# Supporting Information

# $T_g$ Confinement Effect of Random Copolymers of 4-*tert*-Butylstyrene and 4-Acetoxystyrene with Different Compositions

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**Method to synthesize the P(TBS-*r*-AS) copolymers**

4-*tert*-butylstyrene (TBS, 90% purity) and 4-acetoxystyrene (AS, 98% purity) were purchased from J & K Scientific Ltd. and purified by chromatography with an alkaline alumina column (100-200 mesh particle size). Azobis(isobutyronitrile) (AIBN, 98% purity) was purchased from Aladdin Chemical Co., Ltd. and purified by recrystallization twice from methanol. 4-cyano-4-(thiobenzoylthio) pentanoic acid (CTA, > 97% purity, purchased from Sigma-Aldrich) was used as received. All other reagents, such as tetrahydrofuran (THF) and absolute methanol were of analytical grade and used as received.

P(TBS-*r*-AS) with different $X_{TBS}$ from 0 to 1 were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Typically, suitable amounts of TBS, AS, CTA and AIBN were sequentially added into an ampoule bottle of 50 mL in an $N_2$ environment. The mixture was degassed with three freezing-evacuation-thawing cycles. After sealing, the mixture was heated to 50 or 80 ºC in an oil bath where polymerization took place. The reaction lasted for various amounts of time depending on the feeding of monomers, and was terminated by quenching with liquid $N_2$. The reaction product was diluted with THF and precipitated with absolute methanol thrice. After drying at 50 ºC under vacuum for 12 h, P(TBS-*r*-AS) copolymers in powder form resulted.

**Method to prepare the substrates and polymer films**

Silicon covered by a native oxide (SiOx) layer was used as substrate for the films, and prepared as follows. Firstly, silicon wafers were sonicated in deionized water for 15 min, then

immersed in a piranha solution at 90 °C for 20 min to remove the organic contaminants. Afterward, the wafers were sonic rinsed in deionized water four times, 5 min each time. After rinsing and nitrogen-drying, the wafers were further cleaned by oxygen plasma for 20 min. Polymer films were prepared by spin-coating solutions of polymer in toluene with concentrations of 0.5-10.0 wt % onto cleaned substrates at a spinning speed of 4500 rpm. Afterward, the films were annealed at 150 °C under a vacuum of ~1 Pa for various times of 1, 5 or 9 h.