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Synthesis and Polymerization of Multiacrylic Dendritic Molecules

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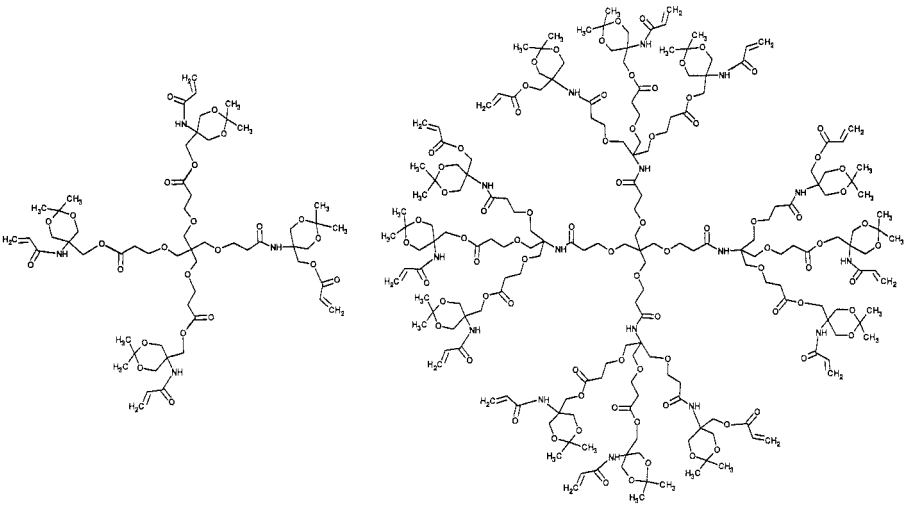
Summary

The first and second generation multiacrylic dendrimers were obtained in good yields following the strategy proposed by Newkome et al. based on the reaction between pentaerythritol and acrylonitrile. Both compounds were thermally polymerized in solution and in bulk through a radical addition reaction. The soluble products were characterized by IR, ^{1}H and ^{13}C-MNR spectroscopies and GPC. The crosslinking products were studied by IR, swelling indexes, DSC and TGA.
Second generation monomers produced highly crosslinked materials, more compact and less-swellable than those obtained from the first generation monomer. These dendritic monomers showed typical behavior previously described in macromonomers chemistry.

Introduction

Monodendrons and dendrimers are some of the most powerful synthetic building blocks that can be employed in the construction of supramolecular and macromolecular systems with well-defined shapes and controllable size. However, only in the last years have dendrimer synthesis and related characterization methods matured sufficiently to allow the study of dendron monomers or dendritic macromonomers, as well as to exploit their potential for the synthesis of new polymers[1-7]. Several research groups have synthesized and characterized dendritic macromolecules with interesting functionalities for various purposes [8-11].
On the other hand, the development of a thermosetting oligomer which would both decrease the viscosity of the resin formulation and increase the cure speed, while also concurrently improving the physicochemical properties of cured materials, has thus become a great challenge. Therefore, macromonomer with a dendritic structure and a high number of functional groups are expected to give low viscosity and good cured properties. It has been demostrated by Ranby [12-14] and Moszner [15], who showed that dendritic multiacrylates are very promising monomers for the preparation of composites for industrial applications due to their relatively low viscosity and efficient incorporation into the formed polymer network. Therefore, dendritic monomers which will produce polymer networks with improved mechanical properties, have to must be synthesized [16]
As an extension of our previous work about the synthesis of a first generation (G1) of a novel dendritic multiacrylic monomers [17], we have expanded the research and

here we now report the synthesis and characterization of a second generation of a multiacrylic dendrimers (G2). The synthesis of the dendritic compounds (**1** and **2**) was designed to have monomers bearing acrylic functional groups, only one for each arm, and masked hydroxyl groups. Besides, is our interest to know the behavior and properties of those crosslinking dendritic networks.



1 **2**

Figure 1: Multiacrylic dendritic monomers: **1**, first generation. **2**, second generation (Idealized structures)

Experimental

Materials and methods: pentaerythritol was obtained from Riedel de Häen, acrylonitrile from Carlo Erba, tris (hydroxymethyl)-aminomethane (TRIS) from Anedra, silica gel 60 from Merck, 1,1'-carbonyldiimidazole (CDI), acryloyl chloride, triethylamine (TEA), 2,2'-azobisisobutyronitrile (AIBN), $CDCl_3$ and D_2O from Aldrich. All chemicals were used without purification. Solvents were obtained from Sintorgan, purified by distillation, and dried with 4Å molecular sieves when necessary.

Calorimetric experiments were conducted on a Hi-Res Modulated TGA 2950, Thermogravimetric Analyser and TA Instruments 2920, Modulated Differential Scanning Calorimeter, at a rate of 10 °C/min under a nitrogen atmosphere. Gel Permeation Chromatography (GPC) experiments were performed on a Perkin Elmer HPLC, poly(styrene-divinylbenzene) column, and refraction index detector, using THF as solvent (0.5 mL/min) at 20°C and polystyrene as standard. Fourier Transform Infrared Spectra (FT-IR) were obtained in a Nicolet 5 SXC FTIR spectrometer on KBr discs. NMR spectra were obtained in $CDCl_3$, unless otherwise indicated, using a Bruker 200 MHz NMR spectrometer. The equilibrium volume swelling ratio, S_w, was calculated by the ratio of the volume of samples in the swelling equilibrium state (V_{sw}) and the volume of samples in the dry state (V_{dry}). It was measured using graduated tubes after the samples have been soaked for 24 h in an excess of different solvents.

I) Monomer Synthesis: *the syntheses of compounds **3** and **11** (Figure 2) have been previously reported [17].*

Amine **7** (Cyanoethylation). TRIS **5** (1 g, 8.25 mmol) was reacted with acrylonitrile **6** (ratio: 1:2 equivalents) 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 82%.
FT-IR (cm^{-1}): Hydroxyl band disappearance (2500-3300, ν OH), new signal at 2256 (ν CN). ^{13}C NMR ($CDCl_3$): δ(ppm)= 118.6 (CN); 73.2 ($H_2NC(-CH_2O-)_3$); 65.9 (OCH_2CH_2); 56.7 ($H_2NC(-CH_2O-)_3$); 19.4 (CH_2CN). ^1H NMR ($CDCl_3$): δ(ppm)= 1.59 (NH_2); 2.59 (t, 8H, CH_2CN); 3.42 (s, 8H, $C(-CH_2O-)_4$); 3.67 (t, 8H, OCH_2CH_2)

Dodecanitrile **8**. To obtain tetraacidchloride **4**, $SOCl_2$ (2 mL) was added to tetraacid **3** (2.01 g; 4.7 mmol) in CH_2Cl_2 (2mL) and allowed to react for 1 h under reflux. The excess of $SOCl_2$ was evaporated under vacuum and the crude product was used for the amidation step. A mixture of amine **7** (5.6 g; 20 mmol.) and TEA (2.8 mL; 20 mmol) in 30 mL of THF was added to tetraacidchloride **4** dissolved in THF (10 mL) and allowed to react for 15 hours 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. Yield was 85%.
FT-IR (cm^{-1}): 2262 (ν CN). Disappearance of carbonyl acid band at 1720 (ν C=O). New amide bands at 1690 (ν C=O) and 1557 (ν NH). ^{13}C NMR ($CDCl_3$): δ(ppm)= 171.6 (C=O); 118.1 (CN); 69.5 and 68.9 ($C(-CH_2OCH_2-)_4$); 67.4 ($CONHC(-CH_2O-)_3$); 65.7(OCH_2CH_2); 59.7($CONHC(-CH_2O-)_3$); 45.4 ($C(-CH_2O-)_4$); 37.4 ($-CH_2CONH-$); 18.7 (CH_2CN). ^1H NMR ($CDCl_3$) δ (ppm): 2.37 (t, 8H, CH_2CONH); 2.56 (t, 24H,CH_2CN); 3.33 (s, 8H, $C(-CH_2O-)_4$); 3.62 (t, 32H, OCH_2CH_2); 3.76 (s, 24H,$CONHC(-CH_2O-)_3$). Anal. Calcd. for $C_{69}H_{100}N_{16}O_{20}$ (1473): C, 56.17; H, 6.85; N, 15.20; O, 21.78. Found: C, 55.43; H, 6.76; N, 14.72; O, 23.09.

Dodecamethyl ester **9** (Esterification). Dodecanitrile **8** (2.0 g, 1.36 mmol) was dissolved in 20 mL of dry methanol acidified with HCl (g), and the reaction mixture was refluxed for 30 min. After the solvent was removed under vacuum, the crude product was dissolved in chloroform and washed with water, and the organic phase was dried with $CaCl_2$, filtered and dried. Yield was 50% .
FT-IR (cm^{-1}): disappearance of 2262 (ν CN) band, new ester signal at 1743 (ν C=O).
^{13}C NMR ($CDCl_3$): δ(ppm)= 172.0 and 171.9 (-COO- and CONH); 69.9 and 69.0 ($C(-CH_2OCH_2-)_4$); 67.4 and 66.6 ($CONHC(CH_2OCH_2)_3$); 58.7 ($CONHC(CH_2OCH_2)_3$); 51.5 (CH_3); 45.4 ($C(-CH_2OCH_2-)_4$); 34.6 ($-CH_2CONH-$).^1H NMR: ($CDCl_3$) δ (ppm): 2.39 (t, 8H, CH_2CONH); 2.53 (t, 24H,CH_2CN); 3.34 (s, 8H, $C(-CH_2OCH_2-)_4$); 3.64 - 3.71 (m, 92H, OCH_2; CH_3). Anal. Calcd for $C_{81}H_{136}N_4O_{44}$ (1869): C, 52.00; H, 7.33; N, 3.00; O, 37.67. Found: C, 50.50; H, 6.99; N, 2.92; O, 39.59.

Dodecacarboxylic acid **10** (Hydrolysis of dodecamethyl ester **9**). Dodecamethyl ester **9** (1.1 g, 0.59 mmol) was mixed with 2.4 mL of an aqueous 3M NaOH solution for 30 minutes at room temperature. When the reaction was complete, the product was acidified with HCl 1N, dried and extracted with THF. Yield was 60%.
FT-IR (cm^{-1}): disappearance of ester signal at 1740 (ν C=O), new signal of carbonyl acid at 1720 (ν COOH). ^{13}C NMR (D_2O) δ(ppm)= 176.0 and 174.1 (C=O); 69.7 and

68.9 ($C(-CH_2O-CH_2-)_4$); 67.8 and 67.2 ($CONHC(CH_2OCH_2)_3$); 60.4 ($CONHC(CH_2OCH_2)_3$); 45.6 ($C(-CH_2OCH_2-)_4$); 34.8 ($-CH_2CONH-$). ^1H NMR: (D_2O) δ (ppm): 2.41 (t, 8H, CH_2CONH); 2.56 (t, 24H,CH_2COOH); 3.32 (s, 8H, $C(-CH_2OCH_2-)_4$); 3.65 (m, 56H, $-OCH_2$). Anal. Calcd. for $C_{69}H_{112}N_4O_{44}$ (1701): C, 48.68; H, 6.64; N, 3.29; O, 41.39. Found: C, 47.86; H, 6.65; N, 4.01; O, 41.48.

Dendrimer **12** (Esterification-Amidation of Dodecacarboxylic acid **10** with hydroxylamine **11**). Dodecacarboxylic acid **10** (0.5 g, 0.27 mmol) was dissolved in THF and CDI (0.57 g, 3.5 mmol) was added. After 45 min, hydroxylamine **11** (0.59 g, 3.5 mmol) was added and the reaction was allowed to proceed for 15 hours. When the reaction was complete, the solvent was evaporated under vacuum at room temperature, and the crude product was dissolved in chloroform and washed with water, and the organic phase was dried with $CaCl_2$, filtered and dried.
FT-IR (cm^{-1}): 1739 (ν C=O ester), 1660 (ν C=O amide) and 1543 (ν NH amide), disappearance of carbonyl acid signal at 1720 (ν C=O). ^{13}C NMR ($CDCl_3$): δ(ppm)= 172.5 and 171.3 (-COO- and CONH); 98.5 ($C_{acetal}(CH_3)_2$); 69.9 and 69.0 ($C(-CH_2OCH_2-)_4$); 67.3 and 66.7 ($CONHC(CH_2OCH_2)_3$); 63.0 ($-CH_2OH$); 59.7 ($CONHC(CH_2OCH_2)_3$); 54.6 ($C_{tris}(-CH_2O-)_3$); 45.5 ($C(-CH_2OCH_2-)_4$); 37.1 and 34.7 ($-CH_2CONH-$); 24.2 and 22.7 (CH_3). ^1H NMR: ($CDCl_3$) δ (ppm): 1.40 and 1.43 (s, 72H, CH_3); 2.43 (t, 8H, CH_2CONH); 2.58 (t, 24H, CH_2COOH); 3.35 (s, 8H, $C(-CH_2OCH_2-)_4$); 3.67 (m) and 4.13 (s) (128H, $-OCH_2$). *Anal.* Calcd. for $C_{153}H_{268}N_{16}O_{68}$ (3418): C, 53.71; H, 7.90; N, 6.55; O, 31.83. Found: C, 51.81; H, 7.27; N, 6.48; O, 34.44.

Multiacrylic Dendrimer **2**. To a solution of product **12** (0.5 g, 0.15 mmol) and triethylamine (0.065 mL, 0.45 mmol) in 1.5 mL of THF, acryloyl chloride (0.025 mL, 0.30 mmol) dissolved in 0.5 mL of THF was added dropwise at 0°C. After the solution was allowed to warm to room temperature, it was stirred for 3h. The solvent was then evaporated under vacuum and the residue was dissolved in chloroform and washed with water to remove the ammonium salts. Yield was 78%.
FT-IR (cm^{-1}): 1747 (ν C=O ester), 1668 (ν C=O amide) and 1555 (ν NH amide).
^{13}C NMR ($CDCl_3$): δ(ppm)= 171.8 and 168.7 (-COO- and CONH); 165.9 (-OCO-CH=CH_2); 134.5-126.6 (-CH=CH_2); 98.6 ($C_{acetal}(CH_3)_2$); 69.9 and 68.9 ($C(-CH_2OCH_2-)_4$); 67.8 and 66.6 ($CONHC(CH_2OCH_2)_3$); 62.2 ($-CH_2OH$); 59.7 ($CONHC(CH_2OCH_2)_3$); 52.8 ($C_{tris}(CH_2O-)_3$); 45.5 ($C(-CH_2OCH_2-)_4$); 37.1 and 34.8 ($-CH_2CONH-$); 25.4-18.7 (CH_3). ^1H NMR ($CDCl_3$) δ (ppm): 1.41 and 1.49 (s, 72H, CH_3); 2.40 (t, 8H, CH_2CONH); 2.55 (t, 24H,CH_2COOH); 3.35 (s, 8H, $C(-CH_2O-)_4$); 3.66 (m) and 4.52(s) (128H, $-OCH_2$); 5.62 and 6.20 (m, 36H, CH=CH_2). *Anal.* Calcd. for $C_{189}H_{292}N_{16}O_{80}$ (4067): C, 55.77; H, 7.25; N, 5.51; O, 31.47. Found: C, 55.03; H, 7.11; N, 4.96; O, 32.90.

II) Polymerization experiments: thermal polymerization of both dendritic monomers **1** and **2** was performed under a nitrogen atmosphere using 1% w/w of AIBN as the initiator at 60°C. Reaction times are reported in Table 1. DMF was used as the solvent for polymerizations in solution 0.3M, and then vacuum eliminated. When the reaction were complete, the crude products were washed with $CHCl_3$ and the soluble and insoluble fractions separated. Gel fraction was calculated as %w/w of the insoluble product compared to the initial weight of the reagents.

Results and Discussion

I) Monomer Synthesis: the monomer cores were synthesized following the strategy proposed by Newkome *et al.,* which is based on the reaction of pentaerythritol and acrylonitrile[18-19]. The synthesis of the first generation of the multiacrylic monomer **1** has been studied and optimized in our laboratory as previously reported [17].

The pathway for the synthesis of the desired second generation dendritic monomer **2** followed the same strategy used in the synthesis of the first generation, as shown in Figure 2.

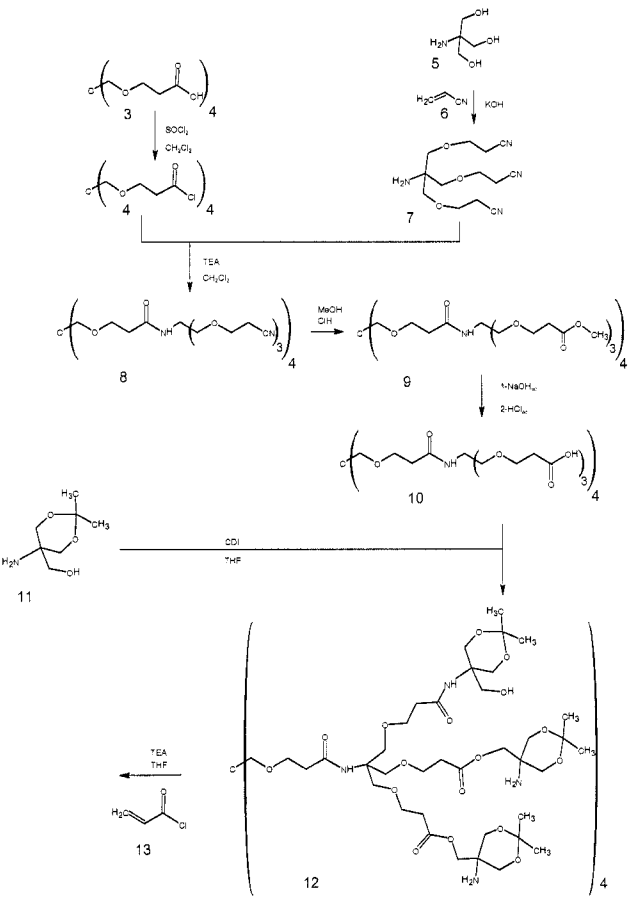


Figure 2: Synthetic patway leading to the dendritic monomer **2.**

The reaction conditions were optimized to improve yields in each step. Our first attempt to synthesize the nitrile precursor **8** was the amidation of the tetraacid core **3**, previously activated by 1,1'-carbonyldiimidazole (CDI), with amine **7**. This amine was previously prepared by Michael reaction of TRIS **5** with acrylonitrile **6**. We found that the conversion to amide groups was incomplete under various experimental conditions, probably due to steric hindrance. To overcome this problem, the

carboxylic acid groups of **3** were converted into the more reactive acid chlorides(compound **4**) through reaction with thionyl chloride. Finally, products **4** and **7** were linked through a convergent synthesis in THF to obtain dodecanitrile **8** in 85% yield.
Dodecamethyl ester **9** was obtained in 57% yield by methanolysis of compound **8** in acidic medium. Next, hydrolysis of compound **9** in basic aqueous solution gave dodecacarboxylic acid **10** in 60% yield. Incorporation of hydroxyl and amine end groups was performed by activation of the carboxylic acid groups of **10** with CDI and subsequent reaction with hydroxylamine **11**. A mixture of amide and ester products (30:70) in **12** was obtained in optimized yields of 60%. The amide/ester ratio is strongly dependent on the reaction conditions. Increasing in reaction time, temperature or concentration of the initial reagents all led to a rise in the amide percentage. These variations may be explained by the attack of a hydroxyl group, which is favored because it is less hindered, followed by an intramolecular rearrangement by attack of the amine at the ester carbonyl to yield the amide[20].
Once compound **12** was attained, the reaction of its free amine and hydroxyl groups with acryloyl chloride **13** gave the multiacrylic dendrimer **2** in 75% yield, with an average of 12 acrylic groups per molecule. The number of acrylic groups was estimated by ^{1}H NMR from the ratio of the integral of vinylic protons at 5.6 ppm and the methylene protons of the dendritic core at 2.6 ppm.
Multiacrylic compounds **1** (first generation) and **2** (second generation) were used as monomers in thermal polymerization assays.

II) Polymerization: polymerization assays of dendritic monomers **1** and **2** were performed using 2,2´-azobisisobutyronitrile (AIBN) as the thermal initiator at 60° C under a nitrogen atmosphere. Time and type of polymerization technique were varied to determine the effect of reaction conditions on the crosslinked product yield, which was measured as the insoluble product (gel fraction). The results are shown in Table 1. As can be observed in Table 1, addition polymerization reactions render crosslinked and/or soluble products in different yields. Solution polymerization conditions gave only soluble products, as unreacted monomers and dimers, while bulk polymerization conditions gave soluble and insoluble products. The presence of soluble products and their characteristics were confirmed by GPC studies (see section III). Comparison of the polymerization reactions conducted in bulk with those carried out in solution reveals that the degree of polymerization and conversion of macromonomers are higher in bulk. This can be attributed to the need for high concentrations of the macromonomers, due to the steric congestion of their active centers. Increasing the reaction time in bulk polymerization favored the formation of insoluble products up to 15 h. Longer reaction times did not improve the yields, probably due to matrix stiffness diminishing the mobility of the reactive sites.
Polymerizations with the second generation monomer produced yields up to 90%, which is due to the greater number of acrylic groups on this second generation dendrimer. Considering the lack of solubility of the polymerized structures (crosslinked polymer), the deprotection assays of hydroxyl groups were not performed.

III) Characterization of Polymerization Products: crosslinked products (reactions VII, VIII, IX and X) were studied by FT-IR, swelling index (Sw), DSC and TGA. Soluble fractions (from reactions I, II, VII, VIII and IX) were studied by GPC and ^{1}H-NMR.

FT-IR spectroscopy of the polymers showed the disappearance of the vinyl group signal at 1625 cm^{-1} (ν C=C). However, it was difficult to perform quantitative measurements due to the strong amide band at 1640 cm^{-1} (ν C=O) which masks the vinyl signal.

Swelling index (Sw), measured as swollen volume (V_{sw}) vs dry volume (V_{dry}), showed the affinity of the matrices for different solvents. The less polar solvents are better incorporated into the matrix, although swelling indexes are quite low in general. They were: polymer from **1**, 1.5 (H_2O), 3.0 (CH_3OH), and 4.0 ($CHCl_3$); polymer from 2, 1.2 (H_2O), 1.5 (CH_3OH), and 1.6 ($CHCl_3$). Second generation products incorporate very little solvent, probably due to cross linking and reduced accessibility of the solvent to inner zones.

Table 1. Polymerization assays of dendritic monomers **1** and **2**.

Polymerization Reaction	Time (h)	Condition	Gel Fraction % w/w
First Generation			
I	2	Solution (DMF 0.3M)	-
II	15		-
III	1	Bulk	-
IV	2		10
V	4		17
VI	8		32
VII	15		45
VIII	24		43
Second Generation			
IX	4	Bulk	63
X	15		90

Thermogravimetric analysis demonstrated that homopolymers of the second generation are slightly more stable than those obtained from the first generation, as observed from the residual mass for increasing temperatures (Table 2). Thermal stabilities are probably related to the number of moieties covalently bonded in the polymeric network; that is, the denser the matrix, the more difficult it is to degrade it.

DSC analysis showed three endothermic peaks for both products. The first, at 75°C for homopolymer 1 and 2, due to the loss of solvent molecules occluded into the matrix. The second, at 252°C for homopolymer 1 and 242°C for homopolymer 2. This behavior could be adjudicated to a beginning of degradation process, where the most labile bonds of the network are broken (outer of the dendritic monomer).The third, between 420-430°C for both products, due to the complete degradation of the network (inner of dendritic molecules).

Table 2. Thermogravimetric assays of dendritic networks

	Weight loss percentage from $w_{initial}$				
	100°C	200°C	300°C	400°C	500°C
Homopolymer 1	2	11	44	66	77
Homopolymer 2	1	9	30	48	63

^{1}H NMR of the soluble fractions of polymerization showed unreacted double bonds

(60-80% of the total acrylic groups), calculated from the ratio of the integral of vinyl protons at 5.6 ppm and methylene protons of the dendritic core at 2.6 ppm.
GPC studies of soluble products showed the presence of unreacted monomers and dimers for the products from solution polymerization. However, only unreacted monomers were detected when bulk polymerization reactions were carried out.

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References

1. Newkome, G.R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives;* VCH:Weinheim, 1996.
2. Tomalia D.; Frechet J. *J. Polym. Sci.:Part A: Polym. Chem.* **2002, 40,** 16, 2719-2728.
3. Grayson, S.; Frechet, J. *Chem. Rev.* **2001, 101**, 12, 3819-3867.
4. Bosman, A. W.; Jansen, H. M.; Meijer, E.W. *Chem. Rev.* **1999,** 99, 1665.
5. Zeng F.; Zimmerman, S.C. *Chem. Rev.* **1997**, 97, 1681.
6. Percec V.; Ahn C.; Cho W.; Jamieson A.; Kim J.; Leman T.; Schmidt M., Gerle M.; Moller M.; Prokhorova S.; Cheng S.; Zhang A.; Ungar G.; Yerdley J. *J. Am. Chem. Soc.* **1998**, *120* (34), 8619-8631.
7. Matyjaszewski K.; Shigemoto T.; Frechet J.; Leduc M. *Macromolecules* **1996**, *29* (12), 4167-4171.
8. Peerlings, H.W..; Van Benthem, R. A. T. M.; Meijer, E. W. *J. Polym. Sci:Part A: Polym. Chem.,* **2001, 39,** 3112-3120.
9. Kim, C.; Kim, H. *J. Polym. Sci.:Part A: Polym. Chem.* **2002, 40**, 326-333.
10. Vögtle, F.; Gestermann, S.; Hesse, H.; Schwierz, B.; Windisch, B. *Progress Polym. Sci.* **2000, 25**, 987-1041.
11. Vetter, S; Koch, S; Schluter A., *J. Polym. Sci. Part A,* **2001**, *39*, (11), 1940-1954.
12. Shi W.; Ranby B. *J. Appl. Polym. Sci.* **1996**, *59*, 1937-1944.
13. Shi W.; Ranby B. *J. Appl. Polym. Sci.***1996**, 59, 1945-1950.
14. Shi W.; Ranby B. *J. Appl. Polym. Sci.* **1996**, *59,* 1951-1956.
15. Moszner N., Volkel T.,Rheinberger V., *Macromol. Chem. Phys.* **1996**, 197, 621.
16. Moszner, N.; Salz, U; *Prog. Polym. Sci.,* **2001,** 26, 535-576.
17. Halabi, A.; Strumia, M.C. *J. Org. Chem.* **2000**, *65* (26), 9210-9213.
18. Newkome G.; Lin X. *Macromolecules* **1991**, *24* (6), 1443-1444.
19. Newkome G.; Weis C. *Org. Perp. Proced. Int.* **1996**, *28*, 242-246.
20. Satterhwait A.; Jencks W. *J. Am. Chem. Soc.* **1974, *96,*** 7018-*7031.*