

Dendronization of Undecylamine with Pentaerythritol Tetra-acrylate (0.5 mole acrylate/NH) Quenched with Morpholine.

Pentaerythritol tetra-acrylate (3.21 g, 9.1 mmol) was dissolved in methanol (5.0 mL) and cooled to 4 °C with an ice-water bath. The solution of undecylamine (1.56 mg, 9.1 mmol in 10 mL methanol) was added during a period of 5 minutes. After the addition, the reaction was stirred at 4°C for 30 min. and allowed to warm to room temperature. The reaction was then stirred at room temperature under dark overnight. A wax like, polymeric solid phased out at the bottom of flask. The solution was checked by MALDI-TOF: calculated for C₂₈H₄₅NO₈ (looped, mono-dendron) (3), 523.66, found, 524.28(M+H), 556.33 (M+K).

Preparation of [core: 1,2-Diaminoethane]; (G=1); dendri{CH₂-CH₂-CO₂-CH₂C(Et)-(CH₂CO₂CH=CH₂)₂}

To a 100 ml round bottom flask with a stir bar was added trimethylolpropane triacrylate (TMPTA) (29.6 g, 0.10 mol) in 15 ml MeOH and cooled to ~4 °C. 1,2-Diaminoethane (1.2 g, 0.02 mol) in 5 mL MeOH was added over 5 minutes. This mixture was stirred at 30 °C for 18 hours. This mixture was cooled to 20 °C and poured into 150 g of stirred methanol. The product phased out by allowing the mixture to stand without stirring for 1 hour. The methanol layer was decanted and this process was repeated two more times. This clear, viscous mixture was evacuated at high vacuum for 3 hours while protecting from light, using aluminum foil, to give 20g (100% based on tri-adduct product and 80% based on tetra-adduct product) of material indicating that most of the material was the tri-dendron dendrimer adduct. A MALDI-TOF mass spectrum of this product exhibited a major peak at 950 daltons corresponding to the tri-dendron adduct with theoretical MW = 949 daltons, structure (7). A very slight peak at 1245 daltons was observed for the tetra-dendron adduct. ¹³C-NMR (500 MHz, CDCl₃) δ 172.10, 165.69, 131.26, 128.04, 64.05, 63.88, 49.48, 40.86, 40.77, 32.38, 23.14, 23.00, 7.45.

Preparation of [core: 1,4-Diaminobutane];(G=1); dendri{CH₂-CH₂-CO₂-CH₂C-(CH₂CO₂CH=CH₂)₃}₄ with 4 moles PTA per NH and Conversion to Morpholine Surface.

To a 50 mL round bottom flask containing a stir bar was added pentaerythritol tetraacrylate (PTA) (19.0 g, 32 mmol, 4 moles per NH) and 10 mL MeOH. To this mixture cooled at 4 °C was added 1,4-diaminobutane (303 mg, 3.3 mmol) in 5 mL MeOH. This mixture was stirred at 25 °C for 18 hours under N₂. While stirring, this mixture was added dropwise over ~ 5 minutes into 40 mL of MeOH containing morpholine (28 g, 321 mmol, 1.5 moles per acrylate). After stirring for 18 hours at room temperature, this crude reaction mixture was devolatilized on a rotary evaporator, followed by submission to high vacuum for 3-5 hours to give 37.17 g of crude material. An aliquot (2.8 g) was purified on a Sephadex LH – 20 column (void volume 365 mL) in methanol taking 30 x 8 mL fractions. A TLC (MeOH) indicated the product eluted in fractions 2 – 16. These collected fractions were stripped of volatiles to a constant weight giving 600 mg (8.0g, 96% yield for a (4:1); tetradendron adduct with theoretical, MW = 2540).

¹H-NMR (300 MHz, CDCl₃): δ 1.35 (bs, 4 H), 2.41 (bs, 36 H), 2.45 – 2.58 (bs, 30 H), 2.59 (bm, 18 H), 2.62 (bm, 13H), 3.37(bs, 4 H), 3.41 (bs, 6H), 3.52 (bm, 4H), 3.63 (bs, 36 H), 4.0 – 4.2 (bm, 29 H).

¹³C-NMR (75 MHz, CDCl₃): δ 24.84, 32.13, 42.42, 42.56, 43.03, 43.15, 43.88, 43.07, 48.92, 53.50, 54.00, 54.16, 61.99, 62.14, 62.48, 66.79, 66.89, 67.00, 171.73, 171.03, 172.06.

FTIR (neat) ν_{\max} 2956, 2818, 1738, 1449, 1252, 1117, 1054, 1011, 859 cm⁻¹.

Preparation of [core: 1,6-Diaminohexane]; (G=1); dendri{CH₂-CH₂-CO₂-CH₂C-(CH₂CO₂CH=CH₂)₃}₄ (2 moles PTA per NH) and Conversion to Morpholine Terminated Adduct.

To a 50 mL round bottom flask containing a stir bar was added pentaerythritol tetraacrylate (PTA) (9.7 g, 27.6 mmol) and 10 mL MeOH. After cooling to 4 °C, 1,6-diaminohexane (400 mg, 3.4 mmol) in 10 mL MeOH was added. This mixture was stirred at 25 °C for 18 hours under N₂. After cooling this mixture to ~ 15 °C, it was added dropwise over ~ 5 minutes into 40 mL stirred MeOH containing morpholine (14.4 g, 165 mmol, 1.5 moles per acrylate) cooled to 4 °C. This mixture was stirred for 19 hours at room temperature, devolatilized on a rotary evaporator, followed by submission to high vacuum for 3-5 hours to give 22 g crude material. An aliquot (1.0

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g) was purified on a Sephadex LH – 20 column (void volume 105 mL) in methanol taking 30 x 3 mL fractions. A TLC (MeOH) indicated the product eluded in fractions 1-16. These collected fractions were stripped of volatiles to a constant weight to give 250 mg (5.5 g, 89% yield of the tri-dendron adduct).

¹H-NMR (300 MHz, CDCl₃): δ 1.20 (bs, 4 H), 1.35 (bs, 4H), 2.39 (bs, 48 H), 2.43 – 2.8 (bm, 64 H), 3.40 (bs, 4H), 3.52 (bs, 4H), 3.61 (bs, 48 H), 4.0 – 4.2 (bs, 32 H).

¹³C-NMR (75 MHz, CDCl₃): δ 27.64, 32.22, 42.61, 43.10, 44.02, 49.05, 53.60, 54.09, 54.27, 62.10, 62.60, 66.92, 67.02, 171.88, 172.22.

FTIR (neat) ν_{\max} 2956, 2818, 1738, 1449, 1252, 1117, 1054, 1011, 859 cm⁻¹.

Preparation of [core: 1,12-Diaminododecane]; (G=1); dendri{CH₂-CH₂-CO₂-CH₂C-(CH₂CO₂CH=CH₂)₃}₄, (4 moles PTA per NH) and Conversion to Morpholine Terminated Adduct.

To a 50 mL round bottom flask containing a stir bar was added pentaerythritol tetraacrylate (PTA) (19.9 g, 50 mmol, 2.2 moles per NH) and 10 mL MeOH. To this mixture cooled at 4 °C was added 1,12-diaminododecane (706 g, 5.8 mmol) in 20 mL MeOH. This mixture was stirred at 25 °C for 18 hours under N₂. This mixture was added dropwise over ~ 5 minutes to a mixture of 40 g MeOH containing morpholine (29 g, 333 mmol, 1.5 moles) cooled at 4 °C and then stirred at room temperature for 18 hours. The resulting mixture was evacuated of volatiles with a rotary evaporator, followed by high vacuum for 3-5 hours to give 39.25 g of crude product. An aliquot (2.8 g) was purified on a Sephadex LH – 20 column (void volume 365 mL) in methanol taking 30 x 8 mL fractions. A TLC (MeOH) indicated the product eluded in fractions 2-16. These collected fractions were stripped of volatiles to a constant weight to give 600 mg (94% yield of the (4:1), tetra-dendron adduct with theoretical MW = 2658).

¹H-NMR (300 MHz, CDCl₃): δ 1.22 (bs, 14 H), 1.39 (bs, 4 H), 2.41 (bs, 24 H), 2.45-2.58 (bs, 18 H), 2.59 – 2.68 (bs, 10 H), 2.68 – 2.78 (bs, 6H), 3.41 (bs, 4 H), 3.52 (bs, 2 H), 3.64 (bs, 24 H), 4.0-4.2 (bs, 18 H).

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^{13}C -NMR (75 MHz, CDCl_3): δ 27.76, 29.94, 32.22, 32.29, 42.61, 42.61, 43.11, 43.23, 44.06, 49.07, 49.09, 53.60, 54.09, 54.28, 62.11, 62.24, 66.91, 67.03, 171.80, 172.18, 172.23, 172.55.

FTIR (neat) ν_{max} 2956, 2818, 1738, 1449, 1252, 1117, 1054, 1011, 859 cm^{-1} .