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Polyfunctional MDI oligomers through dendrimerization

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Abstract

An accessible pathway to synthesize dendronized MDI oligomers was studied. Two dendrons bearing –CN and –*t*-butyl functional groups on the periphery were obtained following the synthetic strategy proposed by Newkome et al. Dendrons with one focal point were converted from nitro into amino precursors and used as modifiers in the preparation of new functionalized materials. The coupling reaction of dendrons on oligomers with isocyanate groups was carried out through an easy and quick procedure. The dendronized oligomers showed conformation changes according to the polarity of the solvents, allowing a prediction of a "stimuli-responsive" behavior.

Keywords: Dendron; Dendrimerization; Dendronized polymers; Polyfunctional polymers; Dendronized MDI

1. Introduction

Various dendrimer construction strategies have been developed on the basis of classical organic and inorganic chemistry [1–4]. In the last decades, the concept of dendritic growth in particular has had a significant impact, since it allows the development of polymers or building blocks with rigorously controlled molecular weights, number of branch and terminal groups. A case in point is the synthesis of conical molecules, or dendrons, which are structurally characterized by having exactly one focal point and end groups in multiple branches.

There are numerous examples of dendrons or building blocks used in the construction of supramolecular functionalized structures [5–7] or in the rapid dendronization of materials and surfaces [8–11]. The possibility of handling different synthetic strategies allows the obtention of new materials in the field of dendritic chemistry, which may be a starting point for the development of interesting technologies and applications [11–16]. Moreover, dendritic research has been lately shifted from simple preparation methods to material applications with specific functions [17–22]. It was recognized that if dendritic fragments (dendron) could be attached to polymer it would be possible to form

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a new kind of macromolecule. The architecture of this macromolecule would then be characterized by a rigid or flexible backbone which is wrapped about by wedges that increasingly branch as they go from the inner to the outer regions. For example, because of its abundance in nature, cellulose is a prime polymer candidate that can be selectively dendronized to afford an easy avenue to tailored polymeric chiral architectures which are of utilitarian interest. The properties of the cellulose derivatives depend not only on the nature of the substituents but also on the position of the substitution and the distribution of functionality along the cellulose chain [23].

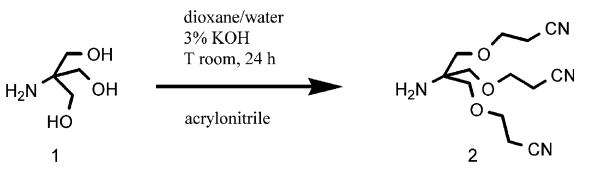
In this paper we studied the effects of dendronization on MDI oligomers. Therefore, the synthesis and characterization of two polyfunctional dendrons from 5-nitroisophthalic acid and their use as polymer modifiers are reported. An oligomer of methyl phenyl diisocyanate (MDI) was functionalized and specifically characterized.

2. Results and discussion

Firstly, we present the synthesis and characterization of the dendrons and secondly, their use as modifiers of MDI. The property studies of the dendronized MDI were made mainly through the observation of their behavior in solvents with different polarity. Those studies were corroborated by molecular dynamics simulations.

2.1. Synthesis and characterization of dendrons used as modifiers

Dendrons were synthesized in agreement with the scheme shown in Schemes 1 and 2 which correspond to a procedure previously reported by Newkome et al. [1,8,24–26]. Some steps were experimentally modified and adapted to the availability of our labs, such as the amidation and hydrogenation reaction. Within this framework, the construction of these molecules was based on a synthetic strategy to obtain dendritic effect on the properties of the resultant products subsequently constructed from that building block. 5-nitroisophthaloyl chloride was chosen because the nitro moiety could be subsequently further reduced to an amino functionality when desired, thus allowing its incorporation in other structures.



Scheme 1. Divergent synthesis of dendron **2**.

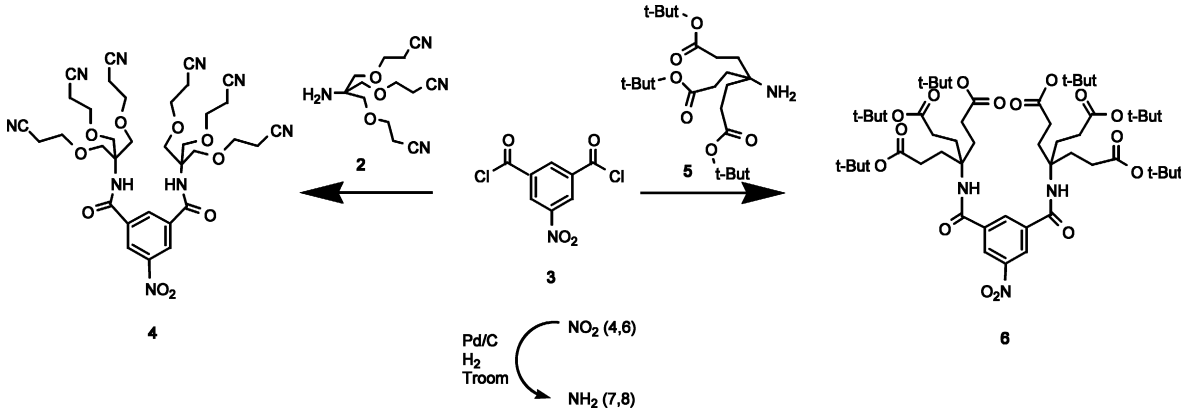
First, dendron **2** was prepared following a divergent method (Scheme 1). Therefore, tris[(cyano-ethoxy)methyl]aminomethane **2** was obtained by Bruson's method [27] from tris(hydroxymethyl) aminomethane **1** with 50 meq of acrylonitrile, and KOH as catalyst. This reaction afforded (80%) of **1**, as a yellowish oil, which was supported by a new peak ^{13}C NMR at 118.6 ppm corresponding to nitrile carbon and a band FT-IR at 2252 cm^{-1} corresponding to triple bond stretching CN.

Then, 5-nitroisophthalic acid was converted into diacid chloride with thionyl chloride to yield product **3** which was characterized by a band (FT-IR) at 1800 cm^{-1} of acid chloride formation. Subsequently, 5-nitroisophthaloyl chloride **3** was used as a functionalized core following a convergent pathway. Therefore, **3** was covalently bonded to tris[(cyano-ethoxy)methyl]aminomethane **2** and Behera's amine **5** [28] by a conventional amidation procedure, to render products with different functional groups on the periphery (nitrile and *t*-butyl ester).

This yielded 75% yellow oil of the nitrile precursor **4** and 80% white solid **6**. Scheme 2 shows the synthesis of the different dendrons and alternative pathways.

According to ^{13}C NMR analysis corresponding to product **4** a new signal at 167.7 ppm was assigned to the carbonyl amide group and FT-IR spectrum showed the nitrile signal at 2252 cm^{-1}. On the other hand, the ^{13}C NMR spectrum of product **6** presented a signal at 163.3 ppm assigned to the carbonyl amide group and the carbonyl absorption band of ester occurred at 1736 cm^{-1} in FT-IR spectrum. FT-IR spectroscopy of those products, **4** and **6**, showed the secondary amide with a strong amide band I at 1667 cm^{-1} and a band II at 1535 cm^{-1} resulting from N–H bending vibrations.

Then, the final products were prepared by a catalytic hydrogenation of the nitro group to amine using Pd on C catalyst in methanol to yield 95% yellow oil of dendrons **7** and yellow solid **8**. The structural composition of these products was supported by the shift of the ^{13}C NMR signal corresponding to aromatic carbons in *para* and *ortho* positions to the nitrogen groups. Table 1 shows these signals.



Scheme 2. Synthesis of the dendron **4** and **6**.

Table 1
^{13}C NMR ($CDCl_3$) shift of aromatic carbon of dendrons **4**, **6**, **7** and **8** and modified oligomers **9** and **10**

Dendron				Product	
4		**7**		**9**	
	δ (ppm)		δ (ppm)		δ (ppm)
C_1–NO_2	142.5	C_1–NH_2	142.3	C_1–NHCON	147.7
$C_{2\text{ and }6}$–*ortho* NO_2	126.9	$C_{2\text{ and }6}$–*ortho* NH_2	118.3	$C_{2\text{ and }6}$–*ortho* NHCON	114.9
$C_{3\text{ and }5}$–*meta* NO_2	131.6	$C_{3\text{ and }5}$–*meta* NH_2	131.6	$C_{3\text{ and }5}$–*meta* NHCON	131.6
C_4–*para* NO_2	128.6	C_4–*para* NH_2	119.3	C_4–*para* NHCON	116.1
6		**8**		**10**	
C_1–NO_2	148.3	C_1–NH_2	148.3	C_1–NHCON	148.3
$C_{2\text{ and }6}$–*ortho* NO_2	124.1	$C_{2\text{ and }6}$–*ortho* NH_2	118.0	$C_{2\text{ and }6}$–*ortho* NHCON	114.7
$C_{3\text{ and }5}$–*meta* NO_2	136.9	$C_{3\text{ and }5}$–*meta* NH_2	136.9	$C_{3\text{ and }5}$–*meta* NHCON	136.9
C_4–*para* NO_2	131.7	C_4–*para* NH_2	116.0	C_4–*para* NHCON	116.0

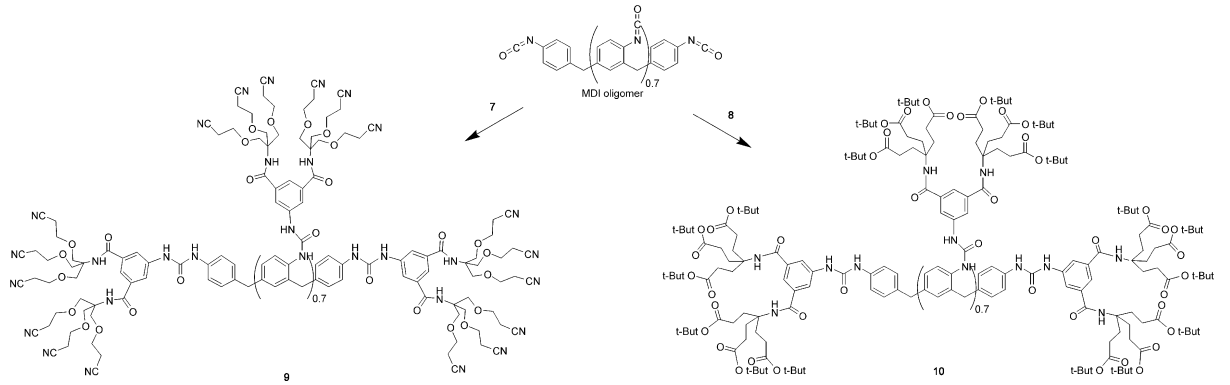
2.2. Synthesis and characterization of dendronized oligomers

Dendrons **7** and **8**, which carried out different terminal functional groups in the surface and were of easy obtention, could be interesting molecules used as agents of material modification. Therefore, investigations in the preparation of dendronized products were carried out on MDI oligomers using a convergent procedure, which offers the advantage of obtaining products which have quasi-equivalence of dendrimers and very good yields through a rapid and simple synthetic method.

In the present study, dendrons **7** and **8** were attached to the end of an oligomer capped with isocyanate groups and the products were characterized. Scheme 3 shows the synthetic strategy to obtain the dendronized MDI oligomer. This substrate (with 2.7 equivalents of isocyanate groups per mol) and each dendron were mixed with a ratio of equivalents of 1:2 of MDI and dendron, respectively. The reaction was carried out in anhydrous THF and triethylamine as catalyst at room temperature during 6 h to render, after purification, products which yielded between 40–55% of yellow oil.

The SEC chromatogram showed that samples **9** and **10** contain higher weight oligomers than pure MDI, according to the retention time. Fig. 1 shows that **9** presents two principal products and **10** presents only one principal product.

According to NMR and FT-IR analysis of purified samples, a successful coupling addition of dendrons to MDI oligomers could be observed, which can be easily detected by the characteristic signal of urea groups in ^{13}C NMR and FT-IR spectra of products **9** and **10**. Urea carbon signal ^{13}C NMR appeared at 154.5 ppm and FT-IR spectra showed the urea group with a band at 1653 cm^{-1}, while the isocyanate signal at 2283 cm^{-1} vanished. The MDI oligomers were functionalized across all their



Scheme 3. Dendronizations of MDI oligomers.

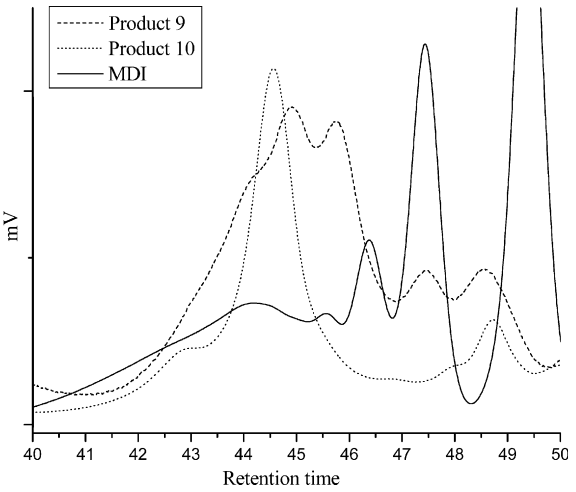


Fig. 1. SEC chromatograms of MDI, products 9 and 10.

isocyanate groups according to ^{1}H NMR spectra quantitative analysis of products **9** and **10** which showed a ratio of dendron:MDI 2.67 and 2.21, respectively.

A comparative analysis of spectra of ^{13}C NMR of dendrons and modified oligomers revealed an interesting shift of specific bands, summarized in Table 1. Significant changes were observed in the aromatic carbon signals which confirms the proposal structures. The most important change corresponded to the signal of the *ortho* position to urea group from about 118 to 114 ppm.

MDI, dendrons and dendronized products showed different solubility. MDI was soluble in non-protic solvents (benzene, chloroform, acetone, THF, DMF), while dendrons **7** and **8** were soluble in polar solvents (chloroform, acetone, THF, DMF) and protic solvents (alcohols). Dendronized product **9** was soluble in polar solvent (chloroform, acetone) but it could not be dissolved in non-polar solvents (benzene). Dendronized product **10** was soluble in polar solvents (chloroform, acetone), protic solvents (alcohols) and non-polar solvents (benzene).

On the other hand, products **9** and **10** responded to changes in their environment through changes in their conformation front to solvents of different polarity. These changes showed adjustment in their molecular conformation and were evidenced by ^{1}H NMR in chloroform, acetone and benzene. Fig. 2.

Product **9**, which in this structure contains a more polar building block **7**, showed in chloroform and acetone discrete signals corresponding to each methylene group of aliphatic chain ($OC\boldsymbol{H}_2C\boldsymbol{H}_2CN$) and the methylene group of MDI. Aromatic

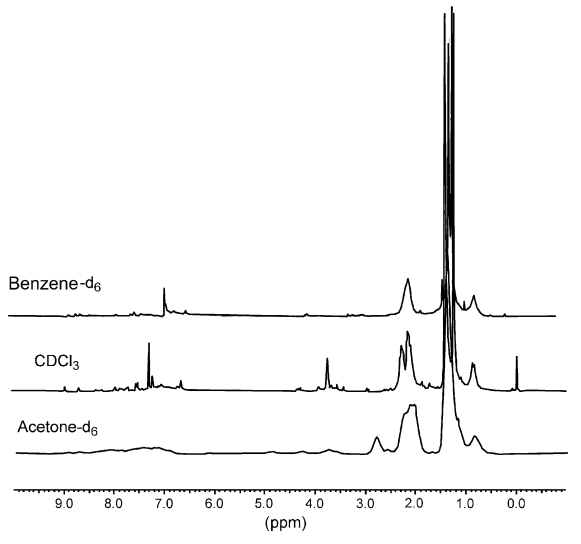


Fig. 2. ^{1}H NMR of 10 in different solvents.

protons corresponding to dendron **7** and MDI also showed discrete signals. In this case, the polarity of the combination of dendron **7** and oligomer is widely different, therefore product **9** exhibited an amphiphilic behavior.

Product **10** in chloroform exhibited discrete signals with optimal and higher resolution. Methyl groups from *t*-butyl esters ($COC(CH_3)_3$) around dendron periphery were clearly detected as two signals, thus revealing slight differences in the chemical environment. Each methylene group (CCH_2-CH_2CO) from the Behera's unit appeared as a multiplet. The methylene group of MDI also showed a slight signal at 4.29 ppm. When the spectrum of the product in acetone was examined, all signals widened, the intensity lowered, and the spectrum lost resolution. Terminal methyl groups were detected as a single wide signal, just as the methylene groups of the Behera's amine chain. The CH_2 of the MDI was a very wide low intensity signal. Finally, when the spectrum was studied on benzene, the signals were wide, but of an intensity between that observed for chloroform and that for acetone.

These observations could be explained as follows: in chloroform, in which both dendrons and oligomer are readily soluble, **10** expands to adopt their fully extended conformation. In polar solvent (acetone), product **10** adopts a conformation consisting of a compactly packed block. Probably, the dendronized oligomers associated themselves to protect their hydrophobic moiety (oligomer) surrounded by hydrophilic parts (dendrones), whereas in benzene **10** acquired an extended/collapsed intermediate configuration.

2.3. Study of molecular dynamics simulations

With the aim of confirming the observation found from NMR in different polarity solvents, the conformational properties of products **9** and **10** were investigated in the same solvents by means of numerical simulations using the Molecular Dynamics (MD) method.

From the saved coordinates, we have evaluated the mean radius of gyration of the structures and have also calculated the mean core-end distance between the center of the middle core phenyl ring of MDI to the center of the end C–N bonds for **9**, and from the same core point to the main C-atom of the *t*-butyl group for **10**. The results are shown in Table 2. In the case of **9**, it can be observed that the core-end distance is significantly higher for the chloroform systems, showing also a slightly higher radius of gyration in this solvent. According to these data, the smaller chloroform molecules are more able to interact with this product. Snapshots of different configurations seem to confirm that the chloroform molecules interact more actively with the product branches, while acetone molecules tend to interact with the surface. Therefore, this interaction should have a small effect on the global size or branch extension of the product and may explain the solubility of **9** in this particular solvent. For structure **10**, the core-to-end distance is also higher for chloroform, however the radius of gyration is higher for the benzene solution. It may be assumed that the more bulky benzene molecules are able to penetrate into this product, increasing the global size of the whole molecule. The smaller chloroform molecules, however, are more able to induce more extended branches. Acetone molecules seem to affect less both the molecule size and the branch extension of this product. This is compatible with a smaller penetrability of this solvent.

Table 2
Molecular dynamics simulations of products **9** and **10**

		Core-end distance (Å)	Radius of gyration (Å)
Product **9**	Chloroform	9.0	11.1
	Acetone	8.0	10.6
Product **10**	Chloroform	9.0	11.8
	Acetone	8.0	11.9
	Benzene	7.9	12.5

3. Experimental section

3.1. Materials

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 phenyl 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 (Aldrich) and silica gel 60 (Merck). Potassium bromide 99% FT-IR grade (Aldrich); Chloroform-*d* 99.8%D (Aldrich); benzene-d_6 99.5%D (Sigma); acetone-d_6 99.5%D (Sigma) All commercial chemicals were used without purification.

Solvents were obtained from Sintorgan, purified by distillation, and dried with 4 Å molecular sieves when necessary.

3.2. 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 $CDCl_3$, acetone-d_6 or benzene-d_6, 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).

3.3. Methods

3.3.1. 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 was purified by liquid chromatography on silica gel and eluted with acetone. Yield was 80%.

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

^{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).

^1H NMR ($CDCl_3$): (δ, ppm) = 3.60 (t, 6H, OCH_2CH_2); 3.42 (s, 6H, NCH_2O CH_2); 2.60 (t, 6H, CH_2CN); 1.60 (NH_2).

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

3.3.2. Dendritic molecules **4, 6**

To obtain diacidchloride, **3**, $SOCl_2$ (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 **4** and **6**, the reaction was carried out using the ratio of equivalents of tris[(cyano-ethoxy) methyl]aminomethane **2**, (1.000 g) and Behera's amine **5**, (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 **3** 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 yellow oil (**4**) and white solid (**6**) [mp 165.6–166.1 °C] were obtained and purified by column chromatography through silica gel using acetone as eluent.

Yield was 75% and 80%, respectively.

*3.3.2.1. Product **4**.* 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 (*C*NO_2); 131.6 ($C_{3\,and\,5}$ aromatic); 128.6 (C_4 aromatic); 126.9 ($C_{2\,and\,6}$ aromatic); 118.2 (*C*N); 70.9 (C*C*H_2O); 65.9 (O*C*H_2CH_2); 48.2 (NH*C*CH_2O); 18.83 (CH_2*C*H_2CN).

^1H NMR ($CDCl_3$): (δ, ppm) = 8.71 (s, 2H, C*H* aromatic); 8.39 (s, 1H, C*H* aromatic); 3.93 (s, 12H, OCH_2CH_2); 3.69 (t, 12H, OCH_2CH_2CN); 2.60 (t, 12H, OCH_2C*H*$_2$CN).

*3.3.2.2. 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 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_3*C*O); 58.4 (*C*NHCH_2); 30.3 (*C*H_2CH_2CO); 29.9 (CH_2*C*H_2CO); 27.9 (OC*C*H_3).

^1H NMR ($CDCl_3$): (δ, ppm) = 8.77 (s, 2H, C*H* aromatic); 8.69 (s, 1H, C*H* aromatic); 2.25 (m, 12H, CCH_2C*H*$_2$CO); 2.08 (m, 12H, CC*H*$_2$CH_2CO); 1.36 (s, 54H, OC(C*H*$_3$)$_3$).

3.3.3. Hydrogenation

Dendritic molecules (**4** and **6**) (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 **7** and **8**

[mp 184.7–185.3 °C] were obtained. Yields were 95%.

FT-IR (cm^{-1}) = 7 and 8 present a similar pattern to 4 and 6, respectively. The overlapping signals corresponding to amide and amino groups did not allow a conclusion to be drawn.

^1H NMR ($CDCl_3$): (δ, ppm) = **7** and **8** present a similar pattern to **4** and **6**, respectively.

3.3.3.1. Product 7. ^{13}C NMR ($CDCl_3$) (δ, ppm) = 119.3 (C_4 aromatic); 118.3 ($C_{2\,and\,6}$ aromatic); the rest of the signals did not change with respect to **4**.

^1H NMR ($CDCl_3$): (δ, ppm) = 6.37 (s, 2H, C*H* aromatic); 6.63 (s, 1H, C*H* aromatic), the rest of the signals did not change with respect to product **4**.

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

3.3.3.2. Product 8. ^{13}C NMR ($CDCl_3$) (δ, ppm) = 116.0 (C_4 aromatic); 118.0 ($C_{2\,and\,6}$ aromatic); the rest of the signals did not change with respect to **6**.

^1H NMR ($CDCl_3$): (δ, ppm) = 7.25 (s, 2H, C*H* aromatic); 7.38 (s, 1H, C*H* aromatic), the rest of the signals did not change with respect to product **6**.

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

3.3.4. Dendritic molecules – methyl phenyl diisocyanate (MDI)

Polyurethane oligomer end-capped with isocyanate groups (118 mg, 0.4 mmol) was linked to dendritic molecules **4** and **6** (2 mmol) in anhydro THF under nitrogen (ratio 1:2 mol) for 4 h at room temperature. The crude products were purified by liquid chromatography on silica gel and eluted with chloroform:acetone 90:10, yellowish oils (**9, 10**) were obtained. Yields were 42% (**9**), and 44% (**10**).

FT-IR (cm^{-1}): Disappearance of the signal at 2283 (NCO stretching vibrations) corresponding to the isocyanate group and appearance of a new signal at 1653 (C=O stretching vibration) corresponding to the urea group.

3.3.4.1. Product 9. ^{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 (aromatic *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 (C*C*H_2O); 65.9 (O*C*H_2CH_2); 48.2 (NH*C*CH_2O); 18.83 (CH_2*C*H_2CN).

^1H 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).

3.3.4.2. Product 10. ^{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_3*C*O); 58.4 (*C*NHCH_2); 30.3 (*C*H_2CH_2CO); 29.9 (CH_2*C*H_2CO); 27.9 (OC*C*H_3).

^1H 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)$_3$).

3.3.5. Molecular dynamics simulations

The conformational properties of **9** and **10** in chloroform, acetone and benzene were investigated by means of numerical simulations using the molecular dynamics (MD) methods. The construction of the molecular structures, the preparation of simulation boxes and the generation of the MD classical trajectories were performed using the "Materials Studio" software package from Accelrys.

Once the dendronized structures were built, they were minimized in order to obtain a moderate initial potential energy. Each minimized structure was subsequently included in a simulation box together with 50 solvent molecules. The volume of the boxes was set so that density was 1.0. In order to create the simulation boxes we used the "Amorphous Cell" module of the software package. This module also performs a preliminary energy optimization of the system. Finally, the MD simulations were carried out at constant volume and temperature (mean value 303.2 K) with the Nose thermostat. Minimizations and MD simulations were carried out using the "Discover" module in which the standard force field PCFF was employed. The final MD simulations were run to cover a total of 2 ns with a time step time of 0.5 fs, i.e. these performed 4×10^6 steps. According to the output information on temperature and energy, both the initial and final results were consistent with the mean and standard deviation values; in systematic deviations along the trajectories they were not observed.

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