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One-pot polymer brush synthesis *via* simultaneous isocyanate coupling chemistry and "grafting from" RAFT polymerization

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SUPPORTING INFORMATION

Experimental

Materials. Unless otherwise stated, all materials were obtained from Sigma-Aldrich and used without any further purification. Benzyl amine (97%), toluene (99.5%), *N, N′*-dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino)pyridine (DMAP, ≥99%), and dicholoromethane (DCM, ≥99.8%) were all used as received. Dodecyl isobutyryl azide trithiocarbonate (DIAzTC) and isocyanate-terminated RAFT grown polystyrene were prepared according to conditions previously described in the literature.[1] Butyl dimethyl acetic acid trithiocarbonate (BDMAATC) was prepared by adapting a method described in the literature.[2] Styrene (≥99%) was de-inhibited by passing through basic alumina prior to use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Methods. *Gel Permeation Chromatograph (GPC).* Molecular weight analysis was also performed on a Shimadzu LC-20AD liquid chromatography system using a Jordi Gel DVB 500Å guard column (50×7.8 mm) followed by two PL gel, 5 μm, MIXED-C (300×7.5 mm) columns. THF, heated to 40 °C, was used as an eluent with a flow rate of 1.0 mL·min^{-1} and with 0.5 vol% toluene as a flow rate marker. Polystyrene standards were used to calibrate the system. Samples were filtered through a polytetrafluoroethylene (PTFE) membrane with a 0.2 μm pore size before injection (100 μL sample volume). Experimental molar mass ($M_{n,SEC}$) and dispersity ($Đ$) values of the synthesized polymers were determined by conventional calibration using ASTRA for Windows software (Version 6.90.08) with known RI detector calibration constant.

As can be seen in Figure S1, the α-isocyanate terminated PS generated during the solution polymerization of styrene monomer with DIAzTC RAFT agent resulted in a monomodal polymer with

dispersity (*Đ*) of 1.12 and a M_n of 9,300 g/mol. This shows the highly controlled nature of the carbonyl azide RAFT agent when the polymerization reaction is free from moisture which could result in side reactions with the in situ generated isocyanate group.

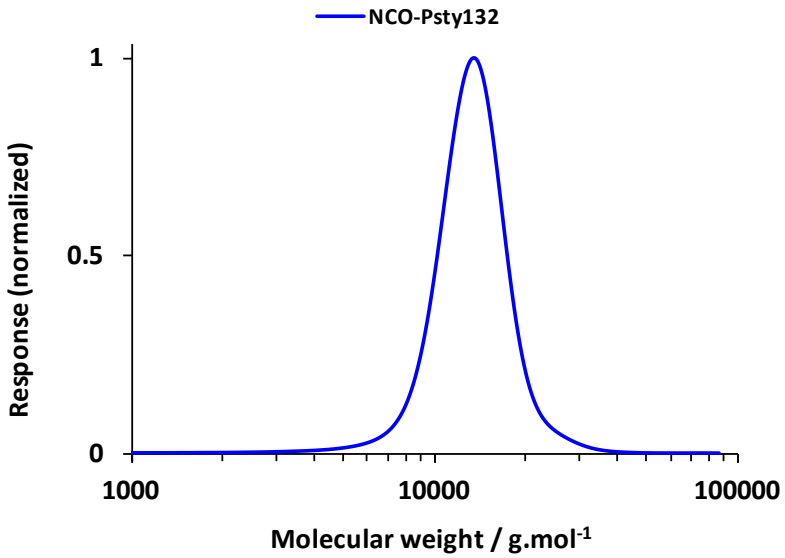


Figure S1. GPC analysis of polystyrene generated using DIAzTC RAFT agent.

NMR Spectroscopy. ^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) solvent on a Bruker Avance 200 working at 200 MHz. All chemical shifts were reported in ppm (δ). The α-isocyanate terminated PS generated was used in the benzyl amine coupling reactions. Figure S2 shows the ^{1}H NMR of the resulting coupled polystyrene. The urea linkage formed from the coupling of the terminal isocyanate group from the polystyrene and the amine of the benzyl amine is evident (δ of 4.0 and 3.89 ppm). Furthermore, by integrating this group relative to the methylene group of the benzyl amine we were able to determine the coupling efficiency of the reaction. Comparing the integrals showed that the coupling reaction had roughly a 96% efficiency, proving that the terminal isocyanate group is highly reactive towards primary amine functional groups.

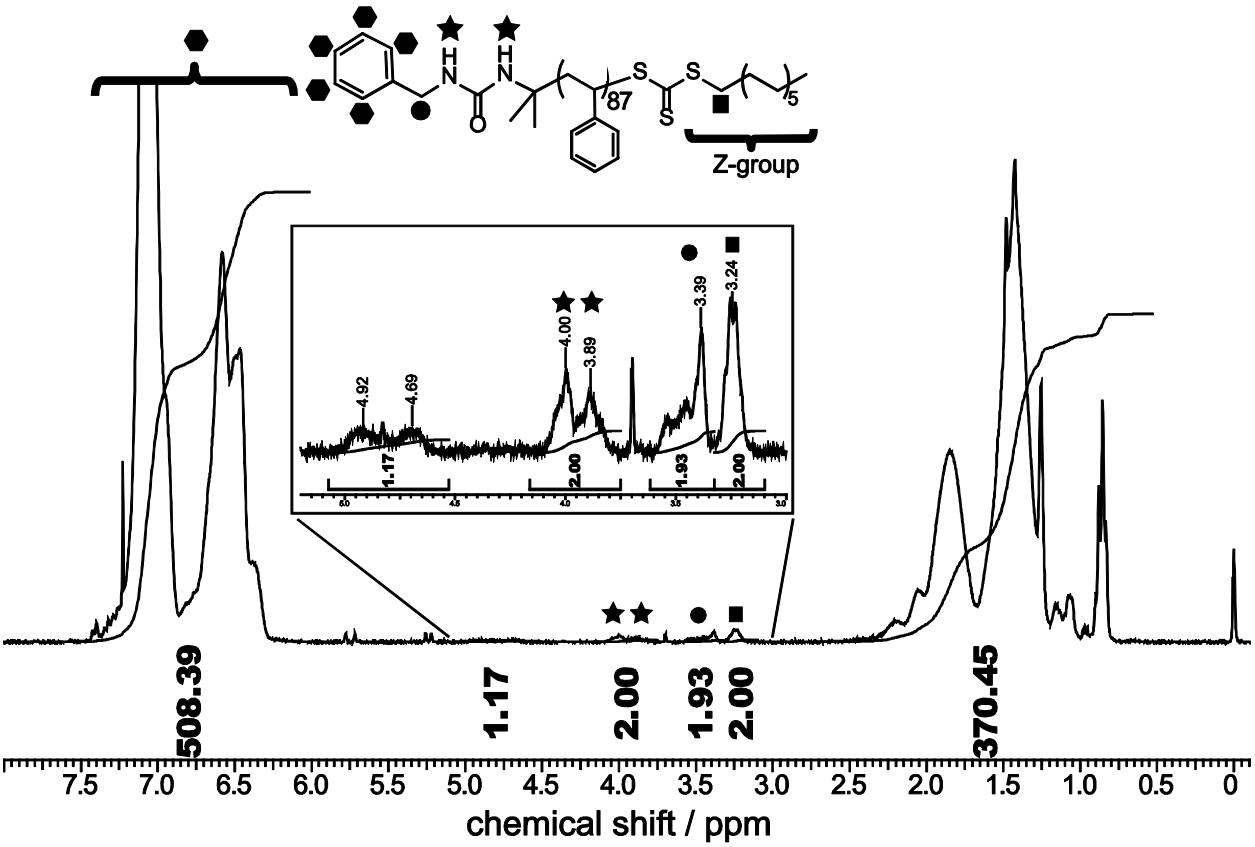
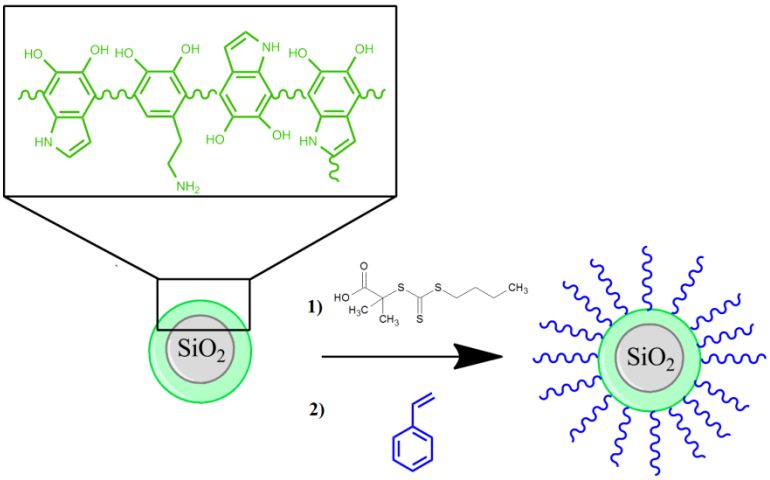


Figure S2. ^{1}H NMR spectrum of the precipitated polystyrene obtained after one-pot RAFT/benzyl amine-isocyanate coupling (DP_{NMR} = 87 = 508 / 5 * 0.86 (theoretical fraction of chains possessing the CH_2 from the Z-group). Yield of the coupling = 1.93 / 2 * 100 ≈ 96%

Traditional 'grafting from' RAFT Polymerization of Styrene in the Presence of PDA Surfaces. Polydopamine particles (0.1 g), BDMAATC (6.51×10^{-2} g, 2.6×10^{-4} mol), DCC (5.9×10^{-2} g, 2.86×10^{-4} mol) and DMAP (3.17×10^{-3} g, 2.6×10^{-5} mol) were combined in a flask with 20 mL anhydrous DCM. The mixture was stirred at 30 °C overnight. The resulting mixture was washed with tetrahydrofuran, acetone and dichloromethane and filtered to capture the particles. After drying in a vacuum oven at 40 °C for four hours, ATR-FTIR analysis was completed to confirm the successful deposition of the BDMAATC RAFT agent on the surface of the polydopamine particles.

The BDMAATC modified polydopamine particles (0.1g) were placed in a flask and degassed under vacuum for 20 minutes. Extra BDMAATC RAFT agent (6.51×10^{-2} g, 2.6×10^{-4} mol) was added to a second flask along with styrene (6.931 g, 6.65×10^{-2} mol) and AIBN (8.7×10^{-3} g, 5.3×10^{-5} mol). This flask was degassed by bubbling nitrogen through the solution for 20 minutes prior to cannula transfer to the flask containing the RAFT

modified particles. The polymerization proceeded for 21h at 65 °C, then the solution was removed from heat and the particles washed with THF, filtered, and dried in a vacuum oven at 40 °C for four hours. The free polymer, collected from the filtered solution after removing the solvent under vacuum, was analyzed using GPC while the polystyrene grafted particles were analyzed using ATR-FTIR and TGA.



Scheme S3. Traditional 'grafting from' PS brush synthesis. (1) BDMAATC RAFT agent was coupled to PDA particles using DCC coupling reaction followed by (2) surface initiated RAFT polymerization of styrene.

As can be seen from Figure S4, the 'free' polystyrene generated during the 'grafting from' polymer brush reactions using surface bound BDMAATC RAFT agent has a comparable molecular weight and dispersity (M_n = 11,900 g/mol and $Đ$ = 1.14) to that generated by the carbonyl-azide RAFT agent during the one-pot 'grafting from' polymerization process. This is critical for determining polymer brush grafting densities and ensuring that the comparison between a traditional 'grafting from' process and this new one-pot 'grafting from' process are on an even footing. Figure S5 depicts the ATR-FTIR spectra of the BDMAATC RAFT surface modified particles as well as the subsequent polystyrene brushes. The thermogravimetric analysis of these brushes resulted in a weight loss of 35% due to the PDA and polymer brush layers. This weight loss data equates to a grafting density of 0.31 chains/nm^2 when using the grafting density equation.

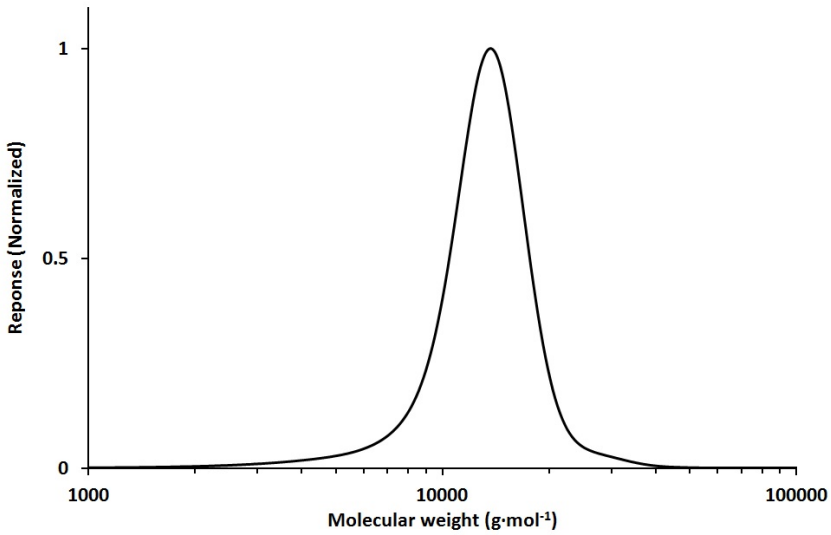


Figure S4. GPC analysis of polystyrene generated using BDMAATC RAFT agent during 'grafting from' brush synthesis.

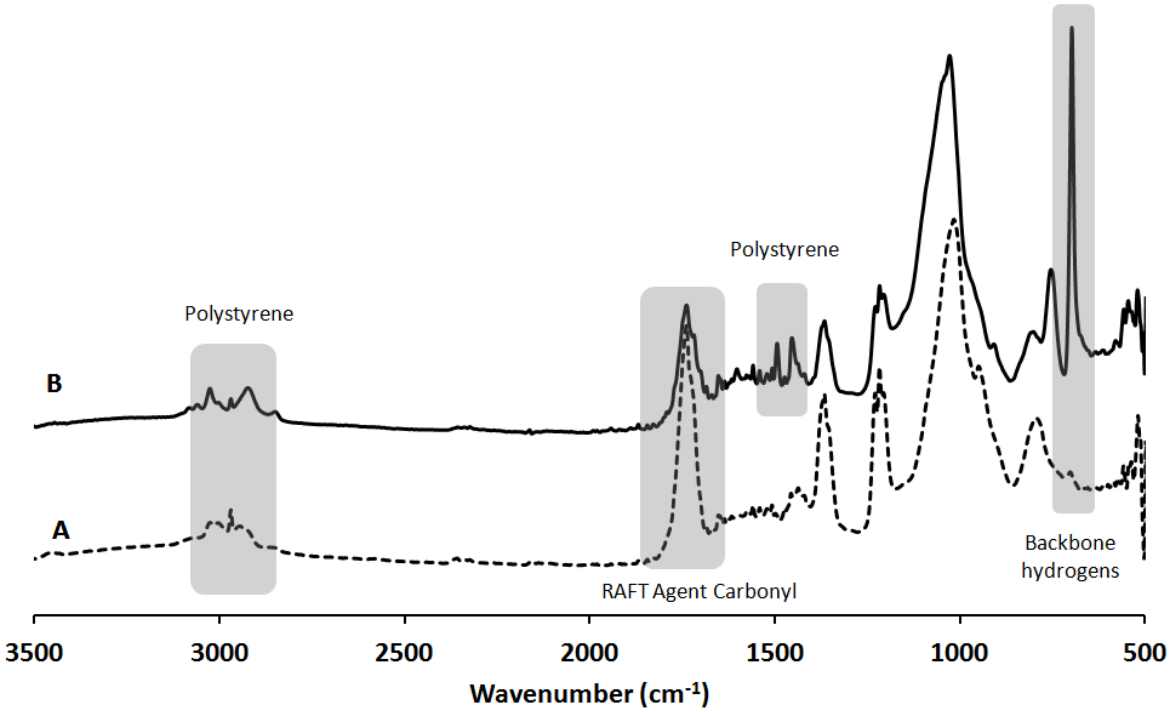


Figure S5. ATR-FTIR analysis of (A) BDMAATC RAFT agent bound to PDA particles and (B) 'grafting from' polymer brush synthesis of polystyrene.

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[1] Gody, G.; Rossner, C.; Moraes, J.; Vana, P.; Maschmeyer, T.; Perrier, S. *J. Am. Chem. Soc.* **2012**, *134*, 12596.
[2] Convertine, A. J.; Lokitz, B. S.; Vasileva, Y.; Myrick, L. J.; Scales, C. W.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2006**, *39*, 1724.