Supporting Information

Synthesis and properties of couplable ABCDE star copolymers by orthogonal CuAAC and Diels-Alder click reactions

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Experimental section

Materials

All the monomers were purchased from Sigma-Aldrich, and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd unless otherwise stated. *N*-Isopropylacrylamide (NIPAM, 97%) was recrystallized twice from mixtures of hexane and toluene, *tert*-butyl acrylate (*t*BA, 98%) was passed through a basic alumina column to remove the inhibitor, *ε*-caprolactone (CL, 99%) was distilled from calcium hydride under reduced pressure, L-lactide (LLA, 99%) was recrystallized twice from toluene. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Stannous octoate ($Sn(Oct)_2$, 97%, Sigma-Aldrich), sodium azide (99%, Alfa Aesar), 1,8-diazabicycloundec-7-ene (DBU, 97%, Sigma-Aldrich), 2,2-bis(hydroxylmethyl) propionic acid (Bis-HMPA, 98%), 4-(chloromethyl)phenyltrimethoxysilane (95%, ABCR GmbH & Co. KG), 9-anthracenemethanol (97%, Accela ChemBio Inc), epichlorohydrin (99%), triphenylphosphine (96%), and succinic anhydride (99%, Aladdin) were used as received. 4-Cyanopentanoic acid dithiobenzoate (4-CPDB),[1] propargyl 5-cyano-5-phenylthiocarbonyl sulfanylpentanoyloxy-2-hydroxymethyl-2-methylpropanoate (PCP),[2] 5-methyl-5-allyloxy carbonyl-1,3-dioxan-2-one (MAC),[3] *N*-hydroxyethyl maleimide (HEMI),[4] 4-(2-(2,2-bis(hydroxyl methyl)propionyloxy)ethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (PMI-$(OH)_2$),[5] and azide- and alkyne-functionalized silica particles (with loadings of 0.612 mmol g^{-1} for Si-N_3 and 0.398 mmol g^{-1} for Si-Ak)[6,7] were synthesized and purified according to literature procedures.

Synthesis of 9-anthracenylmethyl 3-chloro-2-hydroxypropyl succinate (ACHS)

9-Anthracenemethanol (3.00 g, 14.4 mmol), succinic anhydride (1.50 g, 15.0 mmol), and dry toluene (100 mL) were added to a round flask under nitrogen, and the solution was subjected to reaction at 90 °C overnight. The solution was cooled down, and then epichlorohydrin (1.85 g, 20.0 mmol) and triphenylphosphine (0.10 g, 0.38 mmol) were added to the flask under nitrogen. The mixture was stirred at 110 °C for 30 h, and most of toluene and epichlorohydrin were removed by evaporation. The crude product was partitioned between DCM and water, and the organic layer was thoroughly washed with deionized water, collected and dried with $MgSO_4$ overnight. After purification by flash column chromatography eluting with hexane/DCM (2:1, v/v), ACHS (4.82 g, 83.5% yield) was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H, Ar*H*), 8.34 (d, *J* 8.8, 2H, Ar*H*), 8.04 (d, *J* 8.4, 2H, Ar*H*), 7.58 (t, *J* 6.4, 2H, Ar*H*), 7.50 (t, *J* 8.0, 2H, Ar*H*), 6.18 (s, 2H, ArCH_2O), 4.33 and 3.87 (m, 2H, CH_2O), 3.08 (m, 1H, C*H*OH), 2.76 and 2.58 (m, 2H, CH_2Cl), 2.67 (s, 4H, CH_2CH_2COO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.21, 171.78 (*C*=O), 131.18, 130.86, 129.11, 128.96, 126.57, 125.85, 125.00, 123.78 (Ar*C*), 64.97 (Ar*C*H_2O), 59.02 (*C*H_2O), 49.07 (*C*HOH), 44.44 (*C*H_2Cl), 28.96, 28.82 (*C*H_2CO). IR (KBr): 3451, 3063, 2998, 2966, 2932, 1736, 1623, 1524, 1475, 1446, 1413, 1374, 1359, 1335, 1248, 1208, 1152, 1132, 1060, 981, 960, 942, 896, 855, 787, 756, 737, 716, 631 cm^{-1}.

Synthesis of 2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)ethyl 5-cyano-5-phenylthiocarbonylsulfanylpentanoyloxy-2-hydroxymethyl-2-methylpropanoate (DCP)

PMI-$(OH)_2$ (2.40 g, 7.38 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 1.24 g, 6.0 mmol), 4-dimethylamino pyridine (DMAP, 25.0 mg, 2.0 mmol), and DCM (100 mL) were added to a round flask under nitrogen. The mixture was cooled with an ice-water bath, and followed by slow addition of 25 mL of DCM solution containing 4-CPDB (1.50 g, 5.37 mmol) in 1 h. The reaction mixture was warmed to ambient temperature and further stirred overnight. After filtration, the solution was thoroughly washed with deionized water and dried with $MgSO_4$. The crude product was purified by flash column chromatography eluting with hexane/DCM (3:1, v/v), and 2.16 g (68.6% yield) of DCP was obtained as a red-brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92, 7.58, 7.42 (m, 5H, Ph*H*), 6.52 (s, 2H, C*H*=C*H*), 5.29 (s, 2H, C*H*O), 4.2-4.5 (m, 4H, CH_2O), 3.5-3.9 (m, 4H, CH_2N and CH_2OH), 2.89 (s, 2H, C*H*C*H*), 2.3-2.8 (m, 4H, CH_2CH_2CO), 1.94 (s, 3H, CH_3CCN), 1.17 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 222.33 (*C*=S), 176.42, 176.28, 173.81 (*C*=O), 144.48, 133.05, 128.58, 126.66 (Ph*C*), 136.51 (*C*H=*C*H), 118.46 (*C*N), 80.94 (*C*HO), 66.31 (CH_2OCO), 64.97 (CH_2OH), 61.66 (NCH_2CH_2O), 48.39, 45.72 (CCH_3), 47.51 (*C*HCO), 37.97 (CH_2N), 33.30, 29.66 (CH_2), 24.12, 17.36 (CH_3). IR (KBr): 3455, 3058, 2929, 2851, 1775, 1733, 1697, 1627, 1589, 1538, 1445, 1430, 1401, 1364, 1336, 1312, 1286, 1193, 1153, 1048, 1019, 1000, 916, 878, 854, 764, 720, 689 cm^{-1}.

Preparation of anthracene-functionalized silica particles (Si-An)

To a slurry bearing activated flash silica (10 g) and toluene (100 mL) was added 4-(chloromethyl)phenyltrimethoxysilane (4.0 g, 15.4 mmol) under nitrogen, and the mixture was heated to 90 °C for 20 h. The benzyl chloride functionalized silica (Si-Cl) was filtered and thoroughly washed with toluene, THF and acetone, and 10.2 g of Si-Cl was isolated after vacuum drying. Based on the equation $G_p = (W_{\text{Si-Cl},100}/W_{\text{Si-Cl},600} - W_{\text{SiO2},100}/W_{\text{SiO2},600})/M_n(\text{g})$ (where $W_{\text{Si-Cl},T}$ and $W_{\text{SiO2},T}$ are the residual weight percent of Si-Cl and pristine SiO_2 at temperature of T, and $M_n(\text{g})$ is molecular weight of grafted moiety ($M_n(\text{g}) = 125.6$ g mol^{-1})), the loading of benzyl chloride was determined to be 0.774 mmol per g silica by TGA analysis.

9-Anthracenemethanol (1.04 g, 5.0 mmol), NaOH (0.18 g, 4.5 mmol), and DMF (25 mL) were added to a round flask, and the mixture was stirred at room temperature for 1 h. To the mixture was added 2.0 g of Si-Cl under nitrogen, and the reaction was conducted at 45 °C for 24 h. The anthracene-functionalized silica particles were filtered and thoroughly washed with deionized water, THF and acetone, and 1.9 g of Si-An was obtained after vacuum drying. On the basis of the equation of $G_p = (W_{\text{Si-An},100}/W_{\text{Si-An},600} - W_{\text{Si-Cl},100}/W_{\text{Si-Cl},600})/M_n(\text{g}))$ (where $W_{\text{Si-An},T}$ and $W_{\text{Si-Cl},T}$ are the residual weight percent of Si-An and Si-Cl at temperature of T, and $M_n(\text{g})$ is the molecular weight difference between benzyl chloride and 9-anthracenylmethyl benzyl ether ($M_n(\text{g}) = 171.8$ g mol^{-1})), the loading of anthracene moiety was estimated as 0.320 mmol per g silica (corresponding to 41% substitution).

Preparation of maleimide-functionalized silica particles (Si-MI)

3-Isocyanatopropyltriethoxysilane (1.24 g, 5.0 mmol), HEMI (0.706 g, 5.0 mmol), and dry toluene (10 mL) were added to a round flask under nitrogen. The mixture was heated to 50 ^{o}C for 30 h, and 0.5 mL of solution was drawn to check ^{1}H NMR spectrum of 2-(2,5-dioxo-2*H*-pyrrol-1(5*H*)-yl)ethyl 3-(triethoxysilyl)propylcarbamate (DETPC). The residual solution was added to a flask bearing 2.0 g of flash silica and 20 mL toluene, and the reaction was performed at 95 ^{o}C for 30 h. The crude product was filtered and thoroughly washed with toluene, THF and acetone, and 2.2 g of Si-MI was isolated after vacuum drying. The sample was subjected to TGA analysis, and the loading of maleimide was determined to be 0.537 mmol per g silica by using the equation $G_p = (W_{\text{Si-MI},100}/W_{\text{Si-MI},600} - W_{\text{SiO2},100}/W_{\text{SiO2},600})/M_n(\text{g})$ (where $W_{\text{Si-MI,T}}$ and $W_{\text{SiO2,T}}$ are the residual weight percent of Si-MI and pristine SiO_2 at temperature of T, and $M_n(\text{g})$ is molecular weight of grafted moiety ($M_n(\text{g})$ = 225.2 g mol^{-1})).

Synthesis of PCL (A)

ACHS (0.100 g, 0.250 mmol), CL (0.856 g, 7.50 mmol) and $Sn(Oct)_2$ (20.3 mg, 0.050 mmol) were added to an ampoule under nitrogen, and dry toluene was added until the total volume was 2.5 mL. The solution was deoxygenated with several standard freeze-pump-thaw cycles, and then the ampoule was flame sealed and placed in a stirred oil bath thermostated at 90 ^{o}C for 20 h. After removing toluene by evaporation, the crude product was dissolved in 20 mL of DMF. To the solution was added 0.18 g (2.76 mmol) of NaN_3, and the mixture was stirred at 50 ^{o}C for 48 h. After filtration, the filtrate was evaporated under reduced pressure to remove most of DMF, and the product was partitioned between DCM and water. The organic layer was repeatedly washed with deioniced water and dried with $MgSO_4$ overnight. After concentration and precipitation into methanol thrice, 0.930 g (97.0% yield) of PCL was obtained as white powders. Apparent number-average molecular weight ($M_{n,\text{GPC}}$) and polydispersity (PDI) of PCL estimated by GPC analysis were 5650 g mol^{-1} and 1.09, and the M_n value determined by ^{1}H NMR analysis ($M_{n,\text{NMR}}$) was 3830 g mol^{-1}.

PCL: ^{1}H NMR ($CDCl_3$): δ 8.53 (s, Ar*H*), 8.33 (t, *J* 8.4, Ar*H*), 8.05 (d, *J* 8.0, Ar*H*), 7.57 and 7.50 (m, Ar*H*), 6.19 (m, ArC*H*$_2$O), 3.8-4.5 (m, C*H*$_2$O of PCL, C*H*$_2$O and C*H*O), 3.65 (t, *J* 6.4, terminal C*H*$_2$OH), 3.42 (m, C*H*$_2$N$_3$), 2.67 (m, C*H*$_2$C*H*$_2$COO), 2.31 (t, *J* 7.6, C*H*$_2$CO of PCL), 1.65 (m, C*H*$_2$CH$_2$C*H*$_2$CH$_2$CO of PCL), 1.38 (m, CH$_2$C*H*$_2$CH$_2$CH$_2$CO of PCL). IR (KBr): 3441, 2946, 2895, 2866, 2100, 1725, 1633, 1471, 1420, 1398, 1367, 1295, 1243, 1189, 1109, 1047, 962, 934, 840, 733, 708 cm^{-1}.

Synthesis of P*t*BA-*b*-PLLA (BC)

PCP (86.7 mg, 0.200 mmol), *t*BA (2.56 g, 20.0 mmol), and AIBN (3.3 mg, 0.020 mmol) were added to a glass tube with a magnetic stirring bar, and toluene was added until the total volume was 6.7 mL. The tube was sealed with a rubber septum, and the contents were flushed with nitrogen for 20 min. The tube was subsequently immersed into an oil bath thermostated at 60 °C for 20 h. The reaction mixture was precipitated in methanol/water mixture, and 1.38 g (50.5% conversion) of P*t*BA was obtained after vacuum drying. GPC and NMR analyses: $M_{n,GPC}$ = 7320 g mol^{-1}, PDI = 1.06, and $M_{n,NMR}$ = 6590 g mol^{-1}. P*t*BA (B): ^{1}H NMR ($CDCl_3$): δ 7.96, 7.53, 7.37 (m, Ph*H*), 4.74 (s, CH≡CCH_2O), 4.33 and 4.27 (dd, *J* 10.0, CH_3CCH_2O), 3.71 (s, CH_2OH), 0.8-2.8 (m, C*H*, CH_2 and CH_3 originating from CTA and P*t*BA). IR (KBr): 3436, 2979, 2935, 2875, 1729, 1481, 1454, 1393, 1369, 1334, 1258, 1150, 1033, 909, 846, 801, 753, 690 cm^{-1}.

To a Schlenk tube were added P*t*BA (0.659 g, 0.100 mmol), LLA (0.721 g, 5.00 mmol) and Sn(Oct)$_2$ (8.1 mg, 0.020 mmol) under nitrogen, and toluene was added until the total volume was 2.5 mL. The tube was degassed by three freeze-pump-thaw cycles and then placed in an oil bath thermostated at 90 °C for 20 h. After precipitation into diethyl ether, 1.21 g (76.4% conversion) of P*t*BA-*b*-PLLA was obtained. GPC and NMR analyses: $M_{n,GPC}$ = 12800 g mol^{-1}, PDI = 1.08, and $M_{n,NMR}$ = 12100 g mol^{-1}. P*t*BA-*b*-PLLA (BC): ^{1}H NMR ($CDCl_3$): δ 7.96, 7.52, 7.37 (m, Ph*H*), 5.17 (m, C*H* of PLLA), 4.72 (s, CH≡CCH_2O), 4.37 and 4.23 (m, terminal C*H*OH of PLLA and CH_3CCH_2O), 0.7-2.8 (m, C*H*, CH_2 and CH_3 originating from CTA, P*t*BA and PLLA). IR (KBr): 3429, 2980, 2943, 2877, 1761, 1730, 1618, 1459, 1386, 1369, 1257, 1214, 1189, 1134, 1096, 1045, 922, 871, 846, 756, 692 cm^{-1}.

Synthesis of PNIPAM-*b*-PMAC (DE)

NIPAM (1.81 g, 16.0 mmol), DCP (0.117 g, 0.20 mmol) and AIBN (6.6 mg, 0.040 mmol) were added to a glass tube with a magnetic stirring bar, and dioxane was added until the total volume was 5.3 mL. The tube was sealed with a rubber septum, and the contents were flushed with nitrogen for 20 min. After polymerizing at 70 °C for 18 h, the polymer solution was precipitated in diethyl ether, and 1.29 g (64.8% conversion) of PNIPAM was isolated. GPC and NMR analyses: $M_{n,GPC}$ = 6300 g mol^{-1}, PDI = 1.08, and $M_{n,NMR}$ = 6240 g mol^{-1}. PNIPAM (D): ^{1}H NMR ($CDCl_3$): δ 7.96, 7.56, 7.39 (m, Ph*H*), 5.7-7.2 (m, C*H*=C*H* and N*H* of PNIPAM), 5.28 (s, C*H*O), 4.28 (m, CH_2O), 4.00 (s, C*H*NH of PNIPAM), 3.79 (t, *J* 4.8, CH_2N), 3.67 (m, CH_2OH), 2.90 (s, C*H*), 0.7-2.6 (m, other C*H*, CH_2 and CH_3 originating from CTA and PNIPAM). IR (KBr): 3302, 3071, 2973, 2934, 2876, 1651, 1545, 1459, 1387, 1367, 1328, 1243, 1172, 1130, 1061, 987, 926, 879, 840, 807, 689 cm^{-1}.

PNIPAM (0.624 g, 0.10 mmol), MAC (1.60 g, 8.0 mmol) and DBU (7.6 mg, 0.050 mmol) were added to a Schlenk tube under nitrogen, and dioxane was added until the total volume was 4.0 mL. The tube was degassed by three freeze-pump-thaw cycles and then placed in an oil bath thermostated at 70 ^{o}C for 18 h. After precipitation into diethyl ether, 1.39 g (47.9% conversion) of PNIPAM-*b*-PMAC was obtained. GPC and NMR analyses: $M_{n,GPC}$ = 13700 g mol^{-1}, PDI = 1.11, and $M_{n,NMR}$ = 13400 g mol^{-1}. PNIPAM-*b*-PMAC (DE): ^{1}H NMR ($CDCl_3$): δ 7.3-8.0 (m, Ph*H*), 5.8-7.2 (m, C*H*=C*H*, N*H* of PNIPAM, and C*H*=CH_2 of PMAC), 5.2-5.4 (m, C*H*O and CH=CH_2 of PMAC), 4.64 (s, OCH_2CH=CH_2 of PMAC), 4.1-4.5 (m, CH_2O of PMAC), 4.00 (s, C*H*NH of PNIPAM), 3.7-3.9 (m, CH_2N and terminal CH_2OH), 2.86 (s, C*H*), 0.8-2.7 (m, other C*H*, CH_2 and CH_3 originating from initiator, PNIPAM and PMAC). IR (KBr): 3430, 3078, 2973, 2936, 2878, 1738, 1649, 1548, 1461, 1385, 1369, 1266, 1171, 1153, 1132, 1052, 983, 928, 880, 840, 789, 691 cm^{-1}.

Synthesis of PCL-P*t*BA-PLLA-PNIPAM-PMAC (ABCDE) star

To a Schlenk tube were added PCL (0.192 g, 0.050 mmol), P*t*BA-*b*-PLLA (0.665 g, 0.055 mmol), PNIPAM-*b*-PMAC (0.737 g, 0.055 mmol) and 15.9 mL of DMF. The reaction mixture was degassed by three freeze-pump-thaw cycles, and then $Cu(PPh_3)_3Br$ (46.5 mg, 0.050 mmol) was added under nitrogen. The tube was subsequently immersed into an oil bath thermostated at 110 ^{o}C for 48 h, and 0.20 mL of solution was drawn to check GPC trace of crude product. To remove unreacted low component polymers, Si-Ak (0.42 g, 0.15 mmol of alkyne functionality), Si-N_3 (0.27 g, 0.15 mmol of azide functionality) Si-An (0.54 g, 0.15 mmol of anthracene functionality), and Si-MI (0.31 g, 0.15 mmol of maleimide functionality) were added to the tube under nitrogen, and the mixture was further vigorously stirred at 110 ^{o}C for 20 h. The mixture was cooled down, diluted with 100 mL of THF, and passed through an alumina column. The polymer solution was concentrated under reduced pressure and precipitated into cold methanol, and 1.25 g (85.1% yield) of ABCDE star was obtained. GPC analysis: $M_{n,GPC}$ = 24200 g mol^{-1}, PDI = 1.08. Number-average molecular weights determined by GPC-MALLS and ^{1}H NMR analyses were $M_{n,LS}$ = 30200 g mol^{-1} and $M_{n,NMR}$ = 29600 g mol^{-1}, respectively.

ABCDE star: ^{1}H NMR ($CDCl_3$): δ 7.0-7.9 (m, Ph*H*, Ar*H* and C*H*N), 5.91 (m, C*H*=CH_2 of PMAC), 4.9-5.7 (m, CH_2O, C*H* of PLLA, and CH=CH_2 of PMAC), 4.76 (m, C*H* connecting with aromatic ring and maleimide unit), 4.64 (s, OCH_2CH=CH_2 of PMAC), 3.6-4.5 (m, CH_2O, CH_2N, terminal C*H*OH and CH_2OH, CH_2O of PMAC and PCL, and C*H*NH of PNIPAM), 3.32 (m, COC*H*C*H*CON), 0.7-2.8 (m, other C*H*, CH_2 and CH_3 originating from initiator, PCL, P*t*BA, PLLA, PNIPAM and PMAC). IR (KBr): 3432, 3068, 2973, 2941, 2874, 1759, 1734, 1649, 1546, 1460, 1386, 1369, 1247, 1192, 1135, 1096, 1045, 983, 871, 845, 781, 735, 688 cm^{-1}.

Synthesis of PCL-PAA-PLLA-PNIPAM-PMAC (AB'CDE) star

To a solution of 300 mg of ABCDE star in 20 mL of DCM was added 0.30 mL of trifluoroacetic acid (TFA) under nitrogen, and the mixture was stirred at room temperature for 20 h. The solution was concentrated and precipitated into a large amount of hexane, and 250 mg of star copolymer bearing PAA (B') segment was obtained after vacuum drying.

AB'CDE star: ^{1}H NMR ($CDCl_3$): δ 7.0-7.9 (m, Ph*H*, Ar*H* and C*H*N), 5.91 (m, C*H*=CH_2 of PMAC), 4.9-5.7 (m, CH_2O, C*H* of PLLA, and CH=CH_2 of PMAC), 4.76 (m, C*H* connecting with aromatic ring and maleimide unit), 4.64 (s, OCH_2CH=CH_2 of PMAC), 3.6-4.5 (m, CH_2O, CH_2N, terminal C*H*OH and CH_2OH, CH_2O of PMAC and PCL, and C*H*NH of PNIPAM), 3.32 (m, COC*H*C*H*CON), 0.7-2.8 (m, other C*H*, CH_2 and CH_3 originating from initiator, PCL, PAA, PLLA, PNIPAM and PMAC). IR (KBr): 3434, 3088, 2976, 2942, 2878, 1757, 1732, 1678, 1654, 1547, 1460, 1386, 1371, 1205, 1138, 1046, 983, 929, 873, 840, 802, 723, 707 cm^{-1}.

Characterization

Apparent molecular weight ($M_{n,GPC}$) and polydispersity (PDI) of linear polymers were measured on a Waters 150-C gel permeation chromatography (GPC) using three MZ-Gel SDplus columns (pore size 10^3, 10^4 and 10^5 Å, with molecular weight ranges within 1000−2000000) with 10 μm bead size at 40 °C. DMF was used as an eluent at a flow rate of 1.0 mL min^{-1}, and the samples were calibrated with PMMA standard samples. Gel permeation chromatography with multiple angle laser scattering detection (GPC-MALLS) systems was used to determine number-average molecular weight ($M_{n,LS}$) and polydispersity (PDI) of star copolymer. GPC was conducted in THF at 35 ^{o}C with a flow rate of 1.0 mL min^{-1}. Three TSK-GEL H-type columns (pore size 15, 30 and 200 Å, with molecular weight range within 100–400000) with 5 μm bead size were used. Detection consisted of a RI detector (Optilab rEX), a multi-angle (14-145^{o}) laser light scattering (MALLS) detector (DAWN HELEOS) with the He-Ne light wave length at 658.0 nm, and on-line viscosity detector (ViscoStar). The refractive index increment d*n*/d*c* for samples were measured off-line by Optilab rEX refractive index detector (λ = 658 nm) at 25 °C using a series of different concentration solutions. Data were collected and processed by use of ASTRA software from Wyatt Technology, and molecular weights were determined by the triple detection method. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian spectrometer at 25 °C using $CDCl_3$ or DMSO-d_6 as a solvent. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 2000 spectrometer using KBr discs. Differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a Q200 DSC instrument (TA Instruments–Waters LLC) with a heating rate of 10 °C min^{-1}. Dynamic light scattering (DLS) measurements were carried out at 25°C using a Zetasizer Nano-ZS from Malvern Instruments equipped with a 633 nm He–Ne laser using back-scattering detection. Transmission electron microscopy (TEM) images were obtained through a Hitachi H-600 electron microscope.

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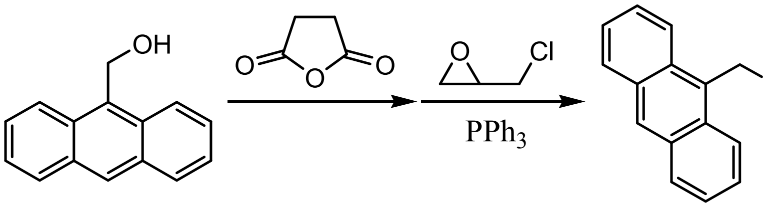
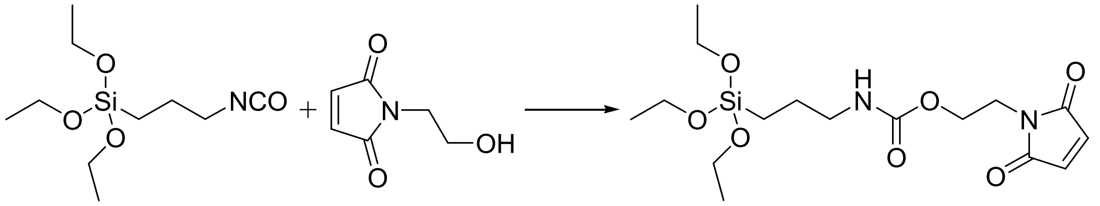
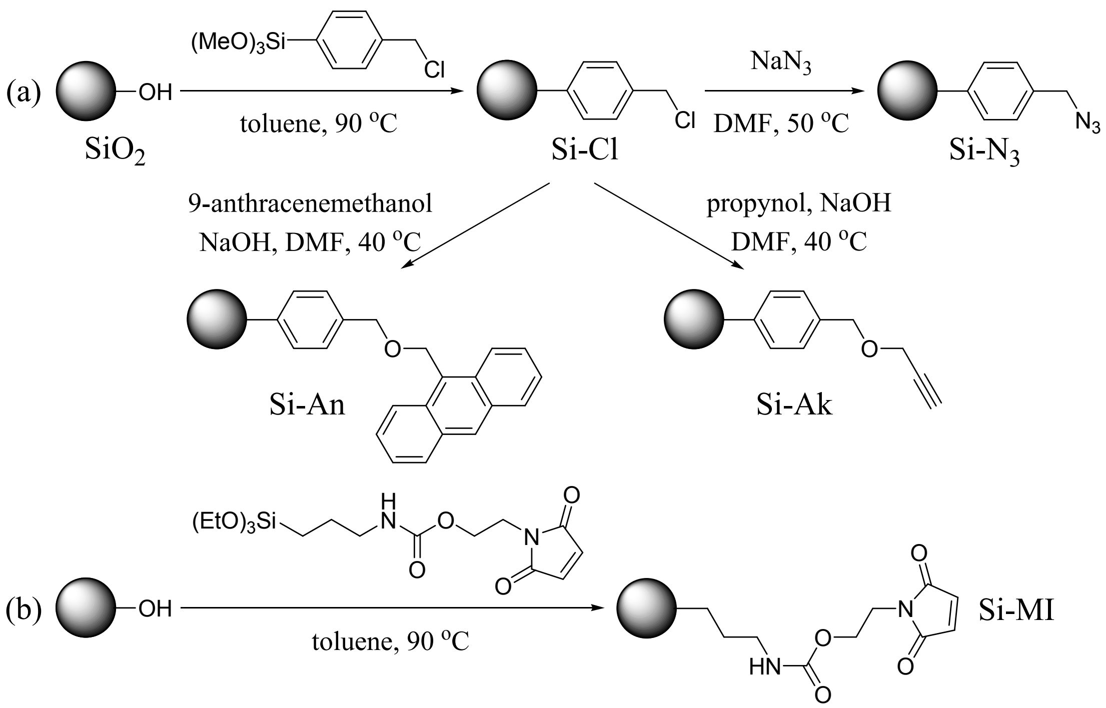


Scheme S1 Synthetic routes to 9-anthracenylmethyl 3-chloro-2-hydroxypropyl succinate (ACHS).



Scheme S2 Synthesis of 2-(2,5-dioxo-2*H*-pyrrol-1(5*H*)-yl)ethyl 3-(triethoxysilyl) propylcarbamate (DETPC).



Scheme S3 Synthetic routes to benzyl chloride (Si-Cl), azide (Si-N_3), alkyne (Si-Ak), anthracene (Si-An), and maleimide (Si-MI) tethered silica particles.

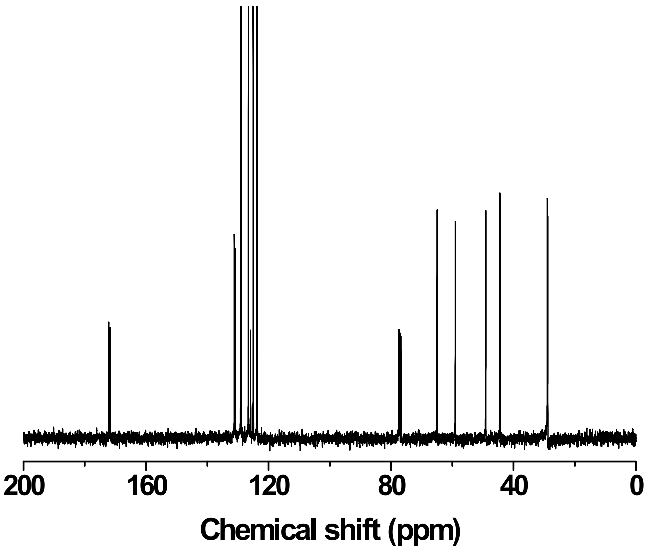


Fig. S1 ^{13}C NMR spectrum of ACHS.

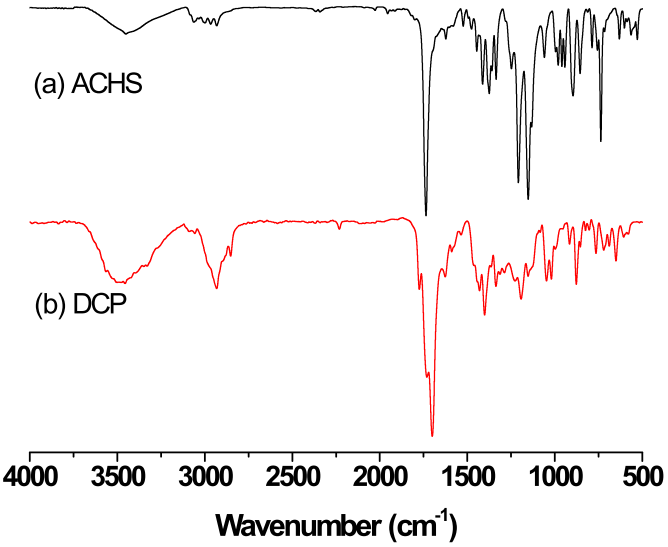


Fig. S2 IR spectra of ACHS and DCP.

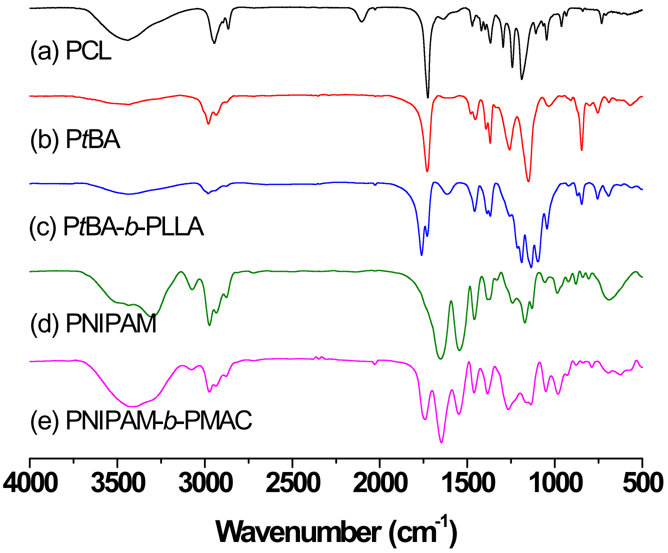


Fig. S3 IR spectra of various homopolymers and diblock copolymers.

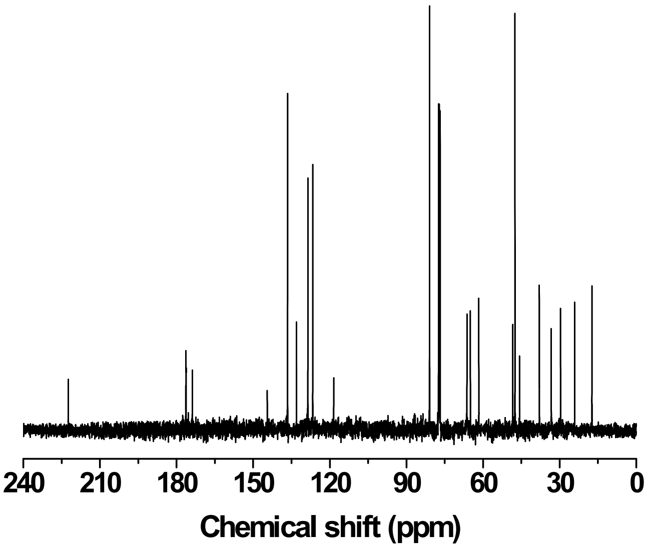


Fig. S4 ^{13}C NMR spectrum of DCP.

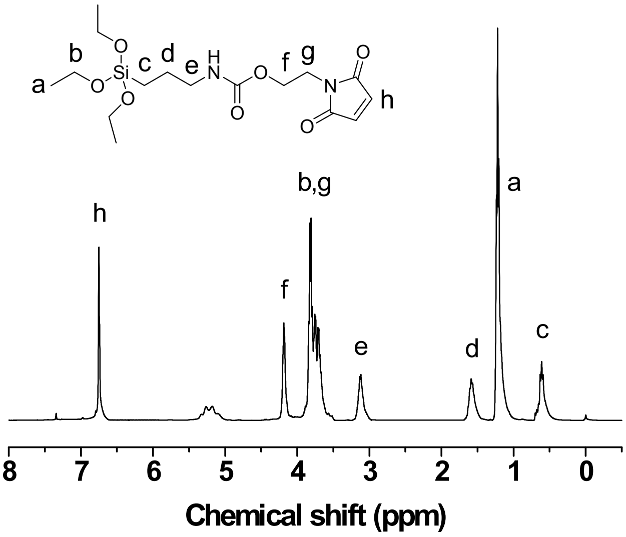


Fig. S5 ^{1}H NMR spectrum of 2-(2,5-dioxo-2*H*-pyrrol-1(5*H*)-yl)ethyl 3-(triethoxysilyl)propyl carbamate (DETPC).

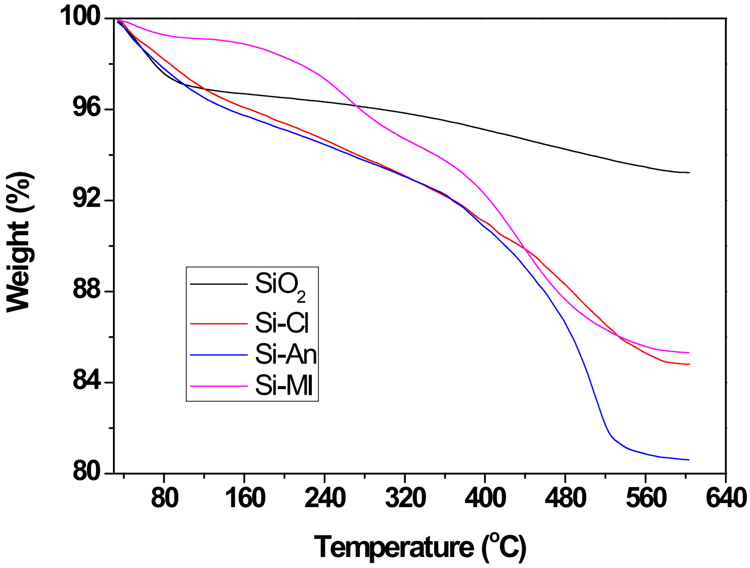


Fig. S6 TGA curves of pristine silica particles, benzyl chloride tethered silica (Si-Cl, 0.774 mmol g^{-1}), anthracenyl modified silica (Si-An, 0.320 mmol g^{-1}) and maleimide grafted silica (Si-MI, 0.537 mmol g^{-1}).

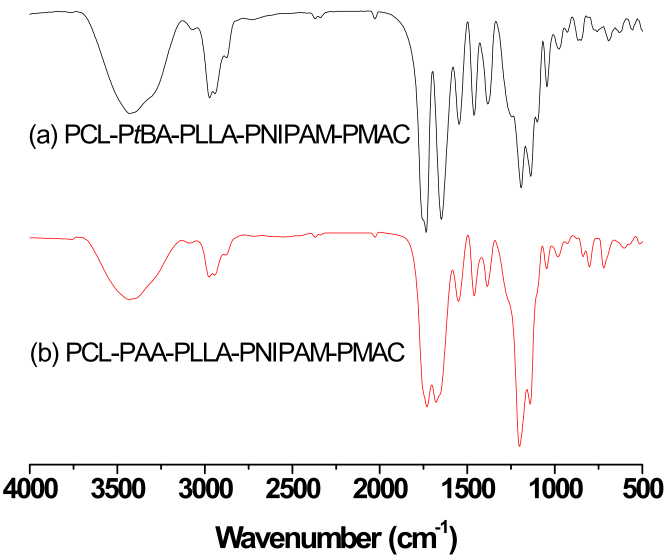


Fig. S7 IR spectra of ABCDE (a) and AB'CDE (b) star copolymers.

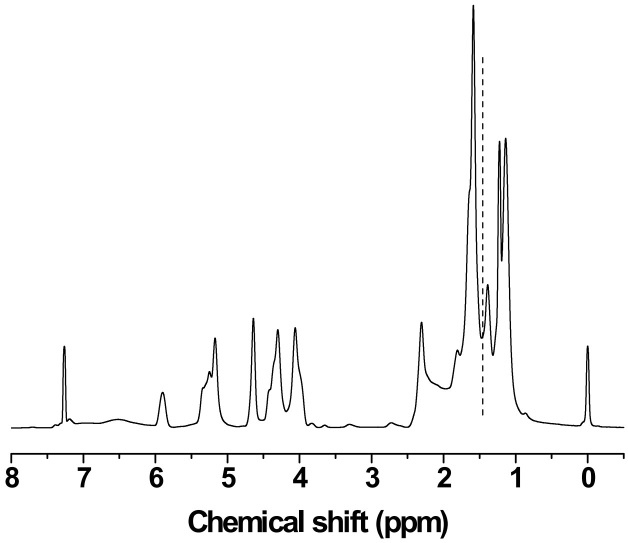


Fig. S8 ^{1}H NMR spectrum of PCL-PAA-PLLA-PNIPAM-PMAC (AB'CDE) star copolymer.