Janus Long-Chain Hyperbranched Copolymer of PSt and POEGMA from Self-Assembly Mediated Click Reaction

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Synthesis of alkynyl-(PSt-N_3)$_2$ and alkynyl-(POEGMA-N_3)$_2$

Figure S1 shows ^{1}H-NMR spectrum of alkynyl-(PSt-N_3)$_2$. Two meso-protons of phenyl groups of styrene units have the signal in the range of 6.3~6.9 ppm. The signals of methylene protons and methine proton of PSt backbone are loacated in the range of 1.0~2.3 ppm. Importantly, the signal of methylene protons from propargyl group appears at 4.52 ppm and that of methine proton next bromo end-group at 3.94 ppm.

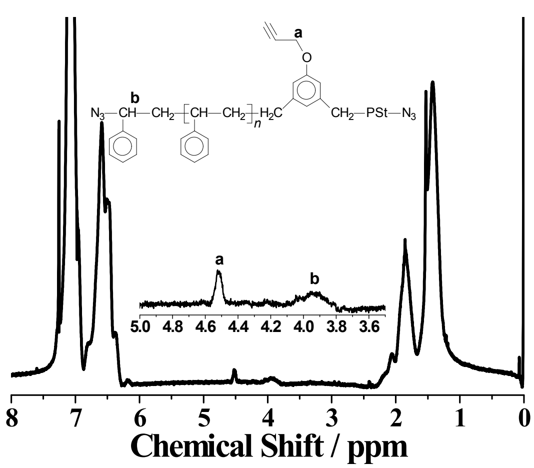

Figure S1. [1]H-NMR spectrum of alkynyl-(PSt-N_3)$_2$ seesaw macromonomer

POEGMA with one alkynyl group at the chain center and two azido groups at each chain end [alkynyl-(POEGMA-Br)$_2$] was prepared through atom transfer radical polymerization (ATRP) of OEGMA with PBMPMP as the initiator and the conversion of bromo end groups into azido end groups. Figure S2 shows [1]H-NMR spectrum of alkynyl-(POEGMA-N_3)$_2$. Based on the integral heights of the signal at 3.67 ppm (methylene protons from OEG) and that at 4.25 ppm (methylene protons from propargyl group), real number-averaged molecular weight ($M_{n,NMR}$) of alkynyl-(POEGMA-N_3)$_2$ is 15000.

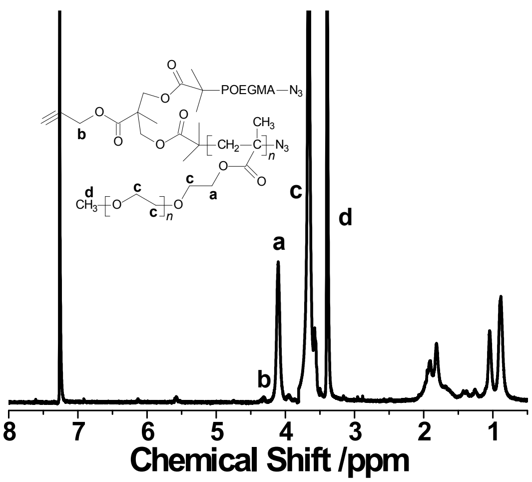

Figure S2. [1]H-NMR spectrum of alkynyl-(POEGMA-N_3)$_2$ seesaw macromonomer

Contact angle imaging of different copolymer films

Different *μ*-(PSt-N_3)$_2$(POEGMA-N_3)$_2$ films were obtained by casting real solution in THF and micelle dispersion in one selective solvent. Contact angles to water (CA_w) and oil (CA_o) were imaged with digital camera, as shown in Figure S3.

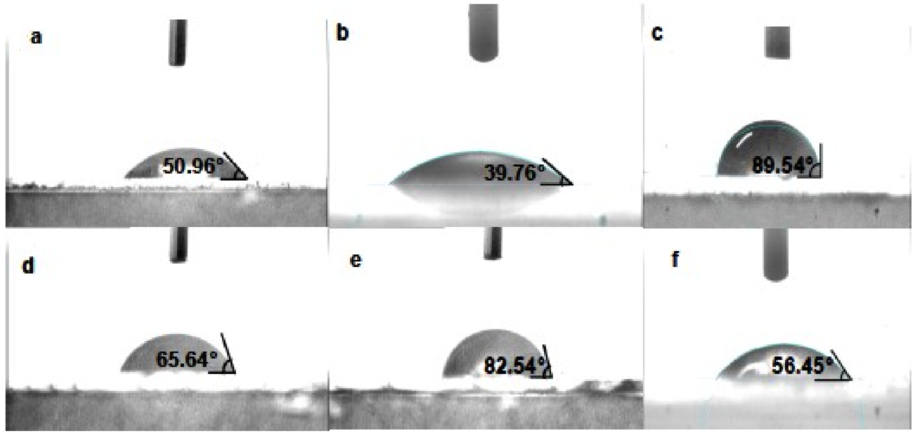

Figure S3. Contact angles of μ-(PSt-N_3)$_2$(POEGMA-N_3)$_2$ films casting from different solvents [CA_w: THF (a), methanol (b), cyclohexane (c); CA_o: THF (d), methanol (e), cyclohexane (f)]

Camera images of different μ-(*lhb*-POEGMA)(PSt-N_3)$_2$ films are shown in Figure S4.

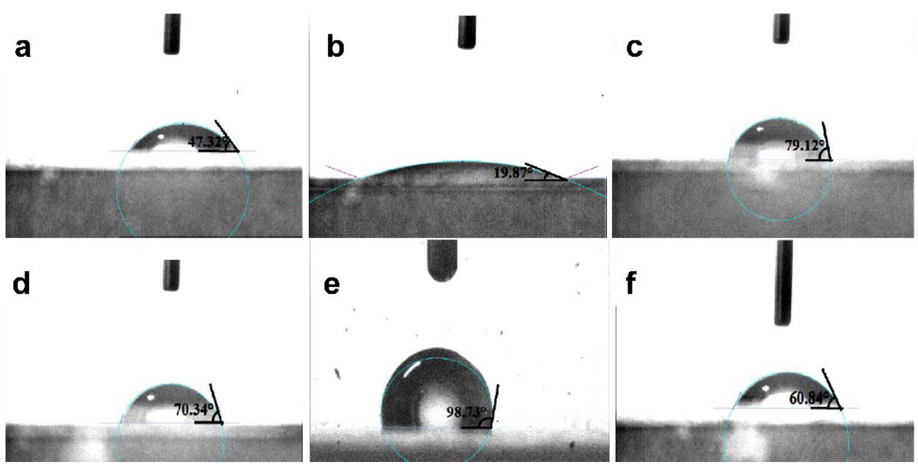

Figure S4. Contact angles of μ-(*lhb*-POEGMA)(PSt-N_3)$_2$ films from THF (a: CA_w, d: CA_o), methanol (b: CA_w, e: CA_o) and cyclohexane (c: CA_w, f: CA_o)

Camera images of different μ-(*lhb*-POEGMA)(*lhb*-PSt) films are shown in Figure Ss.

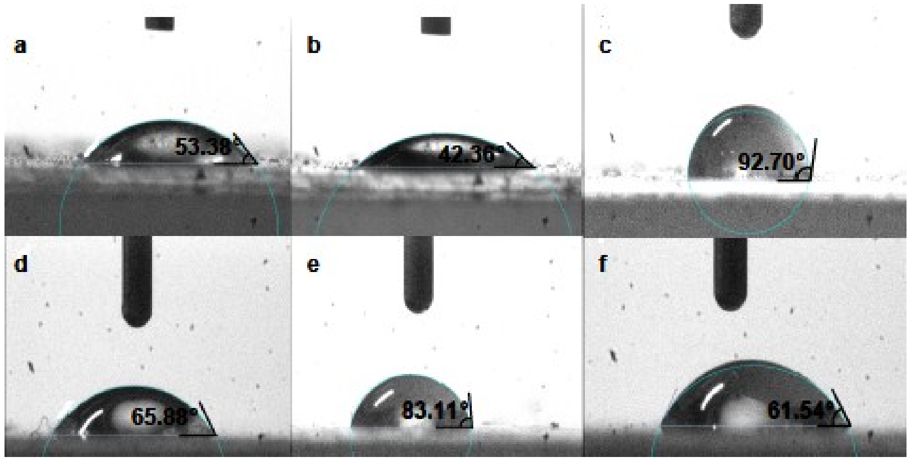

Figure S5. Contact angles of μ-(*lhb*-POEGMA)(*lhb*-PSt) films casting from different solvents THF (a: CA_w, d: CA_o), methanol (b: CA_w, e: CA_o) and cyclohexane (c: CA_w, f: CA_o)

Table S1. Contact angles of different copolymer films cast from different solvents

sample	THF		CH_3OH		cyclcohexane	
	CA_w	CA_o	CA_w	CA_o	CA_w	CA_o
μ-$(PSt\text{-}N_3)_2(POEGMA\text{-}N_3)_2$	50.0º	65.6º	39.8º	82.5º	89.5º	56.4º
μ-(*lhb*-POEGMA)$(PSt\text{-}N_3)_2$	47.3º	70.3º	19.9º	98.7º	79.1º	60.8º
μ-(*lhb*-POEGMA)(*lhb*-PSt)	53.4º	65.9º	42.4º	83.1º	92.7º	61.5º