

Supporting Information

for

Molecular Dynamics in Polystyrene Single Chain Nanoparticles

Panagiotis. A. Klonos[†], Nikolaos Patelis[‡], Emmanouil Glynos[§],

Georgios Sakellariou^{‡,*}, and Apostolos Kyritsis^{†,*}

[†] Department of Physics, National Technical University of Athens, Zografou Campus, 15780, Athens, Greece

[‡] Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15, Athens, 771, Greece

[§] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, Heraklion, Crete, 711 10, Greece

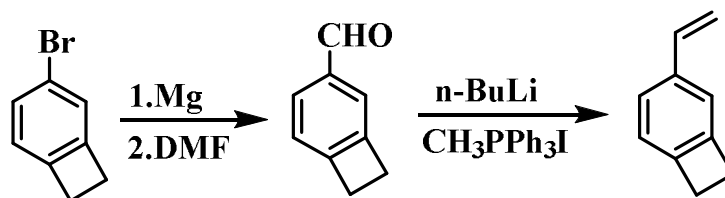
*Corresponding authors e-mail addresses: akyrits@central.ntua.gr (A.K.), gsakellariou@chem.uoa.gr (G.S.)

S1. Materials, synthesis and shape characterization of SCNPs

S1.1 Materials

All chemicals were purchased from Aldrich Chemical Co., except 4-bromobenzocyclobutene (97%), which was generously donated by the Dow Chemical Company. 4-Vinylbenzocyclobutene was

synthesized from 4-bromobenzocyclobutene (Scheme S1) as reported in the literature¹. The monomer was purified by distilling from CaH₂ on the vacuum line and was then stored in a schlenk flask. ¹H NMR (400 MHz, CDCl₃) δ : 7.27 (d, 1H, ArH), 7.2 (s, 1H, ArH), 7.05 (d, 1H, ArH), 6.73 (dd, 1H, CH), 5.7 (d, 1H, CH₂), 5.2 (d, 1H, CH₂), 3.22 (s, 4H, CH₂) (Figure S1).



Scheme S1: Synthesis of 4-Vinyl benzocyclobutene (4-VBCB).

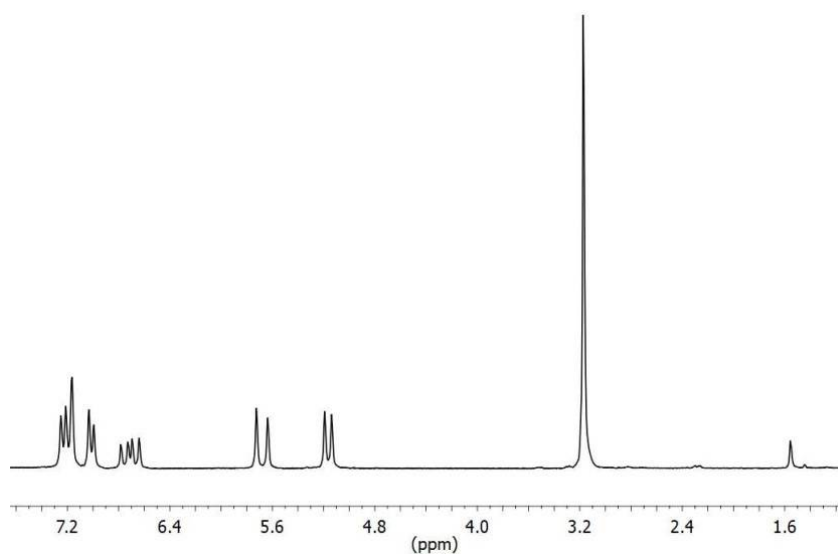


Figure S1. ¹H-NMR spectrum of 4-VBCB.

S1.2 Synthesis of random copolymer PS-co-PVBCB

Styrene (3.0 g, 28.84 mmol) and 4-VBCB (0.2 g, 1.5 mmol) ampoules were attached on a polymerization apparatus, containing the alkoxyamine initiator (7 mg, 0.022 mmol) and a stir bar. The apparatus was attached to the vacuum line, degassed three times and removed by heat sealing. Then, it was placed in an oil bath at 125 °C and the polymerization was allowed to proceed for 7h (Scheme 1).

The polymer product was dissolved in THF and precipitated into cold methanol, giving a white powder (~3.0 g). SEC eluogram and ^1H -NMR spectrum are shown in Figures S2 and S3, respectively.

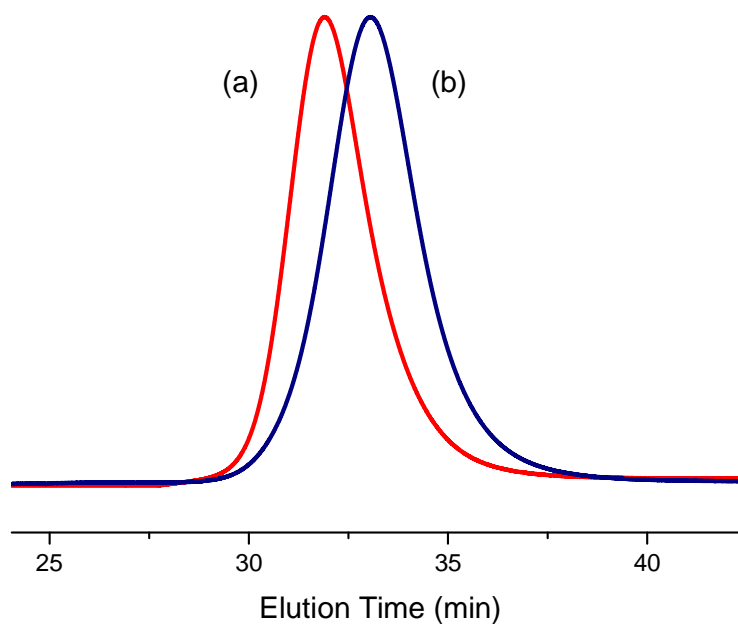


Figure S2. Size exclusion chromatography eluograms of (a) PS-*co*-P4VBCB linear polymer (entry number 2 at the Table 1 in the main article), and (b) the corresponding single chain nanoparticle.

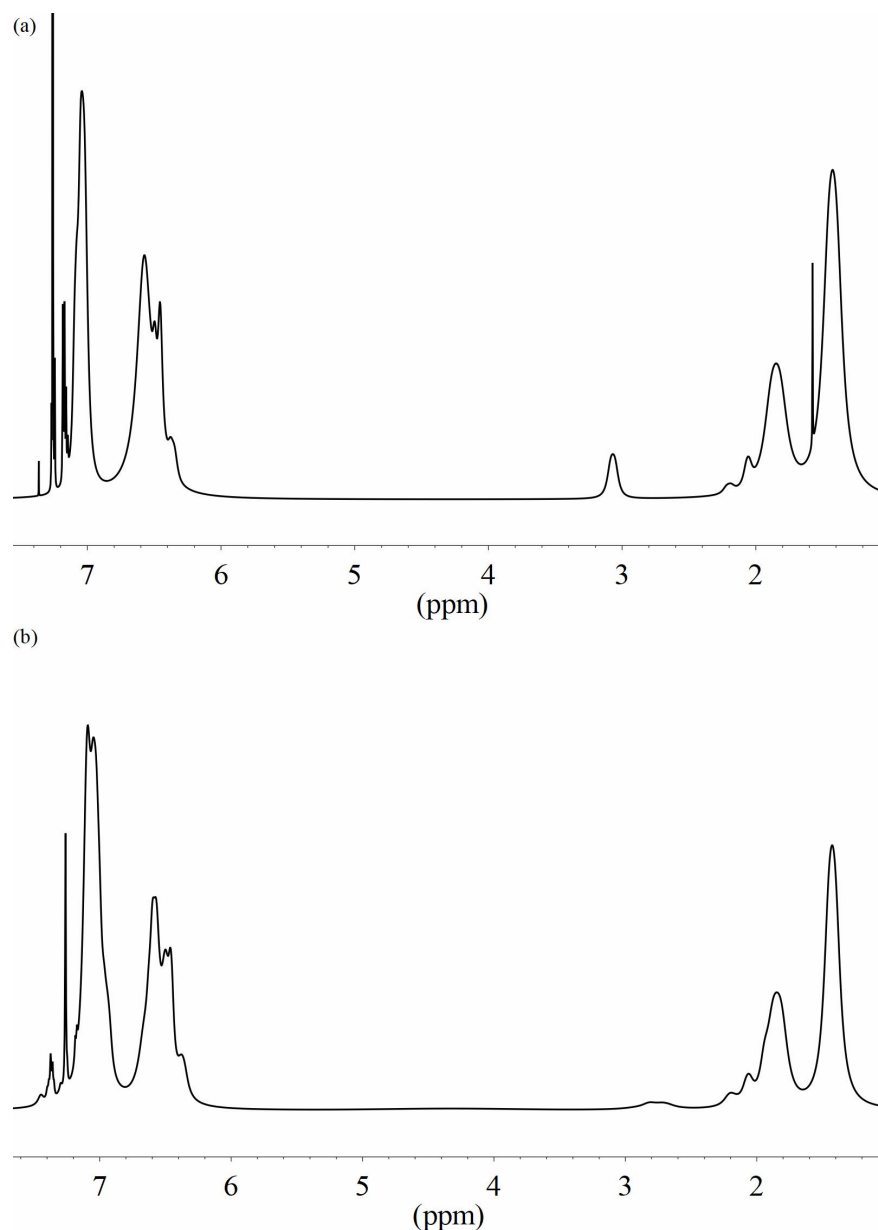
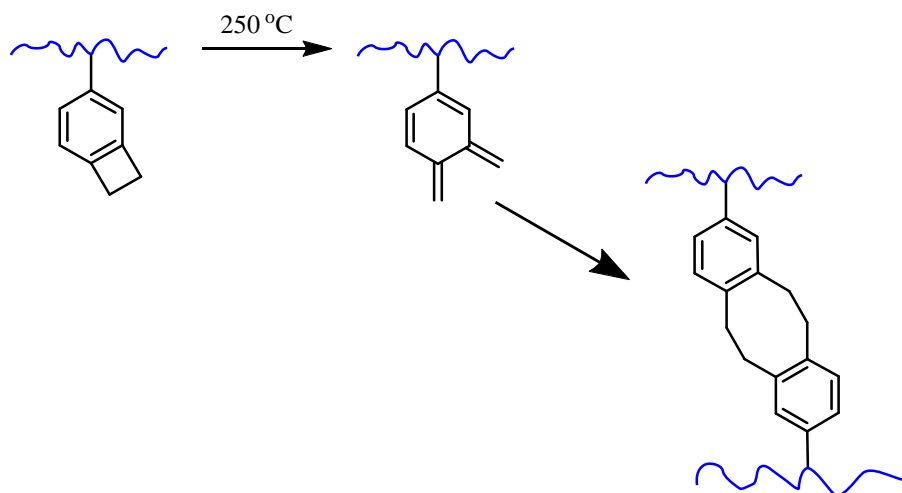


Figure S3. ^1H -NMR spectra of (a) PS-*co*-P4VBCB linear polymer (entry number 2 at the Table 1 in the main article), and (b) the corresponding single chain nanoparticle.

S1.3 Intramolecular cross-linking reaction, Scheme S2

In a 1liter four-necked round bottom flask equipped with an additional funnel, a condenser, an internal thermometer, and an inlet for argon, 600 mL of dry dibenzyl ether were added and heated at 250 °C in a silicone oil bath under constant argon flow. 0.3 gr of linear random copolymer, PS-*co*-PVBCB, ($M_n=140$ Kg/mol, PDI=1.2, entry number 2 at the Table 1 in the main article) diluted in 120

mL dibenzyl ether were added dropwise (30 mL/h) through the additional funnel under vigorous stirring². After complete addition, the solution has heated for an additional 1 ½ hrs. Subsequently, the solution was condensed under reduced pressure, dissolved in THF and precipitated in cold methanol (with powder). The single chains nanoparticles were dried in a vacuum oven overnight.



Scheme S2: Intramolecular coupling reaction of 4-Vinyl benzocyclobutene.

S2. Shape and size of the SCNPs

The PS precursors in dilute solutions adopt conformations like in Θ conditions (their hydrodynamic radius, R_h , scales with M_n like $R_h \sim M_n^{0.52}$ (Figure S4)), instead of expanded coil conformations in good solvents ($R_h \sim M_n^{0.59}$), while in the globular state $R_h \sim M_n^{0.33}$.

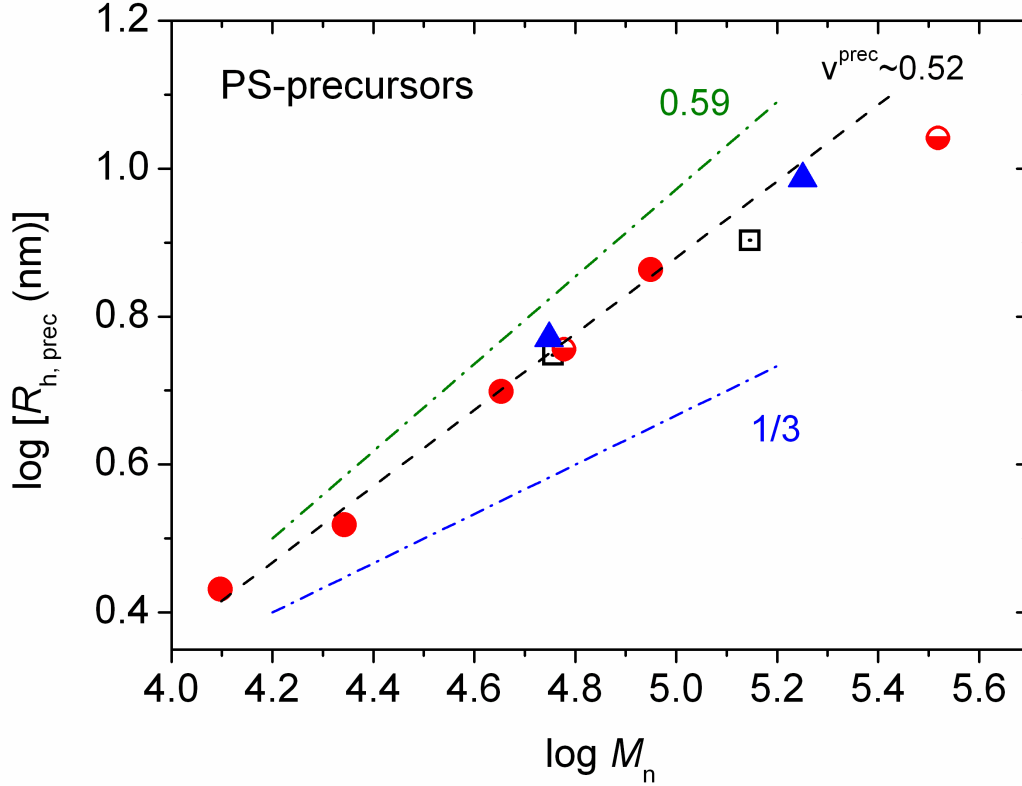


Figure S4. Molecular weight dependence of the hydrodynamic radius of PS precursors. The lines correspond to the power law dependence $R_{h, \text{prec}} \propto M_n^{v^{\text{prec}}}$. The experimental data reveal an exponent $v^{\text{prec}} = 0.52$ for the PS linear chains. The theoretical lines corresponding to exponents $v=0.59$ (ideal solution) and $v=1/3$ (globular state) are also included.

The SCNPs deviate from the shape characteristics of the precursors. The data in Table 1 and Figure S5 suggest that the SCNPs adopt less expanded conformations than PS linear precursors, since $R_{h, \text{SCLNP}} < R_{h, \text{precursor}}$ and $R_{h, \text{SCLNP}} \sim M_n^{0.46}$. Moreover, the data in Table 1 and Figure S5 imply that a few

SCNPs formed by short PS precursors ($M_n < 30k$) with ~25% CrF or by longer precursors ($M_n > 50k$) with ~45% CrF are close to the globular state.

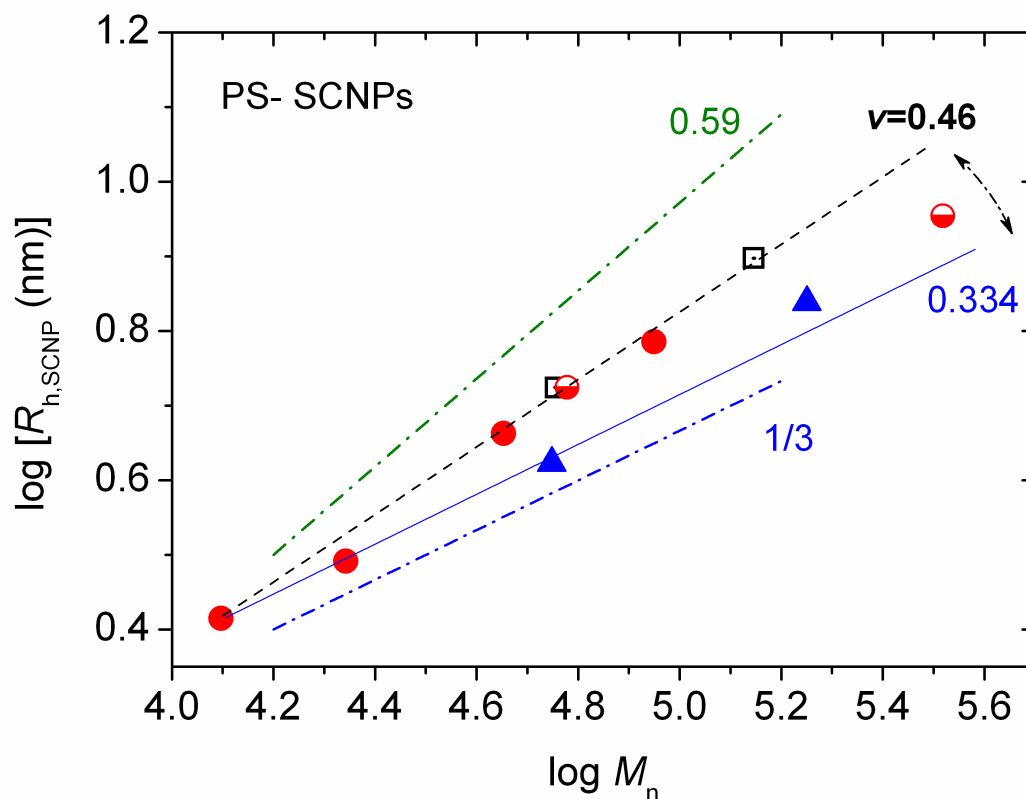


Figure S5. Molecular weight dependence of the hydrodynamic radius of PS SCNPs. The lines correspond to the power law dependence $R_{h,SCNP} \propto M_n^v$. The experimental data suggest an exponent $v = 0.46$ for the SCNPs. Careful sorting of the experimental points reveals that the experimental points may be considered as to follow two distinct power laws with exponent $v=0.46$ and 0.334 , respectively. The theoretical lines (dashed dot lines) corresponding to exponents $v=0.59$ (ideal solution) and $v=1/3$ (globular state) are also included.

S3. Additional DSC data

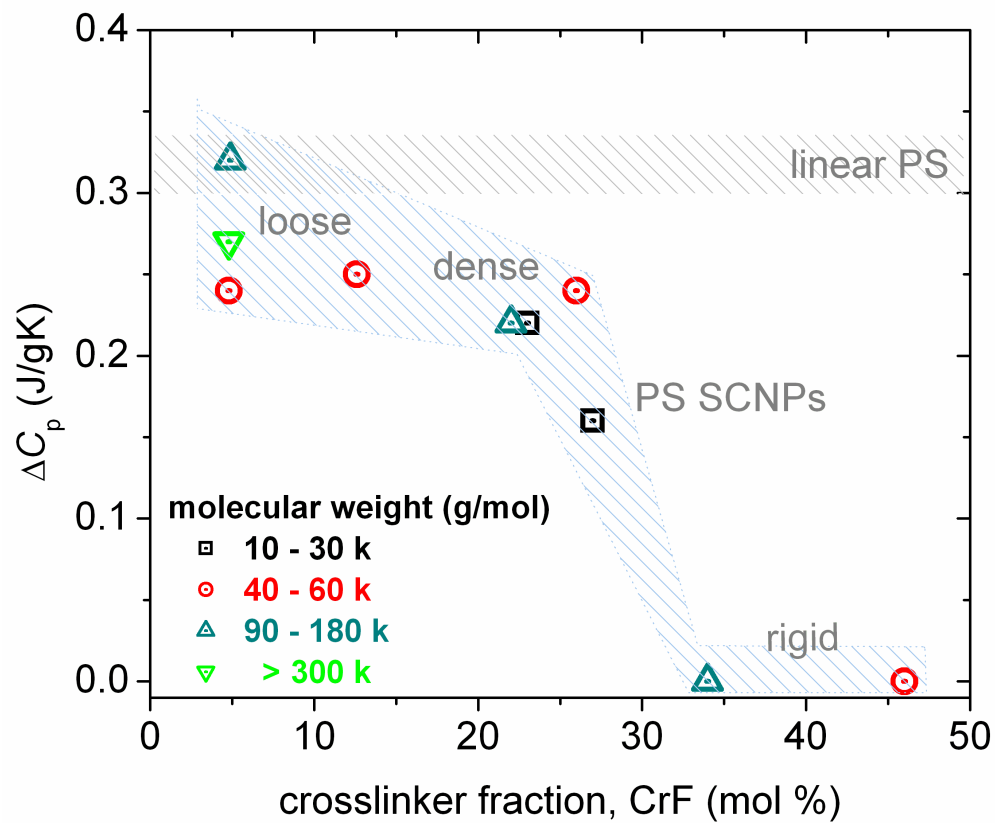


Figure S6. Heat capacity increment, ΔC_p , during glass transition in PS SCNPs against the fraction of crosslinker, CrF, and the molecular weight of the linear PS precursors. The shadow areas mark the values obtained on PS precursors of various M_n s and on SCNPs, respectively.

S4. BDS analysis data

Dielectric strength of segmental (α) and local-like (β^*) relaxation⁴

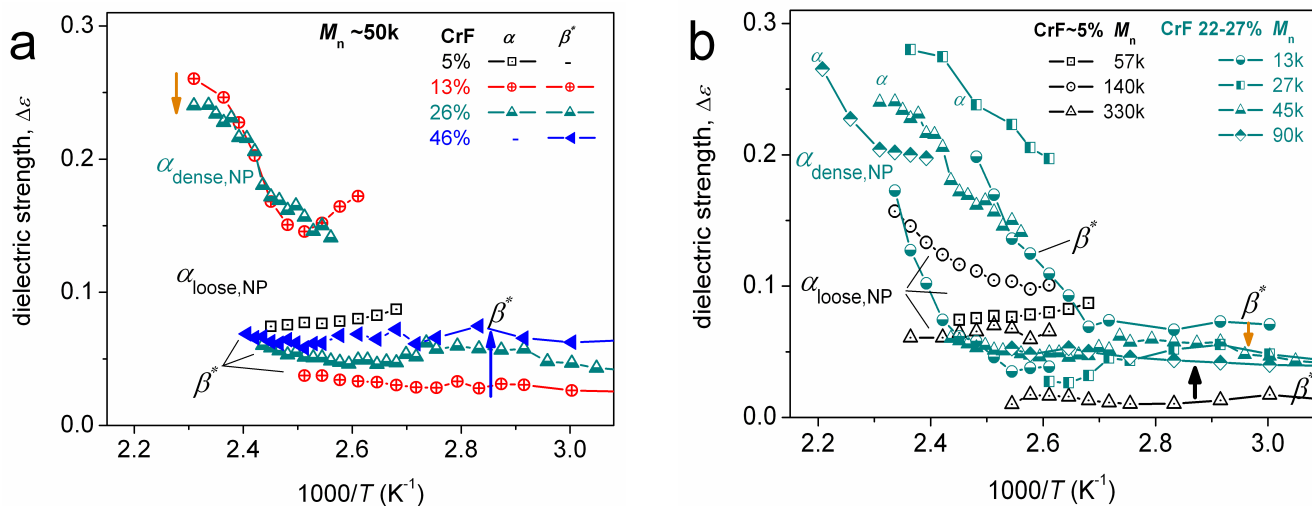


Figure S7. Dielectric strength, $\Delta\epsilon$, of the segmental (α) and local-like dynamics (β^*) relaxations for the SCNPs indicated on the plots.

HN shape parameter⁵ for the segmental α relaxation

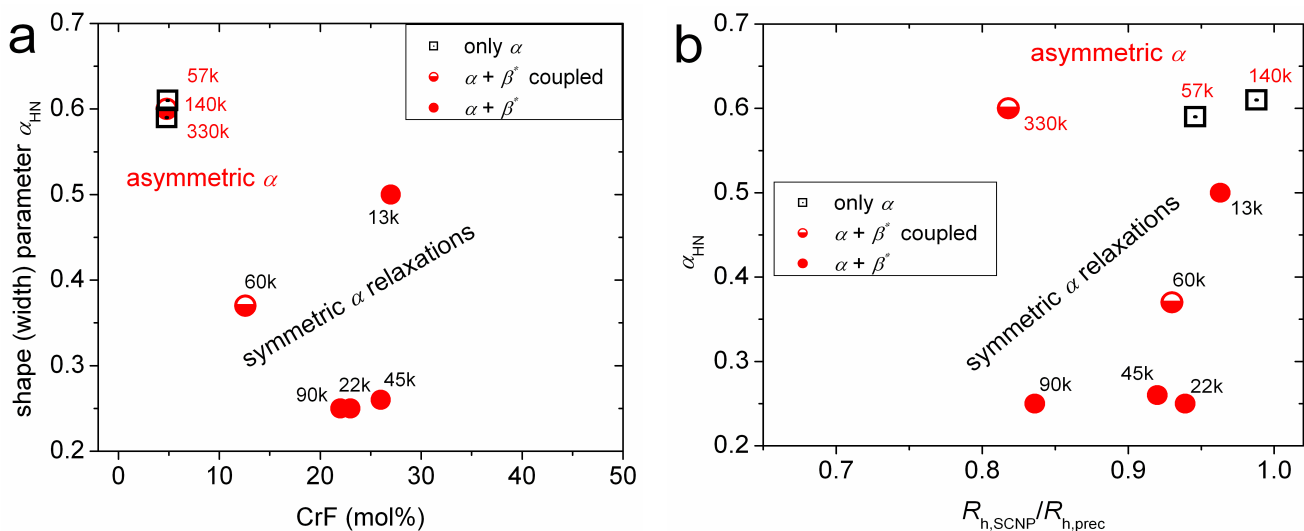


Figure S8. The Havriliak-Negami parameter connected with the broadening of the distribution of relaxation times, α_{HN} , for the segmental α process vs the crosslinker fraction (a) and the $R_{h,SCNP}/R_{h,prec}$ ratio (b). The MWs of the initial linear PS chains are indicated together with the notification for the symmetry of the distribution of the underlying molecular relaxation times.

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