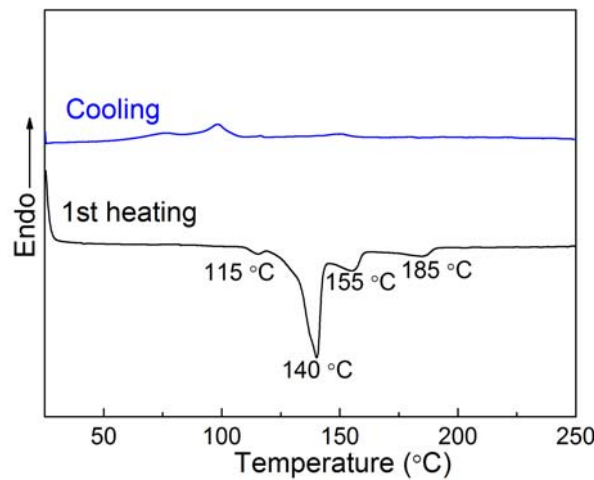
R : Gas constant;

$\Delta H_u$  : Molar heat fusion of repeating unit, (kJ·mol<sup>-1</sup>);

2 : Represent that the chain has two ends.

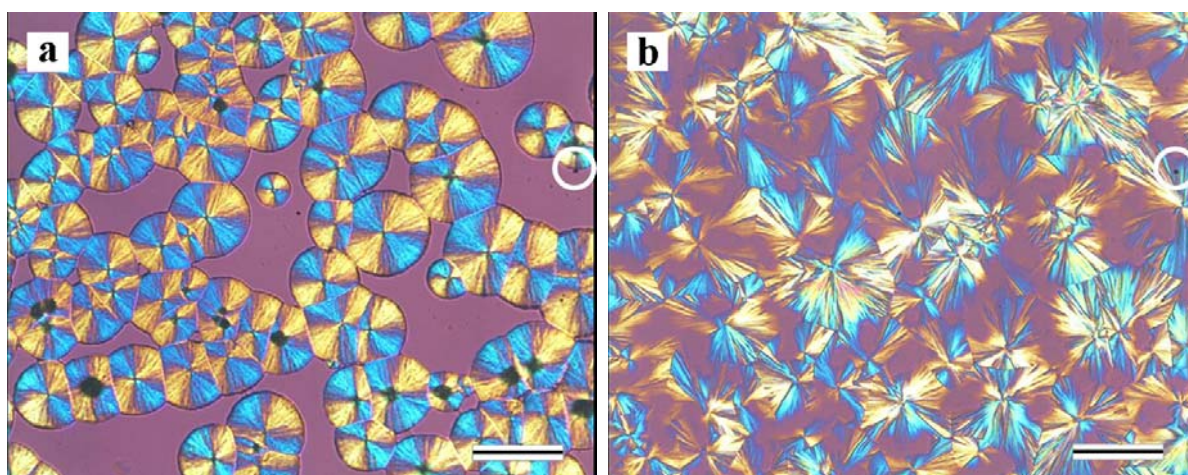
$P_n$  : Number average polymerization degree .

According to Equation ESI 1,  $T_m$  will be depressed with the decrease of the  $P_n$  (molecular weight). In this study, namely, crystals, in ring-banded regions, constructed by low molecular weight pCBT fractions (S-pCBT) should possess low  $T_m$ . This agrees to the in situ melting process (Figure ESI 3).



**Figure ESI 5.** DSC curves of neat CBT. Heating and cooling rate: 10 °C min<sup>-1</sup>

Differential scanning calorimetry (Mettler Toledo DSC I) was calibrated with an indium standard and sample mass of ca.5 mg was adopted for experiments. As shown in Figure ESI 5, above 160 °C, no crystalline peak can be found during cooling, namely, when the sample was quenched from 250 °C to  $T_C$  (160~185 °C), above the main melting point of CBT (120~160 °C, Figure ESI 5, 1<sup>st</sup> heating). The molten residual CBT may play a role of self-compatible “diluent”.



**Figure ESI 6.** POM images of PBT (Ultradur B4500, BASF). (a) Obtained from solution casting; (b) Heating up to 250 °C, holding for 5 min, followed by quenching (liquid nitrogen) to  $T_C$ . Circles represent a reference point for accurate recording the positions. Scale bars: 20 $\mu$ m.

## References

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- (3) Hu, W. B. Molecular segregation in polymer melt crystallization: simulation evidence and unified-scheme interpretation. *Macromolecules*, **2005**, 38(21): 8712-8718.
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