

Supporting Information

**Successful Synthesis of Distinct Dendritic
Unimolecular Initiators Suitable for Topologically
Attractive Star Polymers.**

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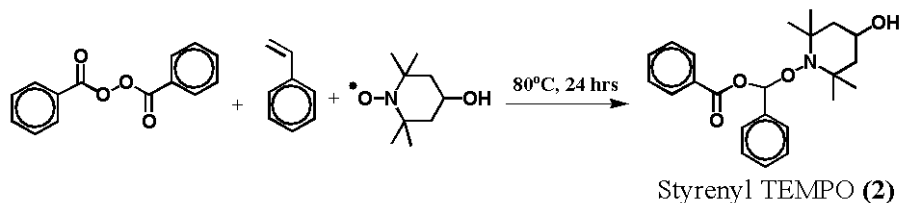
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Experimental Section:

Materials and Measurements. Blocked isocyanate-terminated G1, G2, G3 and G4 polyurethane dendrimers were prepared according to our very recent report^{26b}. Unimolecular initiator **1** was prepared according to a literature method²⁴. 2,2,6,6-Tetramethylpiperdinyloxy (TEMPO) (Sigma-Aldrich), 4-hydroxy TEMPO (Sigma-Aldrich) and dibutyltin dilaurate (DBTDL) (Sigma-Aldrich) were used as received. Benzoyl peroxide (Loba), styrene (Alfa-aesar), N,N'-dimethylformamide (Merck), tetrahydrofuran (Merck) and toluene (Merck) were purified using standard procedures.

Measurements. FT-IR spectra were recorded by the KBr pellet method on a ABB MB3000 instrument. High resolution mass spectra were recorded using a Q-TOF-Mass Spectrometer. NMR spectra were recorded on a Bruker AV 500 (¹H NMR: 500 MHz; ¹³C NMR 125 MHz) or a Bruker AV 400 (¹H NMR: 400 MHz; ¹³C NMR 100 MHz) or a Bruker AV 300 (¹H NMR: 300 MHz; ¹³C NMR 75 MHz). Chemical shift values (δ) were given in ppm and were calibrated on residual non-deuterated solvent peaks (CDCl₃: ¹H NMR: 7.26 ppm, ¹³C NMR: 77.0 ppm; DMSO-*d*₆: ¹H NMR: 3.43, 2.54 ppm, ¹³C NMR: 39.5 ppm) as internal standard. MALDI-TOF MS spectra were recorded by positive mode on a Bruker Ultra flex instrument using dithranol as matrices. The absolute molecular weight of dendritic unimolecular initiators were determined using SEC-MALLS at 60°C (SEC: Shimadzu LC-20AD, Shimadzu DGU-20A3R and two numbers of PL gel 5 μ m MIXED-C column. MALLS: Wyatt mini DAWN TREOS and Wyatt Optilab rEx). DMF containing 0.1mol/l of lithium bromide was used as eluents. In the case of polymers, the SEC-MALLS experiments were carried out at room temperature using stabilized THF as eluent. The nitrogen content of the compounds was estimated using KELPLUS (Pelicon) nitrogen estimation system.

Synthesis of styrenyl-TEMPO (Unimolecular initiator) (2). To a solution of benzoyl peroxide (2 g, 6.2 mmol) in distilled styrene (100 mL) was added 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-hydroxy TEMPO) (3 g, 18.2 mmol) and the solution was heated at 80°C under nitrogen for 24 hours. After cooling to room temperature, the solution was evaporated to dryness and purified by column chromatography initially eluted with pure hexane and then polarity of the eluent was gradually increased to 1:20 ethyl acetate/hexane to give the product, as a pale yellow powder. Yield (58.9%), M.p:38-40°C, IR (KBr, cm^{-1}) 3510 (-OH), 1697 (C=O), 1540 (C-O-C), 1265 (N-O). ^1H NMR (300 MHz, CDCl_3): δ 7.93-7.26 (m, 10H), 5.07-5.04 (s, 1H), 4.85-5.80 (m, 1H), 4.55-4.49 (m, 1H), 1.50-1.06 (m, 18H), ^{13}C NMR (75 MHz, CDCl_3): 166.36, 140.68, 132.83, 130.20, 129.57, 128.28, 128.05, 127.62, 83.94, 40.41, 34.07, 29.71, 17.15. Calcd: $[\text{M}]^+$ $m/z = 397.2253$. Found: HR-MS = 397. Nitrogen content for $\text{C}_{23}\text{H}_{29}\text{NO}_4$: Calcd: 3.65%; Found: 3.55%



Scheme S1: Synthesis of unimolecular initiator (Styrenyl-TEMPO) suitable for anchoring on polyurethane dendrimer.

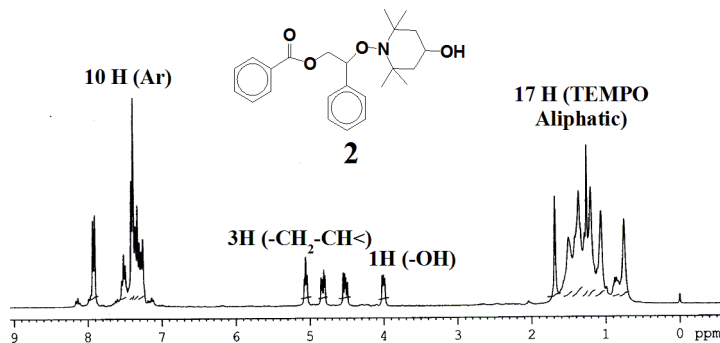


Figure S1: 400 MHz ^1H NMR Spectrum of styrenyl-TEMPO unimolecular initiator (2)

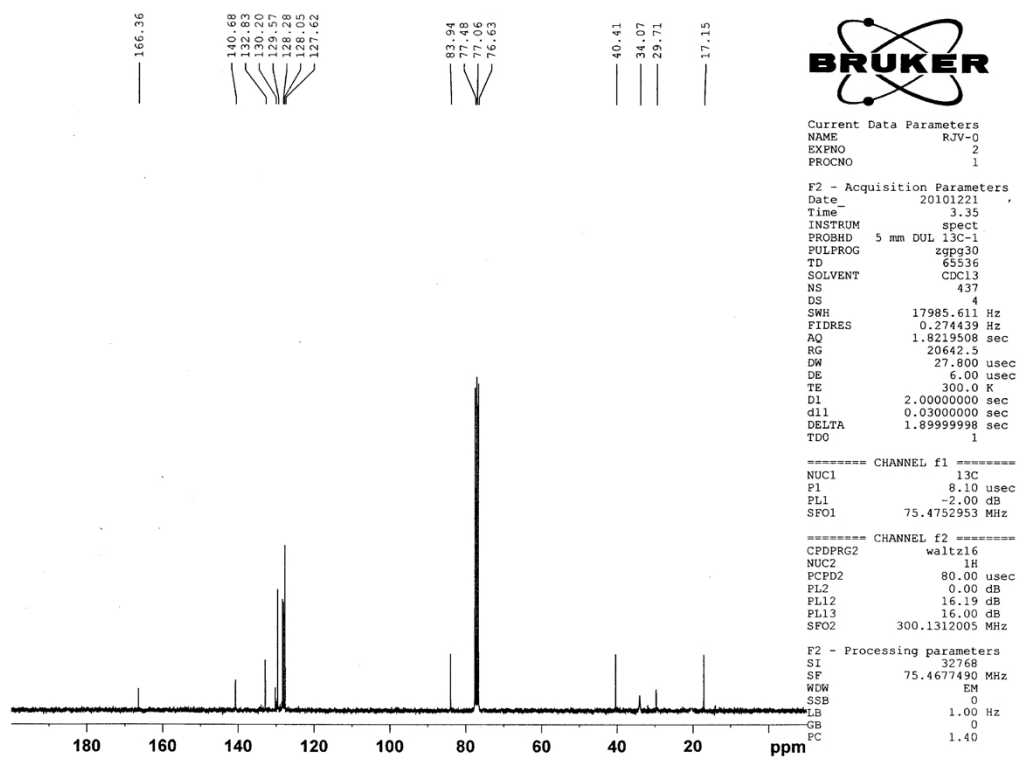


Figure S2: ¹³C NMR Spectrum of Styrenyl-TEMPO (2)

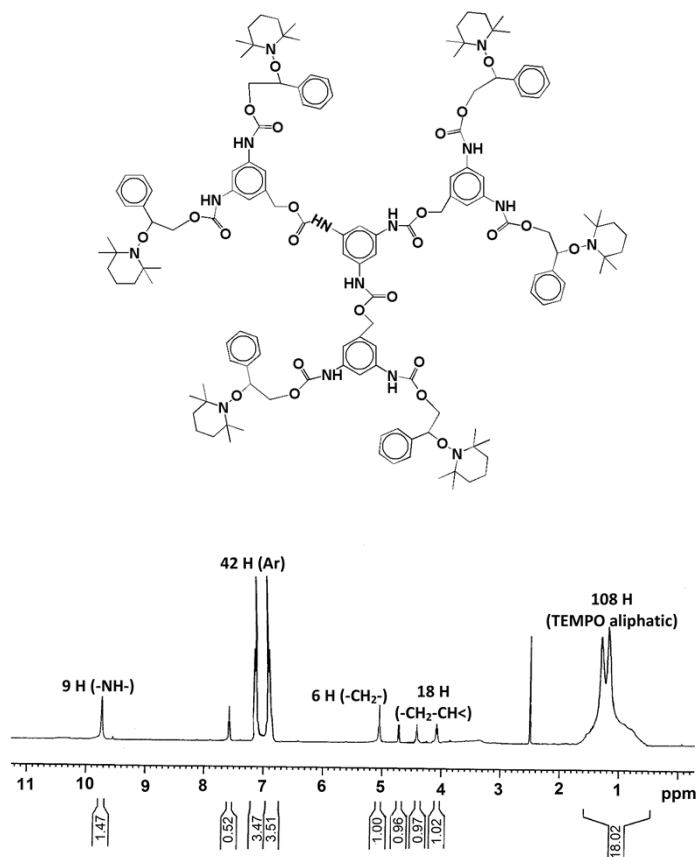


Figure S3: ¹H NMR Spectrum of unimolecular initiator end-capped G1 dendrimer (3).

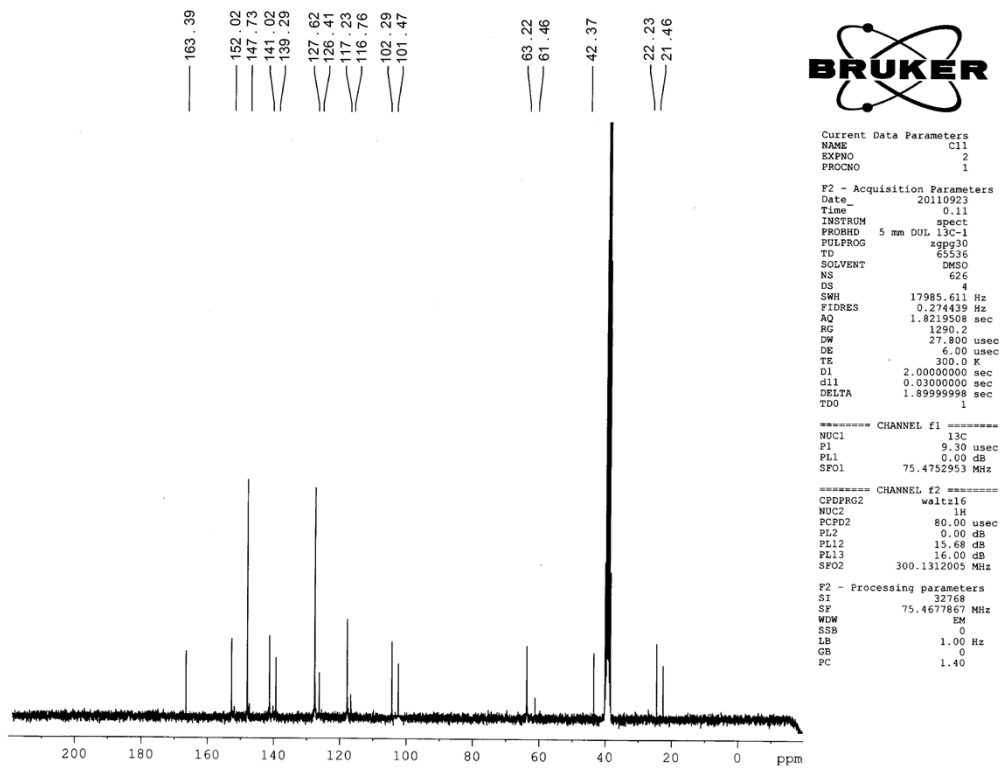


Figure S4: ^{13}C NMR Spectrum of unimolecular initiator end-capped G1 dendrimer.

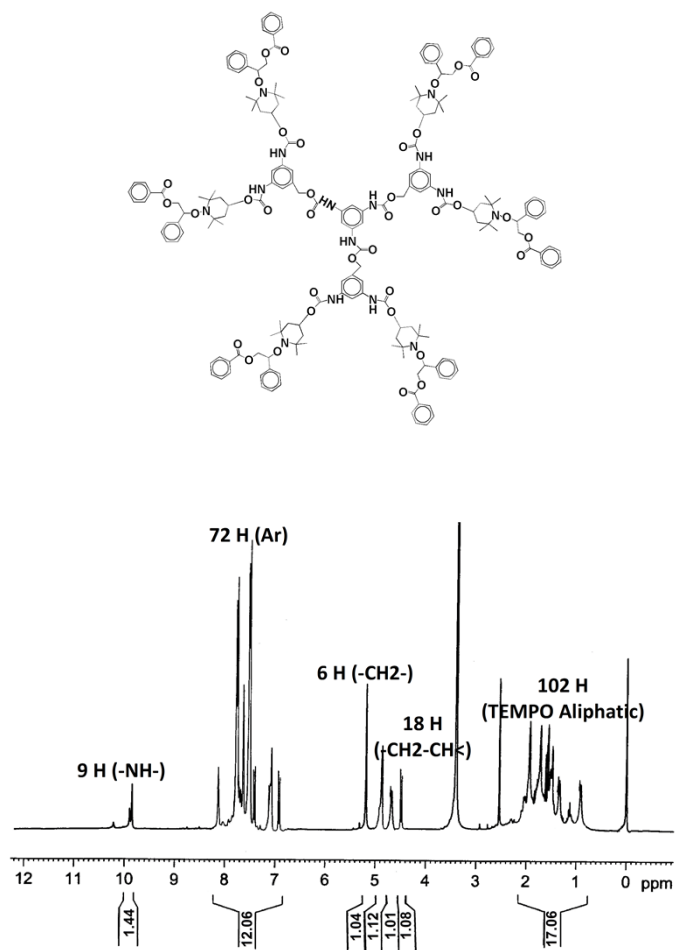


Figure S5: ¹H NMR Spectrum of unimolecular initiator anchored G1 dendrimer.

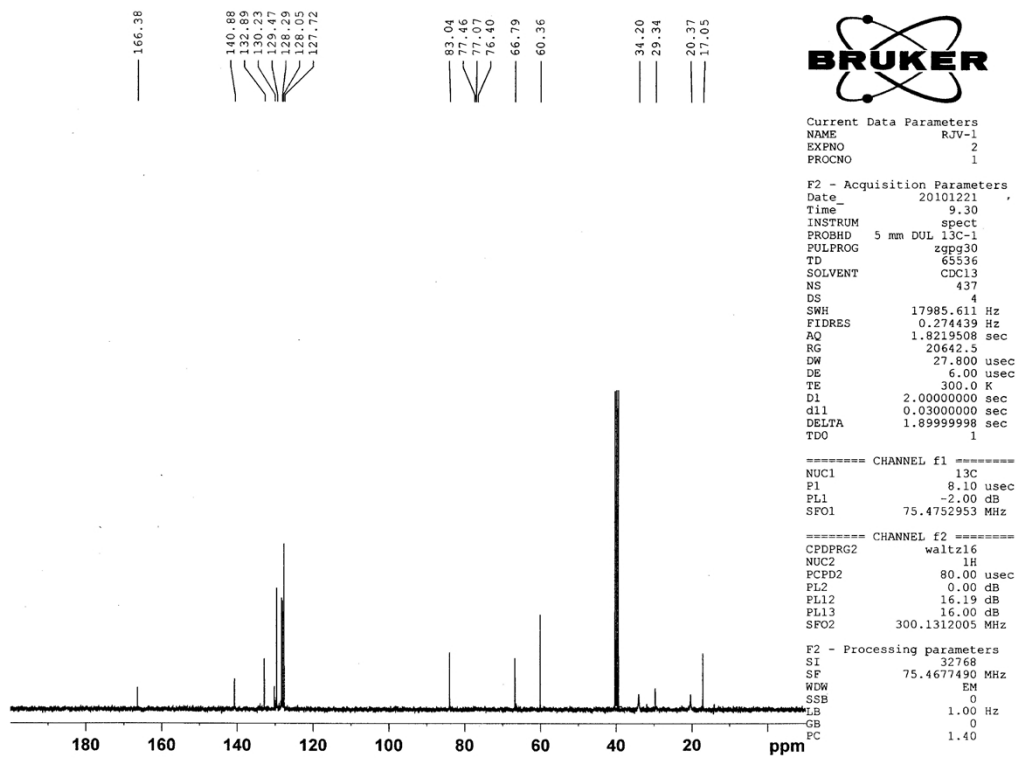


Figure S6: ^{13}C NMR Spectrum of unimolecular initiator anchored G1 dendrimer.

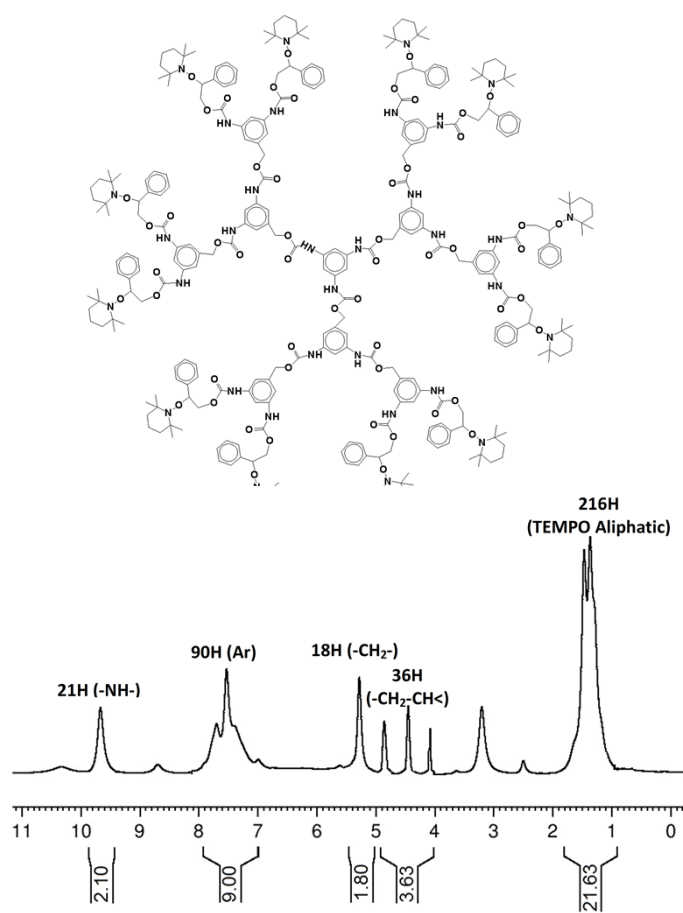


Figure S7: ¹H NMR Spectrum of unimolecular initiator end-capped G2 dendrimer.

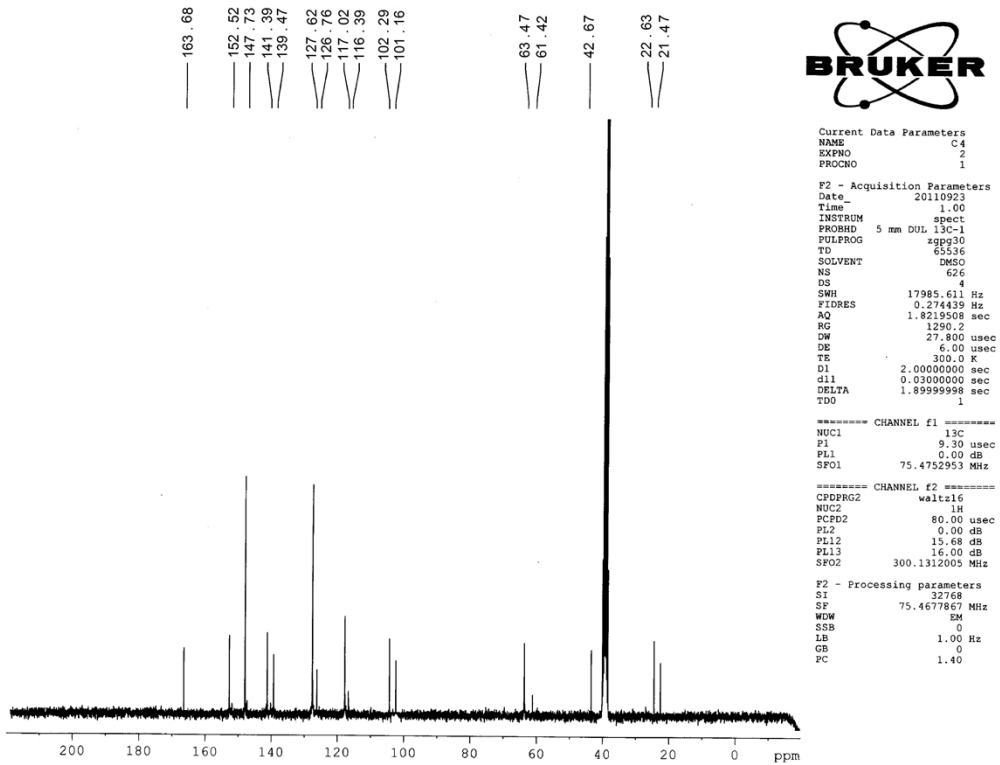


Figure S8: ^{13}C NMR Spectrum of unimolecular initiator end-capped G2 dendrimer.

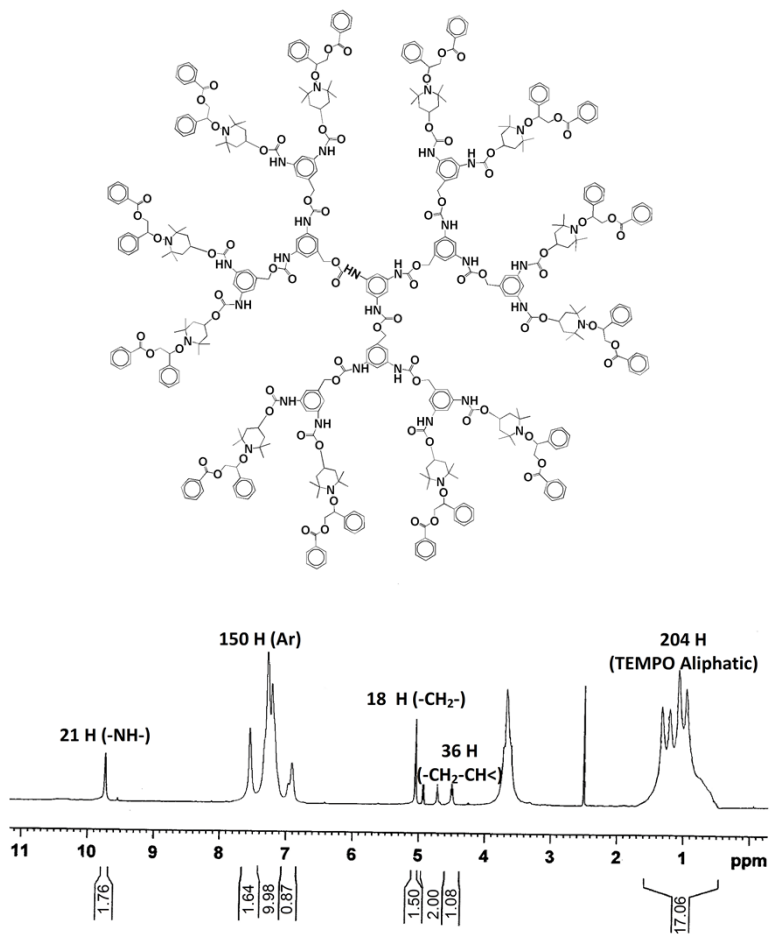


Figure S9: ¹H NMR Spectrum of unimolecular initiator anchored G2 dendrimer.

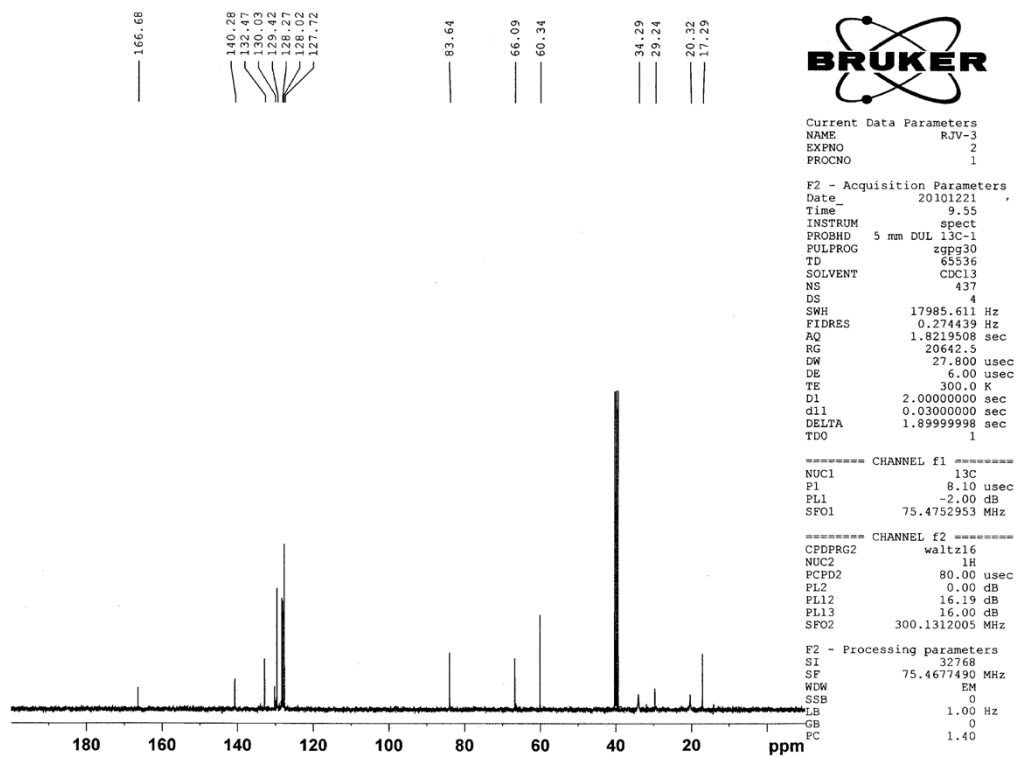


Figure S10: ^{13}C NMR Spectrum of unimolecular initiator anchored G2 dendrimer.

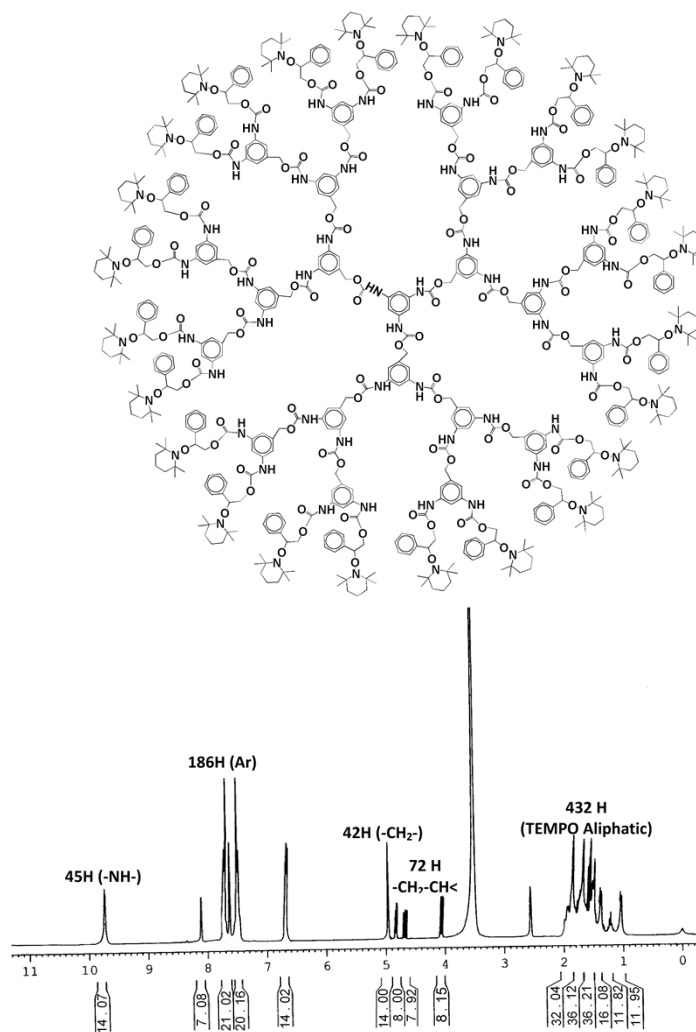


Figure S11: ¹H NMR Spectrum of unimolecular initiator end-capped G3 dendrimer.

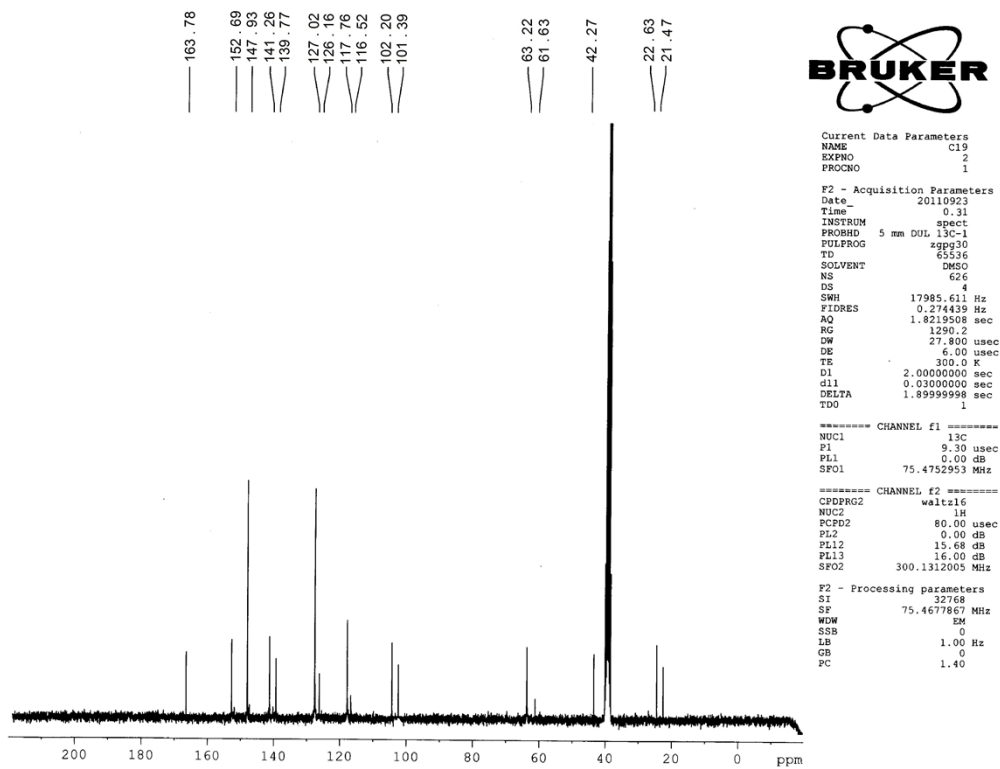


Figure S12: ^{13}C NMR Spectrum of unimolecular initiator end-capped G3 dendrimer.

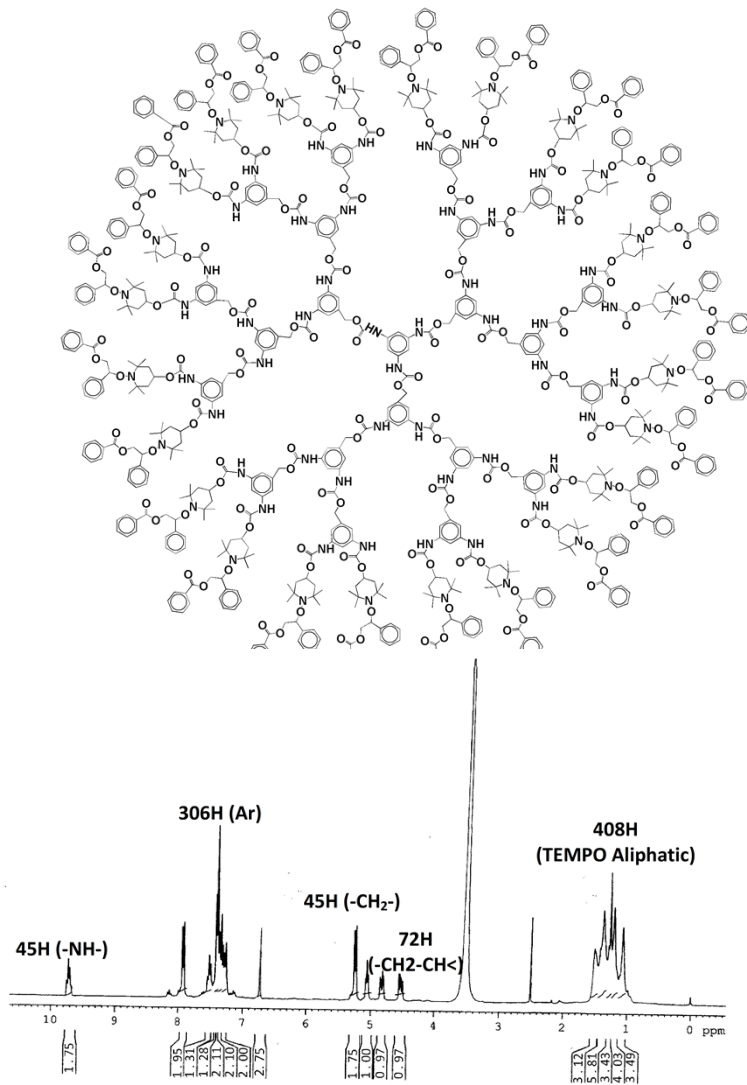


Figure S13: ¹H NMR Spectrum of unimolecular initiator anchored G3 dendrimer.

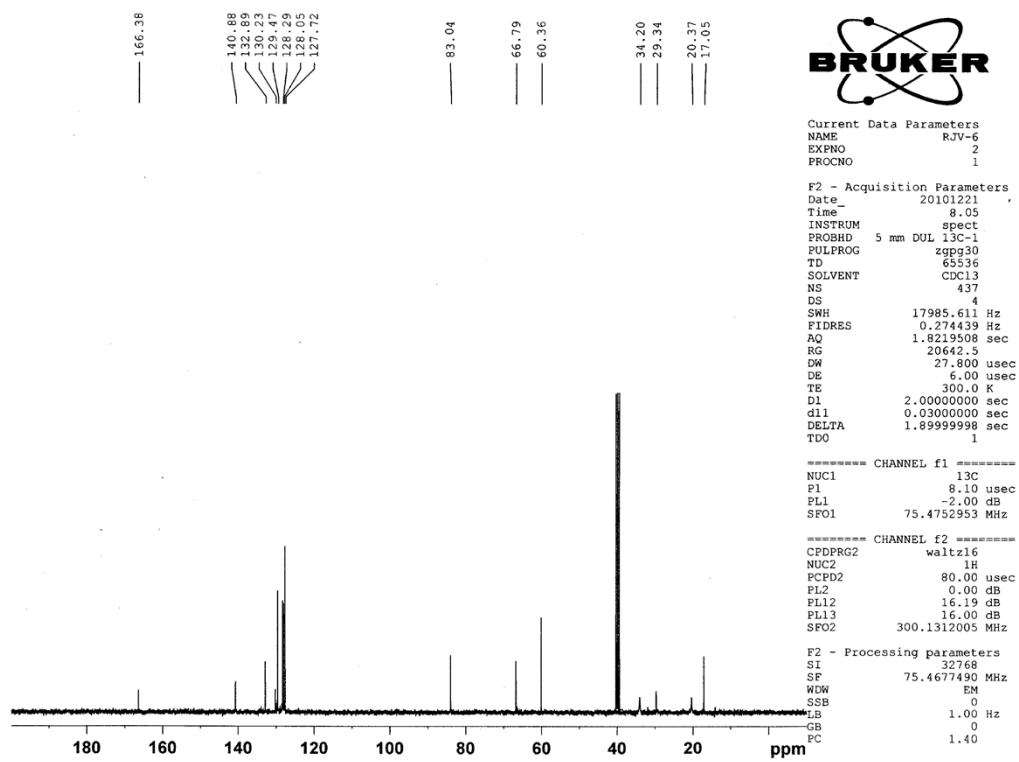


Figure S14: ^{13}C NMR Spectrum of unimolecular initiator anchored G3 dendrimer.

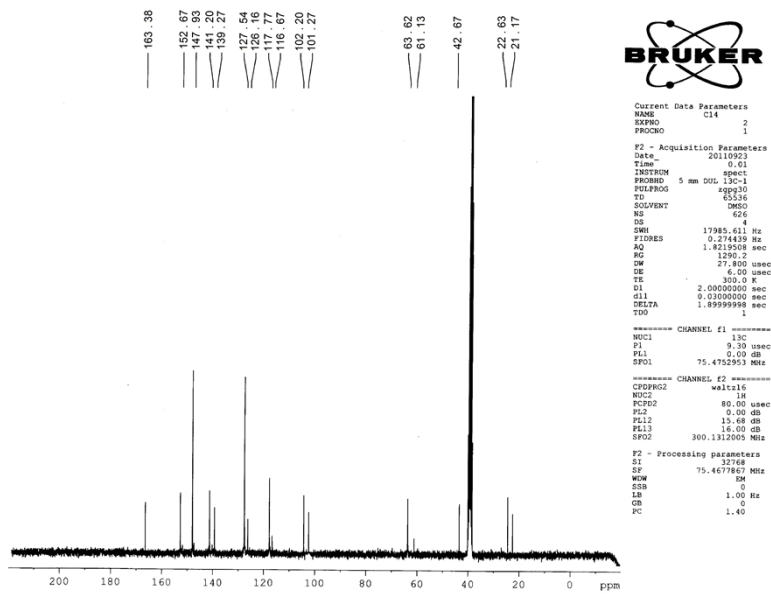


Figure S15: ^{13}C NMR Spectrum of unimolecular initiator end-capped G4 dendrimer.

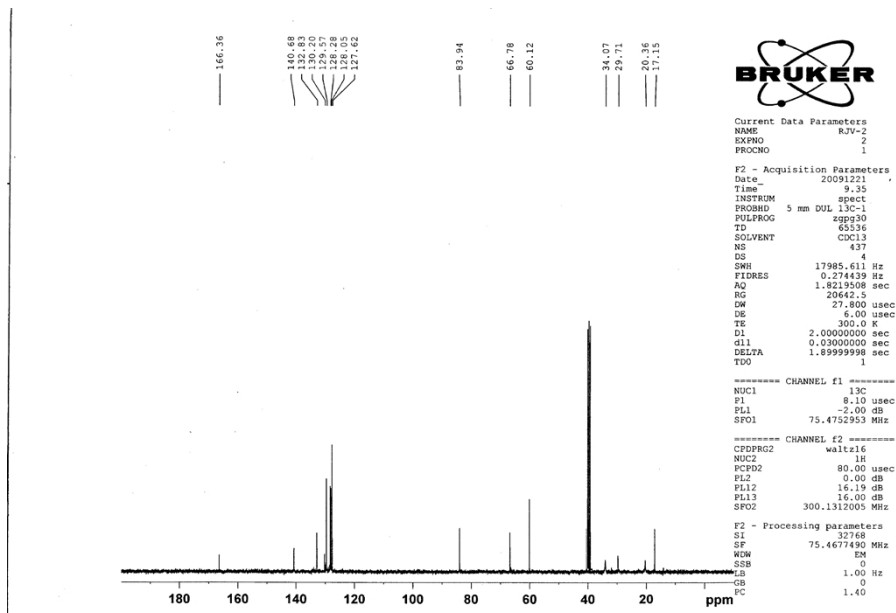


Figure S16: ^{13}C NMR Spectrum of unimolecular initiator anchored G4 dendrimer.

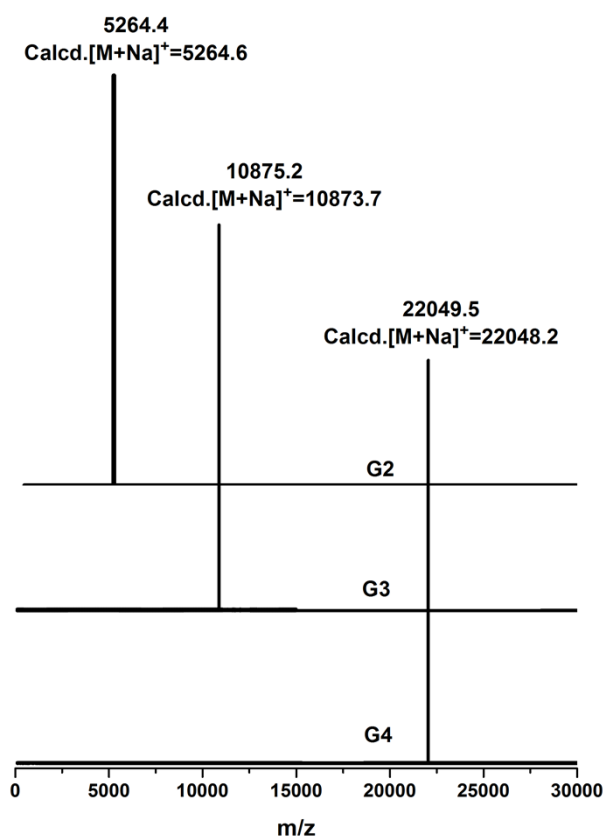


Figure S17: MALDI-TOF MS Spectra of unimolecular initiator end-capped dendrimers.

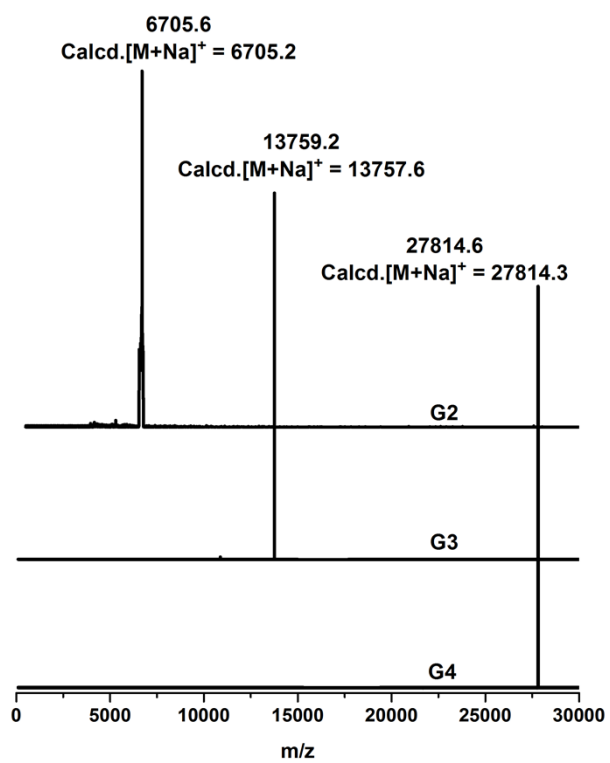


Figure S18: MALDI-TOF MS Spectra of unimolecular initiator anchored dendrimers.

Table S1. Synthesis of multiarm star polymer using styrene monomer and unimolecular initiator end-capped G3 and G4 dendrimers.

Polymer	Initiator used	Functionality of the initiator	[M]equ./[I]equ.	Time (Hrs)	$M_w \times 10^5$ (SEC MALLS) g/mol	PDI
STAR-P1	G3	24	438	30	2.446	1.37
STAR-P2	G4	48	440	30	1.765	1.44

Table S2. Molecular weight data of polystyrene obtained after hydrolysis of inner urethane core of star polymers.

Parent polymer	Polystyrene obtained	Calc. M_w of Single arm (10^3 g/mol)	Observed M_w of single arm (10^3 g/mol)	PDI
STAR-P1	PS-1	9.73	8.61	1.09
STAR-P2	PS-2	3.22	3.09	1.01

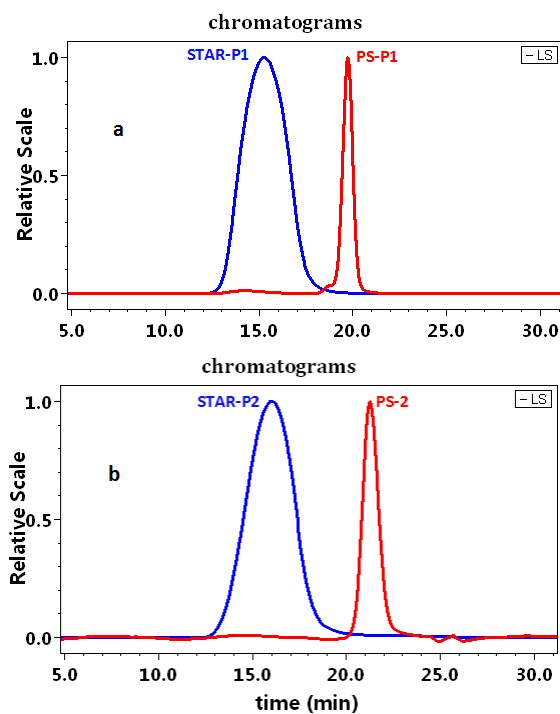


Figure S19: SEC-MALLS chromatogram of star polymers and their corresponding linear polystyrene (obtained after hydrolysis) using (a) unimolecular initiator end-capped G3 dendrimer (b) unimolecular initiator end-capped G4 dendrimer.