Hybrid Dendritic-Linear Copolymers: Synthesis and Reactivity

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Summary: A novel hybrid aromatic dendritic-linear copolymer from Jeffamine® was synthesized by an adaptation of Kakimoto's procedure. Comparative studies of reactivity between aromatic and aliphatic hybrid dendritic-linear copolymers were carried out, through which the best reactivity and the derivatizing capacity of this novel copolymer were clearly demonstrated for the aromatic hybrid dendritic-linear copolymer. Schiff's base formation by reaction with a chromophore (**MFVF**) gave hybrid copolymer interesting crosslinkable properties.

Keywords: crosslinkable properties; dendritic Jeffamine; hybrid dendritic-linear copolymer

Introduction

In the polymer field, dendritic topology has now been recognized as a fourth major class of macromolecular architecture. Numerous synthetic strategies have been reported for the preparation of these materials, which have led to a broad range of dendritic structures.[1–3] Frechet and Hawker were the first to recognize that ''hybrid architectures'' of dendrimers and linear copolymers might be interesting targets in molecular architecture.[4] Therefore, in the last years, by combining the advantages of polymers and dendrimers, several groups have carried out the preparation of the hybrid dendritic-linear copolymers.[5–7] In a dendritic-linear copolymer, both moieties can produce a strong effect on each other's properties and finally they forms a macromolecule with modified and advanced properties.

For example, the presence of the dendritic portion in a hybrid copolymer decreased its viscosity while the presence of the linear polymer increased its flexibility. Moreover, it is known that this kind of copolymers, with a carefully selection of the polarity of each block, could exhibit super-amphiphile behaviour.[8,9]

One of the most suitable materials complying with these requirements consists of oligoether chains, e.g. polyethylene oxide (PEO) or polypropylene oxide (PPO), which remain today as the best structures found, with a variety of potential applications in different fields.[10,11] Similarly, Jeffamines®, a linear oligo(oxyethylene) or poly(oxypropylene) bearing –NH_2 end-groups were extensively used as building blocks in the preparation of different materials. It is known that they could change and improve their properties, such as hydrophilicity/hydrophobicity ratio,[12] biocompatibility[13] and kinetic parameters of solid-phase reactions.[14] Additionally, it has been demonstrated that branched Jeffamines® contribute to improve the final properties of the material.[15,16] Therefore, the branches of these structures could have new and interesting applications, such as grafting or crosslinking agents for the preparation of new materials with specific characteristics, such as amphilicity, tenacity, functionality, etc. Thus, there is a consi-

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derable interest in obtaining a special class of compounds with unusual properties rarely observed in random and coiled polymers, through the design and synthesis of hybrid dendritic-linear copolymers using Jeffamines®.

In a previous work,[17] we presented the synthesis of aliphatic dendritic Jeffamines ($G = 1$ and 2) via Michael addition of acrylonitrile followed by catalytic hydrogenation. There we mentioned their problems of reactivity, evidenced by long reaction times and high temperatures necessary to synthesize the dendritic products. $G = 2$ showed lower reactivity than $G = 1$, and it is even lower than the Jeffamines®, without being modified. This observation can only be explained by a total reduction in the reactivity capacity of aliphatic amine groups or by their extremely poor availability in the dendritic fragments of Jeffamines®. According to Dušek and Matějka,[18] the reactivity of the terminal primary amino groups of these PPO or POE-based amines differs from that of $-NH_2$ groups of aliphatic amines for two main reasons, namely, (i) the fact that the presence of the methyl substitution effect in the amine group reactivity is more negative than that found in aliphatic amines, and (ii) that the intra-and intermolecular interactions are caused by hydrogen bond formation. Consequently, the presence of the ether groups in the Jeffamines®, where the oxygen atoms are a strong H-acceptor, appears to be responsible for the decrease of the amine reactivity, because these amines are implied in the formation of hydrogen bonds. In other products, where $-NH_2$ groups are situated in dendrimers or dendritic moieties, the reduction of their reactivity was also observed.[19–21] In the present study we present an alternative pathway for the synthesis of hybrid linear-dendritic copolymers with the purpose of solving this reduction of reactivity. Therefore, the incorporation of aromatic fragment in the dendritic moiety through Kakimoto's procedure was studied and the increase of the reactivity was demonstrated. The first generation ($G = 1$) of the new product was easily derivatized with a chromophore, and a material with interesting potential photocrosslinking properties gave very good yield.

Experimental

Reagents and Solvents

4,7,10-trioxa-1,13-tridecanediamine (Aldrich, 97%), 3,5-dinitrobenzoyl chloride (Fluka, 98%), thionylchloride (Aldrich), 10% palladium–carbon (Pd-C) (Aldrich), were used as received. 3,5-diaminobenzoic acid was purified by recrystallization from water. Solvents such as chloroform (Ciccarelli), ethanol (Porta), and methylene chloride (CH_2Cl_2) (Ciccarelli) were used without purification. *N,N*-dimethylacetamide (DMAc) (Tedia), and dimethylformamide (DMF) (J.T.Baker) were distilled from calcium hydride. 5methylfurfural (Aldrich, 97%) was purified by fractional distillation.

Equipments

Characterizations by FT-IR were recorded using a Nicolet 5-SXC spectrometer on KBr discs or NaCl plates. ^1H NMR spectra were recorded using a Brüker AC200 in deuterateds dichloromethane, chloroform, water and DMSO solutions. UV–vis spectra were taken with a ThermoSpectronic UNICAMUV 500 using spectrophotometric grade solvents. The irradiations were carried out in a nitrogen atmosphere using a 500W medium-pressure mercury arc equipped with a Pyrex filter to limit the excitation to wavelengths higher than 270 nm. Samples were prepared as follows: methylene chloride copolymer solutions were deposited onto NaCl plates and allowed to dry. It was chosen to work only with the films of about 18 μm thickness.

Synthesis of Tetranitro (3)

In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5dinitrobenzoyl chloride (**2**) (20.0 mmol) and DMAc (40 mL). The solution was cooled at $-5\,^{\circ}C$ and then 4,7,10-trioxa-1, 13-tridecanediamine (**1**) (9.1 mmol) was added. The solution was stirred for 12 h. The reaction mixture was then poured into dilute HCl water (1.5N). The crude was dissolved in CH_2Cl_2, washed with sodium bicarbonate and finally in water, dried ($CaCl_2$) and concentrated in vacuo to obtain the tetranitro compound **3**. The yield was 76%. ^{1}H-NMR ($CDCl_3$) δ: 9.08 (t, 2H,Ar), 9.03 (d, 4H,Ar); 8.07 (t, 2H,CON*H*); 3.65–3.33 (m, 16H, CH_2CH_2O and CH_2CH_2N); 1.85 (q, 4H, $CH_2CH_2CH_2$). FTIR (cm^{-1}): 1102, 1344, 1541, 1659, 2871, 2920, 3098, 3260.

Synthesis of Tetraamine (4)

A stirred EtOH suspension of compound **3** (2.0 mmol), and 10% Pd-C (0.42 g) was degassed and purged with hydrogen several times and then stirred at 60 psi of H_2 and 25 °C for 48 h. The mixture was filtered using Celite-545. The solution was concentrated and dried at room temperature in vacuo. Conversion: quant.; yield: 84%. ^{1}H-NMR (D_2O) δ: 6.58 (d, 4H, Ar), 6.43 (t, 2H, Ar), 3.75 –3.50 (m, 12H, CH_2CH_2O), 3.43 (t, 4H, CH_2CH_2N), 1.88 (q, 4H, $CH_2CH_2CH_2$). FTIR (cm^{-1}): 1449, 1543, 1624, 1688, 1717.

Synthesis of Dendron Tetranitro (6)

In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed 3,5diaminobenzoic acid (**5**) (6.06 mmol) and DMAc (46 mL). The solution was cooled at –5 °C. Then, 3,5-dinitrobenzoyl chloride (**2**) (13.41 mmol in 10 mL of DMAc) was added dropwise during 0.5 h and then the reaction mixture was stirred for 14 h at –5 °C and 14 h at room temperature. The reaction mixture was then poured into dilute HCl water. The crude product was filtered and washed with hot methanol. The product was recrystallized from THF, filtered and dried at 65 °C in vacuo. The yield was 50%. ^{1}H NMR (DMSO-d6) δ: 10.90 (s, 2H,CONH), 9.20 (d, 4H), 9.00 (t, 2H), 8.68 (t, 1H), 8.16 (d, 2H). FTIR (cm^{-1}): 1717 (carboxyl C=O), 1688, 1543 (amide C=O), 1624, 1449 (aromatic).

Synthesis of Octanitro (7)

In a flask, (0.37 mmol) of **6** was dissolved in 5 mL of thionylchloride. Then, DMF were added to the reaction mixture as catalyst, it was stirred for 5 h at reflux. 3,5-Bis(3, 5dinitrobenzoylamino)benzoyl chloride was obtained by distillation of the excess thionylchloride. FTIR (cm^{-1}): 1772 cm^{-1} (C=O).

To the same flask 4 mL of DMAc was added and then a solution of **1** (0.2467 mmol) in 1 mL of DMAc was added at 0 °C. After the solution was stirred at 25 °C for 14 h, the reaction mixture was poured into 50 mL of water. The aqueous mixture was extracted with several aliquots of chloroform and then it was filtrated through silica gel. The complete isolation of this product using column chromatography failed because **7** was retained by the silica gel. The obtained product was analyzed by ^{1}H-NMR ($CDCl_3$) δ: 10.97 (s,4H,CON*H*); 9,35 (d,4H,Ar); 8,90 (t, 8H,Ar); 8,80 (t, 2H,Ar); 8.46 (t,2H, CON*H*); 8,00 (d,4H,Ar); 3.40 (m,12H, CH_2CH_2O); 3.80 (t,4H,CH_2CH_2N); 1.85 (q, 4H,$CH_2CH_2CH_2$).

Synthesis of Compound 8 and 9

The synthesis of the two aliphatic amine hybrids dendritic-linear copolymers (**8** and **9**) was previously published.[17] These molecules were synthesized from **1** (4,7,10- trioxa-1,13tridecanediamine) by a divergent approach using an adaptation of Meijer's methodology. In order words, **8** and **9** were obtained via Michael addition of acrylonitrile followed by catalytic hydrogenation.

Compound 8: to a solution of **1** (2.3mmol) in water (5 mL) at 5 °C, acrylonitrile (18.4 mmol) was added dropwise. After stirring for 1 h at 5 °C, the resulting mixture was heated at 80 °C for 24 h to obtain tetranitrile derivate. After cooling, the solvent and the excess acrylonitrile were removed in vacuo to give a residue that was dissolved in CH_2Cl_2, washed repeatedly with water, dried ($MgSO_4$) and concentrated in vacuo (96% yield). Then, **8** was synthesized by catalytic hydrogenation. A stirred EtOH suspension of tetranitriles (232 μmol), PtO_2 (20 mg) and HCl 37% (130 μL) was maintained at 45 psi of H_2 at 25 °C for 17 h. The solution was then filtered and evaporated in vacuo and extracted with water to obtain the traamines.

Compound 9: it was synthesized using the same procedure as **8,** but on this occasion the Michael addition was performed for 80 h given a 40% yield of octanitriles. Catalytic hydrogenation to obtain **9** was carried out for 24 h at 25 °C.

Synthesis of 5-[2-(5-methyl-furyl-vinylene)]-furancarboxyaldehyde (MFVF or compound 10)

The most adequate experimental conditions providing access to dimer **MFVF** in reasonable yields can be summarized as follows: 20 mL of **5-MF** were mixed with 30 mL of water and 15 mL of methanol, 1.2 g of NaOH was added under magnetic stirring in a nitrogen atmosphere. The resulting mixture was refluxed for 3 h. Purified **MFVF** was obtained in ca. 40% yield by distillation in vacuum. ^{1}H RMN (CD_2Cl_2) δ: 9,53 (s, 1H); 7,23 (d, 1H); 7,04 (d, 1H); 6,76 (d, 1H); 6,48 (d, 1H); 6,40 (d, 1H); 6,07 (m, 1H); 2,33 (s, 3H). FTIR (cm^{-1}): 958, 1018, 1625, 1660, 2946, 3113. p.f.: 86–87 °C.

Synthesis of Schiff-Tetrabase (11)

In a flask equipped with a magnetic stirrer and a nitrogen inlet were placed **MFVF** (4.4 mmol), core tetraamine **3** (1.0 mmol) in methanol (30 mL). The solution was stirred at room temperature for 1 h, and then concentrated using a rotary evaporator and finally dried in vacuo. The reaction mixture was stirred in vacuum and heated at 90 °C for 96 h. Reaction control was performed via IR-spectroscopy (decrease until constant of an aldehyde peack at ≈1670cm^{-1}). Workup: a distillation was made in a secondary ramp of vacuo to eliminate the volatile MFVF that had not reacted. Purification control was performed via IR- spectroscopy (total disappearance of an aldehyde pick at ≈1670cm^{-1}). Conversion: 91% (by ^{1}H NMR); yield: 83%. ^{1}H-NMR (DMSO-d6) δ: 8,05–8,15 (m, 3,7H, Schiff's base); 8,03–7,85 (m, 3,9H, *orto*-imine and *orto*-amide); 7,40–6,10 (m, 23,45H,Ar); 3,70–3,25 (m, 12H, CH_2CH_2O); 2,92–2,77 (m, 4H, CH_2CH_2N); 2,39 (br., 10,95H,$CH3$); 1,91–1,83 (m, 3,8H, $CH_2CH_2CH_2$). FTIR (cm^{-1}): 954, 1024, 1118, 1565, 1641.

Results and Discussion

Synthesis of Hybrid Dendritic-Linear Copolymers by Kakimoto's Procedure

The pathway for the synthesis of the compounds **3**, **4** and **7** from **1** (4,7,10-trioxa-1,13tridecanediamine) is an adaptation of Kakimoto's method for the preparation of dendrimers,[22] where 3,5-dinitrobenzoyl chloride was selected as building blocks (Figure 1).

The compound **4**, G = 1, was synthesized from **1** (4,7,10-trioxa-1,13-tridecanediamine) in two steps, as shown in Figure 1. The first step was to obtain **3** (tetranitro), which was synthesized though an amidation reaction between **1** and **2** (3,5-dinitrobenzoyl chloride). The structure of **3** was confirmed by ^{1}H NMR (8.07 ppm, formation of a new function amide) and FTIR (1541 and 1659 cm^{-1} for the same group). The second step was the hydrogenation of **3** to afford the product **4**. The structure of **4** was confirmed mainly by ^{1}H NMR, by the disappearance of the signals at 9.08 and 9.03 ppm from the aromatic rings substituted by the two nitro groups, and the presence of the new signals at 6.58 and 6.43 ppm corresponding to the protons from the aromatic rings substituted by amine groups.

In order to obtain the compound **7**, G = 1.5, the application of the convergent growth approach was selected,[23] in which the preformed dendron is used as building blocks. This approach allows for the synthesis of the higher dendritic generation hybrids from the compound **1** (linear fragment) in one step. Therefore, it was necessary to synthesize a dendron with four nitro groups and a carboxylic acid at a focal point. For this, **2** was reacted with **5** by the direct amidation reaction to obtain the dendron **6** in a good yield (50%), as shown in Figure 2. The structure was confirmed by ^{1}H NMR (10.90 ppm, formation of a new function amide) and FTIR by the presence

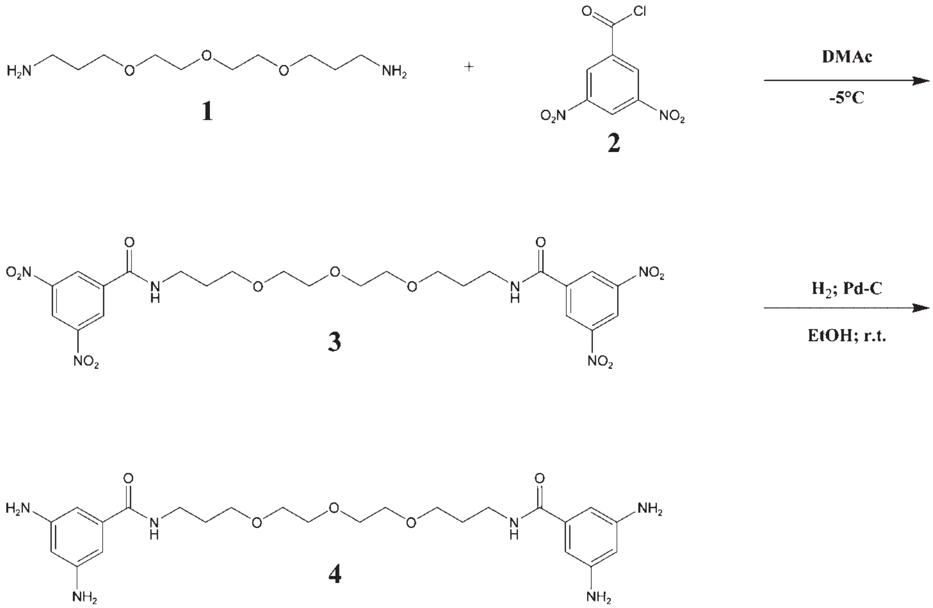


Figure 1.
Synthetic routes of compounds **4** (1G).

of the following peaks: 1717 (carboxyl C=O), 1688 and 1543 (amide C=O).

The hybrid dendritic-linear copolymer **7** was synthesized from dendron **6** and compound **1** through an amidation reaction. For that, **6** was activated using thionylchloride to form the 3,5-Bis(3,5-dinitrobenzoylamino)benzoyl chloride, which was identified by FTIR (1772 cm^{-1} (C=O)). The isolation and purification of final product

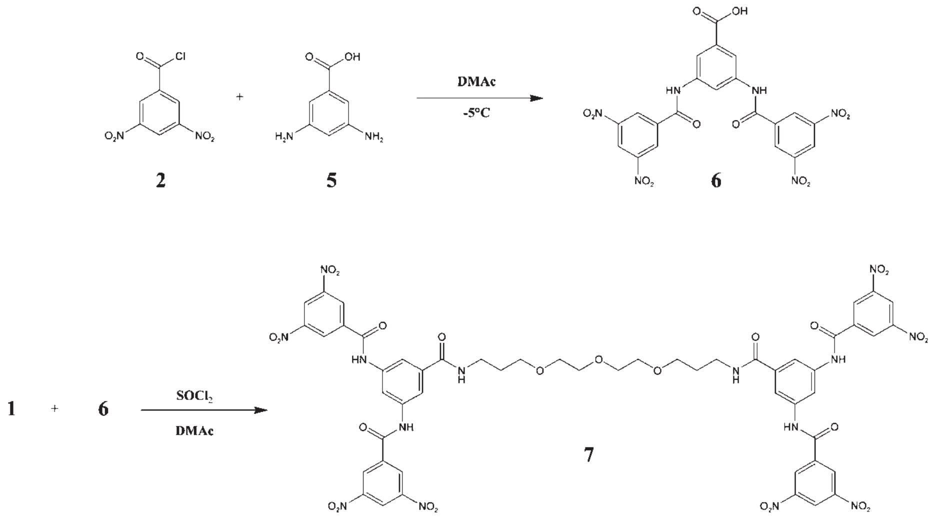


Figure 2.
Synthetic routes of compounds **7** (1.5G).

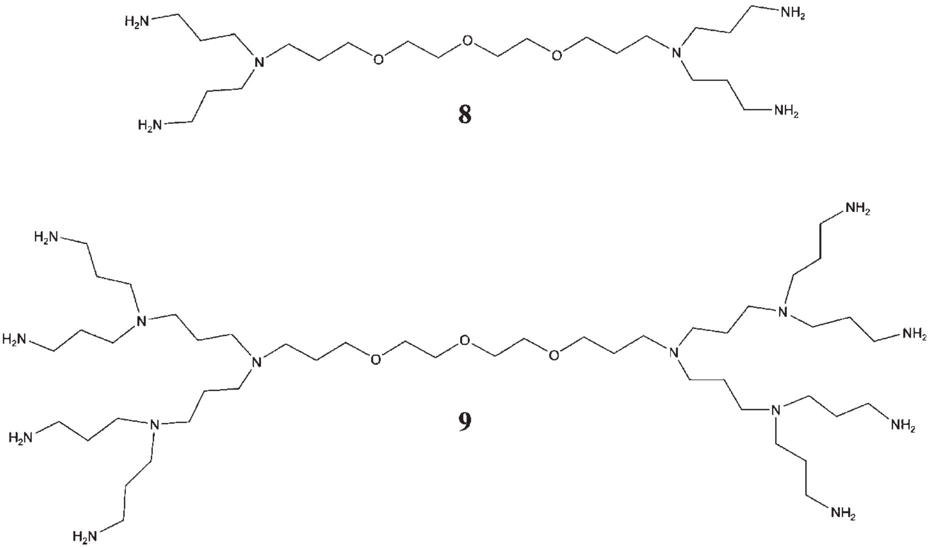


Figure 3.
Structures of aliphatic dendritic Jeffamines® of G1 (**8**) and G2 (**9**).

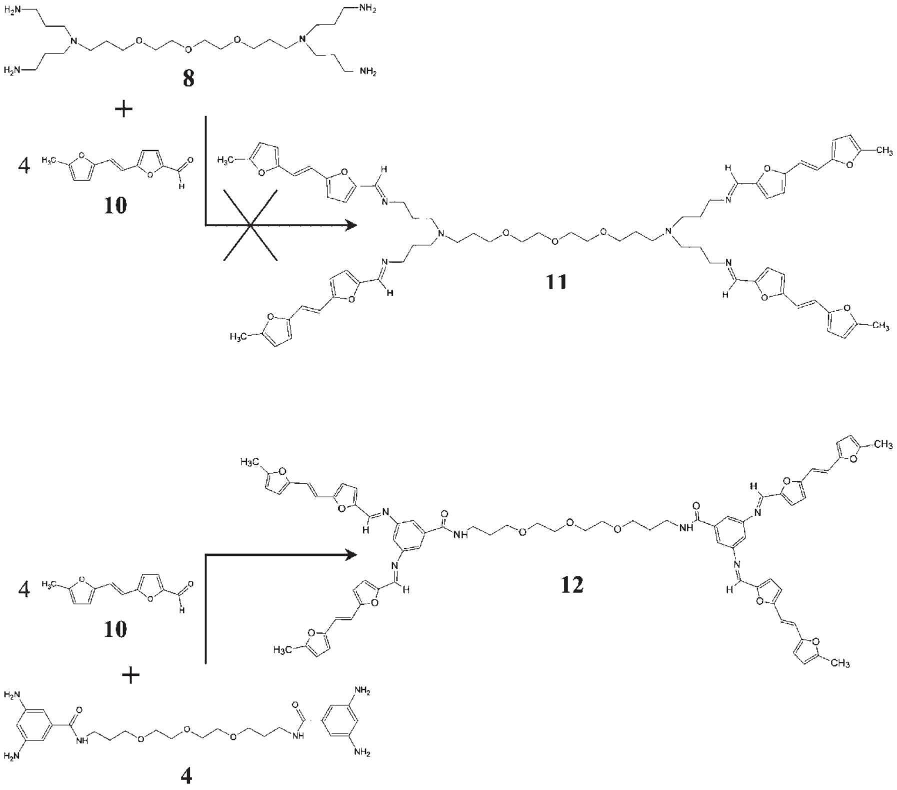
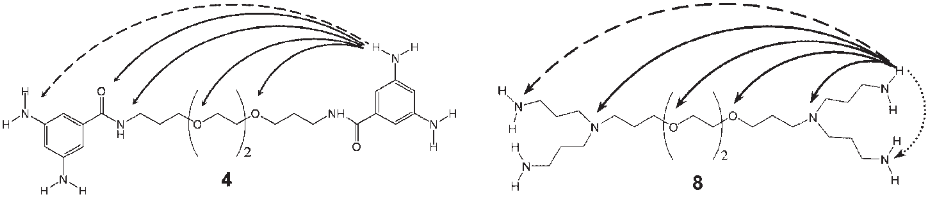


Figure 4.
Preparation of tetra-Schiff's base oligoethers.


4
8

Scheme 1.
The possible hydrogen bonds in the compounds: **4** and **8**.

using several techniques were difficult to achieve and it could only be obtained in low yield.

Study of Hybrids of the First Generation by Reaction with a Chromophore

In a previous work,[17] we presented the synthesis of aliphatic dendritic Jeffamine® of G1 (tetraamine **8**) and G2 (octaamine **9**) as shown in the Figure 3. They were synthesized via Michael addition of acrylonitrile followed by catalytic hydrogenation. As mentioned before, these products showed low reactivity and long reaction times, and high temperatures were necessary for their synthesis. Here, comparative reactivity studies were carried out through Schiff's base formation from G = 1 of aliphatic (**8**) and aromatic (**4**) dendritic-linear copolymers and a chromophore.

The chromophore chosen for this reaction was the compound **10**, which was synthesized and purified following the procedure previously developed by Coutterez and Gandini.[24]

Figure 4 shows the general scheme for the obtention of both products, aliphatic (**11**) and aromatic (**12**), tetra-Schiff's base oligoethers. Several conditions of reaction were assayed for obtaining product **11**, like

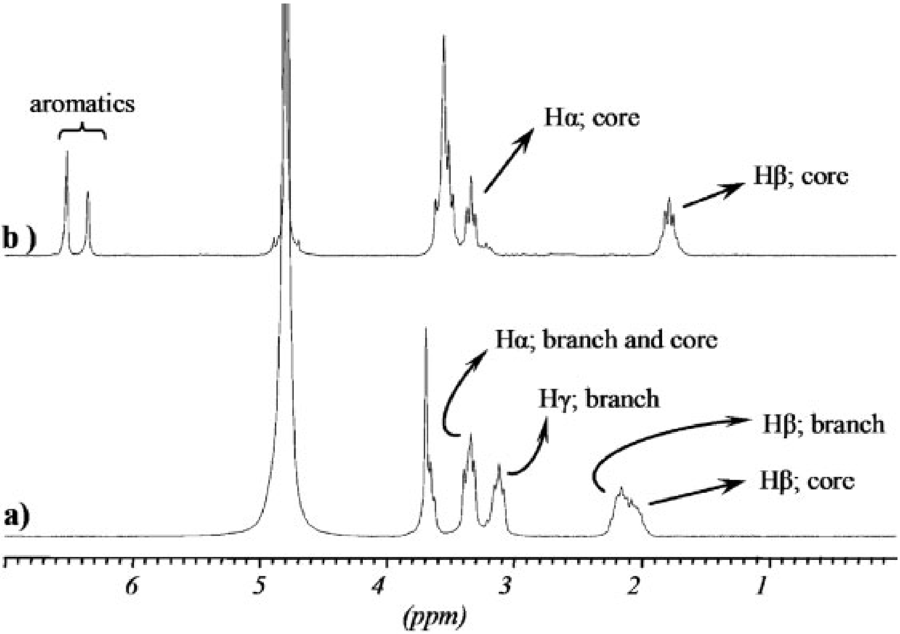


Figure 5.
^{1}H NMR spectra of compounds **4**(b) and **8**(a).

reactions with or without different solvents, various relationships of equivalent of reactive, temperatures and reaction times. Nevertheless, it could not be synthesized under any conditions. However, compound **4** reacted easily with **10**, giving product **12** in a good yield. In both cases, reaction control was performed via IR-spectroscopy, where the diminution of the aldehyde peak at $\approx$1670 cm^{-1} until constant was observed. ^{1}H NMR spectroscopy allowed calculates the conversion degree for this reaction, which was of 91%.

Study of Hybrids of the First Generation by H^{1}NMR

With the aim of corroborating the reactivity difference between products **4** and **8**, comparative studies were conducted. Thus, the possible hydrogen bonds of both compounds were sorted into three categories, as schematically displayed below for G1 (Scheme 1): those between branches grafted on different nodes (broken arrows), those with the tertiary amines and oxygen of central segments (unbroken arrows), and those between branches grafted on the same node (dotted arrows).

In these hybrids, the hydrogen bonds involve the tertiary and primary amines, the oxygen of ethers as well as the nitrogen and oxygen of amides as acceptors. Most of the interactions with tertiary amines or oxygen occur when a terminal branch or the central segment (hybrid core) folds back and orients its end groups toward the tertiary amine to which it is grafted or towards the oxygen of central segment.

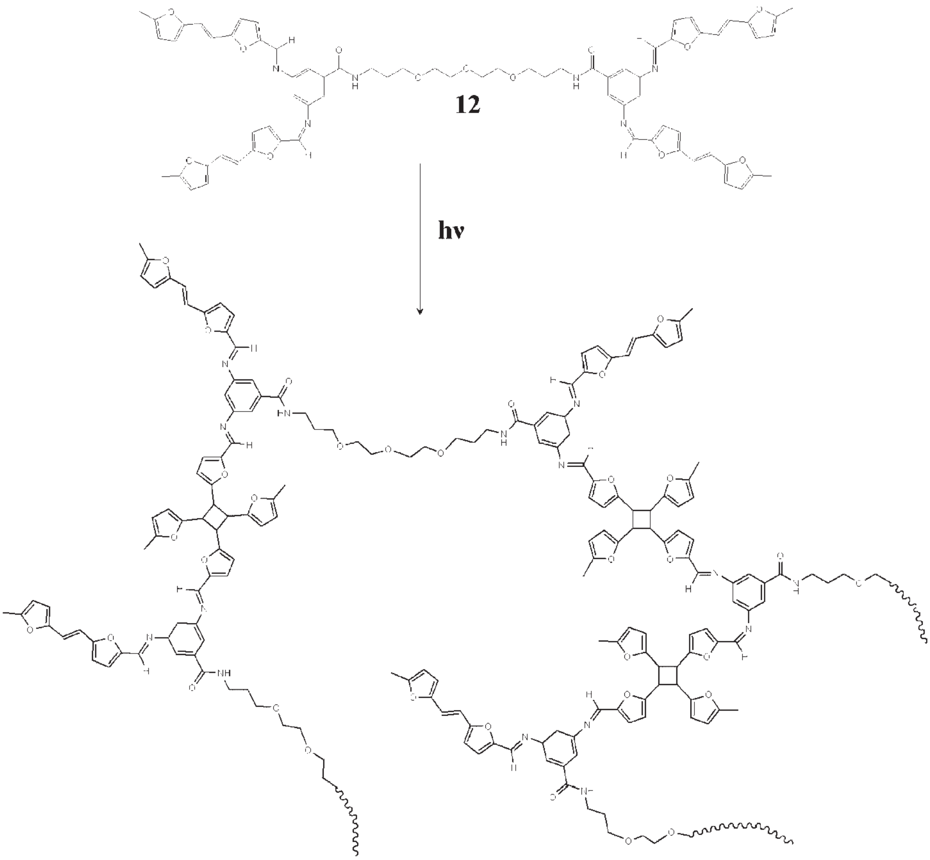


Figure 6.
Photoreticulation mechanism of compound **12**.

Figure 5 shows the ^{1}H NMR of both tetraamines compounds, in which the signals that belong to the $–CH_2C\mathit{H_2}CH_2N=$(Hβ; core) in the central segment are affected by the surroundings. In addition, the spectrum **a)** (compound **8**) shows the signals of $–CH_2–$ in position α, β and γ regarding tertiary amines (each branch) as the broad peaks, whereas the rest of the spectrum displays sharp peaks. This difference in the quality of the signals in the same spectra is caused mainly by the degree of solvatation of each part of the molecule and therefore the quality of the signals shows that the oligoether segment is well solvated, whereas the terminals of these structures are not. This evidences the fact that the primary amine groups of **8** are not available to react easily, because they are in environment in which its mobility is decreased by formation of hydrogen bonds, molecular aggregates or by the backfolding of the branches. These forms of organization of this structure cause great steric hindrance on amines reducing their reactivity.

In order to solve these problems, we synthesized a new hybrid dendritic-linear copolymer of first generation, compound **4**, in which the amine functionality is aromatic instead of aliphatic. The presence of an aromatic ring not only provides a greater rigidity to the dendritic segment where the amine groups are, but also it causes the diminution of their nucleophilicity and basicity. Thus, these three effects are unfavorable to the formation of hydrogen bond or molecular aggregates and therefore no backfolding of end amines can occur, turning the functional groups more available and reactive. This is in agreement with the ^{1}H NMR where all signals corresponding to compound **4** are perfectly defined as shown in Figure 5, spectrum **b)**. This suggests that this molecule does not present any steric restriction of their end groups and therefore the primary amines are available to react.

Preparation of a Photocured Network

Interesting results were obtained when compound **12** was used as crosslinking agent in the preparation of photocured network. A first piece of evidence in favor of a $[\pi2+\pi2]$ cycloaddition mechanism was obtained following the irradiation by FTIR spectroscopy. Thus, the most relevant change was, as expected, the progressive decrease of the alkenyl C=C peak at 1640 cm^{-1}, which was accompanied by the appearance of peaks corresponding to the cyclobutane ring, near 1210 cm^{-1} for CH bending and near 735 cm^{-1} for the ring deformation.

Therefore, coupling between terminal chromophores probably occurred as shown in Figure 6 for the structure photoactive **12**.

Conclusion

Aromatic amine hybrid copolymers showed a better reactivity than the aliphatic amine hybrid copolymers. The presence of a rigid fragment (aromatic ring) appears to be responsible for the decrease of the amine nucleophilicity and basicity, which enhances the availability of amine groups and prevents the intra and intermolecular hydrogen bonds formation. In this way, this study also showed a general procedure that opens up a simple but original method to increase the quantity of chromophores groups per chain oligoether. Thus, a new photoreactive aromatic hybrid dendritic-linear copolymer of first generation with a functionality equal to four (**12**) was synthesized in four steps with very good yields. In agreement with these results, we expect that dendritic Jeffamines® will play an interesting role as enabling building blocks in the preparation of photocrosslinkable materials with interesting application properties in paper and graphic industries. Works to gain a better understanding of these novel materials are in progress.

[1] J. M. J. Frechet, D. A. Tomalia, in: "*Dendrimers and others dendritic polymers*". Wiley, Chichester, **2001**.
[2] D. A. Tomalia and J. M. J. Frechet, *J. Polym. Sci. Part A:Polym. Chem.* **2002**, *40*, 2719.
[3] D. A. Tomalia, *Mater Today* **2003**, *6*, 72.
[4] C. I. Hawker, J. M. J. Frechet, *Polymer* **1992**, *33*, 1507.

[5] I. Gitsov, J. M. J. Frechet, *Macromolecules* **1993**, *26*, 6536.
[6] T. M. Chapman, G. L. Hillyer, E. J. Mahan, K. A. Shaffer, *J. Am. Chem.Soc.* **1994**, *116*, 11195.
[7] Y. Y. Chang, Y. C. Kwon, S. C. Lee, C. Kim, *Macromolecules* **2002**, *33*, 4496.
[8] J. C. Van Hest, D. A. Delnoye, M. W. Baars, M. Van Genderen, E. W. Meijer. *Science* **1995**, *268*, 1592.
[9] J. C. Van Hest, M. W. Baars, R. C. Elissen, M. H. Van Genderen, E. W. Meijer, *Chem. Eur. J.* **1996**, *2*, 1616.
[10] Y. Y. Chang, C. Kim, *J.Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 918.
[11] M. Adeli, R. Haag, *J.Polym. Sci. Part A: Polym. Chem.* **2006**. In press.
[12] G. Eastmond, M. Gibas, W. Pacynko, J. Paprotny, *J. Membr. Sci.* **2002**, *207*, 29.
[13] M. Albert, P. Feiertag, G. Hayn, R. Saf, H. Honing, *Biomacromolecules* **2003**, *4*, 1811.
[14] I. Sucholeiki, J. Perez, P. Wens, *Tetrahedron Lett.* **2001**, *42*, 3279.
[15] M. Meador, V. Cubon, D. Scheiman, W. Bennet, *Chem. Mater.* **2003**, *15*, 3018.
[16] F. Nograro, P. Guerreo, M. Corcuera, I. Mondragón, *J. Appl. Polym. Sci.* **1995**, *56*, 177.
[17] P. Froimowicz, A. Gandini, M. Strumia, *Tetrahedron Lett.* **2005**, *46*, 2653.
[18] K. Dušek, L. L. Matějka, *Adv. Chem. Sci.* **1989**, *222*, 303.
[19] A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chemical Reviews* **1999**; *99*: 1669.
[20] R. Scherrenberg, B. Coussens, P. van Vliet, G. Edouard, J. Brackman, E. de Brabander, K. Mortensen, *Macromolecules* **1998**; *31*: 456.
[21] P. Welch, M. Muthukumar, *Macromolecules* **1998**, *31*: 5892.
[22] Y. Ishida, M. Jikei, M. Kakimoto, *Macromolecules* **2000**, *33*, 3202.
[23] K. L. Wooley, C. J. Hawker, J. M. J. Frechet, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 82.
[24] C. Coutterez, A. Gandini, *Polymer* **1998**, *39*, 7009.