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Synthesis of Dendramines, Dendramides and Their New Application in the Oil Industry

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A series of dendramines and dendramides have been synthesized and some of their "anti-freeze" properties in diesel fuels have been tested, showing that these compounds are good oil additives for reducing the wax-like crystals which block the fuel filters.

INTRODUCTION

Since Vögtle first reported the synthesis of a dendrimer,[1] this compound class has attracted increasing attention in the literature.[2] This is in part because their size and architecture can be specifically controlled in their synthesis. In addition, they have favorable properties, such as low intrinsic viscosity, high solubility (or induced miscibility) and high reactivity. Their many potential uses include nanoscale catalysts, vessels, surfactants, anticoagulators, immuno-diagnostics, agents for delivering drugs or genes into cells, chemical sensors, information processing materials, high performance polymers, adhesives and coatings, separation media and super thin films.[3a-h] The synthesis of dendrimers involves a multistep, repetitive methodology. An important difference, in comparison to a linear polymer, is that dendrimers contain many branches which give rise to a very high number of terminal functional groups in each molecule. It is estimated worldwide that approximately 120 research groups are working with dendrimers and many more potential applications are being discovered and developed.

Dendrimers have not yet been used commercially in the oil industry, partly due to the high cost of multi-stage processing. However, a number of "one pot" processes have been described that may change this.[4] The work described in this paper was carried out to provide a basis upon which additives for diesel fuel could be built. The intended application of the final product was diesel anti-freeze for wax crystal modification in diesel fuel.

Paraffinic (*n*-alkanes) wax separates from diesel fuel in the cold as thin plates that gel the fuel and block fuel filters. Wax crystal modifying additives nucleate smaller wax crystals, and modify their growth to give compact prisms thus, alleviating cold flow problems. Wax crystals may be nucleated by *n*-alkane-like molecules that can form large numbers of wax-like seed nuclei. It was conceived that a dendrimer, which was of sufficient size and coated with long *n*-alkyl groups (e.g. C_{22}), would have good oil solubility (regardless of the polarity of the dendrimer core) and could be large enough (larger than the *n*-alkane crystal critical nucleus size) to act as a heteronuclei for wax crystals. Hence, the synthetic work is divided into two parts: (1) growing a well defined dendrimer core, with reactive chain end groups (these will be primary amine groups by the process described in this paper); (2) reacting these end groups with a suitable derivative of a long chain *n*-alkyl compound; the methodology for this stage was suggested by Tomalia's polyamidoamine approach.[5] Long chain *n*-alkanols (C_{18} to C_{24}) were esterified with acrylic acid and these acrylates were condensed with the primary amine end groups of the dendrimer polyamines. The products are readily soluble in diesel fuel, with low viscosity despite the high molecular weight, and are active as wax crystal modifiers.[6]

In this paper, we report the synthesis of a series of dendramines, dendramides, and their applications as diesel anti-freeze agent in the oil industry.

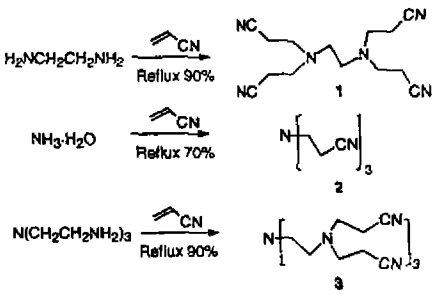
RESULTS AND DISCUSSION

Synthesis of Dendramines

The synthesis of dendramines consisted of an initial Michael addition of a core amine to acrylonitrile, followed by hydrogenation in the presence of Raney nickel catalyst to regenerate a core amine, which can be futher processed in a stepwise manner. The first step is the Michael addition of an amine to acrylonitrile, and products **1**, **2** and **3** (Scheme I) were obtained in excellent yields by the addition of a corresponding amine to acrylonitrile, with acetic acid catalysis.

These compounds have previously been prepared[1] and the melting points and NMR spectra of our materials were consistent with those previously obtained.

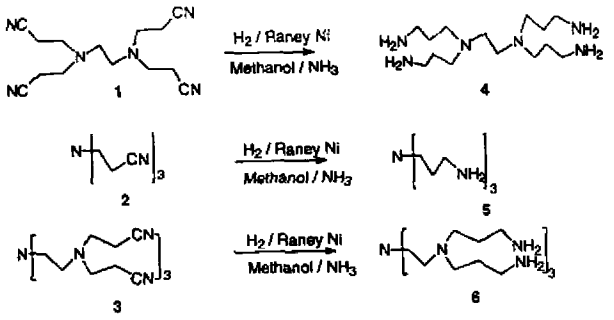
Scheme I



The second step, reduction of the nitrile functionalities to amines, is the most challenging step for the preparation of these dendrimers. Although there are many methods in the literature[7] to reduce nitriles to amines, two types have been reported to reduce multi-nitriles to multi-amines satisfactorily in the preparation of dendrimers: (i) hydride transfer reagents such as $NaBH_4$, in the presence of transition metal salt complexes, and (ii) heterogeneously catalyzed hydrogenation. Vögtle[1] first reported the reduction of a multi-nitrile in 24% yield, by using $NaBH_4$·$CoCl_2$. Difficulties associated with nitrile reduction limited molecular weight obtainable with this dendrimer. Recently, Vögtle reported that the reduction problem was solved by using diisobutylaluminum hydride in a mixed solvent system of THF and hexane,[8] but even a yield of 89% was not good enough for satisfactory synthesis of higher generation polymers. Worner and Mülhaupt[9] used Raney nickel as hydrogenation catalyst and a small amount of sodium hydroxide as the co-catalyst. In this hydrogenation step, the reduction yield is not high (about 70%) because a strong base leads to a retro-Michael reaction. de Brabander-van den Berg and Meijer[10,11] carried out hydrogenation reactions using a large amount of Raney cobalt pretreated with sodium hydroxide as the catalyst, and a large amount of water as the solvent under 30-70 bar H_2 pressure. No side products were detectable under these conditions. It was reported that "*the process window for a quantitative hydrogenation is small*" and several special procedures were utilized to eliminate side reactions to achieve a 99.5% or better selectivity level per conversion. Such control is of critical importance!

The heterogeneously catalyzed hydrogenation method appears to be much better in reducing the multi-nitriles and Raney nickel the most popular catalyst was used. According to the literature,[12,13] ammonia was required to suppress the formation of secondary amino functionality. Thus, a solution of the nitrile in 10 N methanolic ammonia (the ratio of ammonia to each nitrile group was 8 to 1) and Raney nickel catalyst were placed in a hydrogenation bomb. The reaction was carried out under a pressure of 1400 psi and at 130 °C for two days. After cooling, the solvent was removed on a rotary evaporator, and the residue was checked by NMR to determine whether there were any cyano groups left unreacted. If so, the same procedure was repeated.

Scheme II

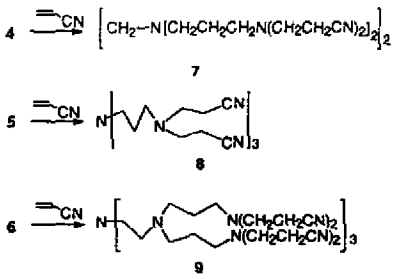


Although we obtained products which showed no cyano signal in their NMR spectra, the unsatisfactory integration of ^{1}H NMR spectra, and many more carbon signals than expected in the ^{13}C NMR, indicated that the compounds **4**, **5** and **6** were still not completely pure. Considerable effort was made to obtain homogeneous multi-amines **4**, **5** and **6** by column chromatography, but all attempts were unsuccessful to concentrate them above about 75%. We also attempted to fractionate the multi-amines by distillation: but there was no improvement in the NMR spectra of either the two fractions obtained with respect to those of the original material.

The crude products **4**, **5**, **6** were therefore used directly for the third step. The same method as above for cyanoethylation was used: amine, excess acrylonitrile, and a catalytic amount of acetic acid were refluxed for two days. After the excess acrylonitrile was removed, the residue was dissolved in $CHCl_3$, and to this solution was added saturated aqueous ammonia solution to neutralize the acetic acid, and the mixture was extracted with $CHCl_3$. The products were subjected to column chromatography. Compounds **7**, **8** and **9** were obtained essentially homogeneous in 90% yields over the two steps but traces of impurities were detected by NMR.

The fourth step consisted of the hydrogenation of compounds **7**, **8**, **9**. The same procedure as for the second step was applied. The reaction was monitored by NMR. No cy-

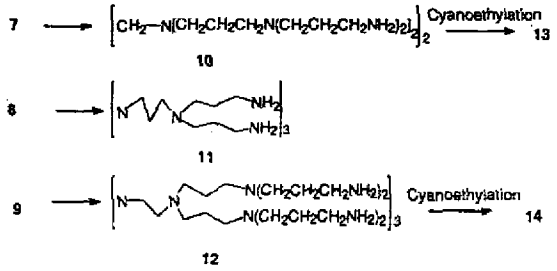
Scheme III



ano groups were detected by the end of the reaction, but the oily products were only *ca.* 75% pure.

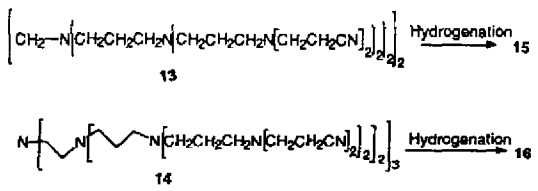
The crude amines **10**, **12** were used directly in the fifth step. The method of cyanoethylation of amine **10** was used as before, *i.e.*, amine, excess acrylonitrile and a catalytic amount of acetic acid were refluxed for two days. After work up, as before, and purification by a short column, **13** in 90% purity was obtained as a yellow oil in 80% yield. A different method was used for the cyanoethylation of amine **12**, *i.e.*: amine **12**, and four equivalents of acrylonitrile were refluxed in water for 24 h, after removing the excess of acrylonitrile, the organic layer was isolated from the resulting clear two-phase system. The nitrile **14** (a colorless oil) was obtained in a 85% yield; *ca.* 90% pure.

Scheme IV



The sixth step was the hydrogenation of compounds **13** and **14**. The same procedure as above was used. The reaction was monitored by NMR. No cyano groups were detected by the end of the reaction, but the oily products **15** and **16** were only *ca.* 70% pure.

Scheme V

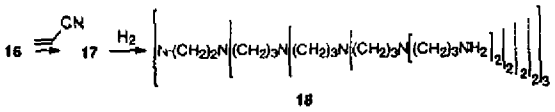


According to the ^{1}H NMR spectra, the purities of compounds **4**, **5**, **6**, **10**, **11**, **12**, **15** and **16** were each higher than 70%. However, in the ^{13}C NMR spectra, there were more signals than required. These could be; (i) from the different stereo-conformations of molecules due to hydrogen bonds, which resulted in complicated carbon signals; (ii) from some by-products, such as secondary amines and imines produced in the reduction, which appear at around 173 ppm in ^{13}C NMR spectra.

Synthesis of Dendramine 18 [94 N (48 P + 46 T)]

We previously obtained dendramine **16**, which contains **24** primary amines and 22 tertiary amines, also called **46 N** (24 P + 22 T). **16** was cyanoethylated with acrylonitrile to form dendrimer **17**, which contains 48 cyano groups. Compound **17** was hydrogenated to give dendramine **18** containing 94 nitrogen atoms, at 130 °C by using Raney nickel as the hydrogenation catalyst and 10 N methanolic ammonia as solvent. The reaction was monitored by NMR, and no cyano groups were detected by the end of the reaction.

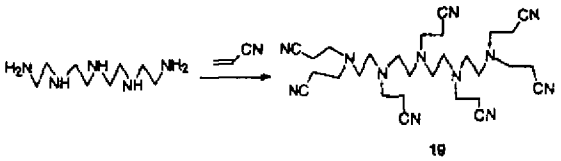
Scheme VI



Using TEPA as the Starting Material to Synthesize a Dendramine

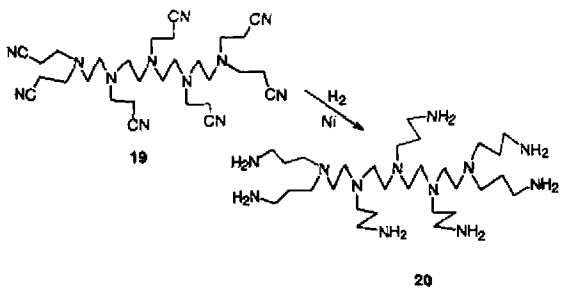
In order to obtain more functional groups in fewer steps, the commercially available TEPA (tetraethylenepentamine) was used as starting material. It contains two primary amino groups and three secondary amino groups. On the treatment of TEPA with excess acrylonitrile, after working up, a white solid **19** (containing 7 cyano groups) was obtained in a yield of 89% (mp 76-79 °C).

Scheme VII



Compound **19** was hydrogenated in the presence of Raney nickel catalyst at 130 °C by using as solvent a mixture of the saturated aqueous ammonia solution and methanol to give **20**. This reaction was monitored by NMR, and

Scheme VIII

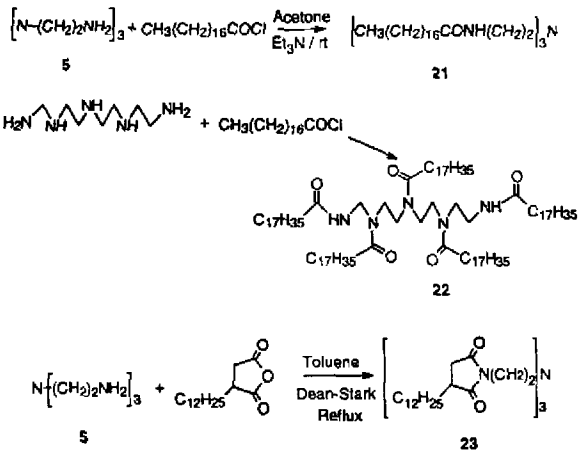


was continued until no cyano groups were detected.

Preparation of Multiple Amides

The amides **21**, **22** were prepared in 99% and 98% yields, respectively by reactions of tris(2-aminoethyl)amine or TEPA with stearoyl chloride in the presence of triethylamine as a base and with acetone as the solvent. Amide **23** was obtained in 90% yield by refluxing tris(2-aminoethyl)amine with dodecylsuccinic anhydride in toluene with a Dean-Stark trap to remove the water. Since the starting material, dodecylsuccinic anhydride bought from Pfaltz & Bauer Inc., was not pure (contained several isomers), the product **23** also consisted of several isomers, and the NMR spectra were more complicated than expected.

Scheme IX



Long Chain Alkyl Dendramine Derivatives as Diesel Anti-freeze Components

Dendramines **6**, **10** and **12**, were reacted with long chain alkyl acrylates at a ratio of one acrylate per primary amine group,[6] to give Michal addition products **24-27**. The acrylate and dendramine were mixed neat and held at 80 °C as a melt for two to three days. The products were re-analysed by ^{1}H NMR which showed that all the acrylate had reacted with the amine.

Dendramine-acrylate fomulations were tested as follows:

(i) 1 mol equivalent (me) hexamine **6** + 6 me eicosyl acrylate → **24**.

(ii) 1 me hexamine **6** + 6 me docosyl acrylate → **25**.

(iii) 1 me octamine **10** + 8 me eicosyl/docosyl (ratio 3/5) acrylate → **26**.

(iv) 1 me dodecamine **12** + 12 me eicosyl/docosy acrylate → **27**.

These alkyl bearing dendramines are totally soluble in diesel fuel and were tested for their ability to aid the reduction of the diesel fuel cold flow fail temperatures (due to wax formation), known as the CFPP (Cold Filter Plugging Point).[14] As usual with diesel cold flow treatment, these materials were tested in combination with an ethylene vinyl acetate copolymer (EVA) having 36 wt% vinyl acetate and Mn of 3000 (relative to polystyrene by gpc). The Table 1 shows that the addition of 200 ppm of EVA depresses the CFPP fomulations **24** through **27** to between -12 °C and -14 °C. Fomulations **24** through **27** also show some CFPP depression when used alone.

EXPERIMENTAL

General

Melting points were determined with a Kofler hot stage apparatus and are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in deuterated chloroform with tetramethylsilane or deuteriochloroform as the internal reference.

Table 1. CFPP of Diesel Fuel Treated with EVA and Dendramine/Acrylate Products[a]

Dendramine/Acrylate Formulation added at 200 ppm	EVA (ppm)	CFPP Result (°C)
None	None	0
None	200	-5
24	200	-13
25	200	-14
26	200	-14
27	200	-12
24	None	-7
25	None	-4
26	None	-4
27	None	-3

[a] The data at 400 ppm of EVA is not available. This particular EVA is commonly used in combination with EVA nucleator and such a total EVA additive gives -16 CFPP at 400 ppm.

Characterization of Compounds

Except for compounds **1-3** which were analytically pure, all compounds were viscous oily. Characterization was by ^{13}C NMR and ^{1}H NMR shown as given. Estimation of purity was by the integration of the proton NMR: impurity peaks *vs* authentic peaks.

Preparation of Nitriles 1, 2, 3, 7, 8, 9, 13, 14, 17, 19 *via* Cyanoethylation

General procedure

Method A (for **1, 2, 3, 7, 8, 9, 13**): Amine (20 mmol) was dissolved in acrylonitrile (20 mL) at room temperature, glacial acetic acid (20 mmol per primary amino function) was added and the solution was heated under reflux for 2 days. Excess acrylonitrile was removed under vacuum, the residue was extracted with chloroform, and concentrated aqueous ammonia solution (40 mL) was added. The organic phase was separated, washed with water, and dried over anhydrous $MgSO_4$. The crude oil was purified by column chromatography with chloroform on silica.

***N,N,N'N'*-Tetra(2-cyanoethyl)ethandiamine (1)**

mp = 61-62 °C, (4.85 g, 90%) [Lit. mp = 61-62 °C];[1] ^{1}H NMR ($CDCl_3$) δ 2.50 (t, 8H, J = 7.0 Hz), 2.70 (s, 4H), 2.90 (t, 8H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 17.3, 49.5, 53.1, 118.8.

***N,N,N*-Tri(2-cyanoethyl)ammonia (2)**

mp = 57-59 °C, (3.21 g, 92%) [Lit. mp = 58-59 °C];[15] ^{1}H NMR ($CDCl_3$) δ 2.52 (t, 6H, J = 7.0 Hz), 2.93 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 17.3, 49.5, 118.8.

Multiple-nitrile 3

oil, (8.40 g, 90%) [Lit. mp = 38-39 °C];[8] ^{1}H NMR ($CDCl_3$) δ 2.54 (t, 12H, J = 7.0 Hz), 2.60-2.70 (m, 12H), 2.92 (t, 12H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.8, 49.8, 51.9, 53.6, 118.9.

Multiple-nitrile 7

oil, [8.00 g, 56% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.55-1.70 (m, 8H), 2.48-2.58 (m, 24H), 2.58-2.70 (m, 12H), 2.80-2.92 (t, 16H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.6, 16.7, 25.5, 49.1, 49.2, 49.3, 50.4, 50.5, 51.2, 52.0, 118.8.

Multiple-nitrile 8

oil, [7.70 g, 76% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.65 (t, 6H, J = 7.0 Hz), 2.48-2.56 (m, 12H), 2.58-2.67 (m, 12H), 2.84 (t, 12H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.4, 16.5, 25.0, 49.0, 49.1, 50.3, 50.4, 50.5, 118.8.

Multiple-nitrile 9

oil,[8] [11.70 g, 52% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.55-1.70 (m, 12H), 2.45-2.70 (m, 60H), 2.80-2.92 (m, 24H); ^{13}C NMR ($CDCl_3$) δ 16.4, 16.6, 18.4, 25.2, 25.5, 44.0, 49.1, 49.2, 49.3, 50.4, 50.5, 51.2, 52.0, 118.8, 119.0.

Multiple-nitrile 13

oil, [11.20 g, 70% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.40-1.70 (m, 24H), 2.45-2.70 (m, 84H), 2.85 (t, 32H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.6, 16.7, 16.8. 25.5, 25.7, 49.2, 49.3, 49.4, 49.5, 50.2, 50.4, 52.0, 53.8, 55.2, 118.8.

Method B (for **14, 17, 19**): Amine (10 mmol), acrylonitrile (50 mL, 0.96 mol), and water (50 mL) were refluxed for 24 h. After removing the excess acrylonitrile, the organic layer was isolated from the resulting clear two-phase system by pouring off the water layer and a reasonably pure nitrile (colorless oil) was obtained by washing the organic layer with water.

Multiple-nitrile 14

oil, [20.80 g, 85% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.40-1.70 (m, 36H), 2.35-2.70 (m, 132H), 2.85 (t, 48H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.4, 16.5, 24.7, 25.0, 48.9, 49.0, 49.1, 49.2, 50.2, 50.5, 50.7, 50.8, 51.0, 55.2, 118.6, 118.7.

Multiple-nitrile 17

oil, [40.20 g, 79% (overall yield of two steps)]; ^{1}H NMR ($CDCl_3$) δ 1.40-1.70 (m, 84H), 2.48-2.65 (m, 276H), 2.85 (t, 96H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2, 16.3, 24.6, 24.8, 48.8, 48.9, 50.1, 50.5, 50.7, 51.2, 55.2, 118.6, 118.7.

Multiple-nitrile 19

mp = 76-79 °C, (5.00 g, 89%); ^{1}H NMR ($CDCl_3$) δ 2.40-2.58 (m, 14H), 2.59-2.72 (m, 16H), 2.80-2.95 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 16.7, 16.8, 17.0, 49.9, 50.1, 50.2, 51.9, 52.2, 52.3, 52.8, 52.9, 53.3, 53.4, 118.8, 119.3.

Preparation of Amines 4, 5, 6, 10, 11, 12, 15, 16, 18, 20 *via* Hydrogenation

General procedure

A high pressure bomb was charged with an appropriate nitrile (10 mmol), Raney nickel catalyst (2 g), and saturated ammonia methanolic solution (the ratio of ammonia to each cyano group is about 8 to 1). The bomb was filled with hydrogen at a suitable pressure and heated at 130 °C for two days. The catalyst was filtered off and the residue was checked by NMR until there was no cyano signals.

Preparation of amides 21-23

Method A (for **21, 22**): A mixture of stearoyl chloride (10 g, 33 mmol), amine, triethylamine (10 mL) and acetone (100 mL) was stirred at room temperature for 3 h. After the acetone was removed and washed with water, a solid formed, which was filtered off and washed with acetone and

the expected product was obtained.

Amide 21

mp = 103-105 °C, (10.30 g, 99%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 9H, *J* = 7.0 Hz), 1.15-1.40 (m, 84H), 1.50-1.70 (m, 6H), 2.16 (t, 6H, *J* = 7.0 Hz), 2.52 (t, 6H, *J* = 6.0 Hz), 3.25 (q, 6H, *J* = 6.0 Hz), 6.80 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 8.6, 14.1, 22.6, 25.9, 29.3, 29.5, 29.6, 29.7, 31.9, 36.5, 37.5, 45.6, 54.2, 174.1.

Amide 22

mp = 60-62 °C, (9.74 g, 98%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 18H, *J* = 7.0 Hz), 1.25-1.40 (m, 192H), 1.60-1.70 (m, 18H), 2.10-2.52 (m, 36H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 24.2, 22.8, 29.1, 29.4, 29.5, 29.6, 31.9, 34.1, 35.3, 169.6.

Method B (for **23**): A mixture of tris(2-aminoethyl)amine (2.92 g, 20 mmol), dodecylsuccinic anhydride (16.08 g, 60 mmol) and toluene (200 mL) were refluxed in a flask equipped with a Dean-Stark trap and condenser for 10 h. Water (1.1 mL) was removed, then the toluene distilled off under vacuum and the residue was purified by a short column with ethyl acetate as the eluent. 16 g of the product was obtained in a yield of 90% (16.10 g), as an oil; ^{1}H NMR ($CDCl_3$) δ 0.80-1.70 (m, 75H), 1.50-2.90 (m, 15H), 3.40-3.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.8, 22.3, 29.1, 31.7, 35.9, 36.1, 51.5, 51.6, 177.0, 177.1.

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Key Words

Dendramines; Dendramides; Synthesis; Application; Oil industry.

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