Synthesis and Characterization of Dendronized Polymers

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Summary: This research aims at the synthesis of several dendrons with different functional groups on their surface, and their use as functionalizing agents of synthetic polymers. Two principal products were synthesized and characterized: dendronized MDI oligomers and dendronized PMMI. The results of the characterization studies of dendronized polymers demonstrated the influence of the polarity of dendrons and the dendronization pathway on the properties of the final products.

Keywords: dendrimers; dendron; dendronized PMMI; dendronized polymer

Introduction

The development of well-defined molecular and supramolecular architectures attracts still increasing scientific interest. Dendrimers are among the most exciting molecular architectures developed in the recent past, and they have paved the way for a new class of materials with promising applications in different fields. Dendronized polymers are a class of polymers produced by the combination of linear polymers and dendritic molecules as side chain pendant moieties.[1–4] Therefore, their preparation combines organic synthesis of dendrons and polymer synthesis, and different synthetic strategies have been developed.[5] Dendronized polymers might be interesting targets and as such be ''the next step'' in molecular architecture.

In addition, when dendritic fragments are attached to polymer chains, the conformation of the polymer chain is strongly affected by the size and chemical structure of the dendritic wedges attached.[6] Dense attachment of dendritic side chain converts a linear polymer into a cylindrically shaped, rigid and nanoscopic dimension. Originally termed ''rod-shaped dendrimers'', they made their first appearance in a patent filed by Tomalia et al. at Dow in 1987;[7] Fréchet and Hawker[8] were the first to recognize these ''hybrid architectures''.

Another property of this class of polymers is that the combination of specific dendrons with linear chains provides an opportunity to design a well-defined amphiphilic dendronized polymer system, which can bring about supramolecular aggregates in an aqueous phase.[9–12]

In this paper, we report the synthesis of a family of specific dendrons bearing different superficial functional groups and their use as grafting agent of linear polymers, such as methyl diphenyl diisocyanate (MDI) and poly (monomethyl itaconate) (PMMI). The dendronized polymers were characterized and the effect of dendronization on the properties of the products was studied.

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Experimental Part

Materials

4-amino-[2-(tert-butoxycarbonyl)-ethyl heptanedioate (Behera's amine) was kindly supplied by Newkome labs. The substrate

5-nitroisophthalic acid was obtained from Sigma, tris-(hydroxymethyl)-aminomethane (TRIS) from Anedra, acrylonitrile from Carlo Erba, methyl diphenyl diisocyanate oligomers with approximately 2.7 eq./mol (MDI) from INTEMA Labs, silica gel 60 from Merck. Triethylamine, TEA 99% from Anedra; thionyl chloride from Merck. Palladium 10 wt.% on activated carbon from Aldrich and silica gel 60 from Merck. Potassium bromide 99% FT-IR grade and Chloroform-*d* 99.8%D from Aldrich. All commercial chemicals were used without purification. Solvents were obtained from Sintorgan, purified by distillation, and dried with 4Å molecular sieves when necessary.

Instruments

Fourier Transform Infrared Spectra (FT-IR) were obtained in a Nicolet 5-SXC FT-IR spectrometer on KBr discs. Nuclear Magnetic Resonance Spectra (NMR) obtained in $CDCl_3$, D_2O unless otherwise indicated, using a Bruker 200 MHz NMR spectrometer.

FAB spectra were obtained in a CH_5DF/FAB instrument in CH_3OH/m–NO_2-Benzyl-OH (matrix).

Elemental analyses were carried out in a Fisons EA 1108 CHNS-O instrument.

Intrinsic viscosities, $[\eta]$, were determined using a capillary type Desreux-Bischoff[13] viscometer and their were calculated according to the classical empirical relations[14] in DMSO at 25 °C.

Methods

A) Tris[(cyano-ethoxy)methyl] aminomethane ***2*** (cyanoethylation)

TRIS (4,0000 g, 0.33 mmol) was reacted with acrylonitrile 26 mL (ratio 1:6 mol) in basic medium (KOH 1%) in a dioxane/water mixture (16:1) to favor substrate dilution. The reaction mixture was stirred for 24 h at room temperature. When the reaction was complete, the solvent was evaporated under vacuum and the residue was dissolved in chloroform and washed with water. The crude product was purified by liquid chromatography on silica gel and eluted with acetone. Yield was 80%.

FT-IR (cm^{-1}): hydroxyl band disappearance (2500–3300, ν OH) and a new signal at 2252 (ν CN) appearance.

^{13}C-NMR ($CDCl_3$): (δ ppm) = 118.6 (*C*N); 73.2 (C*C*H_2O); 65.9 (O*C*H_2CH_2); 55.4 (H_2N*C*CH_2O); 19.4 (*C*H_2CN).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 3.60 (t, 6H, OC*H*$_2$CH_2); 3.42 (s, 6H, NC*H*$_2$O CH_2); 2.60 (t, 6H, C*H*$_2$CN); 1.60 (N*H*$_2$).

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 303.3; found 303.0 $[M+Na]^+$.

B) Tris[((methoxycarbonyl)ethoxy)methyl] aminomethane ***3*** (methanolysis)

tris cyanoamine (1.0000 g, 3.57 mmol) was refluxed in dry HCl saturated anhydro MeOH. The reaction mixture was stirred for 24 h at room temperature. When the reaction was complete, the solvent was evaporated under vacuum and the residue was dissolved in chloroform and washed with Na_2CO_3 solution 10%. Yield was 72%.

FT-IR (cm^{-1}): nitrile band disappeared (2252) and a new signal appeared at 1740 (ν C=O).

^{13}C-NMR ($CDCl_3$): (δ ppm) = 172.0 (*C*=O); 72.7 (H_2N*C*OCH$_2$); 66.8 (O*C*H_2CH_2); 56.0 (*C*NH_2); 51.5 (*C*H_3); 34.8 (*C*H_2CO).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 3.67 (t, 6H, OC*H*$_2$CH_2); 3.67 overlapped (s, 9H, OC*H*$_3$); 3.37 (s, 6H, NC*H*$_2$OCH$_2$); 2.54 (t, 6H, C*H*$_2$CO).

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 380.2; found 380.2 $[M+H]^+$.

C) Dendritic molecules ***6, 7, 8***

To obtain diacidchloride, **5**, $SOCl_2$ (10 mL) was added to diacid (0.4000 g, 16 mmol) in THF (10 mL) anhydro under nitrogen and allowed to react for 4 h under reflux. The excess of $SOCl_2$ was evaporated under vacuum and the crude product was used for the amidation step. To obtain products **6**, **7** and **8,** the reaction was carried out using the ratio of equivalents of *tris[(cyano-ethoxy)methyl] aminomethane* **2** (1.000 g), *tris[((methoxycarbonyl)ethoxy) methyl]aminomethane* **3** (1.3000 g) and *Behera's amine* **4** (1.6600 g), to be 1:2, with respect to diacid. TEA (0.5 mL) in 50 mL anhydrous THF was added to diacid chloride **5** and allowed to react for 24 h at

room temperature. When the reaction was complete, the solvent was evaporated under vacuum and the residue was dissolved in chloroform and washed with water. After removal of the solvent, a pale yellowish oil (**6** and **7**) and a white solid substance (**8**) were obtained and purified by column chromatography through silica gel using acetone as eluent.

Yields were 75, 78 and 80% respectively.

*Product **6***. FT-IR (cm^{-1}): appearance of two new signals at 1667 and 1535 assigned to Band I (C=O stretching vibration) and Band II (N–H bending vibrations), corresponding to the amide group. The C–N absorption band of nitrile appeared at 2252.

^{13}C-NMR ($CDCl_3$): (δ ppm) = 167.7 (C=O amide); 142.5 (CNO_2); 131.6 ($C_{3\ and\ 5}$ aromatic); 128.6 (C_4 aromatic); 126.9 ($C_{2\ and\ 6}$ aromatic); 118.2 (CN); 70.9 (CCH_2O); 65.9 (OCH_2CH_2); 48.2 ($NHCCH_2O$); 18.83 (CH_2CH_2CN).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 8.71 (s, 2H, C*H* aromatic); 8.39 (s, 1H, C*H* aromatic); 3.93 (s, 12H, O*CH*$_2$CH$_2$); 3.69 (t, 12H, O*CH*$_2$CH$_2$CN); 2.60 (t, 12H, OCH$_2$*CH*$_2$CN).

*Product **7***. FT-IR (cm^{-1}): appearance of two new signals at 1667 and 1535 assigned to Band I (C=O stretching vibration) and Band II (N-H bending vibrations), corresponding to the amide group. The carbonyl absorption band of ester appeared at 1739.

^{13}C-NMR ($CDCl_3$): (δ ppm) = 172.0 (*C*=O ester); 164.7 (*C*=O amide); 148.6 (*C*NO_2); 137.2 ($C_{3\ and\ 5}$ aromatic); 130.5 (C_4 aromatic); 125.7 ($C_{2\ and\ 6}$ aromatic); 70.2 (*CC*H$_2$O); 66.8 (O*C*H$_2$CH$_2$); 57.6 (*C*NHCO); 51.6 (*C*H$_3$); 34.7 (*C*H$_2$COOMe).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 8.67 (s, 1H, C*H* aromatic); 8.42 (s, 1H, C*H* aromatic); 6.85 (s, 1H, C*H* aromatic); 3.75 (t, 12H, O*CH*$_2$CH$_2$); 3.55 (s, 18H, O*CH*$_3$); 3.40 (s, 12H, NC*H*$_2$OCH$_2$); 2.54 (t, 12H, C*H*$_2$CO).

*Product **8***. FT-IR (cm^{-1}): appearance of two new signals at 1667 and 1535 assigned to Band I (C=O stretching vibration) and Band II (N–H bending vibrations), corresponding to the amide group. The carbonyl absorption band of ester appeared at 1736.

^{13}C-NMR ($CDCl_3$): (δ ppm) = 173.1 (*C*=O ester); 163.3 (*C*=O amide); 148.3 (*C*NO_2); 136.9 ($C_{3\ and\ 5}$ aromatic); 131.7 (C_4 aromatic); 124.1 ($C_{2\ and\ 6}$ aromatic); 80.9 (CH_3CO); 58.4 (*C*NHCH$_2$); 30.3 (*C*H$_2$CH$_2$CO); 29.9 (CH$_2$*C*H$_2$CO); 27.9 (OC*C*H$_3$).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 8.77 (s, 2H, C*H* aromatic); 8.69 (s, 1H, C*H* aromatic); 2.25 (m, 12H, CCH$_2$C*H*$_2$CO); 2.08 (m, 12H, CC*H*$_2$CH$_2$CO); 1.36 (s, 54H, OC(C*H*$_3$)$_3$).

D) Hydrogenation

Dendritic molecules (**6**, **7**, **8**) (800 mg, 1.00 mmol; 800 mg, 0.90 mmol; 800 mg 0.80 mmol, respectively) dissolved in methanol (20 mL) were reduced at 40 psi H_2 room temperature with 100 mg of Pd/C 10%. After filtration of the catalyst, the solvent was evaporated and products **9, 10** and **11**, were obtained. Yields ranged between 93 and 96%.

FT-IR (cm^{-1}) = **9**, **10**, **11** presented a pattern similar to that of **6**, **7**, **8**, respectively. The overlapping signals corresponding to amide and amino groups did not allow a conclusion to be drawn.

*Product **9***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 119.3 (C_4 aromatic); 118.3 ($C_{2\ and\ 6}$ aromatic); the rest of the signals remained without change with respect to **6**.

^{1}H-NMR ($CDCl_3$): (δ ppm) = 6.37 (s, 2H, CH aromatic); 6.63 (s, 1H, CH aromatic); the rest of the signals did not change with respect to **6**.

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 727.7 found 728.0 $[M+Na]^+$.

*Product **10***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 116.0 (C_4 aromatic); 118.0 ($C_{2\ and\ 6}$ aromatic); the rest of the signals remained without change with respect to **7**.

^{1}H-NMR ($CDCl_3$): (δ ppm) = 6.94 (s, 2H, CH aromatic); 6.71 (s, 1H, CH aromatic); the rest of the signals did not change with respect to **7**.

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 925.9 found 926.4 $[M+Na]^+$.

*Product **11***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 116.0 (C_4 aromatic); 118.0 ($C_{2\ and\ 6}$ aromatic); the rest of the signals remained without change with respect to **8**.

^{1}H-NMR ($CDCl_3$): (δ ppm) = 7.25 (s, 2H, C*H* aromatic); 7.38 (s, 1H, C*H* aromatic); the rest of the signals remained without change with respect to **8**.

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 998.5; found 998.2 $[M+Na]^+$.

*E) Hydrolysis **(12)***

Product **10** (400 mg, 0.5 mmol) was dissolved in 2N NaOH solution at room temperature for three days. The solvent was evaporated immediately. Yield was 80%.

FT-IR (cm^{-1}): The carbonyl absorption band of acid occurred at 1723.

^{13}C-NMR (D_2O): (δ ppm) = 172.0 (*C*=O ester) disappeared; the rest of the signals remained without change with respect to **10**.

^{1}H-NMR (D_2O): (δ ppm) = the methyl ester signal at 3.55 disappeared.

*F) Hydrolysis **(13)***

A solution of **11** (600 mg, 0.6 mmol), in 95% formic acid (15 mL) was stirred at 50 °C for 35 h. After concentration, toluene (5 mL) was added and the solution was once again evaporated under vacuum to remove residual formic acid azeotropically. Finally, **13** was obtained as a viscous oil.

FT-IR (cm^{-1}): the carbonyl absorption band of acid occurred at 1720.

^{13}C-NMR (D_2O): (δ ppm) = 178.3 (*C*=O acid); the rest of the signals remained without change with respect to **11**.

^{1}H-NMR (D_2O): (δ ppm) = the t-butyl ester signal at 1.36 disappeared.

FAB-MS (CH_3OH/m-NO_2-Benzyl-OH matrix) calcd. 738.3 found 738.3 $[M-H]^-$.

G) Dendritic molecules - methyl phenyl diisocyanate (MDI)

polyurethane oligomer end-capped with isocyanate groups (118 mg, 0.4 mmol) was linked to dendritic molecules **2**, **4**, **9**, **11** (2 mmol) in anhydro THF under nitrogen (ratio 1:2 mol) for 4 h at room temperature. Crude products were purified by liquid chromatography on silica gel and eluted with chloroform:acetone 90:10. As a result, a yellowish oil (**14**, **15**, **16**, **17**) was obtained. Yields were 57% (**14**), 42% (**15**), 54% (**16**) and 44% (**17**).

FT-IR (cm^{-1}): the spectra show the urea group with a band at 1653 cm^{-1} (C=O stretching vibration), while the isocyanate signal at 2283 cm^{-1} vanished (NCO stretching vibration).

*Product **14***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 154.5 (*C*=O urea); 138.2-129.0 (aromatics *C* of MDI); 118.6 (*C*N); 73.2 (CCH_2O); 65.9 (OCH_2CH_2); 55.4 (H_2NCCH_2O); 19.4 (CH_2CN).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 7.43-6.91 (aromatics *H* MDI); 4.29 (CH_2 MDI); 3.82 (s, 6H, NCH_2O CH_2); 3.60 (t, 6H, OCH_2CH_2); 2.60 (t, 6H, CH_2CN); 1.60 (NH_2).

*Product **15***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 167.7 (*C*=O amide); 154.5 (*C*=O urea); 147.7 (*C*NHCO); 138.2–129.0 (aromatics *C* of MDI); 131.6 ($C_{3\ and\ 5}$ aromatic); 116.1 (C_4 aromatic); 114.9 ($C_{2\ and\ 6}$ aromatic); 118.2 (*C*N); 70.9 (CCH_2O); 65.9 (OCH_2CH_2); 48.2 ($NHCCH_2O$); 18.83 (CH_2CH_2CN).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 8.71 (s, 2H, C*H* aromatic); 8.39 (s, 1H, C*H* aromatic); 7.43–6.91 (multiple signals corresponding to aromatic protons of MDI); 4.10–3.50 (broad multiplets corresponding to CH_2 of MDI); 3.93 (t, 12H, OCH_2CH_2); 3.69 (t, 12H, OCH_2CH_2CN); 2.60 (t, 12H, OCH_2CH_2CN).

*Product **16***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 173.1 (*C*=O ester); 154.5 (*C*=O urea); 138.2-129.0 (aromatics *C* of MDI); 80.9 (CH_3CO); 56.3 ($NHCCH_2$); 30.3 (CH_2CH_2CO); 29.9 (CH_2CH_2CO); 27.9 ($OCCH_3$).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 7.43–6.91 (aromatics *H* MDI); 4.29 (CH_2 MDI); 2.25 (m, 12H, CCH_2CH_2CO); 2.08 (m, 12H, CCH_2CH_2CO); 1.36 (s, 54H, $OC(CH_3)_3$).

*Product **17***. ^{13}C-NMR ($CDCl_3$): (δ ppm) = 173.1 (*C*=O ester); 154.5 (*C*=O urea); 148.3 (*C*NHCO); 138.2-129.0 (aromatic *C* of MDI); 136.9 ($C_{3\ and\ 5}$ aromatic); 116.0 (C_4 aromatic); 114.7 ($C_{2\ and\ 6}$ aromatic); 80.9 (CH_3CO); 58.4 ($CNHCH_2$); 30.3

(CH_2CH_2CO); 29.9 (CH_2CH_2CO); 27.9 ($OCCH_3$).

^{1}H-NMR ($CDCl_3$): (δ ppm) = 8.77 (s, 2H, C*H* aromatic); 8.69 (s, 1H, C*H* aromatic); 7.43-6.91 (multiple signals corresponding to aromatic protons of MDI); 4.10–3.50 (broad multiplets corresponding to CH_2 of MDI); 2.29 (m, 12H, CCH_2CH_2CO); 2.13 (m, 12H, CCH_2CH_2CO); 1.43 and 1.26 (corresponding to overlapping singlets, 54H, $OC(CH_3)_3$).

H) Dendronization of PMMI

Poly (monomethyl itaconate) was obtained by polymerization of mono methyl itaconate (MMI) at 343 K in bulk under N_2 in the presence of 2,2'-azobisisobutyronitrile (AIBN) following a procedure previously reported.[15]

The PMMI used to carry out the dendronization was obtained from the fractioned precipitation of the PMMI synthesized as described above. The second fraction, used for the dendronization, represented 79% of the initial mass. The molecular weight of the sample precipitated and used, determined by viscosity using parameter values previously measured was 7.25 10^5 Da[15].

A mixture of poly (monomethyl itaconate) (PMMI), amine tris[(cyano-ethoxy)methyl] aminomethane **2**, tris[((methoxycarbonyl) ethoxy)methyl] aminomethane **3**, or Beherás amine **4**, dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (1-HBT) in DMF was stirred at room temperature for 48 h. Then the reaction was filtrated to remove dicyclohexylurea and ethyl ether was added. The precipitate was isolated by filtration and repeatedly washed with chloroform and dried under vacuum to constant weight. The relation of equivalent MMI:DCC:HBT:dendron used was 10: 1:1:4.

Changes in the FT-IR spectra were not observed for the dendronized samples, due to the high intensity of absorption bands of PMMI.

^{1}H-NMR and ^{13}C-NMR spectra of samples **18**, **19** and **20** show the same pattern. The main signals corresponding to the PMMI and the signals characterizing the dendron units are summarized next.

Signals corresponding to the PMMI structure:

^{13}C-NMR (DMSO-d_6): (δ ppm) = 171.9 overlapped (*C*=O ester and acid); 51.5 (OCH_3); 46.6 ($CH_2C(COOH)(CH_2)CH_2$ cuaternary carbon from polymer backbone); 43.2 ($CH_2C(COOH)(CH_2)CH_2$ methylene carbon from polymer backbone); 41.0 (CCH_2CO).

^{1}H-NMR (DMSO-d_6): (δ ppm) = 12.54 (broad, COO*H*); 3.44 (m, 2H, CCH_2CO) overlapped with 3.35 (s, 3H, CH_3); 2.50 (broad, 2H, $CH_2C(COOH)(CH_2)CH_2$).

Signals corresponding to dendrons attached to PMMI:

Product ***18***. ^{13}C-NMR (DMSO-d_6): (δ ppm) = 119.6 (*C*N); 70.2 (CCH_2O); 66.4 (OCH_2CH_2); 58.1 ($NHCCH_2O$); 18.4 (CH_2CH_2CN).

^{1}H-NMR (DMSO-d_6): (δ ppm) = 3.63 (t, OCH_2CH_2CN); 3.41 (s, CCH_2O); 2.77 (t, OCH_2CH_2CN).

Product ***19***. ^{13}C-NMR (DMSO-d_6): (δ ppm) = 172.0 (*C*=O ester); 69.7 (CCH_2O); 67.2 (OCH_2CH_2); 51.8 (*C*NHCO); 51.6 (CH_3); 34.5 (CH_2COOCH_3).

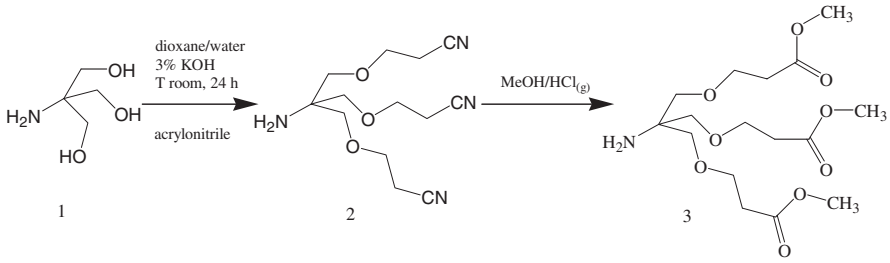
^{1}H-NMR (DMSO-d_6): (δ ppm) = 3.64 (t, OCH_2CH_2); 3.61 (s, OCH_3); 3.35 (s, NCH_2OCH_2); 2.57 (t, CH_2CO).

Product ***20***. ^{13}C-NMR (DMSO-d_6): (δ ppm) = 171.3 (*C*=O ester); 80.5 (CH_3CO); 56.9 ($CNHCH_2$); 30.9 (CH_2CH_2CO); 29.0 (CH_2CH_2CO); 28.2 ($OCCH_3$).

^{1}H-NMR (DMSO-d_6): (δ ppm) = 2.26 (broad, CCH_2CH_2CO); 1.68 (broad, CCH_2CH_2CO); 1.40 (s, $OC(CH_3)_3$).

Results and Discussion

A family of dendrons was synthesized following the scheme presented in Scheme 1 and 2.[16–23] Within this framework, the selection in the construction of these molecules was based on a synthetic strategy to achieve dendritic effect on the properties of the resulting building block

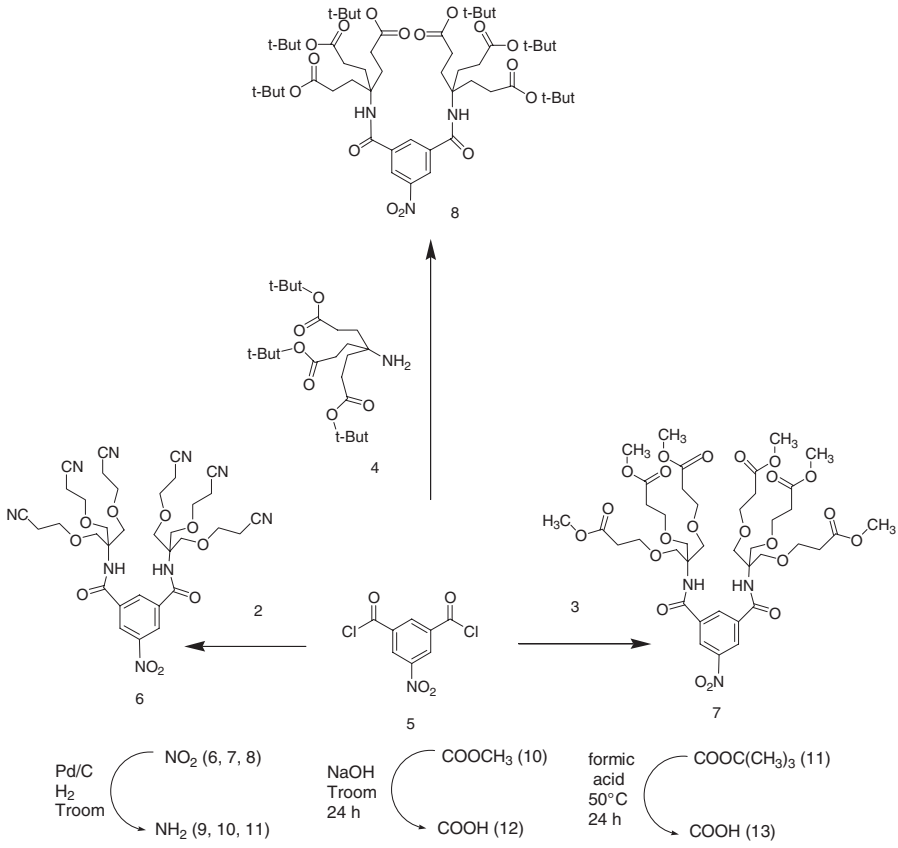


Scheme 1.
Divergent synthesis of dendron 3.

and the subsequently constructed product. 5-nitroisophthaloyl chloride was chosen because the nitro moiety could be subsequently reduced to an amino functionality when desired, thus allowing for its eventual incorporation into other structures.

First, dendron **3** was prepared following a divergent method (Scheme 1). As a result, tris[(cyano-ethoxy)methyl]aminomethane **2** was obtained by Bruson's method[23] from tris(hydroxymethyl) aminomethane **1**.

Next, nitrile **2** was refluxed in a dry HCl saturated MeOH solution to obtain tris [((methoxycarbonyl)ethoxy)methyl]aminomethane **3,** as a pale yellowish oil (yield 72%), which was evidenced by new peaks



Scheme 2.
Synthesis of different dendrons.

(^{1}H NMR) at 3.67 ppm and (^{13}C NMR) 51.5 ppm, assigned to the as ester methyl group. It was noticed that the carbonyl carbon signal ^{13}C NMR rose to 172.0 ppm. Subsequently, the FT-IR nitrile signal at 2252 cm^{-1} disappeared and a new carbonyl ester signal at 1740 cm^{-1} developed from stretching vibrations.

Dendritic molecules **6**, **7** and **8** were prepared by bonding precursors **2**, **3** and **4** to 5-nitroisophthalic acid as a functionalized core following a convergent pathway. Scheme 2 shows the synthesis of the different dendrons.

Previously, 5-nitroisoplhthalic acid was treated with redistilled $SOCl_2$ in dry THF to obtain **5**, which was characterized by a band (FT-IR) at 1800 cm^{-1} of acid chloride formation. Subsequently, samples of **5** were assayed with tris[(cyano-ethoxy)methyl]aminomethane **2**, tris[((methoxycarbonyl)ethoxy)methyl] aminomethane **3** and Beherás amine **4** by a conventional amidation procedure, to yield products with different functional groups on the periphery (nitrile, methyl and t-butyl ester), namely, this nitro precursor yielded 75% to 78% of a yellowish oil (**6**, **7**), and 80% of a white solid matter (**8**). According to ^{13}C NMR analysis a new signal was assigned to the carbonyl amide group. FT-IR spectroscopy showed the secondary amide with a strong amide band I at 1667cm^{-1} and a band II at 1535cm^{-1} resulting from N-H bending vibrations. In addition, the carbonyl absorption band of ester occurred at 1739 cm^{-1} (**7**) and 1736 cm^{-1} (**8**), and the nitrile signal at 2252 cm^{-1} (**6**). Next, the final products were prepared by catalytic hydrogenation of the nitro group to amine using Pd on C catalyst in methanol to yield 95% yellowish oil (**9**, **10**, **11**). Upon reduction, the structural composition of these products was supported by the shift of the ^{13}C NMR signals corresponding to aromatic carbons in *para* and *ortho* position to the nitrogen group.

Finally, dendrons with terminal acid groups (**12**, **13**) were obtained by hydrolysis of the aliphatic ester group in a basic and formic acid medium, respectively (yield 90% in both cases). The complete reaction was tested by proton of methyl or *t*-butyl ester signal disappearance in ^{1}H NMR.

The 70–90% yields at each step, easy purification and characterization make this a viable route to reach a large variety of dendritic molecules of different terminal functional groups and solubility. Additionally, the derivation of key nitro precursors affords access to other possibilities. Dendrons of this kind could be of interest for use as agents of material modification. Accordingly, research on the preparation of dendronized products was performed on MDI and PMMI using a convergent procedure, which offers the advantage of obtaining products with quasi-equivalent dendrimers and very good yields through a rapid and simple synthetic method.

On this occasion, the dendrons were attached to MDI and PMMI; finally, the products were characterized.

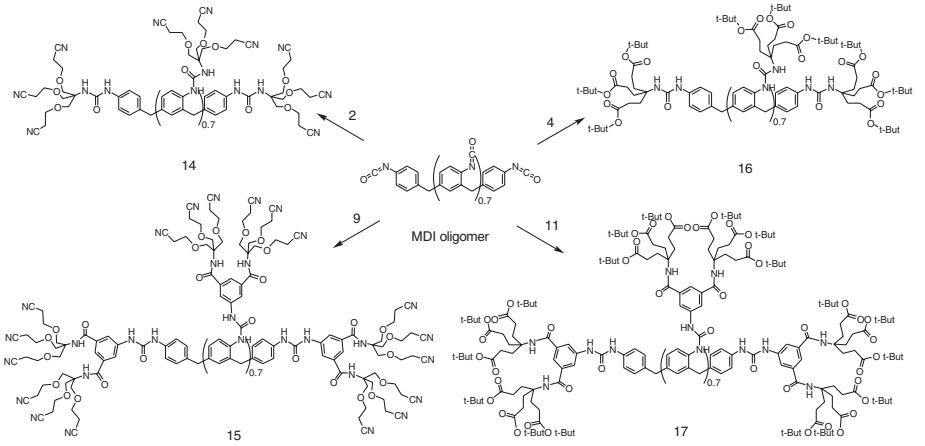
MDI dendronization

Dendrons **2**, **4**, **9** and **11** were attached to the end of an oligomer capped with isocyanate groups of MDI through urea bond formation using a ratio of equivalents of 1:2 of MDI and dendron, respectively. (Scheme 3).

According to NMR, FT-IR and SEC analysis of purified samples, all expected products were obtained with high dendronization degrees (80–98%).

Solubility studies showed interesting changes in the base polymer. MDI was soluble in non-protic solvents (benzene, chloroform, acetone, THF, DMF), while all dendrons were soluble in polar solvents and protic solvents (chloroform, acetone, alcohols, THF, DMF). Dendronized products were soluble in both polar solvents (chloroform, acetone) and protic solvents (alcohols) and non-polar solvents (benzene); except for **15** which could not be dissolved in non-polar solvents. It is clear that the polarity of the dendrons, determined by the functional groups on their surface, modified the solubility of the new dendronized polymers.

In a previous work, we have studied the behaviour of products **15** and **17** in



Scheme 3.
Dendronization of MDI oligomers.

solution.[16] These products responded to changes in their environment with changes in their conformation against solvents of different polarity. These changes showed adjustment in molecular conformation and were evidenced by ^{1}H NMR in chloroform, acetone and benzene. The conformational properties of dendrons **15** and **17** were investigated in the same solvents by means of numerical simulations using the Molecular Dynamics (MD) method, and the proposed changes in molecular conformation were confirmed.

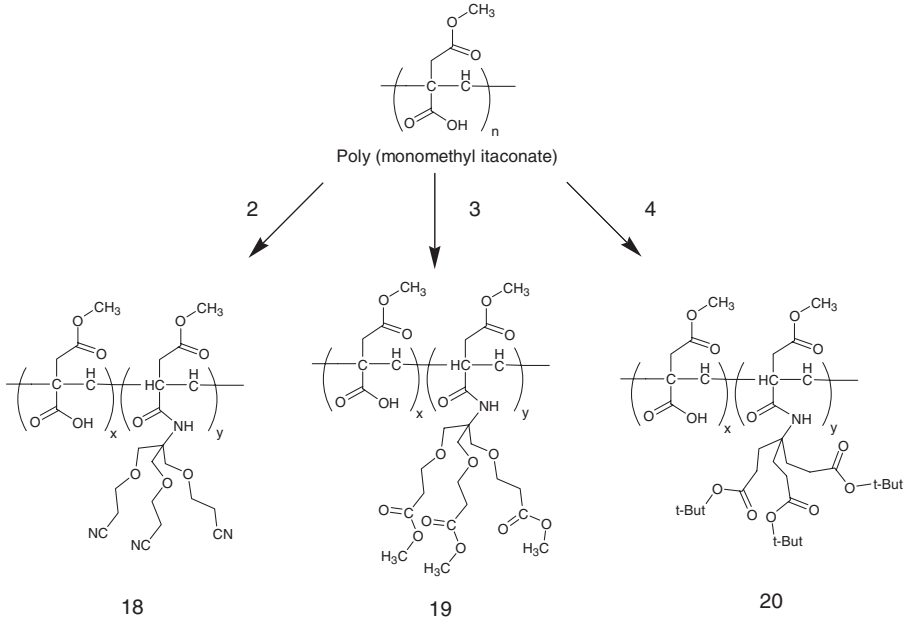
PMMI dendronization

Dendrons **2**, **3** and **4** were coupled to carboxylic groups of PMMI through amidation reaction, where dicyclohexylcarbodiimide (DCC) was used as activate agent and 1-hydroxybenzotriazol (HBT) as catalyst. Three different dendronized polymer samples were obtained, **18**, **19** and **20** respectively.[24] (Scheme 4).

According to NMR and elemental analysis of purified samples, all expected products were obtained. NMR spectra of the dendronized products revealed a signal corresponding to the amide group which confirmed the proposed structures. Dendronization degrees were obtained by elemental analysis and ^{1}H-NMR; the results obtained were 25.0, 7.7 and 5.6% for products **18**, **19** and **20** respectively. The best dendronization degree was obtained for **18**, probably due to greater compatibility and affinity between the polarity of the dendrons and the backbone of the polymer.

Intrinsic viscosities, $[\eta]$, were determined by dilution according to the Huggins relations[14] in DMSO at 25 °C. Table 1 shows the intrinsic viscosity values in DMSO. An important increment of the hydrodynamic volume of the samples was observed due to the incorporation of the dendron units. These results evidenced that the incorporation of dendrons as side groups gave products with a more extended and rigid shape. However, the dendronized polymer **18**, which has the highest dendronization degree, showed the lowest viscosity. This behaviour could be explained by the affinity between the dendrons and the chain, which leads to greater penetration and entanglement with one another. Consequently, they presented a low hydrodynamic volume and therefore a pseudo-globular form.

Finally, the solubility of the dendronized samples in different solvents is summarized in Table 2. The inclusion of dendron units presents different effects on the solubility of the samples. With respect to PMMI, product **18** increased its solubility in polar



Scheme 4.
Dendronization of PMMI.

Table 1.
Viscosimetry determinations in DMSO at 25 °C.

Sample	[η] dL/g
PMMI	0.78
Product 18	2.53
Product 19	3.39
Product 20	3.29

solvent (DMSO, water), while product **20** increased its solubility in non-polar solvent (toluene, methanol/chloroform 25:75, THF). Product **19** and PMMI showed the same solubility (DMSO, methanol and water).

These results demonstrated a clear tendency: dendrons with polar functional groups in the surface (**2**) lead to dendronized polymers soluble in polar solvent. Meanwhile, dendrons with apolar functional groups in the surface (**4**) gave products soluble in apolar solvent. Therefore, the solubility studies of the dendronized polymers showed that when the hydrophobicity of the dendrons increases the products begin to be soluble in solvent of lesser polarity. The contrary tendency was observed for dendrons of higher hydrophilicity.

Conclusion

A family of dendrons bearing different functional groups on their surface were

Table 2.
Solubility of the different samples

Solvent	Water	DMSO	Methanol	THF	Methanol/Chloroform 25:75	Toluene
Product 18	+	+	−	−	−	−
PMMI	+	+	+	−	−	−
Product 19	+	+	+	−	−	−
Product 20	−	+	+	+	+	+

+ soluble.
− insoluble.

synthesized and characterized. Dendrons **2**, **4**, **9** and **11** were used for modification of MDI apolar linear polymer and dendrons **2**, **3** and **4** for PMMI polar linear polymer, through a rapid synthetic procedure. The incorporation of dendrons as side pendant groups resulted in a marked increase of polymeric hydrodynamic volume and changes in solubility.

These results demonstrated that dendronization is a useful tool for changing the properties of base linear polymers through careful selection of the chemical structure of the dendrons.

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