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Synthesis and characterization of supramolecule self-assembly polyamidoamine (PAMAM) G_1-G_1 NH_2, CO_2H end group Megamer

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Abstract

Supramolecule self-assembly polyamidoamine (PAMAM) dendrimer refers to the chemical systems made up of a discrete number of assembled molecular subunits or components. These strategies involve the covalent assembly of hierarchical components reactive monomers, branch cells or dendrons around atomic or molecular cores according to divergent/convergent dendritic branching principles, systematic filling of space around a core with shells (layers) of branch cells. The polydispersity index (PDI) for the supramolecule megamer are pretty closed to one, are in agreement with the Poisson probability distribution. Polyamidoamine (PAMAM) dendrimer G_1-G_1 that it was PAMAM Megamer NH_2, COOH end group synthesized and characterized by FT-IR, ^1H NMR, ^{13}C NMR spectra and Gel Permeation Chromatography (GPC).

Keywords: Supramolecule; polyamidoamin; PAMAM Megamer; self-assembly; dendrimer.

Introduction

In the 1990s, supramolecular chemistry became even more sophisticated with researchers such as James Fraser Stoddart by developing molecular machinery and highly complex self-assembled structures, and Itamar Willner by developing sensors and methods of electronic and biological interfacing. During this period, electrochemical and photochemical motifs became integrated into supramolecular systems in order to increase functionality; research into synthetic self-replicating system and work on molecular information processing devices began. The

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emerging science of nanotechnology also had a strong influence on the subject by building blocks such as fullerenes, nanoparticles, and dendrimers becoming involved in synthetic systems. Supramolecule self-assembly polyamidoamin (PAMAM) dendrimer refers to the covalent assembly of hierarchical components reactive monomers[1,2], branch cells or dendrons around atomic or molecular cores according to divergent/convergent dendritic branching principles systematic filling of space around a core with shells (layers) of branch cells [3-5]. It is provided that the degree of electronic coupling between the molecular component remains small with respect to relevant energy parameters of the component. While traditional chemistry focuses on the covalent bond, supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules [6]. Important concepts that have been demonstrated by supramolecular chemistry include molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically-interlocked molecular architectures, and dynamic covalent chemistry. The study of non-covalent interactions is crucial to understanding many biological processes from cell structure to vision that rely on these forces for structure and function. Biological systems are often the inspiration for supramolecular research [9-11]. Statistical Megamer assemblies have been reported as both *Supramacromolecular* and *supermacromolecular* (covalent) topologies. Many reports on the supramacromolecular self-assembly of these structures leading to dendrimeric clusters and monolayers are prime examples of supramacromolecular Megamers [12-16]. More recently, structures controlled covalent, which are mathematically defined megamers, have been reported [17-20]. They are a major subclass of megamers which also referred to as *core—shell and termini groups* that shown in Figure 1.

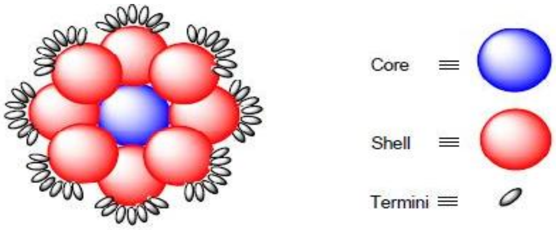


Figure 1. Core-shell and termini groups Megamer

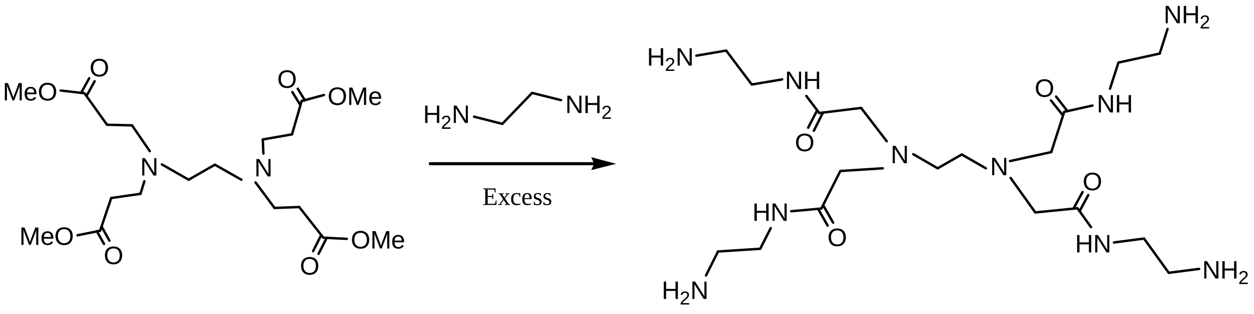
Experimental

General

Ethylenediamine (EDA) core polyamidoamie (PAMAM) dendrimers generation 0.5, succinic anhydride, methyl acrylate, methanol, dimethyl sulfoxide(DMSO), and all the other chemicals and solvents were purchased and used as it was supplied from Merck (Germany). IR spectra of the compounds were obtained on a Shimadzu FTIR-8400s spectrometer using a KBr disk. The ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC 400 Advanced instrument at 400 MHz in dimethyl sulfoxide (DMSO-d6) using tetramethylsilane as an internal standard. Molecular weights and molecular weight distributions were determined with a Gel Permeation Chromatography (GPC, waters-150^{o}C) equipped with a 410 RI detector, a 510 HPLC pump and m-Styragel columns with a pore size of 10^2, 10^3 and 10^4 A^o. The eluent was THF, and the molecular weights were calibrated with polystyrene standards.

Preparation of PAMAM – NH_2 (G_1) dendrimer, (EDA_{Core}), Z_0=2

A solution of PAMAM ($G_{0.5}$) (10 g, 0.025 mol) in methanol (20 mL) was carefully added to a vigorously stirred solution of 1, 2-diaminoethane (85 mL) in methanol (100 mL). The rate of addition was such that the temperature did not rise above 40 °C. The mixture was stirred for 96 h at room temperature. The solvent was removed under reduced pressure maintaining the temperature no higher than 40 °C. The excess of 1, 2-diaminoethane was removed by using an azeotropic mixture of toluene and methanol (9:1) to give the tetra-amine terminated G_1 precursor as a colorless oil (12.5 g, 98%). Synthesis of PAMAM – NH_2 (G_1) dendrimer was shown in Scheme 1.

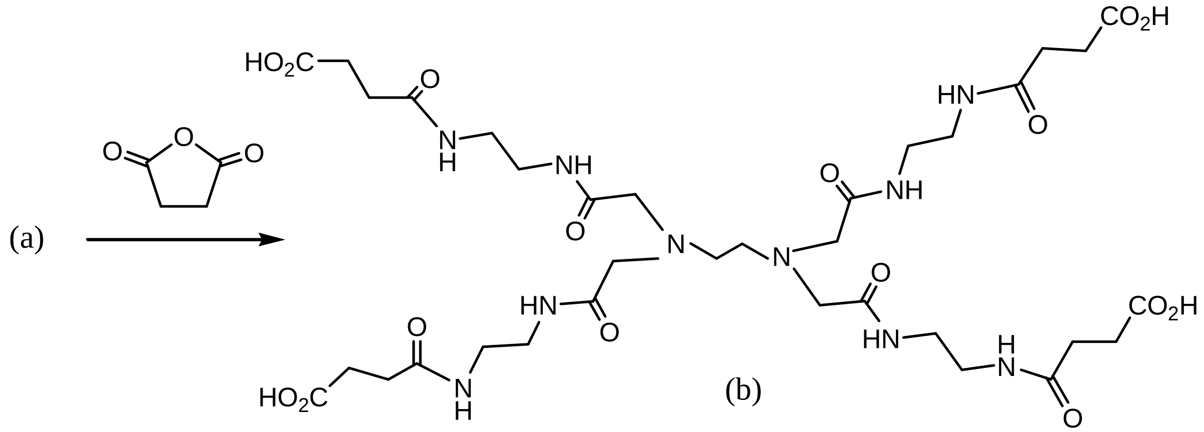


(a)

Scheme 1. The Synthesis of PAMAM – NH_2 (G_1) dendrimer

Preparation of PAMAM –CO_2H (G_1) dendrimer, (EDA_{Core}), Z_0=2

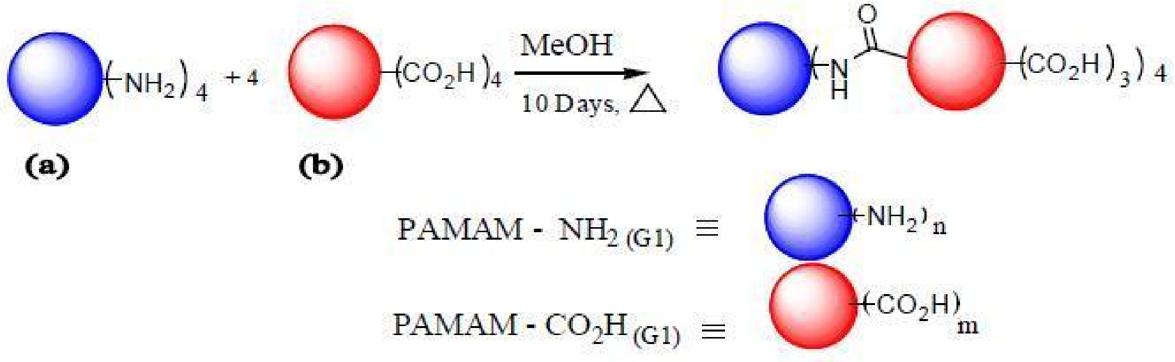
A solution of PAMAM G_1 (10.0000g,(a)) in DMSO (50 mL) was added to the solution of succinic anhydride 7.7423 g in DMSO 50 mL (molar ratio of SAH/−NH_2 =4: 1). It was added under vigorous stirring and reacted for 24 h. The DMSO solution was dialyzed against water to remove the excess amount of succinic anhydride as well as the organic solvent. Obtained product was a white solid weighted 15.6600 g (Yield: 86.7 %). Synthesis of PAMAM – COOH (G_1) dendrimer was shown in Scheme 2.



Scheme 2. The synthesis of PAMAM –CO_2H (G_1) dendrimer

Preparation Polyamidoamine (PAMAM) G_1-G_1 NH_2, CO_2H End Group Megamer

A solution of PAMAM-NH_2 G_1 (0.3043g, (a)) in MeOH (50 mL) was added to the solution of PAMAM-COOH G_1 (2.1600g, (b)) in MeOH(50 mL). It was added under vigorous stirring and reacted for 10 days. Methanol was removed by vacuum distillation at 40 °C. The excess of 1, 2-diaminoethane from the previous relation was removed by azeotropic distillation using a mixture of toluene and methanol (9:1). Obtained product was a dense viscous yellow oil liquid weighted 2.0482 g (Yield: 80.0 %). Synthesis of PAMAM G_1-G_1 NH_2, CO_2H end group Megamer was shown in Scheme 3.



Scheme 3. The synthesis of PAMAM G_1-G_1 NH_2, CO_2H end group Megamer

Selected spectral data PAMAM – NH_2 (G_1) dendrimer, ($^{a}CH_2\ ^{a}CH_2$)[N($^{b}CH_2\ ^{c}CH_2\ ^{d}CO\ ^{e}NH\ ^{f}CH_2\ ^{g}CH_2\ ^{h}NH_2)_2]_2$

Yellow oil, FT-IR (KBr): 3300 cm^{-1} (-NH), 1643 cm^{-1} (stretching C=O); ^{1}H NMR (FT-400 MHz, DMSO): δ; 2.41(s, a, 4H), 2.68 (t, b, 8H), 2.19 (t, c, 8H), 3.24(q, f, 8H), 2.55(m, g, 8H), 2.07 (t, h, 8H), 8.11 (s, e, 8H); ^{13}C NMR (400 MHz, DMSO): δ; 34.18 (c), 39.83 (g), 46.47 (f), 50.55 (a), 50.75 (b), 172.66 (d).

Selected spectral data PAMAM – COOH (G_1) dendrimer, ($^{a}CH_2\ ^{a}CH_2$)[N($^{b}CH_2\ ^{c}CH_2\ ^{d}CO\ ^{e}NH\ ^{f}CH_2\ ^{g}CH_2\ ^{h}NH^{i}CO^{j}CH_2\ ^{k}CH_2\ ^{l}CO_2H)_2]_2$

Yellow oil, FT-IR (KBr): 3420 cm^{-1} (-OH), 1674 cm^{-1} (stretching C=O); ^{1}H NMR (FT-400 MHz, DMSO): δ; 2.45(t, a, j, 12H), 2.64 (t, b, 8H), 2.28 (t, c, 8H), 3.24 (t, g, f, 16H), 2.51 (s, k, 8H), 8.05 (s, e, h, 8H), 11.0 (s, l, 4H); ^{13}C NMR (400 MHz, DMSO): δ; 172.66 (d, i), 177.32 (l), 50.50 (a, b), 39.83 (c, f, g), 32.28 (j, k).

Selected spectral data PAMAM G_1-G_1 NH_2, CO_2H end group Megamer

Yellow solid oil, FT-IR (KBr): 3500 cm^{-1} (-OH), 1650 cm^{-1} (stretching C=O); ^{1}H NMR (FT-400 MHz, DMSO): δ; 2.41(t, 24H), 2.19 (t, 40H), 2.51 (t, 24H), 2.45(m, 36H), 3.28(m, 80H), 2.29 (t, 2H), 3.44(t, 2H), 2.98 (t, 2H), 11.04 (s, 12H), 8.05 (s, 40H); ^{13}C NMR (400 MHz, DMSO): δ; 34.1, 36.8, 39.9, 51.7, 172.20, 174.0.

Results and discussion

Experimental data have been collected according to this fact that the various generations of PAMAM denderimers and supramolecule have been synthesized. In PAMAM – COOH (G_1), amine group disappeared in 3300- 3500 Cm^{-1} as a doublet and against the hydroxyl group appeared in 3400 Cm^{-1} as a wide peak.

In the other hand, analysis data, spectra of FT-IR for G_1 and G_2 were demonstrated that C-O stretching, vibration for metoxy in G_1, G_2 has not been observed. NH at 1556.4 and 1483.2 Cm^{-1} for G_1, G_2 appeared respectively, NH_2 can be seen in 3300-3500(m) Cm^{-1}. In C=O stretching groups, ester has not been shown.

FT-IR spectrum in generation one has shown a CO (broad) stretching vibration in acid end group at 1024 Cm^{-1}. The NH, C-N stretching vibration from 1556.4 (m) to 1562.2 Cm^{-1} in the PAMAM amine termini to PAMAM COOH termini has been changed. C=O stretching vibration acid from 1651 to 1647 Cm^{-1} has been changed and OH peak was appeared in 3500-3000 Cm^{-1}. The double peak for NH_2 in PAMAM COOH end group ($G_{1\text{-}COOH}$) has been removed.

The reaction of PAMAM (G_1) (a) with PAMAM (G_1) COOH end group (b) afforded PAMAM G_1-G_1 NH_2, CO_2H end group Megamer as was shown in Scheme 3. It was fully characterized. The measured molecular weight of the PAMAM –COOH G_1 dendrimer (905g/mol) is slightly lower than the theoretical one (917g/mol), and so the measured molecular weight of the PAMAM –NH_2, G_1dendrimer (508g/mol) is slightly lower than the theoretical one (517g/mol). GPC data can be used in order to derive the precise number of each functional group attached to the carrier. The PAMAM dendrimers and PAMAM Megamer M_i (G_n-G_m) molecular weights and molecular weight distribution given for each generation PAMAM and Megamer were shown in Table 1.

Table 1. Number and weight average molecular weights and molecular weight distribution of PAMAM and PAMAM Megamer

Entry	**Compound**	$^{*}\overline{M}_n, g/mol$	$^{**}\overline{M}_w, g/mol$	$PDI = \frac{\overline{M}_w}{\overline{M}_n}$
1	PAMAM-$COOH_{G1}$	905	910	1.005
2	PAMAM-$NH_{2\ G1}$	508	510	1.004
3	Megamer M_1 (G_1-G_1)	3990	4080	1.022

[*] Number average molecular weight
[**] Weight average molecular weight calculated from GPC data
PDI=Polydispersity Index

Conclusion

The polydispersity index (PDI) for the supramolecule Megamer is indicated in Table 1, Entry 3, which are pretty closed to one, are in agreement with a Poisson probability distribution [15]. The dendrimer of being monodispersitive [3,11], the dendrimer G_1 (amine and carboxyl end group) is monodispersitive as obvious from the data in Table 3, Entries 1 and 2.

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