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# Synthesis and Characterization of Dendrimers from Ethylene Diamine and Trimethylolpropane Triacrylate

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*Dendrimers were prepared from ethylene diamine (EDA) and trimethylolpropane triacrylate (TMPTA) by Michael addition reaction under mild conditions. EDA with four functional groups and TMPTA with three functional groups reacted directly without protection-deprotection steps. The terminated functional groups of the whole dendrimer generation grew at the rate of  $8 \times 6^{n-1}$ , and some objective products could be isolated and purified by washing with selective solvents. The dendrimer structure was characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, elemental analysis and ESI-MS. The influence of reaction conditions on yields and purities of dendrimers was discussed.*

**Keywords** dendrimers, ethylene diamine (EDA), trimethylolpropane triacrylate (TMPTA), Michael addition

## Introduction

Since the pioneering work of highly branched dendritic macromolecules in 1978 by Vögtle et al., interest in dendrimers has been increasing at an amazing rate.<sup>[1]</sup> Up to now, the study of these polymers has been expanded to all areas including theory, synthesis, characterization of structures, properties, functionalization, and investigations of potential applications.<sup>[2]</sup> Compared to traditional linear polymers, dendrimers are three-dimensional ordered, monodisperse, and terminated with multiple functional groups, which makes dendrimers have exhibited potential applications in many areas, such as catalyst, self-assemblies, photoactive and electroactive devices, and biochemical and pharmaceuticals.<sup>[3–5]</sup> However, dendrimers are usually prepared step by step and most synthetic procedures involve the repetitious alternation of a growth reaction and an activation reaction, as well as complex isolating and purifying the products at every step. This limits large-scale preparation and application so that the development of a more efficient synthetic process is highly desirable.<sup>[6]</sup>

Our purpose is to prepare dendrimers with fast growing peripheral functional groups using TMPTA and EDA by simple procedures and mild conditions. All the half and whole

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generation dendrimers are terminated with amino or acrylic double bond and expected to be used as quickly UV-curable oligomers,<sup>[7]</sup> drug delivery and gene transfection agents,<sup>[8]</sup> or further functionalizing precursor.<sup>[9–11]</sup>

## Experimental

### Materials

Ethylene diamine (EDA) and methanol were supplied by the Third Reagent Company of Shanghai (China) and purified by vacuum distillation before used. Trimethylolpropane triacrylate (TMPTA) was a product of UCB Chemicals Company (Belgium) and used without further purification.

### Dendrimer Synthesis

G1.0 ( $\Rightarrow$ ): G1.0 ( $\Rightarrow$ ) was synthesized according to Ref.<sup>[7]</sup>. The analysis results of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis complied with the data in reference.<sup>[7]</sup> G1.5 (NH<sub>2</sub>): Methanol (7.7 ml), Ethylene diamine (EDA) (108 g, 1.80 mol) and G1.0 ( $\Rightarrow$ ) (6.2 g, 0.005 mol) were added to a 250 ml three-necked flask equipped with a mechanic stirrer, thermometer and a condenser. The mixture was stirred well and warmed to 30°C for 24 h, then, the methanol was removed and most of the excess EDA, under vacuum, was washed with 10 g, 10 g, 8 g ethyl acetate three times in turn, dried in vacuum at 30°C and yielded a light yellow, transparent, viscous liquid product G1.5 (NH<sub>2</sub>). Yield: 8.07 g (0.0047 mol, 94%), purity: 98%.

IR spectra (KBr): 3295 ( $\nu_{\text{NH}_2}$ ), 1644 ( $\nu_{\text{C=O}}$ ), 1385, 1115 ( $\nu_{\text{C-N}}$ ). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>- $\delta$ ): 0.75, 0.77, 0.79 (CH<sub>3</sub>, 12H), 1.17, 1.19, 1.21, 1.22 (CH<sub>3</sub>\*CH<sub>2</sub>, 8H), 2.20 (CH<sub>2</sub>COO, 8H, OCOCH<sub>2</sub>, 16H), 2.28–2.31 [\*CH<sub>2</sub>N (CH<sub>2</sub>)<sub>2</sub>, 4H], 2.41 [CH<sub>2</sub>N (\*CH<sub>2</sub>)<sub>2</sub>, 8H], 2.53–2.56 (\*CH<sub>2</sub>NH<sub>2</sub>, 16H), 2.62–2.68 (NH\*CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 16H), 3.07 (\*CH<sub>2</sub>NH, 16H), 3.25 (COOCH<sub>2</sub>, 8H, CH<sub>2</sub>OCO, 16H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>,  $\delta$ ): 7.6 (CH<sub>3</sub>), 21.3, 22.6 (\*CH<sub>2</sub>CH<sub>3</sub>), 33.3 [\*C (CH<sub>2</sub>)<sub>4</sub>], 36.0 (OOC\*CH<sub>2</sub>), 42.1, 43.3 (CH<sub>2</sub>NH<sub>2</sub>), 45.4 [CH<sub>2</sub>N (\*CH<sub>2</sub>)<sub>2</sub>], 49.0, 49.9 (OCOCH<sub>2</sub>\*CH<sub>2</sub>), 51.3 [\*CH<sub>2</sub>N (CH<sub>2</sub>)<sub>2</sub>], 61.8 (OCH<sub>2</sub>), 169.1, 171.5 (C=O). E<sub>LEM</sub>. A<sub>NAL</sub>. (Found/Calcd.) %: C (54.63/54.29), H (8.46/8.82), N (14.23/14.62).

G2.0 ( $\Rightarrow$ ): Methanol (20.0 ml), G1.5 (NH<sub>2</sub>) (2.0 g, 1.16 mmol) and trimethylolpropane triacrylate (TMPTA) (43.9 g, 0.15 mol) were added to a 250 ml three-necked flask equipped with a mechanic stirrer, thermometer and a condenser. The mixture was kept at 30°C for 52 h with stirring, then, removed methanol under vacuum, the clued product was chromatographed on silica gel with a mixture of petroleum ether and ethyl acetate (volume ratio 1.0:3.5) as solvent to yield a colorless, transparent, oily liquid product G2.0 ( $\Rightarrow$ ). Yield: 6.91 g (0.78 mmol, 68%), purity: 98%.

IR spectra (KBr) 1724 ( $\nu_{\text{C=O}}$ ), 1636 ( $\nu_{\text{C=C}}$ ), 810 ( $\delta_{\text{C-H of CH=CH}_2}$ ), 1336, 1111 ( $\nu_{\text{C-N}}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.86–0.95 (CH<sub>3</sub>, 84H), 1.46–1.59 (\*CH<sub>2</sub>CH<sub>3</sub>, 56H), 2.43–2.48 (CH<sub>2</sub>COO, 72H), 2.54–2.57 [\*CH<sub>2</sub>N (CH<sub>2</sub>)<sub>2</sub>, 4H], 2.70–2.77 [CH<sub>2</sub>N (\*CH<sub>2</sub>)<sub>2</sub>, 104H], 3.34–3.67 [OCH<sub>2</sub>C (CH<sub>2</sub>)<sub>3</sub>, 72H], 4.11–4.18 (\*CH<sub>2</sub>OCOCH=CH<sub>2</sub>, 96H), 5.83–6.46 (CH<sub>2</sub>=CH, 144H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.8 (CH<sub>3</sub>), 22.6, 23.5 (\*CH<sub>2</sub>CH<sub>3</sub>), 30.0, 31.5 [\*C (CH<sub>2</sub>)<sub>4</sub>], 32.6, 33.5, 34.1, 35.2 (OOC\*CH<sub>2</sub>), 41.9, 49.1, 49.77 [\*CH<sub>2</sub>N (CH<sub>2</sub>)<sub>2</sub>], 52.8, 53.2 [CH<sub>2</sub>N (\*CH<sub>2</sub>)<sub>2</sub>], 62.4, 64.4, 65.8, 67.1 (OCH<sub>2</sub>), 128.6, 131.7 (CH<sub>2</sub>=CH), 166.1 (C=O). ESI-MS: Calcd. for C<sub>438</sub>H<sub>632</sub>O<sub>168</sub>N<sub>18</sub>: 8828. Found: 971.4 (M + 9H<sup>+</sup>) (Figs. 1 to 4).

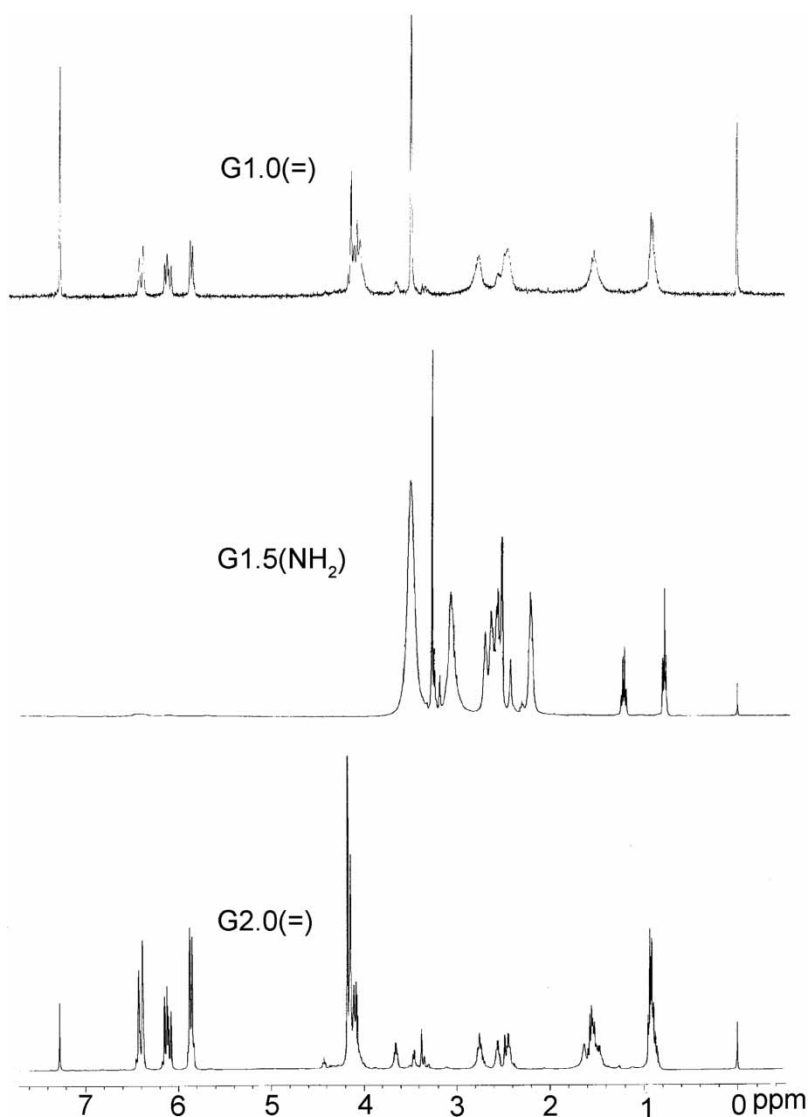
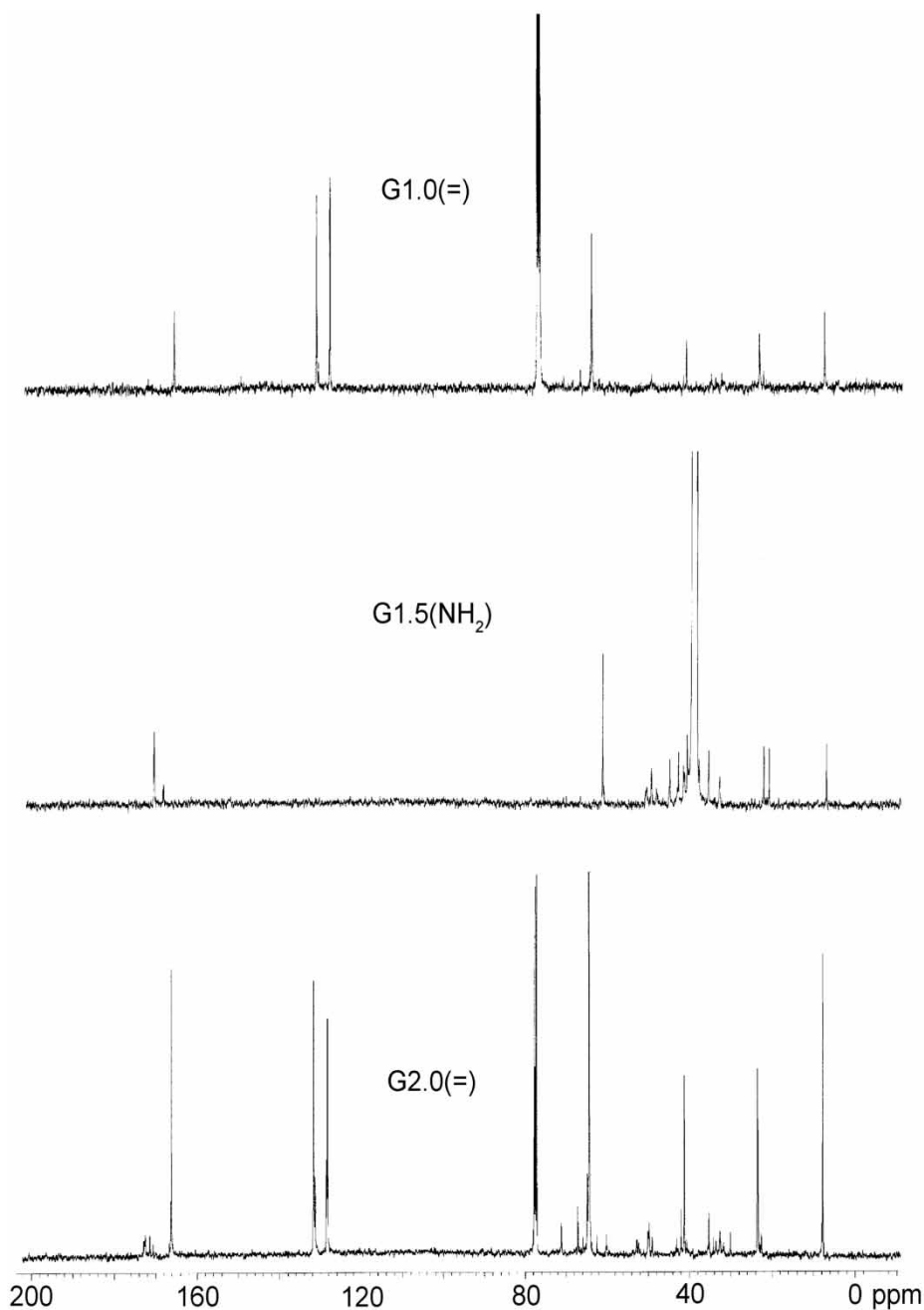


Figure 1.  $^1\text{H}$  NMR spectra of dendrimers.

### Measurements

Infrared (IR) spectra were carried out with a Magna-550 Fourier-transform infrared spectrometer. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) spectra were recorded on an INOVA 400MHz using  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as a solvent. Elemental analysis was carried out with a Shimadzu EA-1110 CHNSO. ESI-MS was recorded on a Finnigan LCQ<sup>TM</sup> ESI mass spectroscope. Nozzle temperature was  $220^\circ\text{C}$ , nozzle potential was 45 V, spray tip potential was 5200 V, flow rate was  $0.2\ \mu\text{l}/\text{min}$  (high purity nitrogen). High efficiency liquid chromatography (HPLC) was performed on a Shimadzu LC-6A using Nova-pak  $\text{C}_{18}$  column ( $3.9 \times 150\ \text{mm}$ ) and a mixture of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  (volume ratio was 4:1) as an eluent (the total flux was  $0.7\ \text{ml}/\text{min}$ ) and the detection



**Figure 2.**  $^{13}\text{C}$  NMR spectra of dendrimers.

wavelength was 239 nm for products with peripheral acrylic double bond, while using C<sub>18</sub> column (4.6 × 250 mm) and mixture of CH<sub>3</sub>CN and H<sub>2</sub>O (volume ratio was 2 : 3) as an eluent (the total flux was 0.7 ml/min), the detection wavelength was 216 nm for products with peripheral amino.

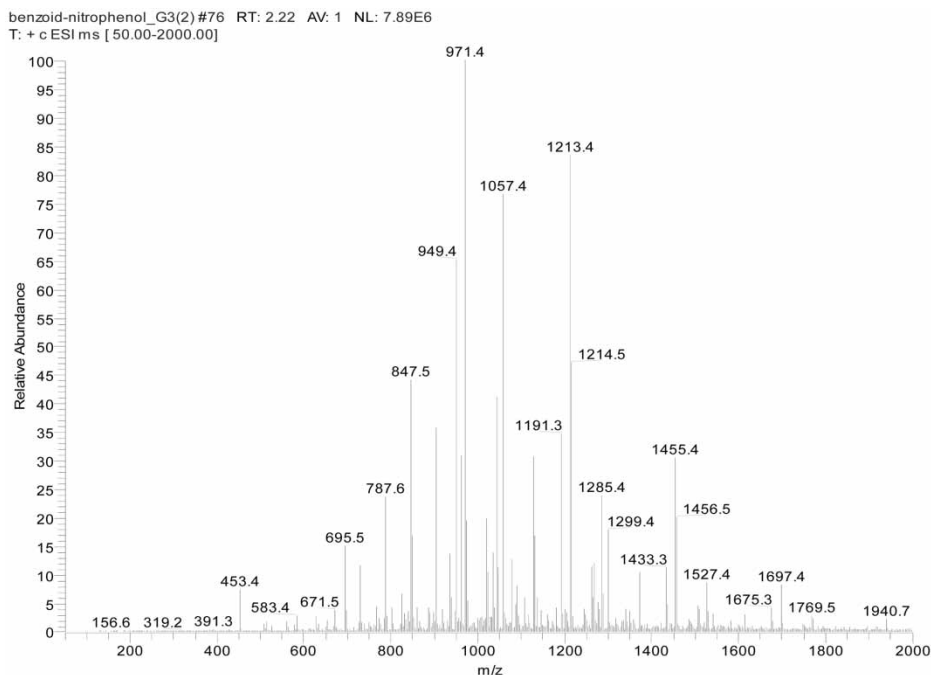


Figure 3. ESI-MS spectra of G2.0 (=).

## Results and Discussion

### The Synthetic Way of Dendrimers

Generally, a required numbers of functional groups are allowed in each step of the dendrimer preparation, therefore, the excessive reactive groups must be protected in one step and deprotected before the next step. However, in the present work, EDA with 3 reactive hydrogen atoms and TMPTA with 3 acrylate double bonds reacted directly without protection-deprotection steps (Sch. 1). The branching monomer was excessive

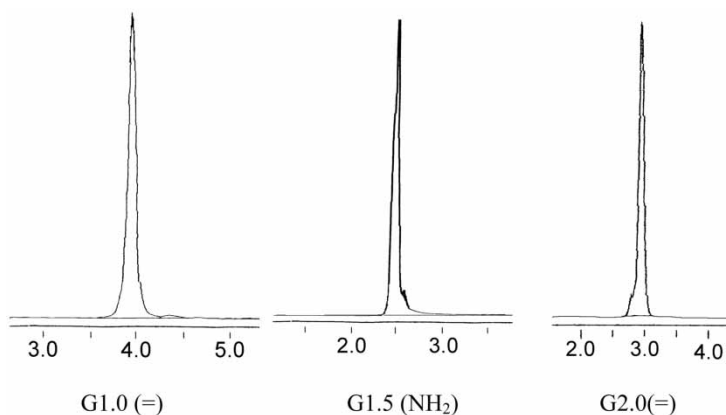
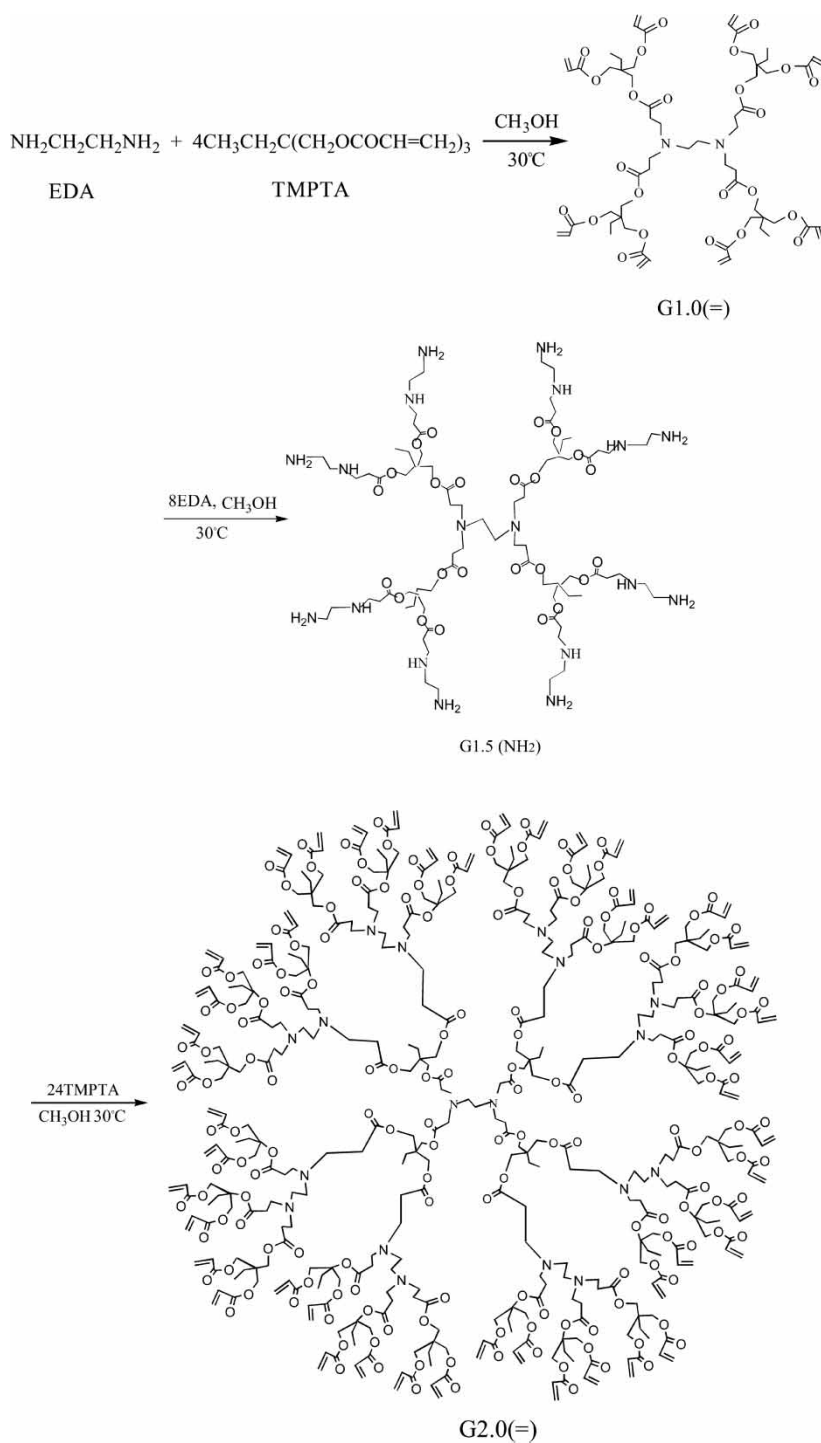


Figure 4. HPLC spectra of dendrimers.



Scheme 1. Synthetic way of dendrimers.

in order to obtain objective dendrimers. Every reaction step made the dendrimer growing efficiently. The number of terminated double bonds of the entire generation dendrimers grew at a rate of  $8 \times 6^{n-1}$ , while most of the reported dendrimers<sup>[12-15]</sup> usually grew according to the law of  $4 \times 2^{n-1}$  or  $3 \times 2^{n-1}$ .

### Effect of Reaction Conditions on Dendrimers

Since the reaction of raw materials with poly reactive groups will produce either highly branched polymers or gel,<sup>[16]</sup> reaction conditions were extremely important to dendrimer synthesis. So, they were carefully investigated in this work, as shown in Table 1-I and II.

The synthesis conditions for G1.0 (=) were optimized in Ref.<sup>[7]</sup>, that is, TMPTA and EDA (mole ratio 5.0:1.0) reacted directly at 30°C for 6 h. In the preparation of G1.5 (NH<sub>2</sub>), EDA must be largely excessive to lower polydispersity, but it could be cycled.

**Table 1**  
Effect of reaction conditions on yields and purities of dendrimers

Mole ratio of G 1.0 (=): EDA	Methanol <sup>a</sup> (%)	Temperature (°C)	Time (h)	Yields (%)	Purities <sup>b</sup> /%
I. G1.5(NH <sub>2</sub> )					
1:240	0	30	24	90	61
1:240	0	40	24	88	25
1:240	0	50	24	89	14
1:240	7.30	30	24	83	66
1:360	0	30	24	91	96
1:360	0	30	48	90	97
1:360	5.16	30	24	94	98
1:480	0	30	24	91	90
1:480	3.94	30	24	96	97
Mole ratio of G 1.5 (NH <sub>2</sub> ): TMPTA	Methanol <sup>a</sup> (%)	Temperature (°C)	Time (h)	Yields (%)	Purities <sup>b</sup> (%)
II. G2.0 (=)					
1:80	34.94	30	5	16	98
1:80	34.94	30	12	22	98
1:80	34.94	30	24	25	98
1:80	34.94	30	52	30	98
1:80	34.94	35	30	12	98
1:80	34.94	35	46	16	98
1:80	34.94	35	52	20	98
1:80	34.94	35	70	22	98
1:128	25.61	30	52	68	98
1:192	18.89	30	74	69	98

<sup>a</sup>Mass percent of methanol in the reaction system.

<sup>b</sup>Mass percent comes from HPLC.



Raising the temperature reduced the purity of G1.5 (NH<sub>2</sub>). A little methanol was a benefit to the purity of G1.5 (NH<sub>2</sub>). Similarly, TMPTA was greatly excessive in the synthesis of G2.0 (≡) and enough reaction time was needed in order to get a higher yield of G2.0 (≡). All in all, G1.0 (≡), G1.5 (NH<sub>2</sub>) and G2.0 (≡) were synthesized in an open system at 30°C for a certain time, so, the reaction conditions were mild.

### *Isolation and Purification of the Dendrimers*

It is well known that isolation and purification of dendrimers is extremely difficult because of similar solubility properties of products, byproducts and the raw material with the same functional groups. However, in this work, G1.0 (≡) and G1.5 (NH<sub>2</sub>) could be easily separated from the reaction systems according to solubility differences between these dendrimers and other components in the mixtures in selective solvents. The experimental results showed that G1.0 (≡) had less solubility in methanol than other parts in the separated mixture, and G1.5 (NH<sub>2</sub>) had a similar situation in ethyl acetate so that they could be separated and purified by washing with these two solvents. To a certain quantity of separated mixture, the amount of solvents existed at an optimum value at which the objective products had good purity and high yields. For G1.0 (≡), the mass ratio of the separated mixture to methanol was 1.0 : 3.5, for G1.5 (NH<sub>2</sub>), it was 1.0 : 1.2. Washing 3 times could give objective products with purity above 96% and yield above 90% (mass percent), further washing only raised purity slightly, while reducing the yields of objective products. The pure G2.0 (≡) was obtained by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (volume ratio 1.0 : 3.5) as solvent.

### **Conclusion**

Dendrimers with fast growing peripheral functional groups were synthesized from TMPTA and EDA by simple producers and under mild conditions. Some dendrimers could be easily isolated and purified by washing with selective solvents. The half and whole generation dendrimers are terminated with amino or acrylic double bond and are expected to be applied in many areas.

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