Supporting Information

Glass Transitions of Poly(methyl methacrylate) Confined in Nanopores: Conversion of Three- and Two-Layer Models

Linling Li,[†] Jiao Chen,[†] Weijia Deng,[†] Chen Zhang,[†] Ye Sha,[†] Zhen Cheng,[†] Gi Xue[*, †] and Dongshan Zhou[*, †,‡]

[†] *Key Laboratory of High Performance Polymer Materials and Technology of Ministry of Education, Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Co-ordination Chemistry, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China*

[‡] *Xinjiang Laboratory of Phase Transitions and Microstructures in Condensed Matters, College of Physical Science and Technology, Yili Normal University, Yining 835000, P. R. China*

Section1: the thermogravimetric analysis for PMMA bulk and PMMA-filled AAO samples

To calculate the amount of PMMA filled in the AAO template, TGA measurement was carried out on the Perkin-Elmer TGA-Pyris system. All the samples were heated from room temperature to 700 ^{o}C at 10 K/min under nitrogen atmosphere. The TGA results for the empty AAO template, $PMMA_{6K}$ bulk, and $PMMA_{6K}$-filled AAO samples are shown in Figure S1.

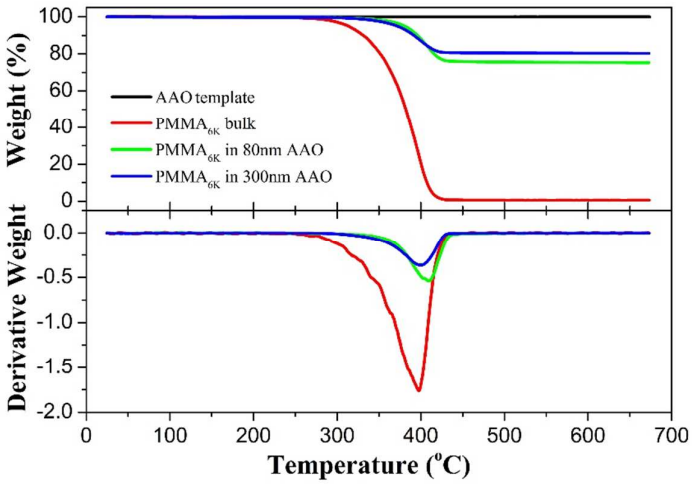

Figure S1. TGA and DTG curves for AAO templates, $PMMA_{6K}$ bulk samples and $PMMA_{6K}$ glasses

confined in AAO nanopores.

Section2: the thermal procedure of sub-T_g annealing experiments to investigate of the nature of the three transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores

To investigate the nature of observed three T_gs, the sub-T_g annealing experiments were carried out. The thermal procedure of the aging tests is shown in Figure S2. After removal of the thermal history, the $PMMA_{6K}$-filled 300 nm AAO samples were firstly cooled from 180 °C at 10 K/min, then annealed at each T_g -5 K for 5h, respectively. After the aging, a subsequent heating at 10 K/min was taken to study the changes in DSC curves. At last, the standard measurement (heating and cooling at 10 K/min, which is identical to that of sample without aging) was carried out for comparison.

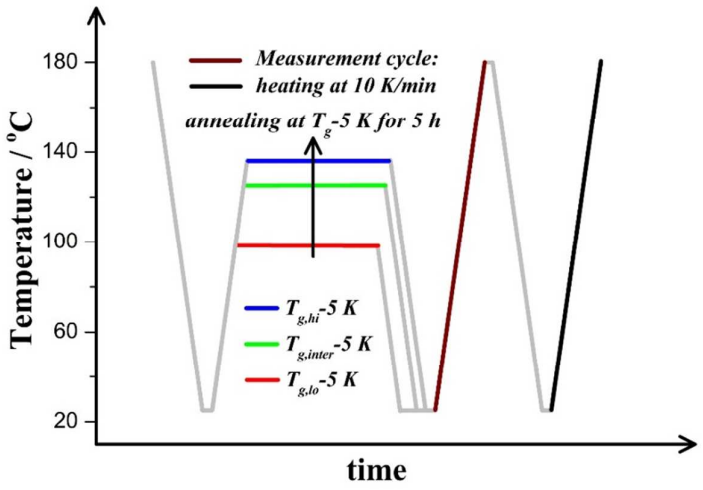

Figure S2. The thermal procedure of sub-T_g annealing experiments to investigate of the nature of the three transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores. All the heating and cooling rates are 10 K/min. The samples were annealed at temperatures of 5 K below each T_g for 5h.

Section3: the thermal procedure of the experiments for investigation of the cooling rate effect on the glass transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores

The thermal procedure of the experiments for investigation of the cooling rate effect on the glass transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores is shown in Figure S3. After removal of the thermal history, PMMA melts were cooled at different cooling rates, and the

subsequent heating at 10 K/min was to trace the variations of glass transitions.

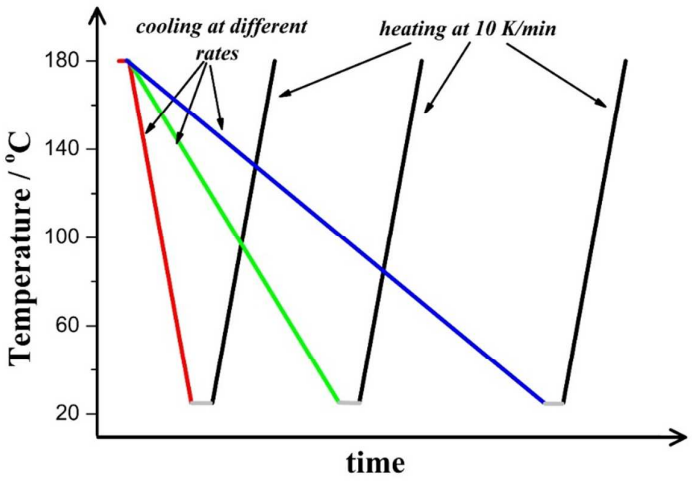

Figure S3. The thermal procedure of the experiments for investigation of the cooling rate effect on the glass transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores.

Section4: the thermal procedure and DSC measurements to investigate the reversibility of the interphase behavior of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores

To investigate the reversibility of the interphase behavior of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores, we design a thermal procedure as shown in Figure S4 (a). The DSC measurement of $PMMA_{6K}$-filled 300 nm AAO sample cooled at 0.5 K/min (segment B) was capped by two standard calorimetric measurements (segment A and C, both of the heating and cooling rates are 10 K/min). Figure S4 (b) presents heating traces of the three segments above. For the cooling rate of 0.5 K/min, the interphase behavior disappears. While, after removing the thermal history, the subsequent heating curve of segment C is identical with that of segment A, and the interphase behavior recovers.

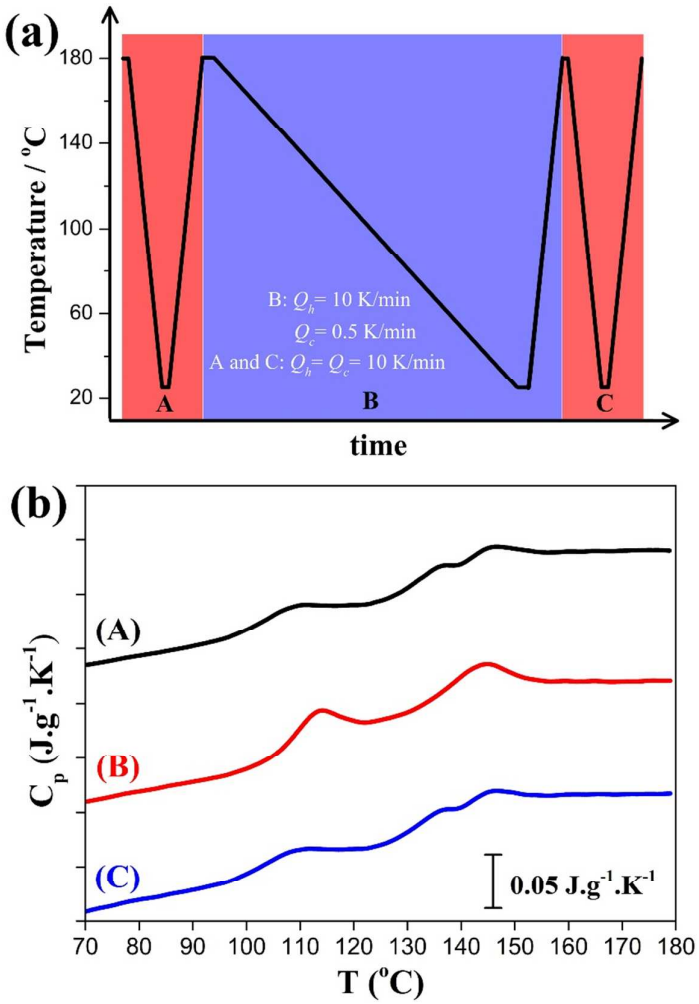

Figure S4. (a) The thermal procedure for investigating the reversibility of glass transitions of $PMMA_{6K}$ oligomer confined in 300 nm AAO nanopores: for A and C segments, both of the heating and cooling rates are 10 K/min; for B segment, the cooling rate is 0.5 K/min and the heating rate is 10 K/min. (b) DSC heating curves of the three segments shown in part (a).

Section5: the glass transitions of three different polymers confined in 300 nm AAO nanopores

To systematically explore the formation of the interphase behavior, the glass transitions of three different polymers confined in 300 nm AAO nanopores were investigated (as shown in Figure S5). The three polymers have the same molecular weight (M_n ~ 6 kg/mol) but different monomer-surface sticking energies. Interestingly, for the high physisorption sticking energy (such as $PMMA_{6K}$ and $P2VP_{6K}$), the interphase behavior can be observed; while for the low physisorption sticking energy (such as PS_{6K}), such behavior is absent.

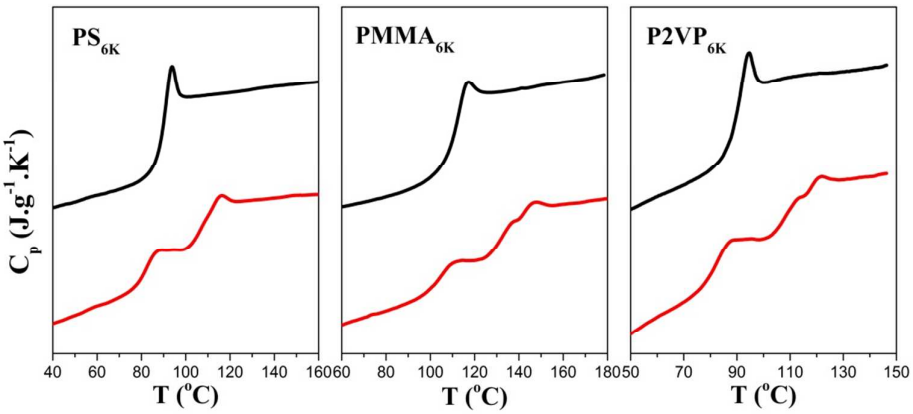

Figure S5. Black curves: DSC heating scans of PS_{6K}, $PMMA_{6K}$ and $P2VP_{6K}$ bulk samples; red curves: DSC heating scans of PS_{6K}, $PMMA_{6K}$ and $P2VP_{6K}$ glasses confined in 300 nm AAO nanopores. Both of the heating and cooling rates are 10 K/min. The subscripts in PS_{6K}, $PMMA_{6K}$ and $P2VP_{6K}$ represent the number-average molecular weight of polymers, which is 6 kg/mol.