A simple phase diagram has been drawn based on the results of our measurements. The sample we chose for this phase diagram is PEO-20K with a number-average molecular weight ($M_n$) of $1.98 \times 10^4$. The phase separation temperature presented in Fig. S1 is mainly obtained from DSC measurements, which varies with the concentration of PEO in solution. It first experiences a decrease and then increases with the growing weight concentration of PEO from 10 wt% to about 90 wt% as the upper curve illustrated in Fig. S1. It’s noteworthy that the temperature at which the solid phase transforms to sol phase stays at about 66 °C according to our measurements, which is indeed the melting point of PEO.