

## **Supplementary material:**

Fig. S1 Variation of storage modulus (G') and correlation length ( $\xi$ ) as a function temperature by oscillatory shear rheology at heating rate 0.5 K/min;  $\omega$ =1 rad/s; shear rate =1%.



Fig. S2 Polarized Optical Microscopy images of PS/PVME 60/40 blend bulk phase separation under quiescent condition with heating 1 K/min (a) 90 °C -miscible state (b) 110 °C - onset of phase separation (c) 115 °C (d) 125 °C [scale :  $20 \mu$ m].



Fig. S3 High speed images along with the corresponding IR thermographic images showing the dynamics of PS/PVME droplets heated at high laser power, I = 0.208 MW.





Fig. S4 SEM images showing final structures of (a) droplets of 20% (wt.) PS/PVME in toluene (at I=0.104MW/m<sup>2</sup>), (b) PS/PVME (without toluene) at 85<sup>o</sup>C, (c) 30% (wt.) PS/PVME in toluene (at I=0.104MW/m<sup>2</sup>) [scale bar is 2  $\mu$ m] and (d) temporal variation of droplet size (20% wt. of PS/PVME in toluene) and temperature (at I=0.104MW/m<sup>2</sup>).