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Dendritic polymers obtained by a single-stage synthesis

M N Bochkarev, M A Katkova

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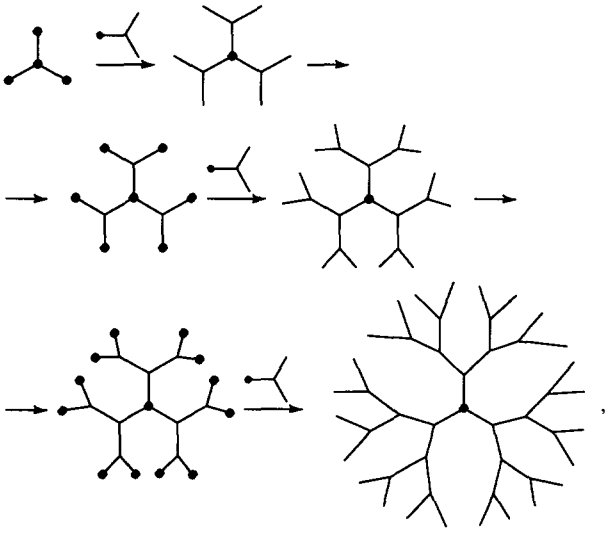
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Abstract. The methods of synthesis, the structure, and properties of the dendritic polymers formed under the conditions of uncontrolled single-stage synthesis are surveyed. The bibliography includes 69 references.

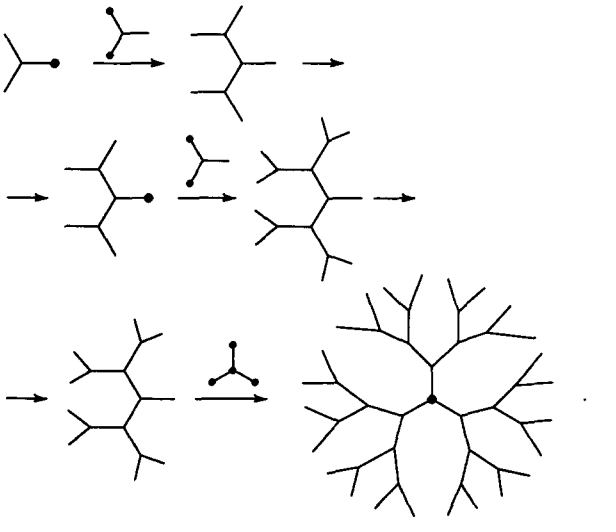
I. Introduction

Studies on polymeric compounds of a fundamentally new type have become one of the most promising and rapidly developing aspects of modern chemistry during the last decade. Their macromolecules have a specific (largely spherical) close-packed shape and the three-dimensional close-packed framework of each molecule consists of concentric layers of branching elementary units. The objects which are studied in this chemical field are so unusual and so difficult to describe within the framework of the IUPAC nomenclature that a new terminology for their designation had to be developed. At the present time, this process is not yet complete and many of the terms, designations, and symbols employed still cannot be regarded as generally accepted. The only firmly established name for the compounds of this class themselves is 'dendrimers' or 'starburst dendrimers' proposed by Tomalia et al.[1] The terms 'arborols' (proposed by Newkome et al.[2]) and 'cascade compounds' are used to a lesser extent. More general designations such as nanomolecules and nanoscopic objects are also employed. The choice of terminology is dictated by the structure of the macrochains, which resembles that of the crown of a tree [dendron (Greek), arbor (Latin) = tree] or a cascade of repeating structural elements, and by the average dimensions of the molecules of these substances (1 – 100 nm). The terms hyperbranched and highly branched polymers have begun to be used recently for the group of dendrimers distinguished by a smaller degree of order in the molecular framework. These objects are in fact the subject of the present review.

One of the fundamental differences between the classical dendrimers and the highly branched polymers is the method of their synthesis. The former are obtained by many repetitions of the chosen sequence of reactions, which makes it possible to grow gradually new generations of layers of elementary fragments around the central atom (or molecule) called the initiator core of the dendritic molecule (divergent scheme), i.e.



or the reverse procedure is employed: the formation of the molecule begins from its periphery and proceeds with increase at each stage in the size of the intermediate dendrons, having a conventional conical shape, the dendrons becoming attached to the core only in the last stage to form the final dendritic macromolecule (convergent scheme), i.e.



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In both cases, the formation of each generation normally includes at least two reactions (for example, the addition of the initial monomer with protected functional groups to the growing molecule and the removal of the protection from the functional groups). Thus both approaches are not only multistep but also multistage. The combination of these methods, i.e. the formation of giant molecules by the addition of monomer molecules or dendrons to the dendrimer molecule previosly synthesised by the divergent or convergent methods, should also be noted. This procedure makes it possible to synthesise heterolayered dendrimers with a high molecular mass.[3]

In contrast to this, highly branched polymers are obtained under the conditions of uncontrolled single-stage synthesis in which the initial monomers employed are compounds of the type $A-R-B_x$ ($x \geqslant 2$), where A and B are functional groups of two types, which under certain conditions enter into a polycondensation or polyaddition reaction with formation of A–B bonds. Such continuous processes and their possible products have in fact been used as models in the theoretical studies of Flory[4] and Stockmayer,[5] whose communications were the first on the subject of hyperbranched formations with a hierarchical architecture of the molecular framework. However, the first specific synthesis of such compounds, achieved 30 years later by Vögtle and coworkers,[6] were carried out according to a multistep divergent scheme. This strategy of the synthesis, i.e. numerous repetitions of the selected reaction sequence, was adhered to by the vast majority of investigators in the field of dendrimers and cascade compounds.[7–10]

The monodispersity of the polymers obtained under these conditions and the predictability of the architecture of the framework, of the number of functional groups on the surface of macromolecules, and of their shape, size, and molecular mass give incontrovertible advantages to the stepwise method. This procedure has been used for the synthesis of diverse dendrimers, such as polyamidoamine dendrimers,[11] compounds with a carbochain skeleton,[12] including optically active,[15] carbosilane,[13] and carbosiloxane[15] compounds, dendrimers with ferrocenyl end-groups,[16] dendrimers with fullerene as the core,[17] dendrimers with coordinated cobalt[18] and ruthenium[19] atoms, carbaboranyl,[20] phenoxy-,[21] phenylethynyl,[22] phosphino-,[23] phosphonio,[24] phenylene,[25] and high-spin polyradical[26] dendrimers, cascade crown-ethers,[27] tetrathiofulvalene dendrimers,[28] etc.

At the same time, together with the above advantages, the stepwise strategy suffers from a series of disadvantages, the most serious of which is the considerable amount of labour involved due to the need for numerous repetition of the operations. Furthermore, the use of large excesses of the reactants creates problems in the isolation and purification of the dendrimers (intermediate generations and target products). Owing to these difficulties, the dendrimers obtained by the multistep synthesis belong to the category of fairly expensive substances which are difficult to obtain.

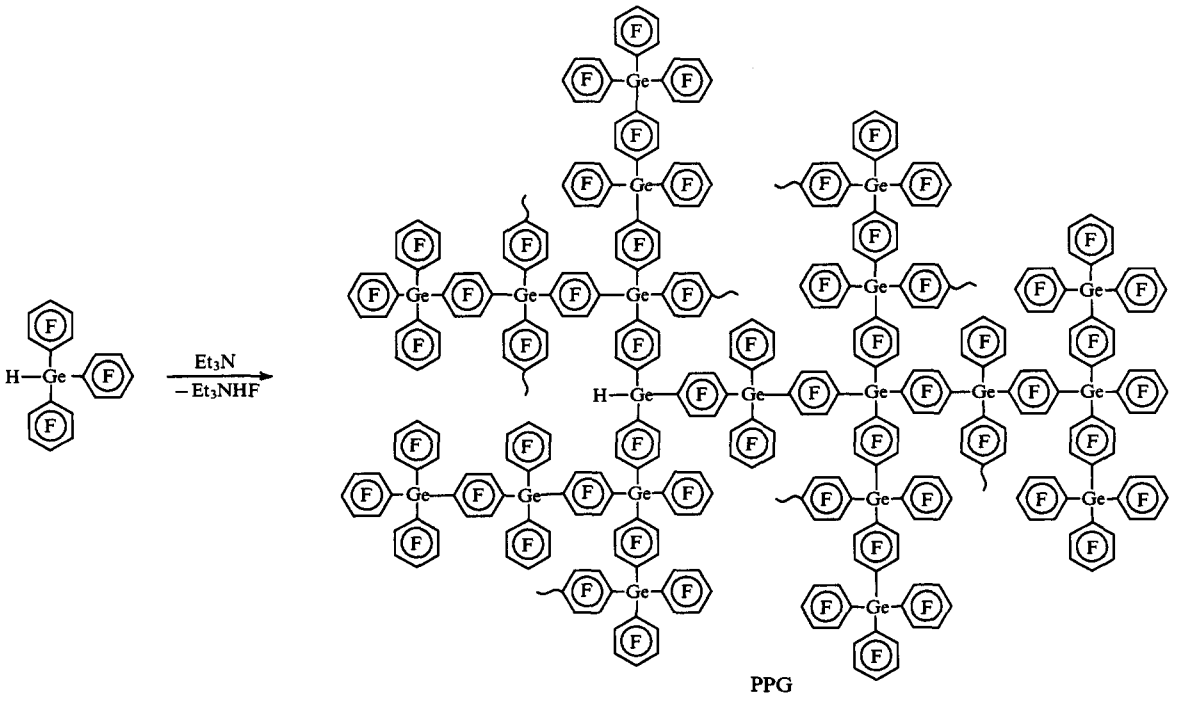
The single-stage method of synthesis of analogous derivatives is free from this disadvantage.

II. Single-stage methods of synthesis and types of dendrimers

As is frequently the case, the invention of compounds with a branched but not cross-linked molecular framework is due to nature, which employs this principle for the formation of glycogen, amylopectin, certain other polysaccharides, and proteins.[29–31]

The first mention of the artificial compounds formed on polycondensation of monomers of the type $A-R-B_x$ and having a cascade structure of the macrochain dates back to the 1920s[32] when the reaction between 2,4,6-trihalophenols and alkali metals with subsequent polycondensation of the resulting phenoxide 2,4,6-$X_3C_6H_2OM$ was carried out. One may assume that weakly ordered dendritic polymers had been obtained even earlier by the Friedel–Crafts polycondensation of benzyl halide derivatives under mild conditions.[33,34] However, in none of these instances were the products considered from the standpoint of the possible organisation of the macromolecules and their belonging to a new class of substances. The same approach to the products, treated as the usual branched polymers without consideration of the specific features of their structure, was also employed in a later study by Kricheldorf et al.,[35] who achieved the cocondensation of 3-(trimethylsiloxy)benzoyl chloride with a small amount of 3,5-bis(trimethylsiloxy)benzoyl chloride. As will be shown below, 3,5-bis(trimethylsiloxy)benzoyl chloride was used subsequently also by other investigators to obtain dendritic polyesters.

Scheme 1



The first specific synthesis of a dendrimeric compound by a single-stage method was achieved by the present authors on the basis of tris(pentafluorophenyl) derivatives of germanium $(C_6F_5)_3GeX$ (X = H, Br, GeR_3).[36-38] The synthesis was based on the earlier observations of the formation of disubstituted tetrafluorophenyl derivatives *p*-MC_6F_4M in the reactions of the organogermanes $(C_6F_5)_3GeX$ with electropositive metals and their organic derivatives.[39-41] A reinvestigation of these reactions and of the substances formed established that in all cases the main organogermanium product is a dendritic polymer — perfluorinated polyphenylgermane (PPG) with the formula $[(C_6F_5)_2.Ge(C_6F_4)]_n$. The best results were obtained when the reaction of the hydride $(C_6F_5)_3GeH$ with triethylamine in tetrahydrofuran (THF) was employed. Synthesis of PPG includes two stages occurring simultaneously: the formation of the anions $(C_6F_5)_3Ge^-$ and their polycondensation as a result of the nucleophilic substitution of the fluorine atoms in the *para*-positions (Scheme 1).

This mechanism of the synthesis of PPG has been confirmed indirectly by the formation of the mercurate complex $\{[(C_6F_5)_3Ge]_3Hg\}^-[(Me_3Si)_2NH_2]^+$ on interaction of $(C_6F_5)_3.GeH$ with $(Me_3Si)_2NH$ in the presence of $[(C_6F_5)_3Ge]_2Hg$ [40] and by the formation of the cross-linked insoluble perfluoropolyphenylenegermanes $[(C_6F_5)_2Ge]_n$ and $[(C_6F_5)_2GeGe(C_6F_5)_3]_n$ from the dihydride $(C_6F_5)_2GeH_2$ and the dihydrodigermane $(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2$.[42] It is interesting to note that the closest analogues of tris(perfluorophenyl)germane $(C_6F_5)_3EH$ (E = C, Si, Sn) as well as the germanol $(C_6F_5)_3GeOH$ do not undergo self-condensation in the presence of amines even on heating.[43] The tin-containing dendritic polymer $[(C_6F_5)_2Sn(C_6F_4)]_n$ was obtained in a low yield by heating $(C_6F_5)_3SnBr$ with alkali metals in THF. The condensation of tris(pentafluorophenyl)silane under the same conditions is accompanied by the elimination of pentafluorophenyl groups.

Side reactions, which lower the yield of the polymer and lead to significant disturbances of the cascade structure of the macromolecules, have been noted also in the polycondensation of the asymmetric digermane $(C_6F_5)_3GeGe(C_6F_5)_2H$ (Scheme 2).[44]

In this case not only the C–F bond but also the Ge–Ge group is subject to attack.

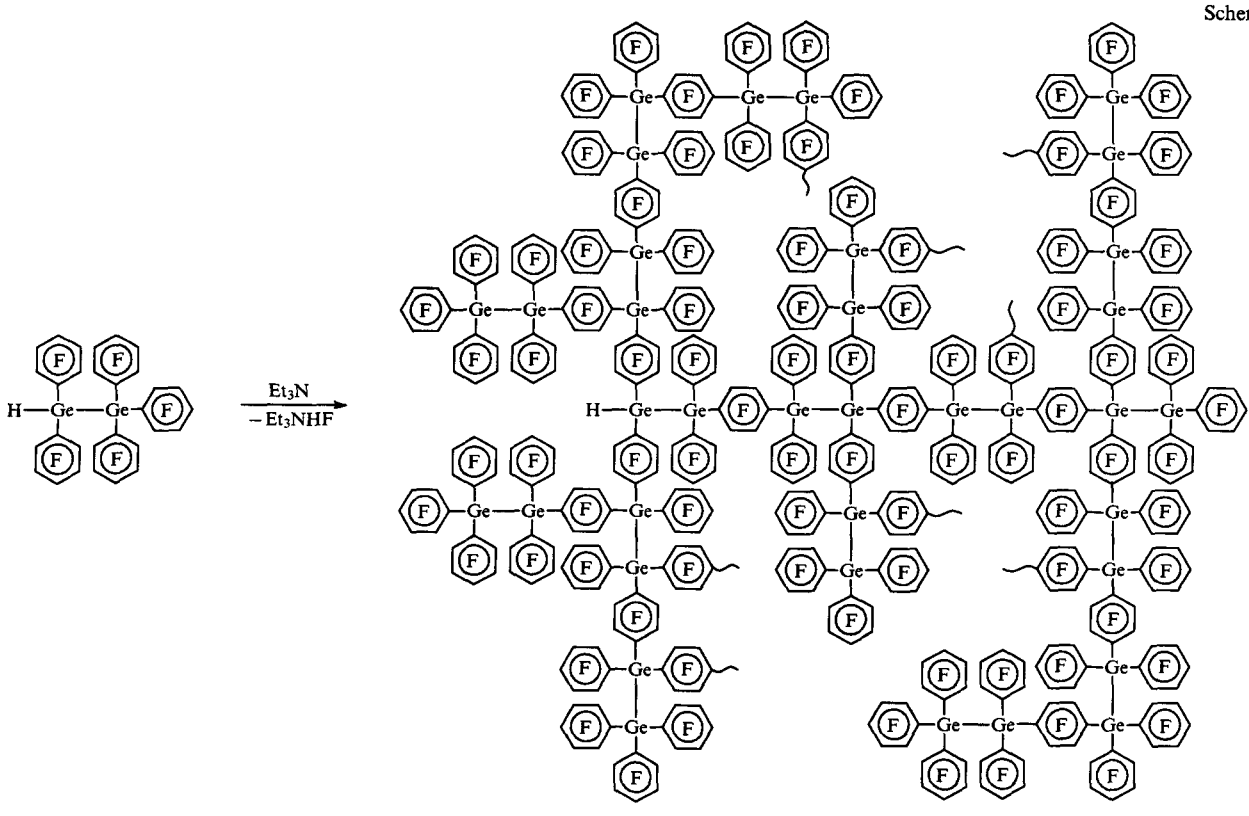
An attempt has been made to synthesise perfluoropolyphenylenegermane from the trihydride $C_6F_5GeH_3$.[45] It might have been expected that the condensation of this monomer in accordance with Scheme 1 would lead to the formation of a dendrimer resembling PPG but having on the surface of the macromolecules the hydride functional groups GeH_3 instead of $(C_6F_5)_3Ge$. The synthesis of such a polyhydrogermane appeared especially attractive, since the high reactivity of the Ge–H group promised to impart to the new polymer properties which would expand its synthetic possibilities. However, in contrast to other pentafluorophenylhydrogermanes, $C_6F_5GeH_3$ does not interact with amines and its reactions with derivatives of reactive metals (RMgX, $C_{10}H_8Na$) lead to linear insoluble polymers $[(C_6F_4)GeH_2]_n$ which are complicated by the elimination of the C_6F_5 groups.

Two brief communications concerning the synthesis of highly branched polyphenylenes by the polycondensation of $3,5\text{-}Br_2C_6H_3MgBr$ (on heating) and $3,5\text{-}Br_2C_6H_3B(OH)_2$ (under catalytic conditions) appeared simultaneously with the first publication on the synthesis of PPG.[46,47] The latter reaction was subsequently investigated in greater detail.[25] The condensation was carried out in an organic solvent–water mixture in the presence of sodium carbonate and $Pd(PPh_3)_4$ (Scheme 3). The mobility of the terminal Br atoms made it possible to employ the dendrimer **1** for the synthesis from it of a series of modified polymeric substances (see Section IV).

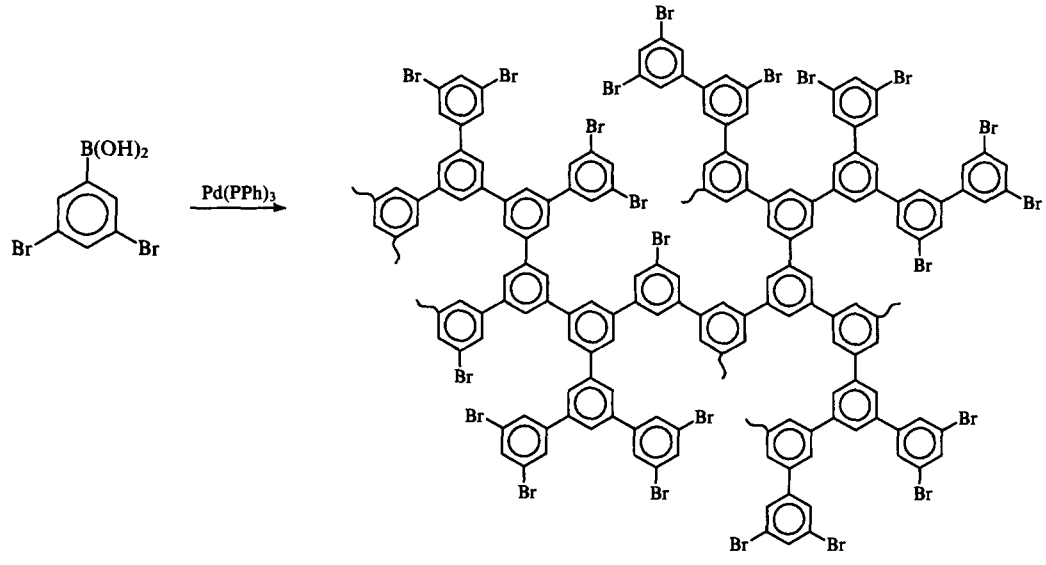
The polycondensation of 3,5-bis(trimethylsiloxy)benzoyl chloride, mentioned above, on heating to 250 °C leads to the formation of a low-molecular-mass and weakly branched polyester in a low yield.[35] By carrying out this reaction with the monomer purified beforehand by distillation, Frechet and coworkers[48] obtained the dendritic polyester **2** in up to 96% yield and a degree of branching of 55%–60%† (Scheme 4).

† The degree of branching is understood as the percentage ratio of the sum of the number of terminal units and the number of units with branching points to the total number of units of the polymer [(see C J Hawker, R Lee, J M J Frechet *J. Am. Chem. Soc.* **113** 4583 (1991)].

Scheme 2

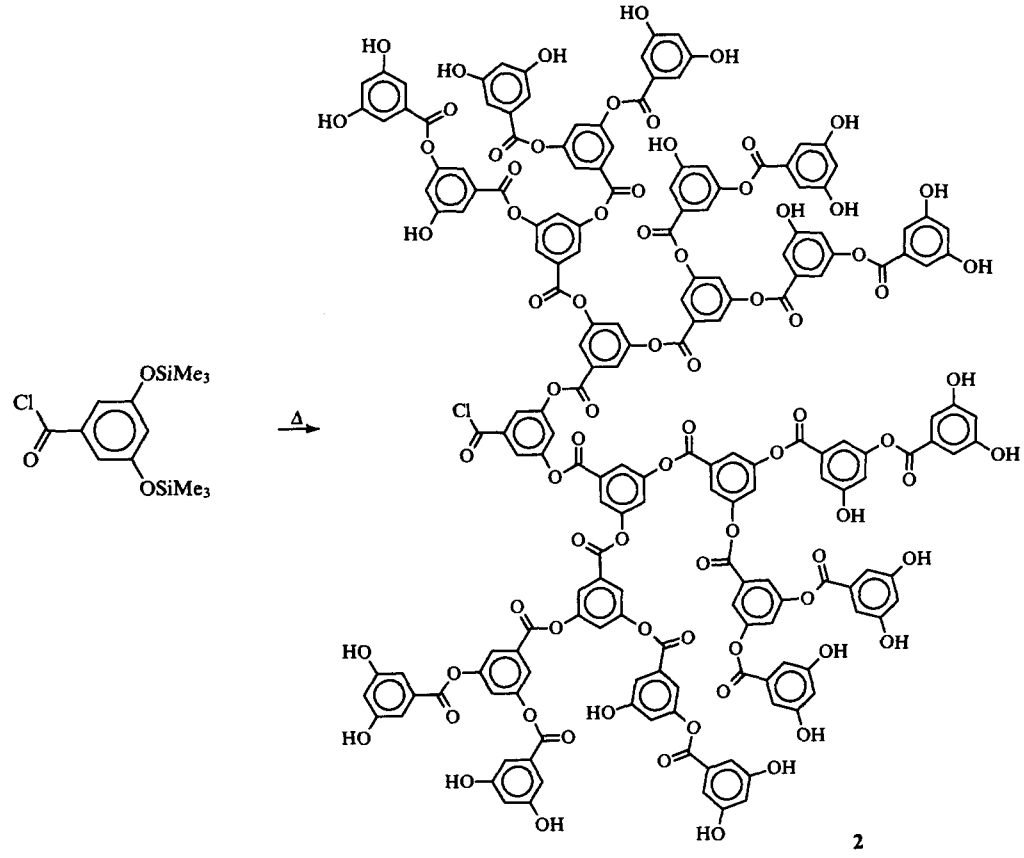


Scheme 3



1

Scheme 4



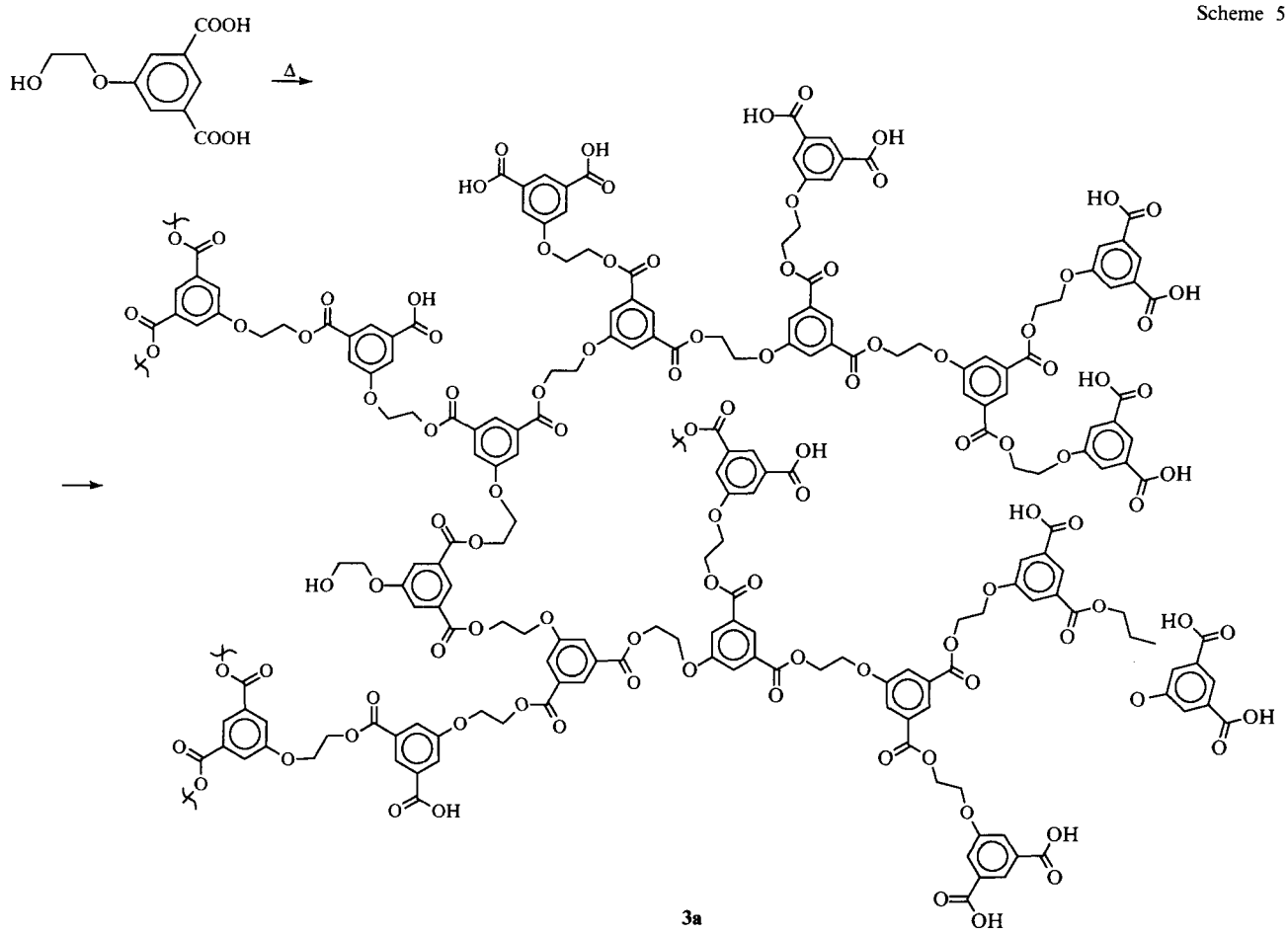
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Apart from $3,5\text{-}(Me_3SiO)_2C_6H_3COCl$, 3,5-diacetoxybenzoic,[49] 5-(2-hydroxyethoxy)isophthalic, and 5-acetoxyisophthalic acids[50,51] have been used to obtain similar polyesters. The reactions were carried out in the monomer melt without a catalyst or in the presence of ammonium salts. The polycondensation of the hydroxyethoxy-derivative takes place at 180 °C in the presence of catalytic amounts of $Bu_2Sn(OCOMe)_2$ (Scheme 5).

The condensation of 5-acetoxyisophthalic acid requires heating to 250 °C, which promotes dehydration of the carboxy-groups and the formation of the cross-linked insoluble polymer **3a**, which is readily converted into the soluble dendrimer **3b** with acid end-groups on refluxing in a THF–water mixture. The COOH end-groups in the polymers **3a, b** were protected by converting them into ester of amide groups. The cocondensation of 5-acetoxyisophthalic acid with 3-(4-acetoxyphenyl)propionic acid, which occurs under similar conditions, leads to dendritic copolymers with different contents of linear fragments.[51]

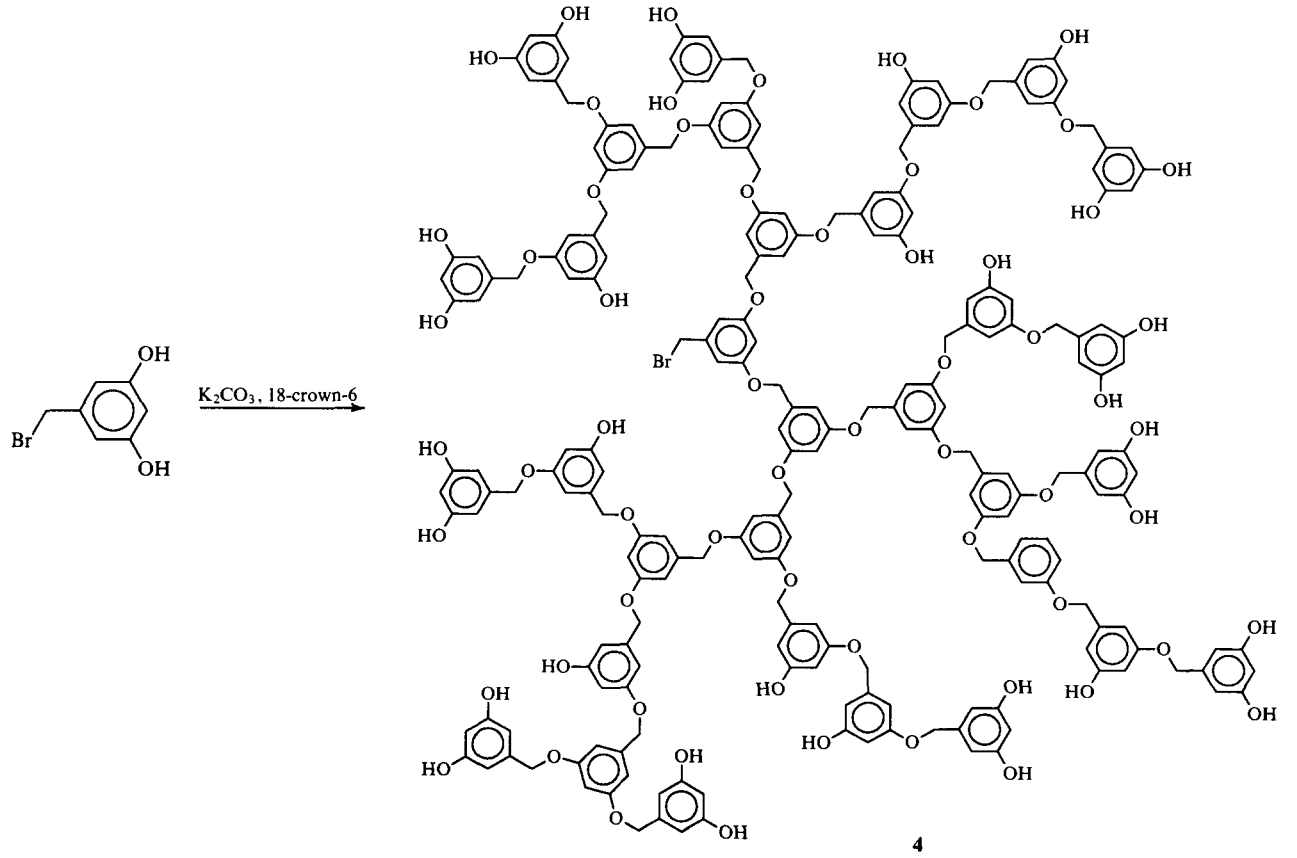
The polyester **4**, based on 3,5-dihydroxybenzyl bromide and having a cascade structure, is synthesised by treatment with K_2CO_3 (Scheme 6).[52,53] Polymer specimens in which the phenolic

Scheme 5



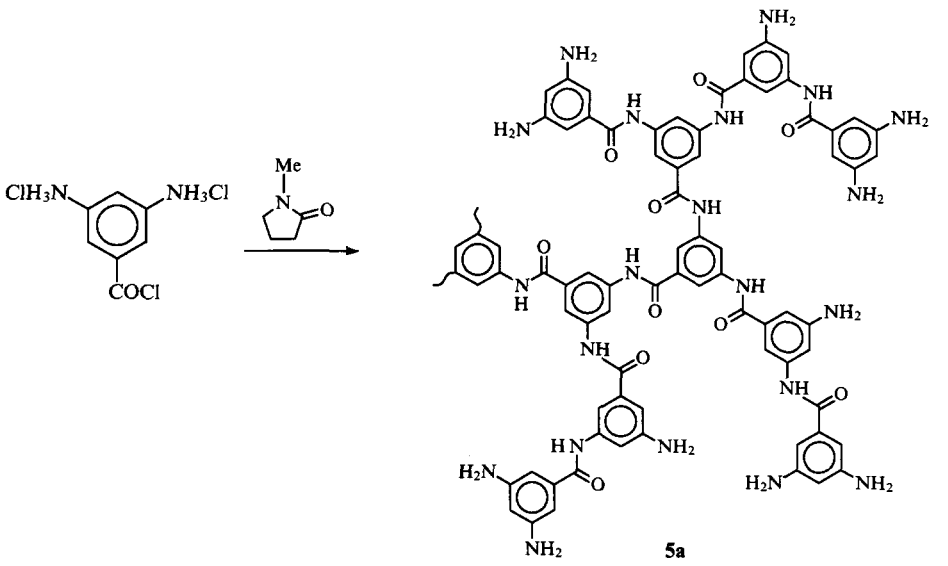
3a

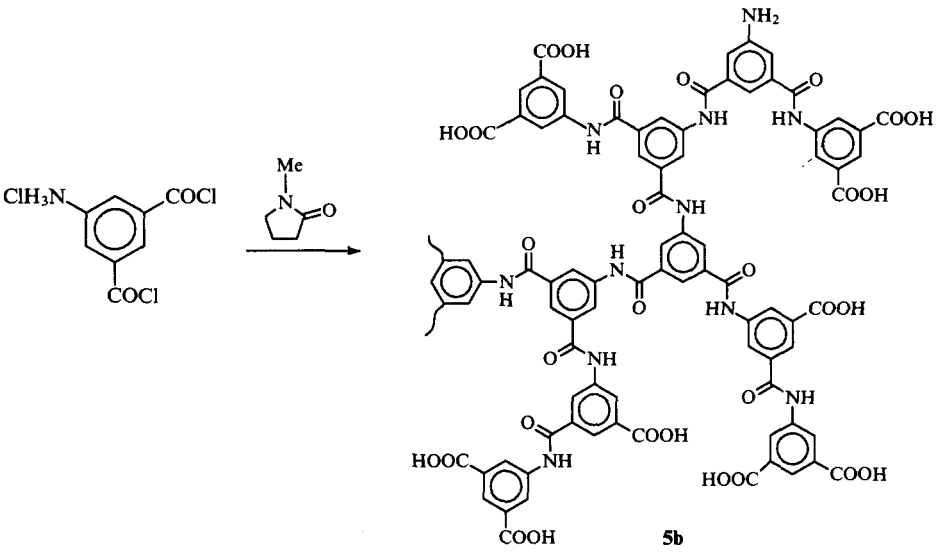
Scheme 6



4

Scheme 7



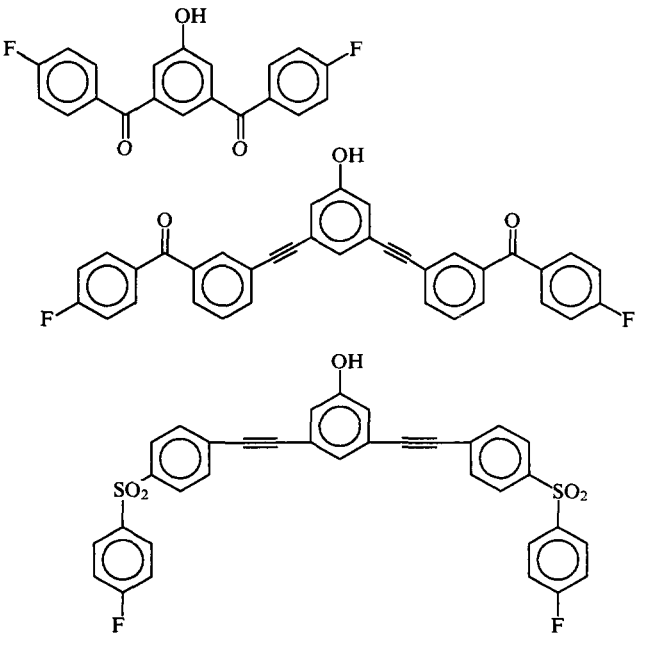


end-groups had been replaced by the inert benzyl groups as a result of the reaction with benzyl bromide were used for subsequent investigations and measurements. The solvent exerts a significant influence on the yield and the molecular mass of the product in this instance: in dichloroethane, the yield does not exceed 38% and $\overline{M}_n$ = 2800, whereas in acetone the yield reaches 73% with $\overline{M}_n$ = 14700. According to ^{1}H NMR data, the polymers formed contain 20%–30% of *C*-alkylated fragments, which are a result of C–C condensation in a side reaction.

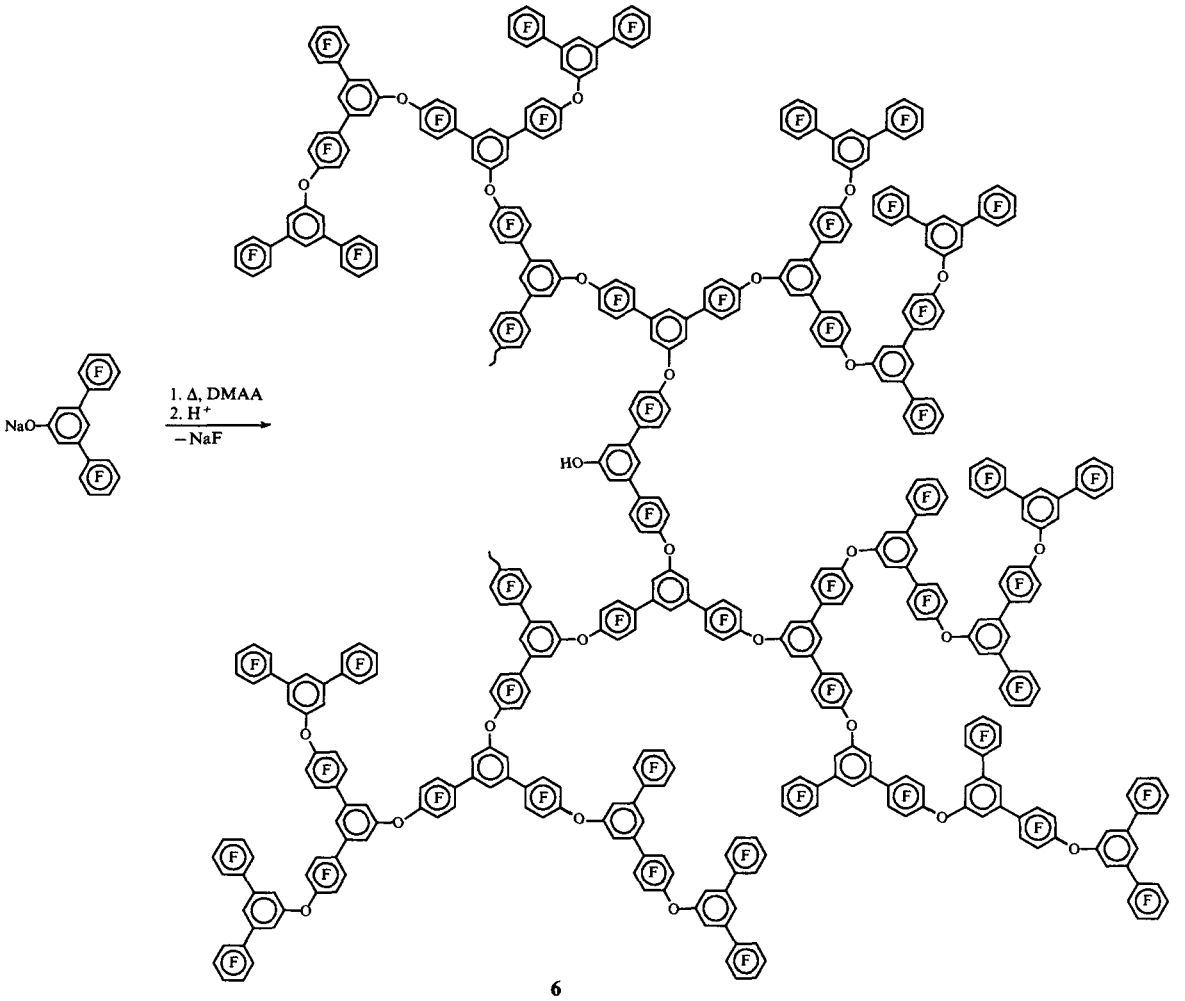
The dendritic aromatic polyamides **5a, b** were obtained from 1,3,5-trisubstituted benzenes in two ways: by the neutralisation of the hydrochloride with subsequent condensation of the resulting free amine (Scheme 7) and by the hydrolysis of the chloride of the sulfinylaminoacid 3,5-$(OSN)_2C_6H_3COCl$ [or 3,5-$(ClCO)_2C_6H_3NSO$].[54]

The dendritic analogues of the well known and widely used linear poly(phenylene oxides) are formed on polycondensation of phenoxides containing pentafluorophenyl or *p*-fluorophenyl substituents in the 3- and 5-positions (Scheme 8).[55]

Other dendrimers of this group were obtained under the same conditions from their monomers



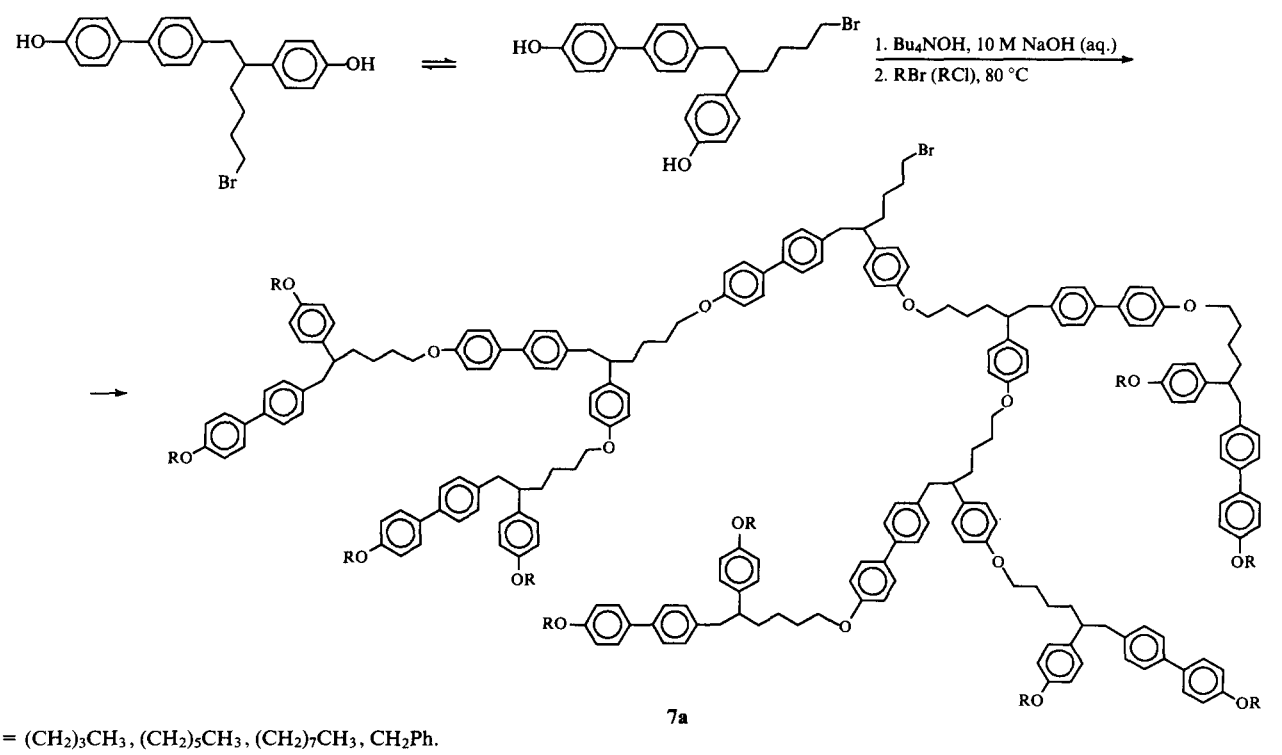
Scheme 8



6

DMAA = *N*,*N*-dimethylacetamide.

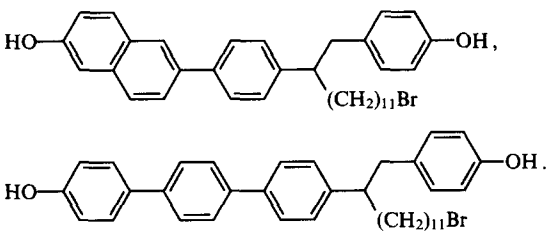
Scheme 9



7a

R = $(CH_2)_3CH_3$, $(CH_2)_5CH_3$, $(CH_2)_7CH_3$, CH_2Ph.

The dendritic polymers **7** of the unusual 'willow-like' type have been synthesised recently from 6-bromo-1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)hexane **7a** and the corresponding decane **7b**.[56,57] The polyesterification was carried out under the conditions of phase transfer catalysis in the presence of tetrabutylammonium hydrogen sulfate with subsequent alkylation of the terminal hydroxy-groups (Scheme 9). Similar polymers have been obtained[57] from the diols

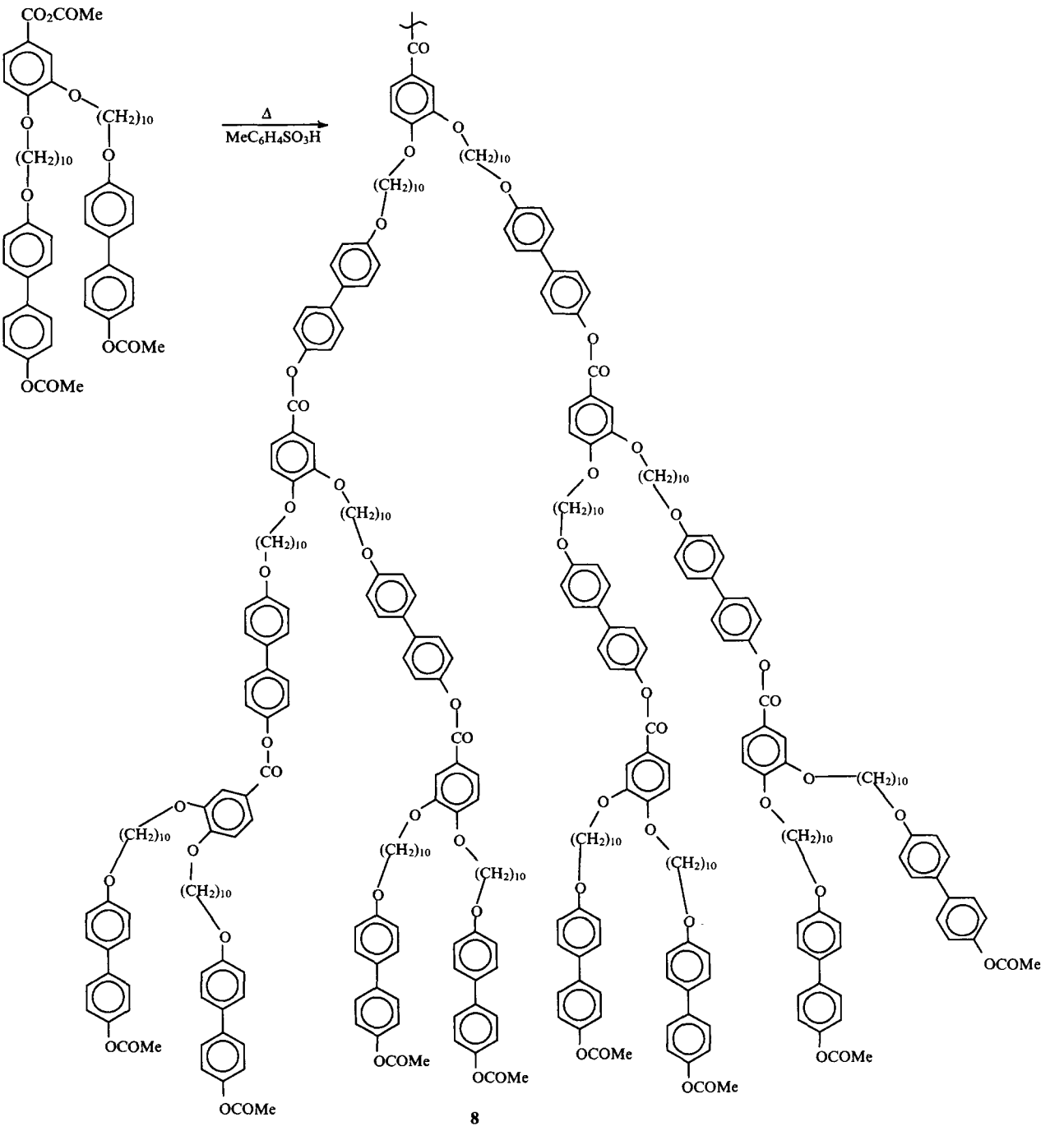


The choice of the monomers for these syntheses was dictated by their mesogenic nature, which permitted the hope that liquid crystal properties might appear in the products.

This was also the aim in the synthesis of the polyester **8** by heating a melt of the monomer at 240 °C in the presence of toluene-*p*-sulfonic acid (Scheme 10).[58] After the polycondensation had been completed, the end-groups were functionalised by adding to the mixture the chloride of a substituted benzoic acid with asymmetric substituents.

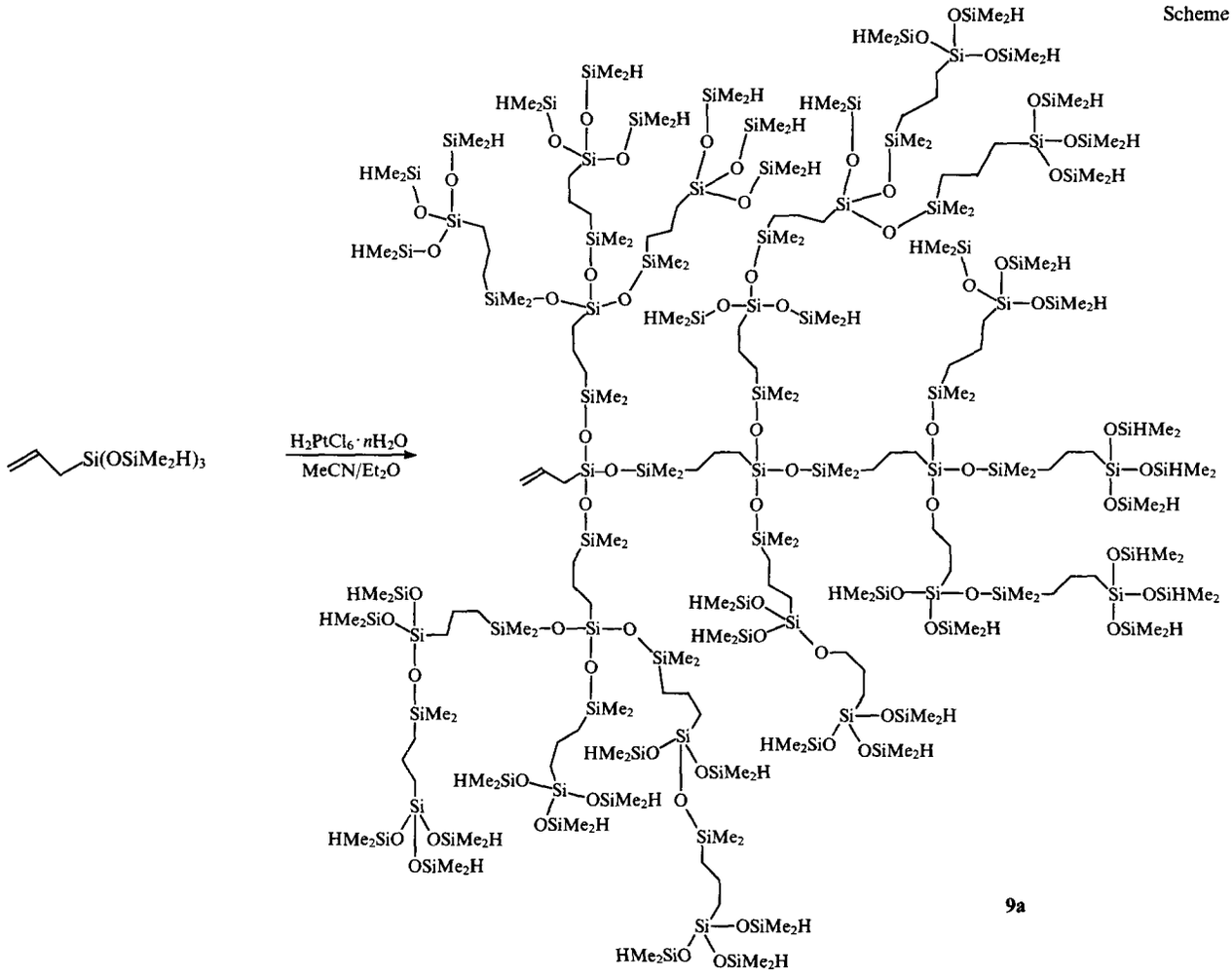
In order to obtain the dendritic polycarbosiloxanes **9a, b**, the allyl(siloxy)silanes $CH_2=CHCH_2Si(OSiMe_2H)_3$ and $CH_2=CHCH_2SiMe(OSiMe_2H)_2$ were synthesised by the cohydrolysis of chlorodimethylsilane with allyldichlorosilane and allyldichloro(methyl)silane respectively.[59,60] The subsequent polymerisation of these monomers in the presence of a platinum catalyst at 52 °C led to dendrimers containing 3–4 layers of monomer units (Scheme 11). In order to prevent intermolecular

Scheme 10

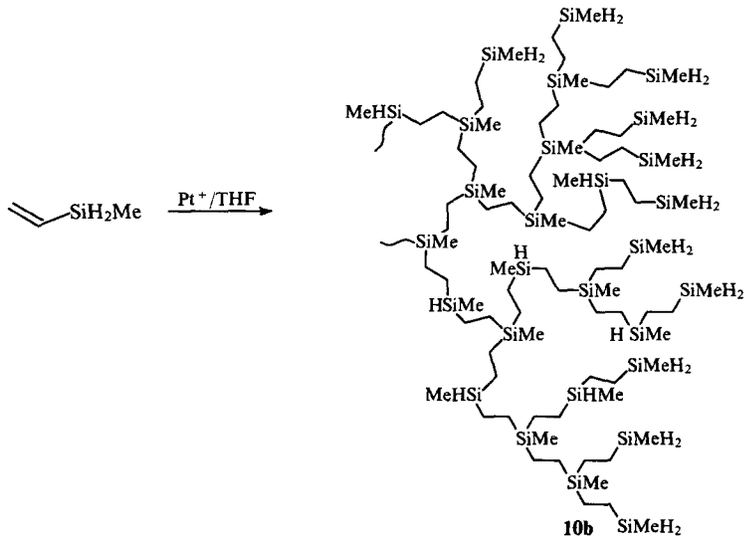


8

Scheme 11



Scheme 12



cross-linking as a consequence of the oxidation of the Si–H end groups and the formation of Si–O–Si bridges, leading to a decrease in the solubility of the polymers, the freshly prepared polysiloxanes **9a**, **b** were treated with allyl phenyl ether. As a result of the addition of the latter, the reactive Si–H groups were replaced by the inert ether end-groups Si–$CH_2CH_2CH_2OPh$.

The same reaction, i.e. catalytic hydrosilylation, was used to obtain the group of dendritic polycarbosilanes **10a–d** from the allyl- and vinyl-silanes $(CH_2{=}CHCH_2)_2MeSiH$, $(CH_2{=}CHCH_2)_3SiH$, $CH_2{=}CH(Me)SiH_2$, and $(CH_2{=}CH)_2{=}MeSiH$ (Scheme 12).[61] All the reactions come to an end after several hours (at 85 °C) and afford high yields of dendritic polymers in the form of viscous transparent liquids. Derivatives with allyl end-groups were then used to obtain modified carbosilanes.

III. The molecular mass, shape, and structure of the macromolecules

In considering the theoretically ideal polycondensation reaction of type $A-R-B_x$ monomers, de Gennes and Hervet [62] concluded that such a reaction should lead to the maximum possible molecular mass, i.e. to a polymer the molecular mass of which is determined solely by the amount of the monomer introduced into the reaction. However, studies have shown that all real processes give rise to dendrimers with a limited molecular mass and size of the macromolecules. The addition in this instance of the initial monomer to the reaction mixture after the completion of the process leads neither to an increase in the molecular mass nor to the appearance of a new fraction of the polymer with a new value of $\overline{M}$.[25,36,61] This finding cannot be rigorously explained, because the molecules of all the dendrimers described above contain on their surface active functional groups capable of combining with additional monomer molecules and hence of giving rise to new generations of layers.

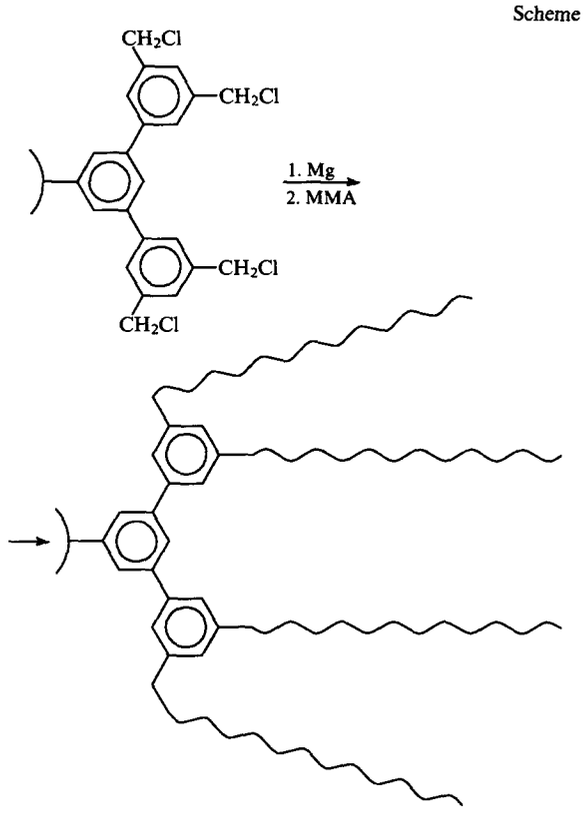
The limitation of the molecular mass of the polymers in real processes has been attributed [25,59,60,63] to steric hindrance, which increases with increase in the size of the macromolecule, or to the formation of an intramolecular ring incorporating group A in the growing dendron $A-[R]_n-B_y$. Apparently this explanation is valid for the convergent mechanism of the formation of the dendritic molecule. However, there are grounds for the hypothesis that, under the conditions of the uncontrolled single-stage synthesis, all versions of the growth occur — convergent, divergent, and their combinations. All three mechanisms are then equally probable in the initial stages. The contributions of the convergent and combined mechanisms ensure a rapid growth of the molecule up to a definite critical size, after the attainment of which the divergent mechanism becomes dominant (as a result of the decreased shielding of the active centres), which leads to a sharp retardation of the increase in $\overline{M}$. (In this respect, there is no doubt about the influence of steric factors.) Hence it follows that the observed limiting values of $\overline{M}$ for all types of dendritic polymers obtained via a single-stage synthesis are only apparent. The introduction of an additional amount of the monomer into the reaction mixture should lead not only to the formation of a new portion of molecules with the 'standard' size but also to some increase in the molecular mass ($\Delta\overline{M}$) of the molecules already present. However, this increase is readily masked against the background of the increase in the overall mass of the polymer.

An indirect confirmation of this hypothesis is provided by the procedure discovered for the rapid increase in the molecular mass of PPG,[36] in which the least soluble fraction and hence the fraction with the highest molecular mass, isolated beforehand from the standard polymer, is introduced into the reaction with a fresh portion of the monomer, where it plays the role of a giant initiator core. The sixfold repetition of this operation made it possible to obtain PPG with a molecular size in excess of 2200 Å for an initial diameter of 50–55 Å. On the other hand, in the synthesis of PPG in the presence of $(C_6F_5)_4Ge$, which plays the role of a kind of inhibitor of the convergent path, a polymer with a lower molecular mass was obtained.[43]

The same principle, i.e. the use of dendritic molecules as the starting compounds, was used in the synthesis of star polymers based on the polyphenylene dendrimer **1** (Scheme 13) [63] and the carbosilane dendrimer **10a**.[61]

The degree of polymerisation n in real cascade compounds obtained in a single stage synthesis varies from 9–15 (for dendrimer **7a**) [56] to 200–300 (for PPG and the polymers **6a–d**).[55] Evidently the type of the monomer and not the rate of reaction exerts a decisive influence under these conditions. Thus, the dendrimer **1** with $n = 25-30$ and PPG with $n = 300$ are formed equally rapidly at room temperature, whereas the triphenylene polymer **6a** ($n \approx 330$) is formed on heating for 0.5–2.0 h.

Scheme 13



The conditions under which the synthesis is carried out affects the degree of polymerisation to a lesser extent. However, in a number of instances a change of the solvent, of the monomer concentration, of the temperature, and of the reaction time entails a change in the degree of polymerisation by a factor of 2–3.[48,55]

The polydispersity of the dendritic polymers obtained by a single stage synthesis does not exceed three in most cases. M_w/M_n exceeds 4 only for certain specimens of the polymers **6a–d** and is up to 10 for the dendrimer **3b**. In the case of the polymer **3b**, the molecular mass distribution of the product is polymodal.[51]

One of the most important characteristics of dendrimers is the shape and linear dimensions of the macromolecules. The construction of three-dimensional models of dendrimers showed that after only 3 generations the molecules approach a spherical shape and become regularly spherical following a further increase in the number of generations. The spherical form of the cascade compounds is apparently in fact responsible for their antifriction properties.[64]

Another characteristic feature of the dendrimer molecules is the presence of cavities, the size of which depends on the geometrical characteristics of the elementary unit.[25,43] In the dendrimers **1** and in PPG, the size of the cavities is 5–6 Å. The presence of unoccupied cavities in the molecules of the dendrimers makes it possible to employ them in compositions of the 'guest–host' type. Such complexes have been obtained for the polyphenylene–*p*-toluidine system.[25]

In the case of PPG,[36–38,43] the molecular diameter was determined by small angle laser scattering (SLS), small angle X-ray scattering, electron microscopy, and the calibrated filter method. The first two methods give rise to a significant scatter. For a PPG specimen with a molecular mass of $(1-1.5) \times 10^5$, which corresponds to $n = 180-270$ and a number of generations $G = 4-5$, it was found that the diameter of the macromolecules is 130–140 Å. Spherical particles with a similar diameter (~200 Å) have been observed by electron microscopy for the same specimen. PPG with a molecular mass of 400 000 has particles of the same size. However, repeated measurements on a standard PPG specimen demonstrated a significantly smaller

average diameter, namely 50–55 Å.[43] The unduly large molecular dimensions obtained from measurements by small angle laser and X-ray scattering are evidently associated with the low accuracy of these methods.

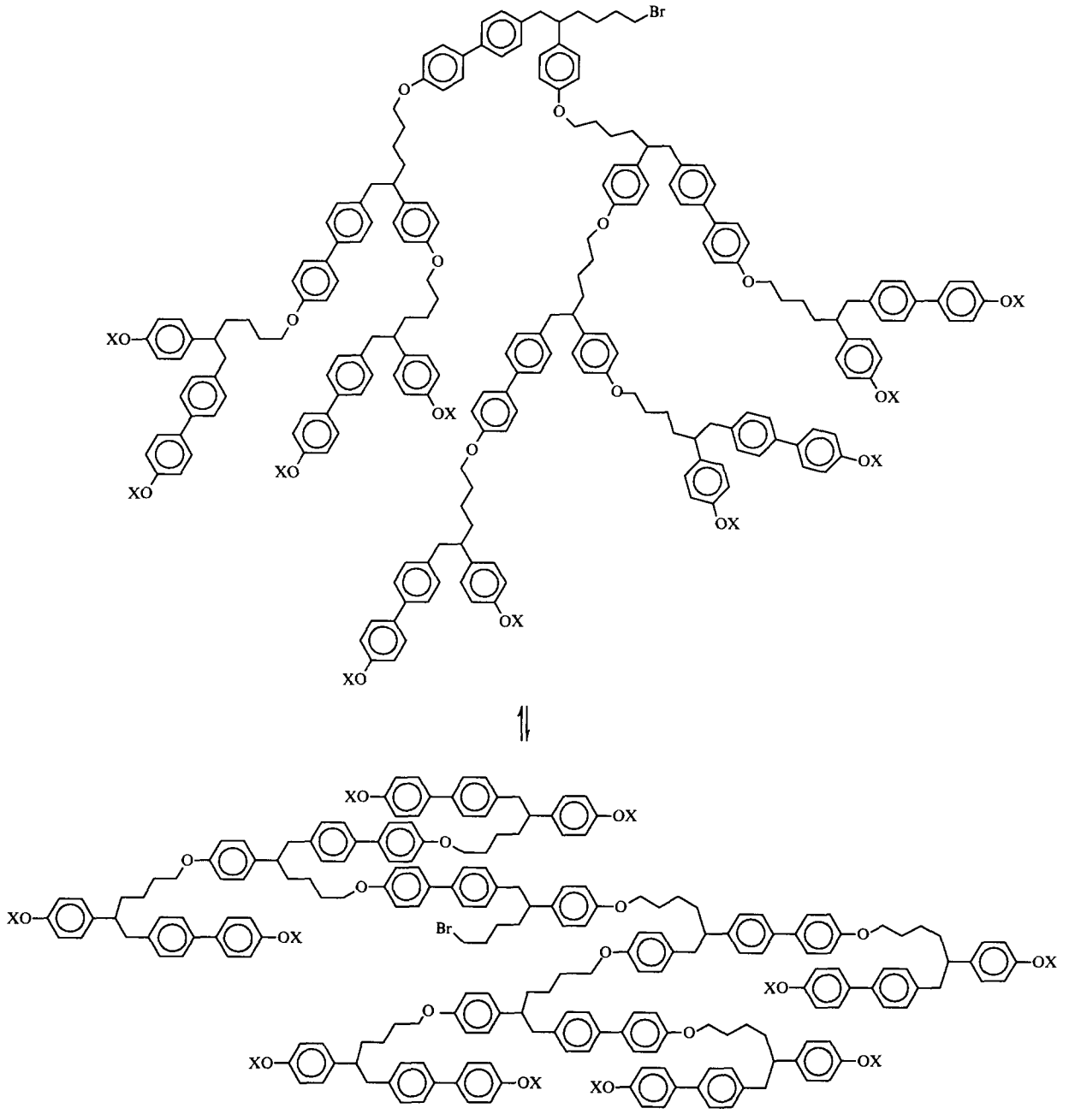
Computer modelling showed that PPG molecules have a diameter of 52.9 Å for $G = 4$ and 63.2 Å for $G = 5$. The calculated molecular masses of the polymer (for a 100% degree of branching) with $G = 4$ and 5 are respectively 90 000 and 270 000. Taking into account the smaller degree of branching in the real polymer, the agreement of the values of $\overline{M}$ obtained with the experimental value of 100 000–150 000 may be regarded as satisfactory.

It has been found for the dendritic polyphenylene **1**[25] and the polyester **2**,[48] in which the multiplicity of the monomer unit is 2, that the degree of branching of these polymers (according to NMR spectroscopic data) does not exceed 60%–70%. In addition, one should take into account the fact that, when the molecule is formed under the conditions of uncontrolled synthesis, the role of initiator core may be assumed not only by the $A-R-B_x$ monomer with a blocked functional group A but also by the ring $[-A-R-B_x-]_n$ formed in the initial stage via intramolecular condensation. As a result of this, the deviation from the ideal dendritic structure is inevitably reflected in the molecular mass and linear dimensions of the macromolecules obtained. It has been suggested that a decrease in the monomer concentration in the initial reaction mixture promotes the formation of intramolecular rings.[55]

IV. Properties

Like the usual flexible-chain polymers, the dendrimers obtained by a single-stage synthesis are viscous liquids, amorphous white powders, or vitreous colourless or pale-yellow substances. Many of them are capable of forming film coatings, but their mechanical properties (for example, their tensile strength) are significantly inferior to those of the usual polymers. However, their employment as modifying additives to rubber compositions based on siloxane raw rubbers leads to a significant increase in the tensile strength of the latter.[61]

Scheme 14



All dendritic polymers are readily soluble in organic solvents such as toluene, chloroform, acetone, and THF. Compared with the linear polymers formed from isotypical elementary units, the solubility of dendrimers is higher. It has been suggested that this is associated with the spherical shape of the molecules, which prevents the close packing of the polymer segments.[48] The peripheral functional groups also exert a considerable influence on the solubility: thus the introduction of alkyl terminal substituents tends to increase the solubility of the polymers in hydrocarbons, whilst the use of carboxylate, hydroxy-, or hydrochloroammonio-end-groups solubilises previously insoluble dendrimers.[25,54,63]

One of the characteristic properties of all dendrimers, including cascade polymers, is a low viscosity of their solutions [the viscosity of PPG solutions is four orders of magnitude lower than that of the solutions of poly(butyl methacrylate) with a similar molecular mass].[65] The molecular mass and concentration of the solutions exert little influence on their viscosity.[36,51,65] In terms of their rheological properties, these substances are closer to suspensions than to solutions of flexible-chain polymers. It is of interest to note that, when a small amount of the dendrimer is added to the normal polymer, the viscosity of the melt of the mixture is significantly reduced.[63]

The spatially fractal nature of the macromolecular framework of dendrimers indicates their possible crystallinity. However, the deviations in the spatial disposition of the elementary units from the ideal sites as well as the reduced degree of branching in the real specimens make it possible to obtain crystals only for first and second generation dendritic compounds.[66] All the remaining polymers of this class are amorphous, which is indicated by the absence of melting points and crystallisation temperatures in these compounds.[55,67] The glass points of isotypical polymers depend little on the molecular mass, but change markedly when the end-groups are altered.

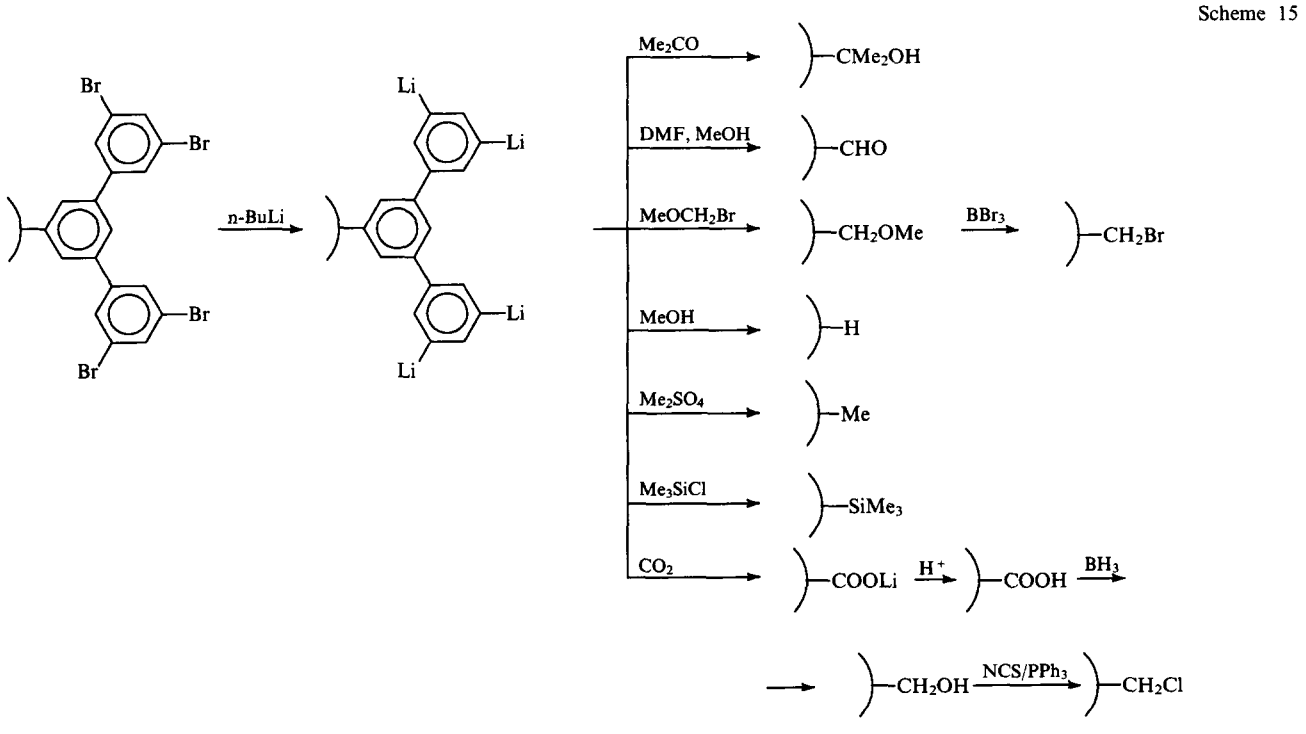
The 'willow-like' dendrimers **7**, obtained by Percec and Kawasumi[56,57] from monomers having mesogenic properties by virtue of their conformational isomerism, are thermotropic liquid crystal substances. It has been suggested that, both in the isotropic phase and in solution, these substances contain mesogenic elementary units in the *gauche*-conformation (or in a *gauche*–*anti* dynamic equilibrium). Such conformation of the units gives rise to the hierarchical architecture of the molecular framework characteristic of dendrimers. On decrease in temperature, the elementary units pass to the *anti*-conformation, which entails a change in the tree-like macromolecular skeleton. They acquire a compact form, corresponding to the nematic mesophase of the polymer (Scheme 14). The transition has been noted in the temperature range from 20 to 40 °C depending on the length and nature of the end-groups of the macrochains.

The existence of a liquid-crystal phase at room temperature has also been noted in a study of solutions of the polymers **5a, b** in amides.[54] For the dendritic polyester **8**, the formation of the cholesteric mesophase has been noted in the temperature range 60–148 °C.[58] By virtue of the presence of chiral end-groups, the same polymer is optically active.

The study of the temperature dependence of the heat capacity of PPG over a wide temperature range (0–550 K) showed that the specific features of the molecular structure of the dendrimer and the molecular shape are hardly reflected in the thermodynamic characteristics of the polymer.[67]

The thermal stability of dendritic polymers is as a rule higher than that of their linear analogues and the corresponding monomeric compounds.[46,48,55,63,68] The polyphenylene dendrimers **1** and **6** belong to the class of the most thermally stable polymeric substances. They begin to decompose in air on heating above 500–550 °C.[55,63] PPG is almost as stable.[68] When PPG is heated at 420 °C for 1.5 h, it loses 4.5% of its mass, the elimination of C_6F_5H and C_6F_6 molecules and partial cross-linking of the macromolecules being noted under these conditions. Among other thermal decomposition products, fluorine and the digermane $[(C_6F_5)_3Ge]_2C_6F_4$ were noted. Decomposition at 580 °C leads to the formation of carbon and germanium. It has been found that the addition of small amounts of dendrimers to the usual polymeric substances frequently increases the thermal stability of the latter.[63,68,69] It has been observed for PPG that the temperature range in which the dendritic polymer exhibits a stabilising activity coincides with the temperature range of its decomposition. This suggests that the substances responsible for the stabilising effect are not the dendrimers themselves but the low-molecular-mass products of their decomposition.[69]

Scheme 15



The possibility of modifying polymers **1** and **4** by replacing the peripheral functional groups has been investigated.[47,52,63] It has been found that the bromine atoms and the phenolic groups in the dendrimer **1** can be replaced by alkyl, aryl, carboxy-, carboxylate, haloalkyl, ethynyl, etc. groups (Scheme 15).

During the modification, 70% – 80% of the functional groups of the initial polymer are as a rule exchanged. It has been noted that a polymer with partially substituted functional groups enters more readily into the subsequent substitution reaction. This property, which has been observed also in relation to other examples,[3] is apparently common to all the dendritic formations. It has been suggested that this may be caused by the local polarisation of the functional groups. Thus the replacement of the functional end-groups, accompanied by significant changes in the solubility and glass point, permits the deliberate alteration of the characteristics of dendritic materials and leads to prospects for the synthesis of micellar and lyotropic systems.

The high reactivity of the peripheral functional groups in the dendrimer **1a** and its derivatives has been used to synthesise polymers of a new type, the so-called star polymers. The macromolecule of such a compound, obtained from compound **1**, closely resembles the shape of the sea urchin.[63] Its 'body' comprises the molecule of the initial dendrimer and the outgoing 'rays (needles)' consist of the linear oligomer and polymer chains. These molecules were synthesised by the successive Br/Li/$SiMe_2R$ (R = CH_3, C_8H_{17}, $C_{18}H_{17}$, $C_{30}H_{61}$) substitution of functional groups or by growing linear polymer chains [of polypropiolactone and poly(methyl methacrylate)] on the surfaces of the spherical molecules, where the dendrimer molecule plays the role of the initiator core.

Thus, one may conclude that, despite the low organisation of the molecular architecture of the dendritic polymers obtained by a single-stage synthesis, their physicochemical properties differ little from those of the dendrimers obtained by the multistep method. Taking into account the advantages of a single-stage synthesis of the dendrimers and the highly promising practically useful properties of such substances, one may confidently predict a vigorous development of this aspect of modern chemistry in the immediate future.

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