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Fast growing dendritic poly(ester–amines) from alternate reaction of EDA and TMPTA

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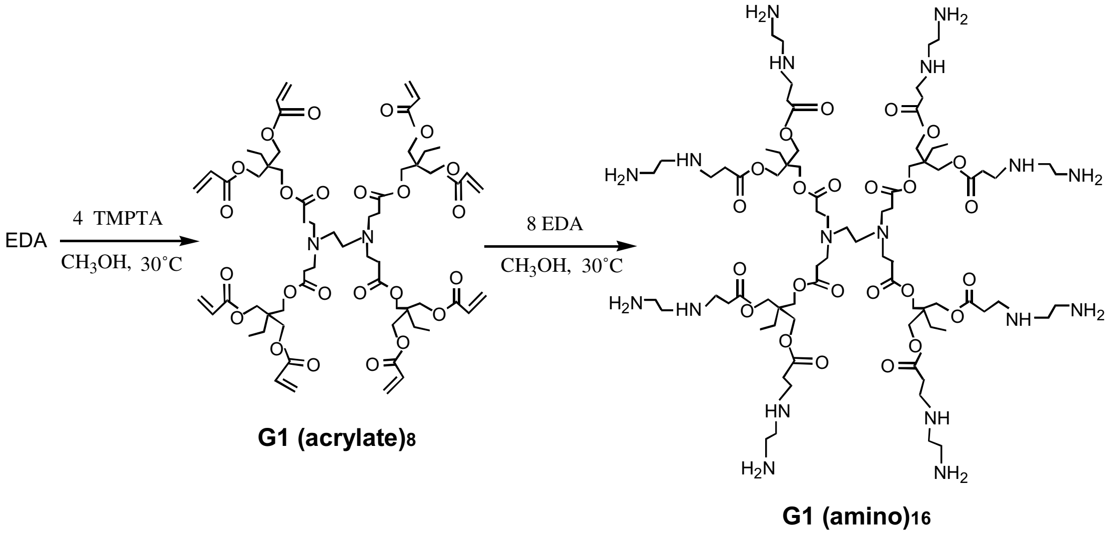
Abstract—Starting with ethylene diamine (EDA) as the core, dendritic poly(ester–amines) were prepared from directly alternate reaction of EDA and trimethylolpropane triacrylate (TMPTA) under mild conditions without protection–deprotection steps. Multiple reactive hydrogen atoms in EDA and acrylate groups in TMPTA led to fast growing of dendrimers and the number of their peripheral groups.

Dendrimers are highly branched, monodisperse, and terminated with multiple functional groups. Their perfect and well-defined structure leads to a number of interesting characteristics and features, including globular, void-containing shapes, low viscosity and good solubility, and compatibility. Therefore, dendrimers have exhibited potential applications in many areas.[1] Dendrimers are usually prepared step by step. In each step, the branching monomer needs more than two functionalities in order to make the dendrimer grow. However, multiple functionalities broaden the polydispersity of dendrimer and even make the reaction system gel. Therefore, most synthetic procedures involve the repetitious alternation of a growth reaction and an



Keywords: Dendritic; Poly(ester–amines); Fast growing.

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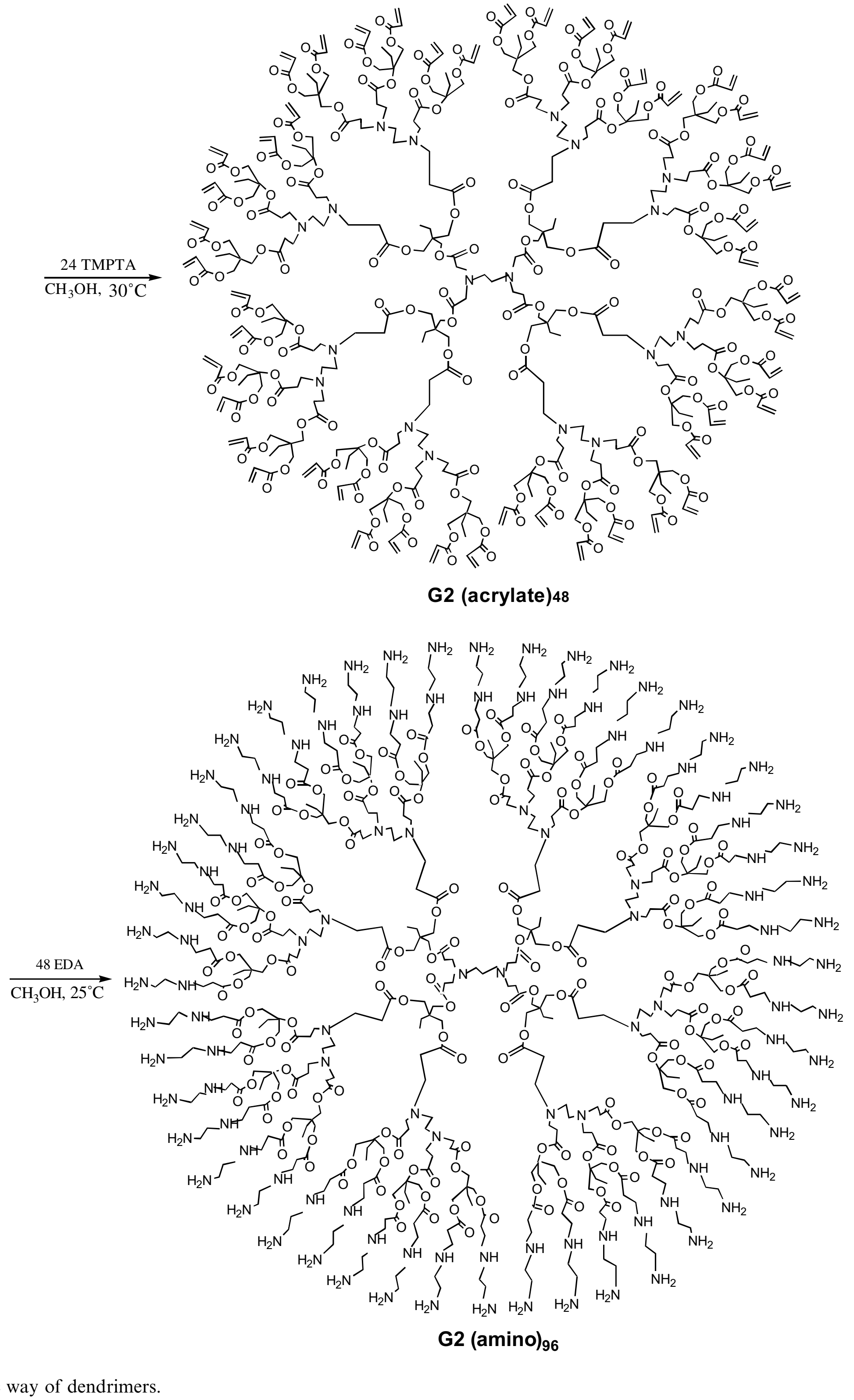
activation reaction (or protection–deprotection steps)[2] as well as complex isolation and purification of the products at every step, which limits large-scale preparation and application, so that the development of more efficient synthetic process is highly desirable.[3]

In previous work, Shi and co-workers[4] prepared dendritic poly(ester–amines) by pseudo one-pot procedure. Each step reaction made the dendrimer grow effectively and the number of peripheral groups grew at the rate of 3×2^n. Sha et al.[5] synthesized hydroxyl terminated



Scheme 1. Synthetic way of dendrimers.

poly(ester–amine) dendrimer from alternate reaction of diethanolamine and acryloyl chloride and the number of peripheral groups grew at the rate of 2×2^n. In each step reaction of Shi and co-workers[4] and Sha et al.,[5] every molecule of the branching monomer only contained one functionality. Here we report a novel dendritic poly(ester–amine), which was, starting with EDA as the core, prepared from alternate reaction of four-functionality EDA and three-functionality TMPTA. In each step reaction, for one branching monomer molecule, only one functionality was needed, as a result, there existed two surplus acrylate double bonds in every TMPTA molecule and three surplus hydrogen atoms in every EDA molecule. However, protection–deprotection steps were omitted. Excess branching monomers were used to suppress the by-reactions and increase the yields of dendrimers. Multiple-functionality EDA and TMPTA reacted directly, leading to fast growing of dendrimers and the number of their peripheral groups, among which the peripheral acrylate groups and amino groups grew at the rate of $8{\times}6^{n-1}$ and $16{\times}6^{n-1}$, respectively. All reactions were carried out under mild conditions.

The synthesis was shown in Scheme 1. The reaction of EDA and 1.2 equiv of TMPTA gave G1(acrylate)$_8$,[6] which reacted with 45 equiv of EDA to produce G1(amino)$_{16}$.[7] Colorless, transparent oil G2(acrylate)$_{48}$ (6.91 g, 67.5% yield) was constructed by G1(amino)$_{16}$ (2.0 g, 1.16 mmol) reacting with 5.3 equiv of TMPTA (43.9 g, 0.148 mol) in 20 mL methanol at 30 °C for 52 h, then removal of methanol under vacuum and purifying the crude product on silica gel (petroleum ether: ethyl acetate = 1.0:3.5). G2(acrylate)$_{48}$ (0.1 g, 0.0113 mmol) reacted with 260 equiv of EDA (8.5 g, 0.142 mol) in 1 mL methanol at 25 °C for 56 h, after removal of methanol and excess EDA under vacuum, the residue was extracted with ethyl acetate (3 × 5 mL), dried under vacuum at 30 °C to give 0.13 g pale yellow, transparent, oily G2(amino)$_{96}$ in 95.8% yield. Dendrimer structures were characterized by IR, ^{1}H NMR, ^{13}C NMR, ESI-MS and elemental analysis.[8]

In conclusion, fast growing acrylate and amino-terminated poly(ester–amine) dendrimers were synthesized efficiently by alternate reactions of multiple functionalities EDA and TMPTA under mild conditions. The excess EDA and TMPTA used as branching monomers could be cycled and the dendrimers might be modified for various applications.

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8. Selected characterization data of two dendrimers. G2 (acrylate)$_{48}$: IR 1724, 1636, 810, 1336, 1111 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 84H, CH_3), 1.46–1.59 (m, 56H, CH_2CH_3), 2.45 (t, 72H, CH_2COO), 2.55 [t, 4H, $\mathit{CH}_2N\ (CH_2)_2$], 2.73 [t, 104H, $CH_2N\ (\mathit{CH}_2)_2$], 3.50 [s, 72H, $O\mathit{CH}_2C\ (CH_2)_3$], 4.11–4.18 (m, 96H, $\mathit{CH}_2OCOCH{=}CH_2$), 5.83–6.46 (m, 144H, $CH_2{=}CH$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 7.8 (CH_3), 22.6, 23.5 ($\mathit{C}H_2CH_3$), 30.0, 31.5 [$\mathit{C}(CH_2)_4$], 32.6, 33.5, 34.1, 35.2 ($OOC\mathit{C}H_2$), 41.9, 49.1, 49.77 [$\mathit{C}H_2N\ (CH_2)_2$], 52.8, 53.2 [$CH_2\ N\ (\mathit{C}H_2)_2$], 62.4, 64.4, 65.8, 67.1 (OCH_2), 128.6, 131.7 ($CH_2{=}CH$), 166.1 ($C{=}O$). Found: C, 59.23; H, 7.10; N, 2.91. $C_{438}H_{632}O_{168}N_{18}$ requires C, 59.54; H, 7.16; N, 2.85. ESI-MS: calcd for $C_{438}H_{632}O_{168}N_{18}$: 8828. Found: 971.4 (M+9H$^+$). G2 (amino)$_{96}$: IR 3333, 1644, 1574, 1385, 1119 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77. (t, 84H, CH_3), 1.17–1.23 (m, 56H, CH_2CH_3), 2.19 (t, 168H, CH_2COO), 2.28 [t, 4H, $\mathit{CH}_2N\ (CH_2)_2$], 2.49 [t, 104H, $CH_2N\ (\mathit{CH}_2)_2$], 2.61 [t, 96H, $\mathit{CH}_2NHCH_2CH_2NH_2$, 96H, CH_2NH_2,], 2.71 [t, 96H, $CH_2NH\mathit{CH}_2CH_2NH_2$], 3.21 [s, 72H, $O\mathit{CH}_2C\ (CH_2)_3$]. ^{13}C NMR (400 MHz, $CDCl_3$): δ 7.5 (CH_3), 21.4, 21.8 ($\mathit{C}H_2CH_3$), 33.4, [$\mathit{C}(CH_2)_4$], 36.0 ($\mathit{C}H_2CO$), 40.9 (CH_2NH_2), 41.3, 42.0 ($\mathit{C}H_2NHCH_2CH_2NH_2$), 43.4, 44.2 [$NHCH_2\mathit{C}H_2$-$N(\mathit{C}H_2CH_2)_2$], 45.6, 45.9 ($NH\mathit{C}H_2CH_2NH_2$), [$NH\mathit{C}H_2$-$CH_2N(CH_2CH_2)_2$], 50.0 [$NCH_2CH_2N(\mathit{C}H_2CH_2)_2$], 51.7 [$N\mathit{C}H_2\mathit{C}H_2N(CH_2CH_2)_2$], 61.6, 61.8 ($CH_2O$), 161.3 ($C{=}O$). Found: C, 54.36; H, 8.73; N, 13.81. $C_{534}H_{1016}O_{168}N_{114}$ requires C, 54.73; H, 8.68; N, 13.63. ESI-MS: calcd for $C_{534}H_{1016}O_{168}N_{114}$: 11708. Found: 901.6 (M+13H$^+$).