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<b>(54) Title:</b> DENSE STAR POLYMERS AND A PROCESS FOR PRODUCING DENSE STAR POLYMERS  <b>(57) Abstract</b> <p>The star polymers of this invention have at least one core branch emanating from a core, each core branch having at least one terminal group provided that (1) the ratio of terminal groups to the core branches is greater than 1:1, (2) the density of terminal groups per unit volume in the polymer is at least 1.5 times that of a conventional star polymer having similar core and monomeric moieties and a comparable molecular weight and number of core branches, each of such branches of the conventional star polymer bearing only one terminal group and (3) a molecular volume that is no more than 60 per cent of the molecular volume of said conventional star polymer. Such star polymers are useful as demulsifiers for oil/water emulsions, wet strength agents in the manufacture of paper and agents for modifying viscosity in aqueous formulations such as paints.</p>		

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DENSE STAR POLYMERS AND A PROCESS  
FOR PRODUCING DENSE STAR POLYMERS

This invention relates to a novel class of branched polymers containing dendritic branches having functional groups uniformly distributed on the periphery of such branches. This invention also relates to processes for preparing such polymers as well as applica-  
5 tions therefore.

Organic polymers are generally classified in a structural sense as either linear or branched. In the case of linear polymers, the repeating units (often  
10 called mers) are divalent and are connected one to another in a linear sequence. In the case of branched polymers, at least some of the mers possess a valency greater than 2 such that the mers are connected in a nonlinear sequence. The term "branching" usually implies that the individual  
15 molecular units of the branches are discrete from the polymer backbone, yet have the same chemical constitution as the polymer backbone. Thus, regularly repeating side groups which are inherent in the monomer structure and/or are of different chemical constitution than the polymer  
20 backbone are not considered as branches, e.g., dependent



methy1 groups of linear polypropylene. To produce a branched polymer, it is necessary to employ an initiator, a monomer, or both that possess at least three moieties that function in the polymerization reaction. Such monomer or initiators are often called polyfunctional. The simplest branched polymers are the chain branched polymers wherein a linear backbone bears one or more essentially linear pendant groups. This simple form of branching, often called comb branching, may be regular wherein the branches are uniformly and regularly distributed on the polymer backbone or irregular wherein the branches are distributed in nonuniform or random fashion on the polymer backbone. See T. A. Orofino, Polymer, 2, 295-314 (1961). An example of regular comb branching is a comb branched polystyrene as described by T. Altores et al. in J. Polymer Sci., Part A, Vol. 3, 4131-4151 (1965) and an example of irregular comb branching is illustrated by graft copolymers as described by Sorenson et al. in "Preparative Methods of Polymer Chemistry", 2nd Ed., Interscience Publishers, 213-214 (1968).

Another type of branching is exemplified by cross-linked or network polymers wherein the polymer chains are connected via tetravalent compounds, e.g., polystyrene molecules bridged or cross-linked with divinylbenzene. In this type of branching, many of the individual branches are not linear in that each branch may itself contain groups pendant from a linear chain. More importantly in network branching, each polymer macromolecule (backbone) is cross-linked at two or more sites to two other polymer macromolecules. Also the chemical constitution of the cross-linkages may vary from that of the polymer macromolecules. In this so-called cross-linked or network branched polymer, the



various branches or cross-linkages may be structurally similar (called regular cross-linked) or they may be structurally dissimilar (called irregularly cross-linked). An example of regular cross-linked polymers is a ladder-  
5 -type poly(phenylsilsesquinone) as described by Sorenson et al., supra, at page 390. The foregoing and other types of branched polymers are described by H. G. Elias in Macro-  
molecules, Vol. I, Plenum Press, New York (1977).

More recently, there have been developed  
10 polymers having so-called star structured branching wherein the individual branches radiate out from a nucleus and there are at least 3 branches per nucleus. Such star branched polymers are illustrated by the poly-  
quaternary compositions described in USP Nos. 4,036,808  
15 and 4,102,827. Star branched polymers prepared from olefins and unsaturated acids are described in USP 4,141,847. The star branched polymers offer several advantages over polymers having other types of branching. For example, it  
is found that the star branched polymers may exhibit higher  
20 concentrations of functional groups thus making them more active for their intended purpose. In addition, such star branched polymers are often less sensitive to degradation by shearing which is a very useful property in formula-  
tions such as paints, in enhanced oil recovery and other  
25 viscosity applications. Additionally, the star branched polymers have relatively low intrinsic viscosities even at high molecular weight.

While the star branched polymers offer many of the aforementioned advantages over polymers having more  
30 conventional branching, it is highly desirable to provide polymers which exhibit even greater concentrations of functional groups per unit volume of the polymer macro-

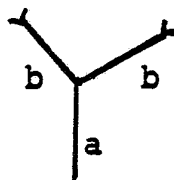


molecule as well as a more uniform distribution of such functional groups in the exterior regions of the macromolecule. In addition, it is often desirable to provide polymers having macromolecular configurations that are more spheroidal and compact than are the star branched polymers.

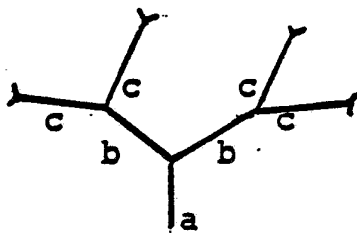
In its broadest aspect, this invention is a dense star polymer having at least one branch (hereinafter called a core branch) emanating from a core, each core branch having at least one terminal group provided that (1) the ratio of terminal groups to the core branches is greater than 1:1, preferably 2:1 or more, (2) the density of terminal groups per unit volume in the polymer is at least 1.5 times that of a conventional star polymer having similar core and monomeric moieties and a comparable molecular weight and number of core branches, each of such branches of the conventional star polymer bearing only one terminal group, and (3) a molecular volume that is no more than 60 percent of the molecular volume of said conventional star polymer as determined by dimensional studies using scaled Corey-Pauling molecular models. For purposes of this invention, the term "dense" as it modifies "star polymer" means that it has a smaller molecular volume than a conventional star polymer having the same molecular weight. The conventional star polymer which is used as the base for comparison with the dense star polymer is one that has the same molecular, same core and monomeric components and same number of core branches as the dense star polymer. In addition while the number of terminal groups is greater for the dense star polymer molecule than in the conventional star polymer molecule, the chemical structure of the terminal groups is the same.



In a somewhat more limited and preferred aspect, this invention is a polymer having a novel ordered star branched structure (herein called starburst structure). Hereinafter this polymer having a starburst structure is called a dendrimer. Thus, a "dendrimer" is a polymer having a polyvalent core that is covalently bonded to at least two ordered dendritic (tree-like) branches which extend through at least two generations. As an illustration, an ordered second generation dendritic branch is depicted by the following configuration:



wherein "a" represents the first generation and "b" represents the second generation. An ordered, third generation dendritic branch is depicted by the following configuration:



wherein "a" and "b" represent the first and second generation, respectively, and "c" represents the third generation. A primary characteristic of the ordered dendritic branch which distinguishes it from conventional branches of conventional polymers is the uniform or

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essentially symmetrical character of the branches as is shown in the foregoing illustrations. In addition, with each new generation, the number of terminal groups on the dendritic branch is an exact multiple of the  
5 number of terminal groups in the previous generation.

Another aspect of this invention is a process for producing the dense star polymer comprising the steps of

(A) contacting

10 (1) a core compound having at least one nucleophilic or one electrophilic moiety (hereinafter referred to in the alternative as N/E moieties) with

15 (2) an excess of a first organic coreactant having (a) one moiety (hereinafter called a core reactive moiety) which is reactive with the N/E moieties of the core compound and (b) an N/E moiety which does not react with the N/E moiety of the core under conditions sufficient to  
20 form a core adduct wherein each N/E moiety of the core compound has reacted with the core reactive moiety of a different molecule of the first coreactant;

(B) contacting

25 (1) the core adduct having at least twice the number of N/E moieties as the core compound with

30 (2) an excess of a second organic coreactant having (a) one moiety (hereinafter called an adduct reactive moiety) which will react with the N/E moieties of the core adduct and (b) an N/E moiety which does not react with the N/E moiety of





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the core adduct under conditions sufficient to form a first generation adduct having a number of N/E moieties that are at least twice the number of N/E moieties in the core adduct; and

5 (C) contacting the first generation adduct with an excess of a third organic coreactant having one moiety that is reactive with the N/E moieties of the first generation adduct and an N/E moiety that does not react with the N/E moieties of the first  
10 generation adduct under conditions sufficient to form a second generation dendrimer. In the foregoing process, the first coreactant differs from the second coreactant, and the second coreactant differs from the third coreactant, but the first  
15 and third coreactants may be the same or different compounds. The third and higher generation dendrimers are formed by repeating steps (B) and (C) of the aforementioned process.

Other aspects of this invention are methods  
20 for using the dense star polymer in such applications as demulsifiers for oil/water emulsions, wet strength agents in the manufacture of paper, agents for modifying viscosity in aqueous formulations such as paints and the like. For example, in a demulsification method, an emulsion  
25 of oil and water is contacted with a demulsifying amount of the dense star polymer under conditions sufficient to cause phase separation.

The dense star polymers of the present invention exhibit the following properties which are unique or  
30 are superior to similar properties of conventional star branched polymers and other branched polymers having similar molecular weight and terminal groups:



- (a) greater branch density;
- (b) greater terminal group density;
- (c) greater accessibility of terminal groups to chemically reactive species; and
- 5 (d) lower viscosity.

In the dense star polymers of the present invention, the core is covalently bonded to at least one core branch, preferably at least two, most preferably at least three, core branches with each core branch having a  
10 calculated length of at least 3 Angstrom units  
(A) (0.3 nm), preferably at least 4 A (0.4 nm), most preferably at least 6 A (0.6 nm). These polymers preferably have an average of at least 2, more preferably at least 3 and most preferably at least 4 terminal groups  
15 per polymer molecule. Preferably, the core branches have a dendritic character, most preferably an ordered dendritic character as defined hereinafter. In preferred dense star polymers, the terminal groups are functional groups that are sufficiently reactive to undergo addition  
20 or substitution reactions. Examples of such functional groups include amino, hydroxy, mercapto, carboxy, alkenyl, allyl, vinyl, amido, halo, urea, oxiranyl, aziridinyl, oxazolinyl, imidazolinyl, sulfonato, phosphonato, isocyanato and isothiocyanato. The dense star polymers  
25 differ from conventional star or star-branched polymers in that the dense star polymers have a greater concentration of terminal groups per unit of molecular volume than do conventional star polymers having an equivalent number of core branches and an equivalent core branch length.  
30 Thus, the density of terminal groups per unit volume in the dense star polymer is at least 1.5 times the density of terminal groups in the conventional star polymer,

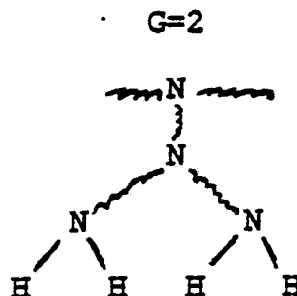
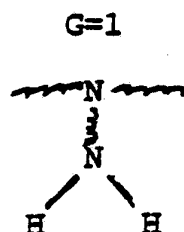


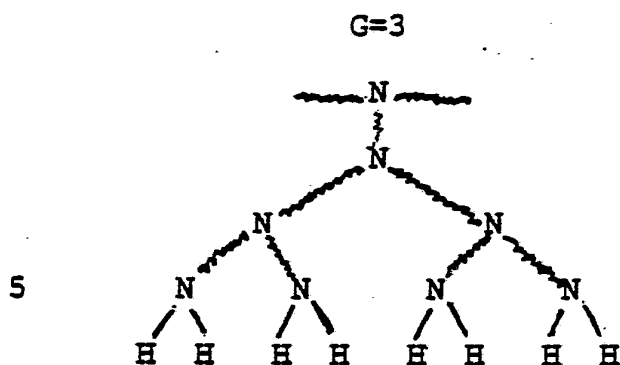
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preferably at least 5 times, more preferably at least 10 times, most preferably from 15 to 50 times. The ratio of terminal groups per core branch in the dense polymer is preferably at least 2, more preferably at least 3, most preferably from 4 to 1024. Preferably, for a given polymer molecular weight, the molecular volume of the dense star polymer is no more than 50 volume percent, more preferably from 16 to 50, most preferably from 7 to 40 volume percent of the molecular volume of the conventional star polymer.

In the preferred polyamidoamine dense star polymers, the density of terminal (primary) amine moieties in the polymer is readily expressed as the molar ratio of primary amine moieties to the total of secondary and tertiary amine moieties. In such polymers this 1° amine:(2° amino + 3° amine) is preferably from 0.37:1 to 1.33:1, more preferably from 0.69:1 to 1.2:1, most preferably from 1.1:1 to 1.2:1.

The preferred dendrimers of the present invention are characterized as having a polyvalent core that is covalently bonded to at least two ordered dendritic branches which extend through at least two generations. Such ordered branching can be illustrated by the following sequence wherein G indicates the number of generations:





Mathematically, the relationship between the number of terminal groups on a dendritic branch and the number of generations of the branch can be represented as follows:

$$\begin{array}{l} \# \text{ of terminal groups} = N_r^G \\ \text{per dendritic branch} \quad \frac{r}{2} \end{array}$$

wherein  $G$  is the number of generations and  $N_r$  is the repeating unit multiplicity which is at least 2 as in the case of amines. The total number of terminal groups in the dendrimer is determined by the following:

$$\begin{array}{l} \# \text{ of terminal groups} = N_c N_r^G \\ \text{per dendrimer} \quad \frac{c}{2} \end{array}$$

wherein  $G$  and  $N_r$  are as defined before and  $N_c$  represents the valency (often called core functionality) of the core compound. Accordingly, the dendrimers of the present invention can be represented in its component parts as follows:

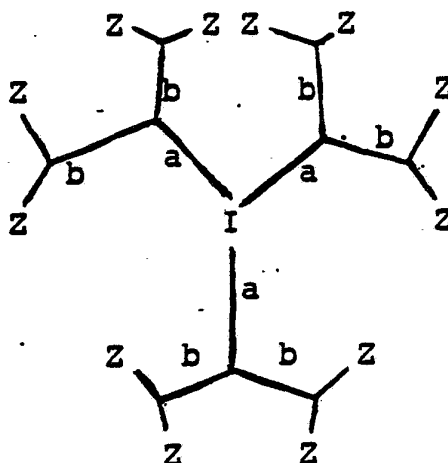


$$(\text{Core}) \left[ (\text{Repeat Unit})_{\frac{N_r G - 1}{N_r - 1}} \left( \text{Terminal Moiety} \right)_{\frac{N_r G}{2}} \right]_{N_c}$$

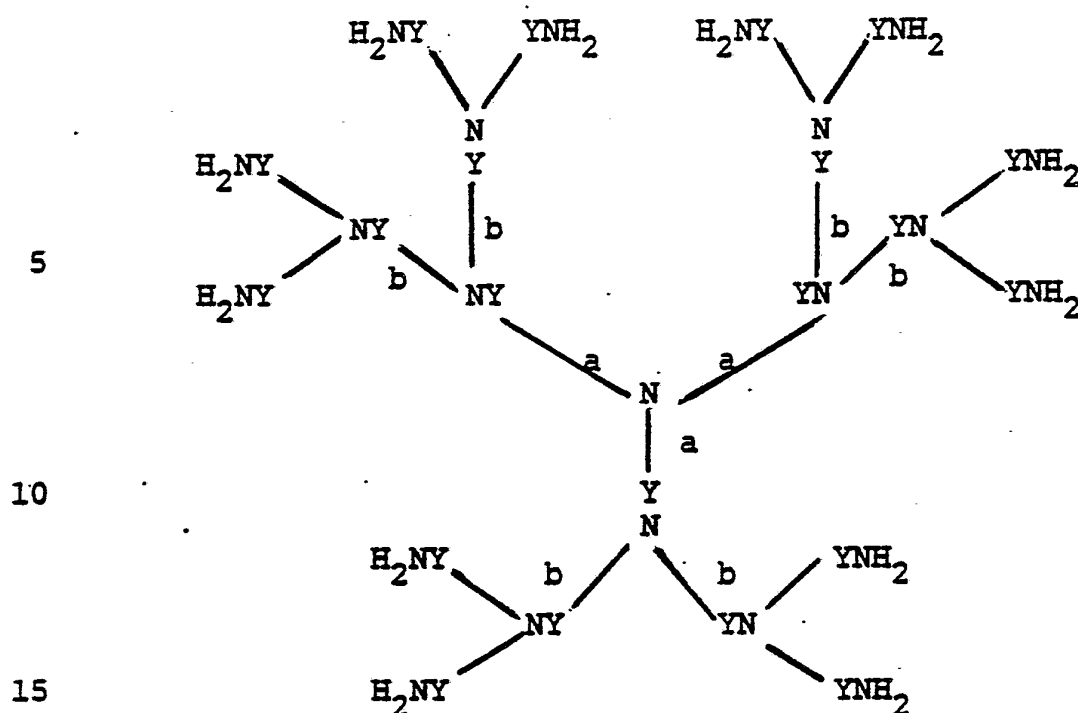
- 5 wherein the Core, Terminal Moiety, G and  $N_c$  are as defined before and the Repeat Unit has a valency or functionality of  $N_r + 1$  wherein  $N_r$  is as defined before.

- 10 An illustration of a functionally active dendrimer of a ternary or trivalent core which has three ordered, second generation dendritic branches is depicted by the following configuration:

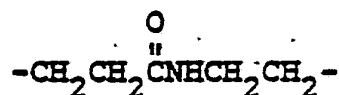
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- 20 wherein I is a trivalent core atom or molecule having a covalent bond with each of the three dendritic branches, Z is a terminal moiety and "a" and "b" are as defined hereinbefore. An example of such a ternary dendrimer is polyamidoamine represented by the following structural formula:



wherein Y represents a divalent amide moiety such as



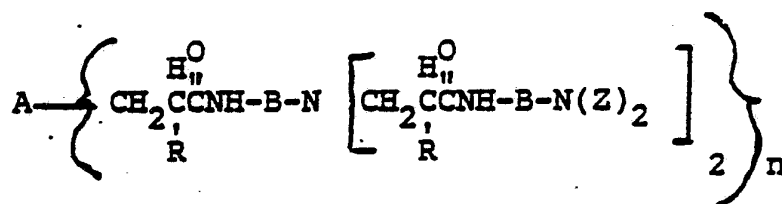
20 and "a" and "b" indicate first and second generations, respectively. In these two illustrations,  $N_c$  is 3 and  $N_r$  is 2. In the latter of the two illustrations, the Repeat Unit is YN. While the foregoing configuration and formula illustrate a trivalent core, the core atom or molecule

25 may be any monovalent or monofunctional moiety or any polyvalent or polyfunctional moiety, preferably a polyvalent or polyfunctional moiety having from 2 to 2300

30 valence bonds or functional sites available for bonding with the dendritic branches, most preferably from 2 to 200 valence bonds or functional sites. In cases wherein the core is a monovalent or monofunctional moiety, the

dense star has only one core branch and must be compared with a linear polymer in order to determine appropriate terminal group density and molecular volume. Accordingly, this dense star must have at least 2 generations in order to exhibit the desired density of terminal groups. Also, Y may be any other divalent organic moiety such as, for example, alkylene, alkylene oxide, alkyleneamine, with the depicted amide moiety being the most preferred. In addition to amine, the terminal groups of the dendrimer may be any functionally active moiety that can be used to propagate the dendritic branch to the next generation. Examples of such other moieties include carboxy, aziridinyl, oxazolinyl, haloalkyl, oxiranyl, hydroxy and isocyanato, with amine or carboxylic ester moieties being preferred. While the dendrimers preferably have dendritic branches having 2 to 6 generations, dendrimers having dendritic branches up to 12 generations are suitably made and employed in the practice of this invention.

More preferably, the amidoamine dendimers of this invention are represented by the formula:

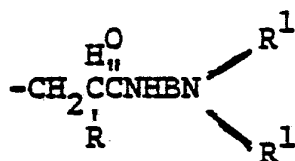


wherein A is a n-valent core derived from a nucleophilic compound, R is hydrogen or lower alkyl, B is a divalent moiety capable of linking amine groups, n is an integer of 3 or more corresponding to the number of the core branches and Z is hydrogen or



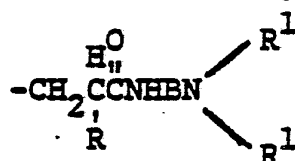
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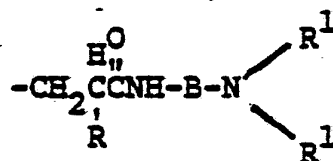
wherein  $\text{R}^1$  is hydrogen or

10



wherein each generation is represented by

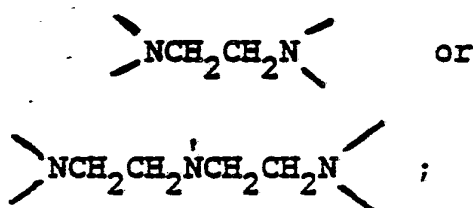
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More preferably A is a core such as



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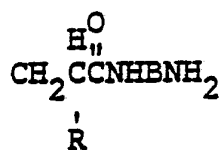


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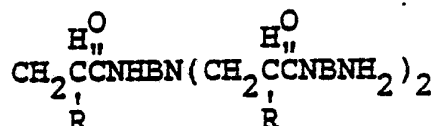
R is hydrogen or methyl; B is the divalent residue of a polyamine, most preferably an alkylene polyamine such as ethylene diamine or a polyalkylene polyamine such as triethylene tetramine; n is an integer from 3 to 2000, more preferably from 3 to 1000, most preferably from 3 to 125, and Z is most preferably





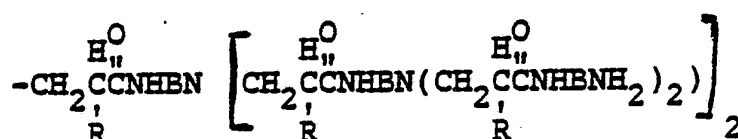


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or

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The dense star polymers of this invention are readily prepared by reacting a compound capable of generating a polyvalent core with a compound or compounds which causes propagation of dendritic branches from the core. In one method of preparing these dendrimers (herein called the successive excess reactant method), it is essential to maintain an excess of coreactant to reactive moieties in the terminal groups in the core, core adduct or subsequent adducts and dendrimers in order to prevent cross-linking and to maintain the ordered character of the dendritic branches. In general, this excess of coreactant to reactive moieties in the terminal groups is from 2:1 to 120:1, preferably from 3:1 to 20:1 on a molar basis.

Alternatively, the compound capable of generating a polyvalent core,  $W(X)_n$ , wherein W is the polyvalent core atom and is covalently bonded to nX reactive terminal groups ( $n \geq 2$ ), is reacted with a partially pro-

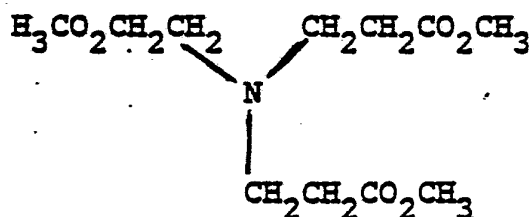


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tected multifunctional reagent,  $T(U)_m$ , wherein U represents a multivalent moiety covalently bonded to  $m$  protected moieties ( $m \geq 2$ ), and to one T, a moiety capable of reacting with X to form  $W[(X'-T')U]_n$ , wherein X' and T' represent the residue of reaction between X and X. This first generation compound is then subjected to activation conditions whereby the  $(U)$  moieties are made reactive (deprotected) and reacted with the partially protected multifunctional reagent,  $T-U$ , to form the second generation protected dendrimer,  $W\{[X'-T']UV\}_m T'-U$ . This protected dendrimer can be activated and reacted again in a similar manner to provide the third generation protected dendrimer. Both the successive excess reactant and the partially protected reactant method are specifically illustrated hereinafter.

The successive excess reactant method of preparing the dendrimers is illustrated by the preparation of the aforementioned ternary dendritic polyamidoamine. In this method, ammonia, a nucleophilic core compound, is first reacted with methyl acrylate under conditions sufficient to cause the Michael addition of one molecule of the ammonia to three molecules of the methyl acrylate to form the following core adduct:

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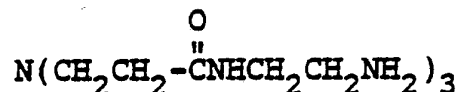


Following removal of unreacted methyl acrylate, this compound is then reacted with excess ethylenediamine under conditions such that one amine group of the ethyl-



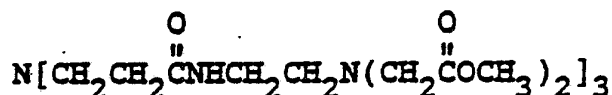
enediamine molecule reacts with the methyl carboxylate groups of the core adduct to form a first generation adduct having three amidoamine moieties represented by the formula:

5



The molar excess of ethylene diamine to methyl acrylate moieties is preferably from 4:1 to 50:1. Following removal of unreacted ethylenediamine, this first generation adduct is then reacted with excess methyl acrylate under Michael's addition conditions to form a second generation adduct having terminal methyl ester moieties:

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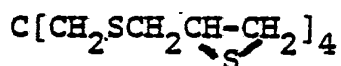


which is then reacted with excess ethylenediamine under amide forming conditions to produce the desired polyamidoamine dendrimer having ordered, second generation dendritic branches with terminal amine moieties. The molar excess of coreactant to reactive moieties in each case is preferably from 1.1:1 to 40:1, most preferably from 3:1 to 10:1. Similar dendrimers containing amidoamine moieties can be made by using organic amines as the core compound, e.g., ethylenediamine which produces a tetra-branched dendrimer or diethylenetriamine which produces a penta-branched dendrimer.

Other dendrimers made by the successive excess reactant method are polysulfides made by (1) reacting a



polythiol,  $C(CH_2SH)_4$ , under basic conditions with epichlorosulfide to form the first generation polyepisulfide,

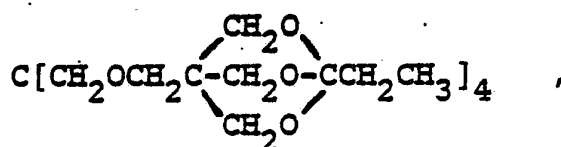


and (2) then reacting this polyepisulfide with hydrogen sulfide to form the first generation polysulfide which can be further reacted with epichlorosulfide and hydrogen sulfide to form subsequent generations. The conditions and procedures which may be suitably employed for polysulfide formation are generally described in Weissberger, Heterocyclic Compounds with Three- and Four-Membered Rings, Interscience Publishers, N.Y., 605 (1964) and Meade et al., J. Chem. Soc., 1894 (1948). Polyaminosulfide dendrimers can be prepared by reacting ammonia or an amine having a plurality of primary amine groups with an excess of ethylene sulfide to form a polysulfide and then with excess aziridine to form a first generation polyaminosulfide which can be reacted with excess ethylene sulfide and then with excess aziridine to form further generations using general reaction conditions described in USP 2,105,845 and Nathan et al., J. Am. Chem. Soc., 63, 2361 (1941). The polyether or polysulfide dendrimers can also be prepared by the excess reactant method by reacting hexahalobenzene with phenol or thiophenol to form a first generation polyarylether or polyarylsulfide and then with excess halogen to form the first generation polyhaloarylpolysulfide and then with further phenol or thiophenol to form further generations according to the procedures and conditions as described by D. D. MacNicol et al., Tetrahedron Letters, 23, 4131-4 (1982).



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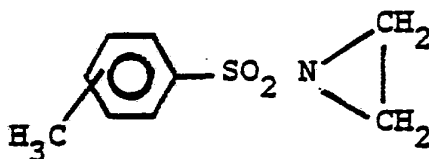
Illustrative of the partially protected reactant method, a polyol such as pentaerythritol,  $C(CH_2OH)_4$ , is employed as the polyvalent core generating compound and is converted to alkali metal salt form, e.g., sodium or lithium, by reaction with alkali metal hydroxide or zero valence alkali metal and then reacted with a molar excess of a partially protected compound such as tosylate ester of 1-ethyl-4-hydroxymethyl-2,6,7-trioxabicyclo[2,2,2]octane to form a protected first generation polyether,



which is then activated by reacting with acid such as hydrochloric acid to form the unprotected first generation polyether,  $C(CH_2O-CH_2C[CH_2OH]_3)_4$ . This polyether is converted to alkali metal salt form by reaction with alkali metal hydroxide or zero valence alkali metal and then reacted with a molar excess of the partially protected tosylate ether to form the protected second generation polyether. The foregoing sequence is repeated as desired for additional generation development according to conditions and procedures described in Endo et al., J. Polym. Sci., Polym. Lett. Ed., 18, 457 (1980), Yokoyama et al., Macromolecules, 15, 11-17 (1982), and Pedias et al., Macromolecules, 15, 217-223 (1982). These polyether dendrimers are particularly desirable for use in highly alkaline or highly acidic media wherein hydrolysis of a poly-amidoamine dendrimer would be unacceptable. As an example of other dendrimers that are suitably prepared by the partially protected reactant method, polyamine dendrimers may be prepared by reacting ammonia or an amine having a plurality of primary amine groups with N-substituted aziridine such as N-tosyl aziridine,



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to form a protected first generation polysulfonamide  
5 and then activated with acid such as hydrochloric acid  
to form the first generation polyamine salt and reacted  
with further N-tosyl aziridine to form the protected  
second generation polysulfonamide which sequence can be  
repeated to produce higher generation polyamines using  
10 the general reaction conditions described in Humrichause,  
C. P., PhD Thesis from University of Pennsylvania, "N-Sub-  
stituted Aziridines as Alkylating Agents", Ref. No. 66-10,  
624 (1966).

In either of the foregoing methods of den-  
15 drimer preparation, water or hydrogen sulfide may be  
employed as nucleophilic cores for the production of  
binary dendrimers. Examples of other nucleophilic core  
compounds include phosphine, polyalkylene polyamines such  
as diethylenetriamine, triethylenetetramine, tetraethyl-  
20 enepentamine and both linear and branched polyethyleni-  
mine; primary amines such as methylamine, hydroxyethyl-  
amine, octadecylamine and polymethylenediamines such as  
hexamethylenediamine; polyaminoalkylarenes such as 1,3,5-  
-tris(aminomethyl)benzene; tris(aminoalkyl)amines such as  
25 tris(aminoethyl)amine; heterocyclic amines such as imid-  
azolines and piperidines; and various other amines such  
as hydroxyethylaminoethylamine, mercaptoethylamine, mor-  
pholine, piperazine, amino derivatives of polyvinylbenzyl  
chloride and other benzylic polyamines such as tris(1,3,5-  
30 -aminomethyl)benzene. Other suitable nucleophilic cores



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include polyols such as the aforementioned pentaerythritol, ethylene glycol and polyalkylene polyols such as polyethylene glycol and polypropylene glycol; 1,2-dimercaptoethane and polyalkylene polymercaptans; thiophenols, and phenols. Of the core compounds, ammonia and the polyalkylene polyamines are preferred for the preparation of polyamidoamine dendrimers by the successive excess reactant method and the polyols are preferred for the preparation of polyether dendrimers by the partially protected reactant method.

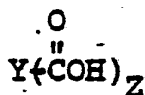
Examples of coreactant materials used to react with the nucleophilic core compounds include  $\alpha,\beta$ -ethylenically unsaturated carboxylic esters and amides as well as esters, acids and nitriles containing an acrylyl moiety such as, for example, methyl acrylate, ethyl acrylate, acrylonitrile, methyl itaconate, dimethyl fumarates, maleic anhydride, acrylamide, with methyl acrylate being the preferred coreactant material. In general other preferred unsaturated reactants are volatile or otherwise readily removed from the core/coreactant reaction products without deleteriously affecting the reaction product.

Examples of the second coreactant materials used to react with the adduct of the nucleophilic core and the first coreactant include various polyamines such as alkylene polyamines and polyalkylene polyamines such as ethylenediamine and diethylenetriamine; benzylic polyamines such as tris(1,3,5-aminomethyl)benzene; alkanolamines such as ethanolamine; and aziridine and derivatives thereof such as N-aminoethyl aziridine. Of these second coreactant materials, the volatile polyamines such as ethylenediamine and diethylenetriamine are preferred, with ethylenediamine being especially preferred.



Alternatively, the dendrimers can be prepared by reacting an electrophilic core such as a polyester with a coreactant such as a polyamine to form a core adduct which is then reacted with a suitable second coreactant such as an unsaturated ester to form the first generation polyamidoamine. Thereafter, this first generation product is reacted with a suitable third coreactant such as polyamine and then with the second coreactant such as unsaturated ester to form the desired second generation dendrimer. Examples of suitable electrophilic cores include the  $C_1$ - $C_4$  alkyl esters of various polycarboxylic acids such as benzene tricarboxylic acid, oxalic acid, terphthalic acid and various other carboxylic acids represented by the formula:

15



wherein Y is hydrocarbyl or a hydrocarbon polyyl wherein the hydrocarbon radical is alkyl, aryl, cycloalkyl, alkyl-ene, arylene, cycloalkylene, and corresponding trivalent, tetravalent, pentavalent and hexavalent radicals of such hydrocarbons; and Z is a whole number from 1 to 6. Preferred electrophilic cores include poly(methyl acrylates), poly(acryloyl chloride), poly(methacryloyl chloride), alkyl acrylate/alkyl methacrylate copolymers, polymers of alkyl fumarates, and polymers of alkyl itaconates. Of the electrophilic cores, alkyl acrylate/alkyl methacrylate copolymers and alkyl acrylate/alkyl itaconate copolymers are most preferred.

30

Suitable first coreactants for reaction with the electrophilic core include polyalkylene polyamines





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such as ethylenediamine, diethylenetriamine, triethylenetetramine and other polyamines represented by the formula:



wherein  $\text{R}^1$  and  $\text{R}^2$  independently represent hydrogen or an alkyl, preferably  $\text{C}_1$ - $\text{C}_4$  alkyl, hydroxyalkyl, cyanoalkyl, or amido;  $n$  is at least 2 and preferably 2 to 6 and  $m$  is 10 2 to 100, preferably 2 to 5. Examples of suitable second coreactants to be used in preparing dendrimers from electrophilic cores include alkyl esters of ethylenically unsaturated carboxylic acids such as methyl acrylate, methyl methacrylate, ethyl acrylate and the like. Exam- 15 ples of suitable third coreactants are those illustrated for the first coreactant.

Thus prepared, the dendrimers can be reacted with a wide variety of compounds to produce the polyfunctional compounds having the unique characteristics that 20 are attributable to the structure of the dendrimer. For example, a dendrimer having terminal amine moieties, as in the polyamidoamine dendrimer, may be reacted with an unsaturated nitrile to yield a polynitrile (nitrile-terminated) dendrimer. Alternatively, the polyamidoamine 25 dendrimer may be reacted with (1) an  $\alpha, \beta$ -ethylenically unsaturated amide to form a polyamide (amide-terminated) dendrimer, (2) an  $\alpha, \beta$ -ethylenically unsaturated ester to form a polyester (ester-terminated) dendrimer, (3) an oxirane to yield a polyol (hydroxy-terminated) dendrimer, or



(4) an ethylenically unsaturated sulfide to yield a poly-mercapto (thiol-terminated) dendrimer. In addition, the dendrimer may be reacted with an appropriate difunctional or trifunctional compound such as an alkyl dihalide or an aromatic diisocyanate to form a poly(dendrimer) having a plurality of dendrimers linked together through the residues of the polyhalide or polyisocyanate. In all instances, such derivatives of the dendrimers are prepared using procedures and conditions conventional for carrying out reactions of organic compounds bearing the particular functional group with the particular organic reactant.

Such reactions are further exemplified by the following working examples. In such working examples, all parts and percentages are by weight unless otherwise indicated.

#### Example 1

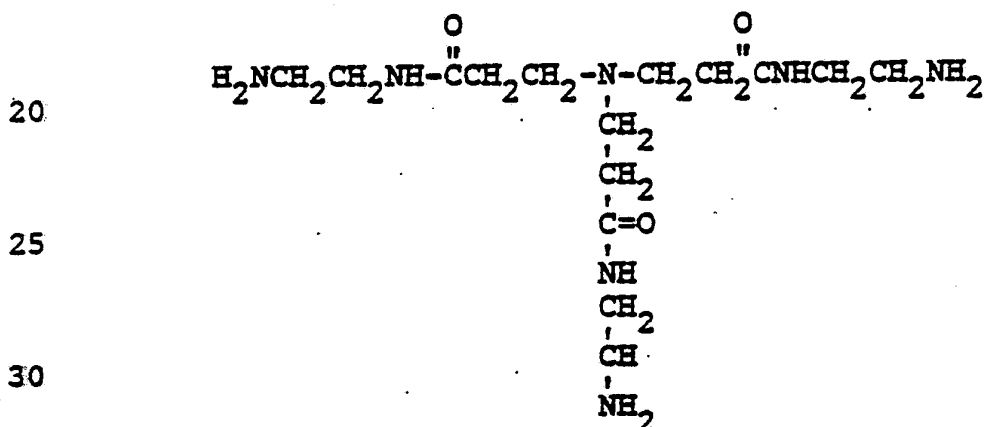
##### A. Preparation of Core Adduct

To a one-liter, 3-neck flask equipped with stirrer, condenser and thermowell, and containing methyl acrylate (296.5 g, 3.45 moles) was added at room temperature with stirring over a 6-hour period ammonia (8.7 g, 0.58 mole) dissolved in 102.2 g of methanol. The mixture was allowed to stand at room temperature for 48 hours at which point excess methyl acrylate was removed by vacuum distillation (1 mm Hg (130 Pa) at 22°C) yielding 156 g of residue. This residue is analyzed by size exclusion chromatography,  $C_{13}$  NMR and liquid chromatography. This analysis indicated the coreactant adduct to be the Michael's addition product of 1 mole of ammonia and 3 moles of methyl acrylate at a 97.8 percent yield.



### B. Preparation of First Generation Adduct

To ethylenediamine (505.8 g, 8.43 moles) dissolved in 215.4 g of methanol in a 3-liter reaction flask equipped with stirrer, condenser and thermowell, was added the aforementioned ammonia/methyl acrylate adduct (28.1 g, 0.1022 mole), and the reaction mixture was allowed to stand at room temperature for 55 hours. The resulting mixture (747.6 g) was subjected to vacuum distillation to remove excess ethylenediamine and methanol at 2 mm Hg (270 Pa) and 72°C. The residue (35.4 g) was analyzed by size exclusion chromatography and other suitable analytical techniques. The analyses indicated that essentially all of the ester moieties of the ammonia/-methyl acrylate adduct had been converted to amides in the form of a compound represented by the following structural formula:

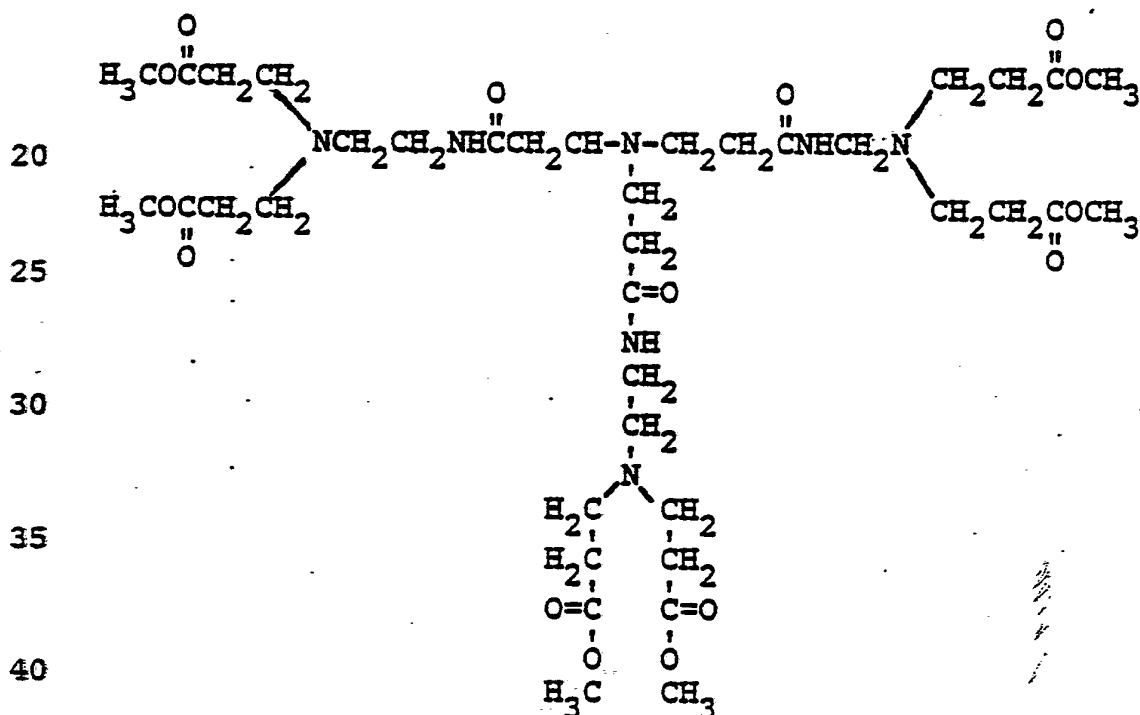


thus indicating a yield of 98.6 percent.



### C. Preparation of Second Generation Polyester Dendrimer

To methyl acrylate (93.2 g, 1.084 moles) in a one-liter flask equipped with condenser, stirrer and thermowell, and heated to 32°C was added the aforementioned first generation adduct (18 g, 0.0501 mole) dissolved in 58.1 g of methanol over 1.5 hours. The resulting mixture was maintained at 32°C for an additional 5 hours and allowed to stand an additional 18 hours at room temperature. The reaction mixture (165.7 g) was stripped of methanol and excess methyl acrylate by vacuum distillation (2 mm Hg (270 Pa) and 50°C) to produce 43.1 g of residue. Analysis by suitable techniques indicated the product to be a second generation polyester dendrimer represented by the following formula:



in 98.4 percent yield.



D: Preparation of Second Generation Polyamine Dendrimer

To ethylenediamine (328.8 g, 5.48 moles) dissolved in 210.2 g of methanol at room temperature in the aforementioned flask was added with stirring the second generation polyester dendrimer (34.9 g, 0.0398 mole) dissolved in 45.3 g of methanol. The resulting mixture was allowed to stand for 66 hours at room temperature at which time excess ethylenediamine and methanol was stripped from the product by vacuum distillation (2 mm Hg (270 Pa) at 72°C) to yield 41.1 g (99.0 percent yield) of product. This product was determined by size exclusion chromatography to be the second generation polyamine of the aforementioned polyester dendrimer.

15 E. Preparation of Third Generation Polyester Dendrimer

To methyl acrylate (65.1 g, 0.757 mole) was added the aforementioned second generation polyamine dendrimer (28.4 g, 0.0272 mole) dissolved in 84.6 g of methanol over a period of 1 hour and 15 minutes. The resulting mixture was allowed to stand for 18 hours at 25°C after which time excess methyl acrylate and methanol were removed by vacuum distillation (2 mm Hg (270 Pa) at 50°C) to yield 56.3 g (100.0 percent yield) of product residue. Analysis of this residue by suitable analytical techniques indicated that it was a third generation polyester dendrimer having 3 core branches with 4 terminal ester moieties per core branch thereby providing 12 terminal ester moieties per dendrimer molecule.



F. Preparation of Third Generation Polyamine Dendrimer

To ethylenediamine (437.6 g, 7.29 moles) dissolved in 192 g of methanol was added the aforementioned  
5 third generation polyester dendrimer (44.9 g, 0.0216 mole) dissolved in 69.7 g of methanol. The addition occurred over a period of 48 hours at 25°C with stirring. The resulting reaction mixture was then allowed to stand for 19 hours at 25°C after which time excess methanol and  
10 ethylenediamine were removed by vacuum distillation (2 mm Hg (270 Pa) at 72°C) to yield 51.2 g of residual product. Analysis of this residue indicated a yield of 85.3 percent of a third generation polyamine dendrimer having 3 core branches with 4 terminal primary amine moieties per core  
15 branch, thereby providing 12 terminal primary amine moieties per molecule of dendrimer. This dendrimer was calculated to have a molecular volume between 50,000 and 97,000 cubic Å (50 and 97 nm<sup>3</sup> and a density of a terminal amine moiety between 1 to 3( $\times 10^{-4}$ ) moieties/cubic Å (0.1  
20 and 0.3 moieties/nm<sup>3</sup>).

Example 2

Following the procedure of Example 1, except that a molar equivalent amount of ethylenediamine was substituted for ammonia as the core compound, a third  
25 generation polyamine dendrimer is prepared. Upon analysis, it is determined that this dendrimer has four core branches with 4 terminal primary amine moieties per core branch, thereby providing 16 terminal primary amine moieties per molecule of dendrimer. This dendrimer has a  
30 molecular volume between 60,000 and 120,000 cubic Å (60 and 120 nm<sup>3</sup>) and a terminal amine density of 2 to 6( $\times 10^{-4}$ ) amines/cubic Å (0.2 and 0.6 amines/nm<sup>3</sup>).

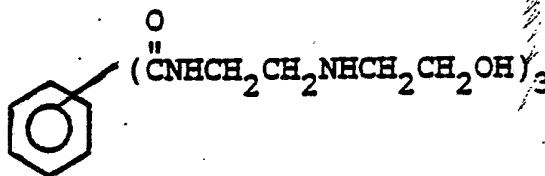


Similar dendrimers were obtained when equimolar amounts of 1,2-diaminopropane, 1,3-diaminopropane and 1,6-diaminohexane (hexamethylenediamine) were substituted for the ethylenediamine as the core compound in the foregoing procedure. When an equimolar amount of dodecyl-amine or benzylamine was substituted for the ethylenediamine as the core compound, the resulting dense star polymers had 2 core branches per molecule with 4 terminal primary amine groups per branch, thereby providing a total of 8 primary amine groups per polymer molecule. Substitution of triaminoethylamine for ethylenediamine as the core compound yielded a dendrimer having 6 core branches with 4 terminal primary amine moieties per core branch, thereby providing 24 terminal primary amine moieties per molecule of dendrimer.

### Example 3

#### A. First Amidation

Following the procedure of Example 1, 5 g (0.0198 mole) of trimethyl-1,3,5-benzenetricarboxylate was mixed with 6.3 g (0.0368 mole) of aminoethylethanolamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$ ) to form a white paste. This mixture was heated at  $120^\circ\text{C}$  for 3 hours to form 9.48 g of a light yellow syrup which infrared and nuclear magnetic resonance spectral analysis indicate was an amidoamine represented by the structural formula:

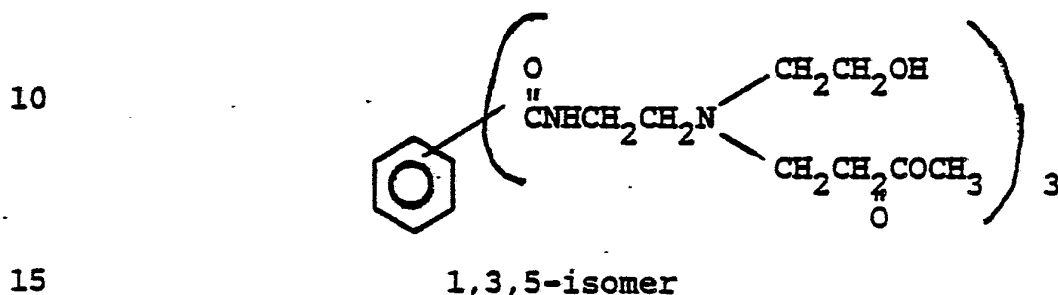


1,3,5-isomer

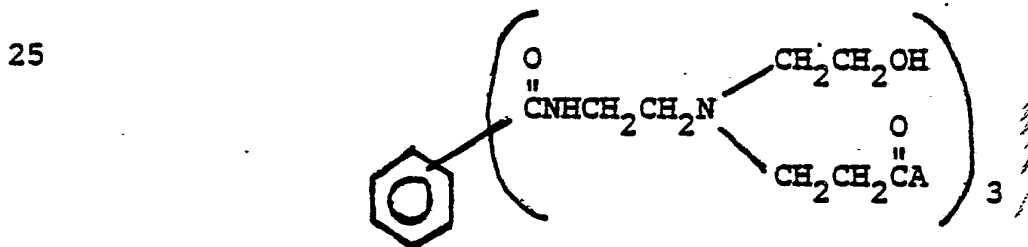


B. First Alkylation

A 9.48 g. (0.0202 mole) of this amidoamine was combined with a stoichiometric excess (11.0 g, 0.127 mole) of methyl acrylate and heated for 24 hours at 80°C which, after devolatilization, was a light yellow syrup weighing 14.66 g. Nuclear magnetic resonance ( $H^1$ ) and infrared spectral analysis of the syrup indicated that it was a triester represented by the structural formula:

C. Second Amidation

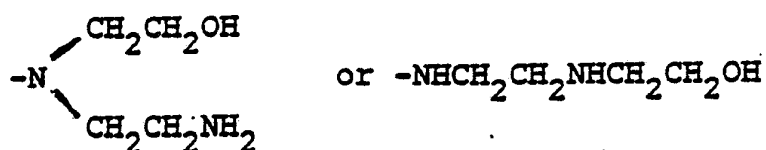
Following the procedure of part A of this example, the triester (4.57 g,  $6.3 \times 10^{-3}$  mole) produced in part B was mixed with 1.96 g ( $1.89 \times 10^{-2}$  mole) of aminoethylethanolamine and heated at 90°C for 48 hours to form 5.8 g of a light yellow, highly viscous syrup. Analysis of this product by nuclear magnetic resonance ( $H^1$ ) (DMSO- $d_6$ ) and infrared spectroscopy indicated that it was triamidoamine represented by the structural formula:





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wherein each A is individually



#### 5 Example 4

##### A. First Amidation

A 27.3-g portion (0.1 mole) of a triester represented by the formula:



was mixed with 30 g (0.405 mole) of N-methyl ethylene-diamine (MEDA) and 16.6 g of methanol and then heated at 63°C for 11 hours. The product was then stripped of  
15 unreacted MEDA and methanol to yield 36.1 g of a triamide represented by the formula:

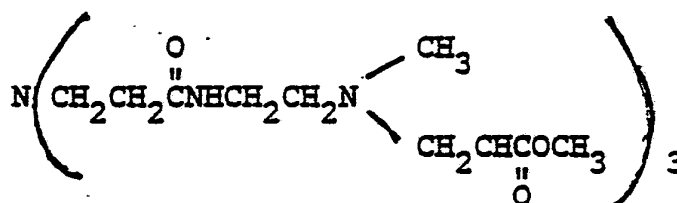


##### 20 B. First Alkylation

To the aforementioned triamide (36.1 g, 0.09 mole) was added 38.5 g of methanol to yield a clear solution to which was added 50.5 g (0.59 mole) of methyl acrylate dropwise over a period of 2 hours at 38°C. The  
25 temperature of the resulting mixture was increased to

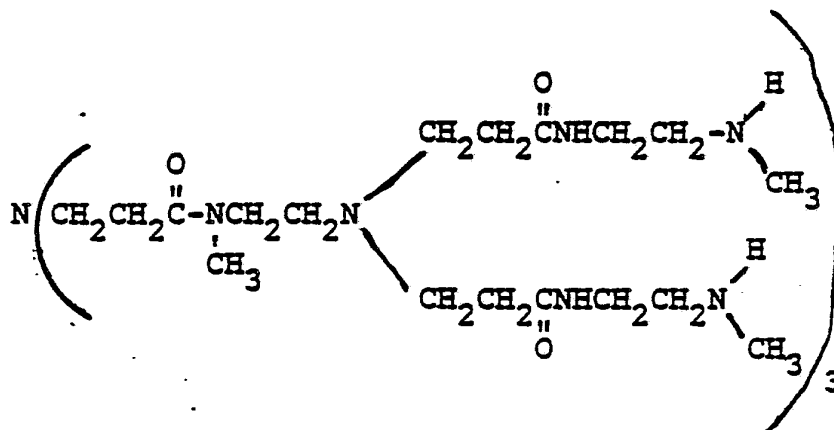
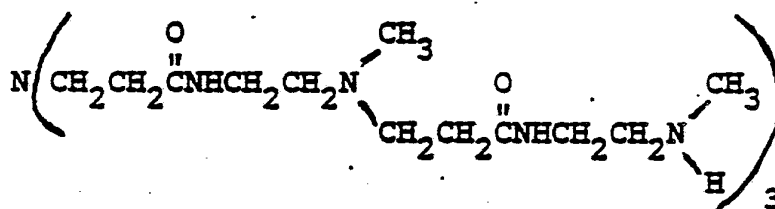


53°C for 5 additional hours after which unreacted methyl acrylate and methanol were removed under vacuum to yield 61 g of a light yellow syrup. Analysis of this product by nuclear magnetic resonance ( $H^1$ ) spectroscopy indicated that it is represented by the formula:



### C. Second Amidation

To 60.8 g of the aforementioned first alkylation product were added with stirring 42.7 g of methanol and 26.6 g (0.359 mole) of MEDA followed by heating the resulting mixture at 65°C for 6 hours. Vacuum stripping of the mixture yielded 72.7 g of a light yellow syrup. Analysis of this product (syrup) indicated that it was a mixture of isomers having the following structures:



D. Second Alkylation and Third Amidation

Alkylation of the aforementioned second amidation product with methyl acrylate and then amidation of the resulting alkylated product with MEDA in accordance with aforementioned procedures yielded a mixture of isomers having core branches with dendritic characteristics.

Example 5 - Demulsification Method

To 100 ml of an oil-in-water emulsion containing about 5 percent of crude oil having a specific gravity of ~0.98 g/ml was added one part per million based on the emulsion of the dendrimer (ethylene diamine core) of Example 2. The emulsion was then shaken for 3 minutes to effectively disperse the dendrimer into the emulsion. The emulsion was allowed to stand for 10 minutes and visually evaluated. After 10 minutes, the emulsion appeared to be completely resolved into two phases having a distinct interface wherein the aqueous phase was essentially transparent.

Following the foregoing procedure except substituting a quaternized form of the foregoing dendrimer for the dendrimer, the emulsion was similarly resolved using 0.5 ppm and 1 ppm of the quaternized form. This quaternized form was prepared by reacting the 32.42 g (0.01 mole) of the dendrimer in 100 ml of methanol with 24.32 g (0.16 mole) of 2-hydroxy-3-chloropropyl trimethyl ammonium chloride in 30 ml of water at 50°C for 12 hours.



CLAIMS

1. A star polymer having at least one core branch emanating from a core, each core branch having at least one terminal group provided that (1) the ratio of terminal groups to the core branches is greater than 1:1, (2) the density of terminal groups per unit volume in the polymer is at least 1.5 times that of a conventional star polymer having similar core and monomeric moieties and a comparable molecular weight and number of core branches, each of such branches of the conventional star polymer bearing only one terminal group, and (3) a molecular volume that is no more than 60 percent of the molecular volume of said conventional star polymer.

2. The star polymer of Claim 1 having (1) at least 2 core branches per core, (2) a terminal group density at least 5 times that of the corresponding conventional star polymer, (3) a molecular volume that is no more than 50 percent of the volume of the conventional star polymer, and (4) a ratio of terminal groups to core branches is 2:1 or more.



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3. The polymer of Claim 1 which is a dendrimer having a polyvalent core that is covalently bonded to at least 1 ordered dendritic branch which extends to two generations such that each dendritic branch has at least four terminal groups and a symmetrical structure.

4. The polymer of Claim 1 wherein the dendritic branches contain amidoamine linkages.

5. The polymer of Claim 1 wherein the core is derived from a nucleophilic compound and the branches are polyamidoamines wherein the terminal groups are primary amine groups.

6. The polymer of Claim 1 wherein the nucleophilic core is derived from a core compound having a plurality of active hydrogens capable of undergoing a Michael's addition reaction with an ethylenically unsaturated group.

7. The polymer of Claim 5 wherein the nucleophilic compound is an amine having a plurality of amine hydrogens.

8. The polymer of Claim 5 wherein the branches are polyamidoamine which is derived from the reaction of an alkyl ester of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid or an  $\alpha,\beta$ -ethylenically unsaturated amide and an alkylene polyamine or a polyalkylene polyamine.

9. The polymer of Claim 8 wherein the nucleophilic compound is ammonia, the ester is methyl acrylate and the polyamine is ethylenediamine.



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10. A process for producing the dense star polymer of Claim 1 comprising the steps of:

(A) contacting

- (1) a core compound having at least one nucleophilic or one electrophilic moiety (N/E moieties) with
- (2) an excess of a first organic coreactant having (a) one core reactive moiety which is reactive with the N/E moieties of the core compound, and (b) an N/E moiety which does not react with the N/E moiety of the core under conditions sufficient to form a core adduct wherein each N/E moiety of the core compound has reacted with the core reactive moiety of a different molecule of the first coreactant;

(B) contacting

- (1) the core adduct having at least twice the number of N/E moieties as the core compound with
- (2) an excess of a second organic coreactant having (a) one adduct reactive moiety which will react with the N/E moieties of the core adduct and (b) a N/E moiety which does not react with the N/E moiety of the core adduct under conditions sufficient to form a first generation adduct having a number of N/E moieties that are at least twice



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the number of N/E moieties in  
the core adduct; and

- (C) contacting the first generation adduct with an excess of a third organic coreactant having one moiety that is reactive with the N/E moieties of the first generation adduct and an N/E moiety that does not react with the N/E moieties of the first generation adduct under conditions sufficient to form a second generation dendrimer, wherein the first coreactant differs from the second coreactant, and the second coreactant differs from the third coreactant, but the first and third coreactants may be the same or different compounds.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US83/02052

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <div style="text-align: center; font-family: monospace;">           INT. CL <sup>3</sup> C08G 73/00            U.S. CL 528/363         </div>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; font-size: small;">Minimum Documentation Searched <sup>4</sup></div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th style="width: 80%;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">U.S.</td> <td style="font-family: monospace;">           528/310, 328, 331, 363            560/155, 169, 171, 215            564/153, 155, 468, 509         </td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">           Documentation Searched other than Minimum Documentation            to the Extent that such Documents are Included in the Fields Searched <sup>5</sup> </div>			Classification System	Classification Symbols	U.S.	528/310, 328, 331, 363 560/155, 169, 171, 215 564/153, 155, 468, 509								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%;">Category <sup>6</sup></th> <th style="width: 60%;">Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 30%;">Relevant to Claim No. <sup>18</sup></th> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 3,578,643 PUBLISHED 11 MAY 1971 WOOD ET AL</td> <td style="text-align: center;">1-10</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 3,580,891 PUBLISHED 25 MAY 1971 RAINIER</td> <td style="text-align: center;">1-10</td> </tr> <tr> <td style="text-align: center;">A</td> <td>US, A, 4,289,872 PUBLISHED 15 SEPTEMBER 1981 DENKEWALTER ET AL</td> <td style="text-align: center;">1-10</td> </tr> </table>			Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>	A	US, A, 3,578,643 PUBLISHED 11 MAY 1971 WOOD ET AL	1-10	A	US, A, 3,580,891 PUBLISHED 25 MAY 1971 RAINIER	1-10	A	US, A, 4,289,872 PUBLISHED 15 SEPTEMBER 1981 DENKEWALTER ET AL	1-10
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A	US, A, 4,289,872 PUBLISHED 15 SEPTEMBER 1981 DENKEWALTER ET AL	1-10												
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents: <sup>15</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top;">           Date of the Actual Completion of the International Search <sup>2</sup>             7 FEBRUARY 1984            International Searching Authority <sup>1</sup>             ISA/US         </td> <td style="width: 50%; vertical-align: top;">           Date of Mailing of this International Search Report <sup>3</sup>   <div style="text-align: center; font-size: large; font-weight: bold;">16 FEB 1984</div>           Signature of Authorizing Officer <sup>7</sup>  <div style="text-align: center;">              HAROLD D. ANDERSON           </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <sup>2</sup>  7 FEBRUARY 1984 International Searching Authority <sup>1</sup>  ISA/US	Date of Mailing of this International Search Report <sup>3</sup>  <div style="text-align: center; font-size: large; font-weight: bold;">16 FEB 1984</div> Signature of Authorizing Officer <sup>7</sup> <div style="text-align: center;">              HAROLD D. ANDERSON           </div>										
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