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Communication

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

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Unimolecular initiator end-capped and anchored dendrimers with initiator functionality up to 48 of G4 dendrimer were prepared quantitatively in a single-step reaction. Polymerization of styrene using these initiators yielded multi arm star polymers with mol. weight ( $M_w$ ) in the order of  $10^5$  g/mol and polydispersity of arm in the range of 1.01 to 1.09.

In the recent past, major developments in the field of polymer science have resulted from macromolecular engineering. The development of polymers with controlled molecular architecture, complexity and attractive star-like topology (for example, dendritic-linear hybrid multiarm polymers with controlled molecular architecture) is topical in research<sup>1</sup>. An executable protocol based on dendritic growth strategy and living polymerization mechanism could produce such kind of materials. However, the intriguing challenge in achieving this task is to make available suitable multifunctional core molecules.

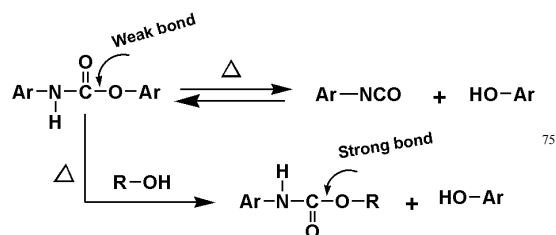
Many kinds of core molecules have been used for synthesis of star (or) multiarm polymers<sup>2,3</sup>. Hawker<sup>4</sup> reported first example of nitroxide based multi-functional initiator for synthesis of three arm star polymers. Subsequently, Frechet<sup>5a</sup> group described TEMPO functionalized polystyrene for the synthesis of branched and highly branched polymers in a tandem approach and also used a styrenyl-TEMPO monomer which underwent self-condensing living free radical polymerization leading to star polymers<sup>5b</sup>. Latter, a mesitylene<sup>6</sup>, a cyclodextrin<sup>7</sup>, a porphyrin<sup>8</sup>, silsesquioxane and an octafunctional derivative of resorcinarene based NMP initiators have been reported<sup>9,10</sup>. In one report, Miura and co-worker<sup>11</sup> used second generation dendritic macro initiators with 12 TEMPO moieties for the synthesis of star and star di-block copolymers. Dendrimers functionalized for living polymerization process are meagre<sup>4,5,11</sup>, and dendrimer functionalized with styrenyl-TEMPO moiety suitable for nitroxide-mediated living radical polymerization leading to multi arm star polymers with number of arm more than 12 is not yet reported.

Herein, we report TEMPO based dendritic unimolecular initiators of two different types having number of initiators up to 48 for the first time. Indeed, these distinct initiators will give similar kind of polymers, but with different topological features that could not be expected from other multi-functional initiators reported so far. Moreover, they can be used to produce well-defined multiarm star polymers at nanoscale with pre-determined

number of arms at higher order.

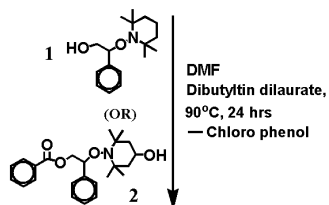
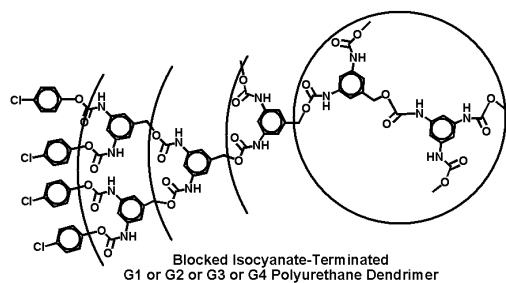
In this work we used two different styrenyl-TEMPO reagents (unimolecular initiators). The unimolecular initiator **1** suitable for end-capping reaction with dendrimers was prepared using a reported procedure<sup>12</sup> and the same **2** suitable for anchoring reaction was prepared according to the Scheme S1 (*see Supporting Information*). The structure and purity of the newly prepared styrenyl-TEMPO reagent **2** were confirmed using FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HR-MS data and nitrogen content estimation. The reason for end-capping and anchoring of unimolecular initiator on dendrimers is to use such initiators in future for the synthesis of multi arm star polymers with distinct topological futures.

The concept of blocked isocyanate chemistry was adapted for end-capping and anchoring of unimolecular initiator on dendrimers. Blocked isocyanate is an adduct usually obtained from an aromatic isocyanate and a phenol. The -NHCOO- group of a blocked isocyanate is thermally weak and at elevated temperature it de-blocks into isocyanate (-NCO) and blocking agent (HO-). Then, the regenerated isocyanate could react with a co-reactant containing aliphatic hydroxyl functional group to form urethane with thermally more stable bonds<sup>13</sup>. The overall reaction can be seen as:



The easy-to-do reaction involving blocked isocyanate group and hydroxyl co-reactant of present work is described in Scheme 1<sup>14</sup>. The substituent on phenol (blocking agent) can influence seriously the de-blocking temperature; the electron withdrawing substituent reduces the de-blocking temperature. Blocked isocyanates with relatively low de-blocking temperature find applications in many chemical processes. In this work, the blocking agent already derived at the surface groups of dendrimer is *p*-chlorophenol which could cleave of easily below 90°C<sup>15</sup>, thus the urethane interchange reaction described in Scheme 1 proceeded smoothly at 90°C in DMF in the presence of dibutyltin dilaurate catalyst. The styrenyl-TEMPO end-capped and

anchored dendrimers (3-6 and 7-10) do not require column purification and it is worth mentioning here that these initiators are found to be highly soluble in 10:1 mixture of styrene and DMF.



Unimolecular Initiator End Capped (3 - 6) or Anchored (7 - 10) Dendrimers (for structures see Fig.1)

Scheme 1 Synthesis of dendritic unimolecular initiators.

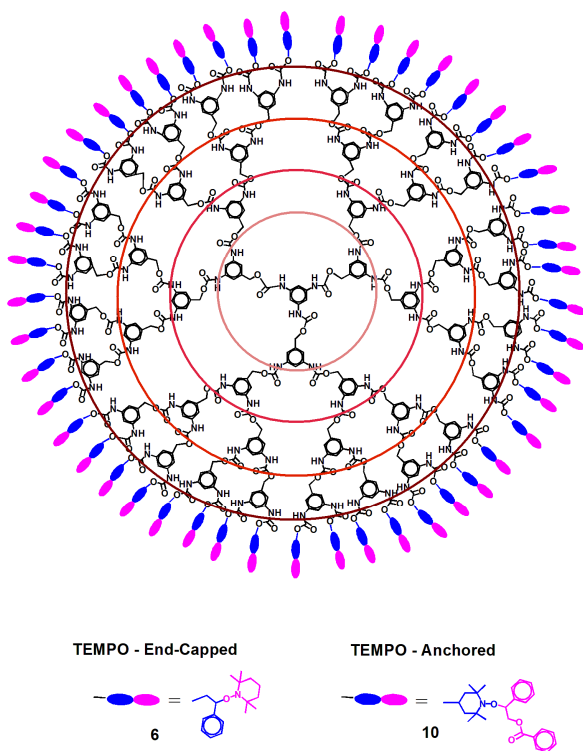


Fig. 1 Structure of G4 dendritic unimolecular initiators.

The  $^1\text{H-NMR}$  and MALDI-TOF MS spectra of these novel initiators of G4 dendrimer are given in Figure 2 and 3 respectively. The  $^1\text{H-NMR}$  spectra show sharp and distinct signals arising from dendritic and reagent part. Moreover, the integration values of hundreds of protons of different types present in the large globular molecules agree well with the

calculated number of protons. One important change observed in the  $^1\text{H-NMR}$  spectra that could be treated as confirmation for quantitative conversion into multifunctional initiators is the complete disappearance of a peak at 10.4 ppm corresponding to urethane  $-\text{NH}$  protons of blocked isocyanate moiety of parent dendrimer. After completion of urethane interchange reaction, the discrepancy in the urethane  $-\text{NH}$  protons had vanished and all the urethane  $-\text{NH}$  protons became uniform; thus, they give only one peak at 9.8 ppm. In the MALDI-TOF MS spectra of styrenyl-TEMPO end- capped and anchored G4 polyurethane dendrimer,

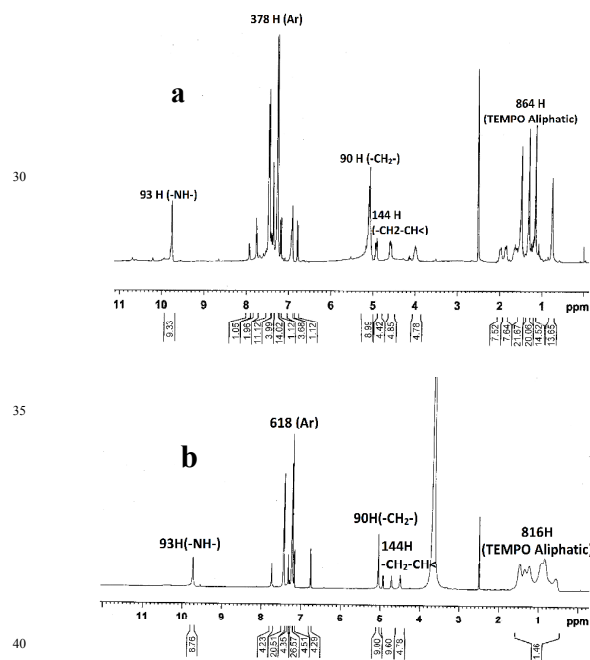


Fig. 2 400 MHz  $^1\text{H}$  NMR Spectrum of (a) unimolecular initiator end-capped and (b) unimolecular initiator anchored G4 dendrimer.

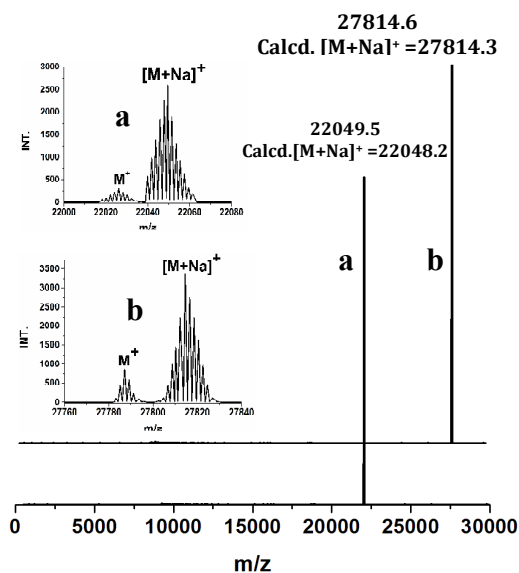


Fig.3 MALDI TOF MS spectrum of (a) unimolecular initiator end-capped and (b) unimolecular initiator anchored G4 dendrimer (insert are isotopes distribution pattern).

no peak was observed even with very trace intensity for any undesired products, and only one peak was observed with 100% intensity at  $m/z$  22049.5 and 27814.6 respectively exactly corresponding to  $[M+Na]^+$  of respective molecules. The labile bond formed between styrene and TEMPO moiety was found stable under MALDI-TOF experimental condition and this is not surprising because similar observations have been reported for many unimolecular initiators<sup>16</sup>. These analytical examinations confirm that the targeted innovative initiators are structurally pure. Analysis of  $^1H$ -NMR and MALDI-TOF MS spectra (See Supporting information) of both such type of initiators based on G1-G3 dendrimers reveals that they also structurally pure.

As we obtained remarkably good  $^1H$  NMR and MALDI-TOF MS spectra which confirm the defect free structure of dendritic unimolecular initiators, it was decided to support these data. Size exclusion chromatography combined with multi angle laser light scattering (SEC-MALLS) technique is an ultimate tool to be used to determine the absolute molar mass and polydispersity index (PDI) of the dendrimers. Elution of all the dendritic initiators in the SEC-MALLS resulted narrow disperse signals (Fig. 4) with estimated molecular weight close to calculated molar mass (Table 1). Specific refractive index increment ( $dn/dc$ ) for each

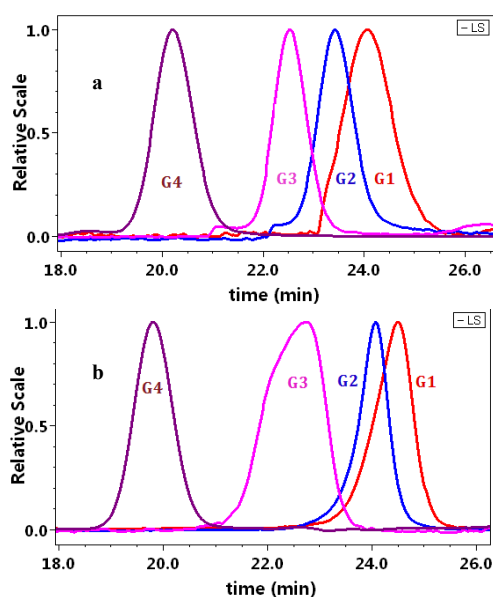


Fig. 4 SEC-MALLS Chromatograms of (a) unimolecular initiator end-capped dendrimers and (b) unimolecular initiator anchored dendrimers.

Table 1. Molecular weight data of unimolecular initiator end-capped and anchored dendrimers.

Initiator	No. of initiator present	$dn/dc$	Theoretical Molecular weight ( $M_n$ ) (g/mol)	SEC-MALLS Molecular weight ( $M_n$ ) (g/mol)	PDI
3	6	0.1661	2436	2319	1.05
4	12	0.1604	5241	4584	1.09
5	24	0.1106	10852	11220	1.01
6	48	0.1374	22,027	28480	1.00
7	6	0.1701	3157	4493	1.14
8	12	0.1213	6683	5557	1.09
9	24	0.1010	13735	13680	1.29
10	48	0.1591	27792	27910	1.00

dendrimer was determined separately in the same solvent used for SEC experiments and used for molecular weight calculation. The  $dn/dc$  value of dendrimer was found decreased with increasing the generation up to G3 and then increased for G4 dendrimer and this trend was found to be common for both types of dendritic initiators. The molecular weight data and unimodal chromatograms with narrow distribution clearly support the  $^1H$  NMR and MALDI-TOF MS spectra of the dendrimers.

The reagents used for end-capping and anchoring process are dormant species in the TEMPO-mediated polymerization and its effectiveness in molecular weight build-up was confirmed beyond any doubt with variety of monomers<sup>17</sup>. Thus, the multifunctional unimolecular initiators reported in this communication could be readily used for the synthesis of dendritic-linear hybrid multiarm polymers. Preliminary work on this line was carried out using the initiator 5 and 6 with an intention to confirm the efficiency of the initiators on tune and control the arms. Polymerization of styrene carried out at 125°C varying the experimental conditions like monomer/initiator ratio and reaction time yielded high molecular weight multiarm star polymers, the molecular weight ( $M_w$ , SEC-MALLS) was in the order of  $10^5$  g/mol. The polydispersity index of multiarm star polymers were found to be in the range of 1.37 to 1.39, however the PDI of arm (after hydrolysis of inner polyurethane core) was highly narrow, in the range of 1.01 – 1.09. This finding i.e., difference in PDI of parent polymers and their hydrolysed into linear chains is consistent with a reported work<sup>4, 5b, 11, 18</sup>. All the chromatograms were unimodal and are given in the Supporting Information along with molecular weight data. Experimentally calculated number of arms were found agree well with the theoretically calculated values and the results confirm that the number of arms of star polymer can be pre-determined, tuned and controlled accurately using these initiators. Polymerization studies in detail including dependence of molecular size of star polymers and their  $dn/dc$  and characterization for topological features at nanoscale would be reported following this communication.

In conclusion, two series of dendritic unimolecular initiators up to fourth generation were prepared in quantitative yield. As these initiators were designed with an intention to produce multiarm star polymers with pre-determined number of arms, their defect-free structures have been established beyond doubt. Use of these initiators in the synthesis of topologically attractive multiarm star polymers enable to tune and control the number of arms and its PDI value were proved.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details (materials, measurements, synthetic procedure of Compound 2), <sup>1</sup>H NMR spectra of compound 2-5 and 7-9, <sup>13</sup>C NMR spectra of compound 2-10, MALDI-TOF MS spectra of compound 4, 5, 8 and 9 and polymerization results of styrene.

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14 **Synthesis of unimolecular initiator end-capped and anchored polyurethane dendrimers (3-6 and 7-10).** 0.5 g of blocked isocyanate-terminated dendrimer (G1 or G2 or G3 or G4) and calculated amount of styrenyl-TEMPO reagent 1 (end-capping reagent) or 2 (anchoring reagent) were taken in a two-necked 100mL flask and were dissolved in 10 mL of dry DMF. To this solution was added 0.02 g of DBTDL. The reaction was carried out in an oil bath maintained at 90°C for overnight. The reaction mass was added dropwise into 100 mL of water to precipitate the product and it was filtered and dried under vacuum. Then, the curd product was washed in chloroform to remove unreacted styrenyl-TEMPO reagent and then re-precipitated in dry THF by the addition of petroleum ether.

55 (3). Yield: 92.4%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.73 (s, 9H), 7.55-6.77 (m, 42H), 5.05 (s, 6H), 4.67 (m, 6H), 4.40 (m, 6H), 4.17 (m, 6H), 1.50-0.50 (m, 108 H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 163.39, 152.02, 147.73, 141.02, 139.29, 127.62, 126.41, 117.23, 116.76, 102.29, 101.47, 63.22, 61.46, 42.37, 22.23, 21.46.

60 (4). Yield: 92.8%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.79 (s, 21H), 7.91-7.12 (m, 90H), 5.28 (s, 18H), 4.84 (m, 12H), 4.42 (m, 12H), 4.09

(m, 12H), 1.57-1.27 (m, 216H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 163.68, 152.52, 147.73, 141.39, 139.47, 127.62, 126.76, 117.02, 116.39, 102.29, 101.16, 63.47, 61.42, 42.67, 22.63, 21.47. Calcd: [M+Na]<sup>+</sup> m/z = 5227.33. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 5264.6.

65 (5). Yield: 94.7%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.97 (s, 45H), 7.91-6.70 (m, 186H), 5.02 (m, 24H), 4.81 (s, 42H), 4.62-4.59 (m, 24 H), 4.11 (m, 24H), 1.86-1.06 (m, 432H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 163.78, 152.69, 147.93, 141.26, 139.77, 127.02, 126.16, 117.76, 116.52, 102.20, 101.39, 63.22, 61.63, 42.27, 22.63, 21.47. Calcd: [M+Na]<sup>+</sup> m/z = 10875.2. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 10873.7.

70 (6). Yield (92.4%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.76 (s, 93H), 7.91-6.77 (m, 378H), 5.11 (s, 90H), 4.99-4.95 (m, 48H), 4.62-4.59 (m, 48H), 4.07-4.03 (m, 48H), 2.1-1.06 (m, 864H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 163.38, 152.67, 147.93, 141.20, 139.27, 127.54, 126.16, 117.77, 116.67, 102.20, 101.27, 63.62, 61.13, 42.67, 22.63, 21.17. Calcd: [M+Na]<sup>+</sup> m/z = 22048.5. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 22048.2.

75 (7). Yield: 96.5%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.69 (s, 9H), 8.15-6.87 (m, 72H), 5.23 (s, 6H), 4.83 (m, 6H), 4.72 (m, 6H), 4.47 (m, 6H), 2.12-0.85 (m, 102H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 166.38, 140.88, 132.89, 130.23, 129.47, 128.29, 128.05, 127.72, 83.04, 66.79, 60.36, 34.20, 29.34, 20.37, 17.05.

80 (8). Yield: 96.2%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.73 (s, 21H), 7.55-6.77 (m, 141H), 5.05 (s, 18H), 4.93 (m, 12H), 4.75 (m, 12H), 4.45 (m, 12H), 1.51-1.11 (m, 204H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 166.88, 140.28, 132.47, 130.03, 129.42, 128.27, 128.02, 127.72, 83.64, 66.09, 60.34, 34.29, 29.24, 20.32, 17.29. Calcd: [M+Na]<sup>+</sup> m/z = 6682.63. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 6705.2.

85 (9). Yield: 94.8%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.96 (s, 45 H), 7.94-7.26 (m, 306), 5.26 (42H), 5.06 (m, 24H), 4.82 (m, 24H), 4.52 (m, 24H), 1.69-0.75 (m, 408H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 166.38, 140.88, 132.89, 130.23, 129.47, 128.29, 128.05, 127.72, 83.04, 66.79, 60.36, 34.20, 29.34, 20.37, 17.05. Calcd: [M+Na]<sup>+</sup> m/z = 13759.2. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 13757.6.

90 (10). Yield (95.6%). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ 9.72 (s, 93H), 7.74-6.75 (m, 618 H), 5.05 (s, 90H), 4.95-4.91 (m, 48H), 4.75-4.70 (m, 48H), 4.55-4.49 (m, 48H), 1.5-0.5 (m, 816H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): 166.36, 140.68, 132.83, 130.20, 129.57, 128.28, 128.05, 127.62, 83.94, 66.78, 60.12, 40.41, 34.07, 29.71, 20.36, 17.15. Calcd: [M+Na]<sup>+</sup> m/z = 27814.3. Found: MALDI-TOF-MS [M+Na]<sup>+</sup> = 27814.6.

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