Unimolecular Micelles and Globular Amphiphiles: Dendritic Macromolecules as Novel Recyclable Solubilization Agents

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The synthesis of dendritic polyether macromolecules based on a 3,5-dihydroxybenzyl alcohol building block and having carboxylate groups as chain-ends is described. These novel macromolecules behave as unimolecular micelles and their ability to solvate hydrophobic molecules has been investigated by UV–VIS spectroscopy. A dramatic increase in the saturation concentration of various polycyclic aromatic compounds in water was observed which was of a magnitude similar to that observed for micelles derived from sodium dodecyl sulfate. A relationship between the solubilizing power of the dendrimer and the electron density of the polycyclic aromatic was found. A linear relationship between the solubilizing ability and the concentration of the dendrimer, even at concentrations as low as 5×10^{-7} mol dm^{-3}, indicates that these materials do not have a critical micelle concentration. Increases in the ionic strength of an aqueous solution of the dendrimer caused an increase in the saturation concentration of the hydrophobic molecules. A recyclable solubilization and extraction system is discussed. The synthesis of a globular dendritic macromolecular amphiphile designed to reside at the interface of an organic solvent and water is also described. This 'hybrid' dendritic amphiphile consisting of two distinct sectors, one hydrophilic and the other hydrophobic is prepared by stepwise alkylation of a core molecule, 4,4'-dihydroxybiphenyl with the two dissimilar dendritic fragments.

There is a growing interest in macromolecules with architectures that differ from the classical linear polymers, as new polymer architectures may exhibit unusual behaviour and possess properties that differ from those of linear materials.[1] One family of macromolecules which has attracted considerable attention is that of the dendritic macromolecules, compounds which are characterized by a large number of terminal groups all emanating from a central core with at least one branch at each repeat unit. Two fundamentally different approaches have been developed for the stepwise synthesis of dendritic macromolecules. In the divergent approach,[2] growth is initiated at a polyfunctional core molecule and occurs by a stepwise series of coupling/activation steps involving a monomer capable of at least one branch per repeat unit. The alternative convergent growth approach[3] is basically the opposite of the divergent approach. Growth is begun at what will become the chain ends of the final macromolecule, and, by the use of a protected AB_x monomer unit and a stepwise series of coupling/activation steps, larger and larger dendritic fragments are produced. The final reaction is attachment to a polyfunctional core molecule. A number of different research groups[2,3] have demonstrated the synthesis of dendritic structures by these methodologies and have defined the advantages of each method.

A fundamental difference between dendritic and linear polymers is the bonding and branching sequence. Dendritic macromolecules contain a large number of symmetrically arranged branches which result in a three-dimensional globular shape. At high molecular weights, these structures may approximate spheres. This globular shape should be relatively fixed in marked contrast to linear polymers which are random coils and depending on the solvent, may vary in shape and size from extended to compact coils. This retention of structure in solution has been exploited by Newkome[4] in a seminal paper describing unimolecular micelles prepared by the divergent growth approach. These unimolecular micelles are a new class of dendritic macromolecules where an interior hydrophobic core is surrounded by a hydrophilic surface layer. In Newkome's system, there is a branching hydrocarbon interior consisting of two generations of nonyl repeat units which is surrounded by a hydrophilic surface layer consisting of 36 carboxylate chain ends. The structure closely resembles that of a micelle except that it is static with all carboxylate or head groups covalently linked to a central core. Therefore, unlike traditional micelles, the structure would be expected to retain its cohesion over the entire range of concentrations and in a greater variety of solvents. Characterization of this novel macromolecule did indeed show that it existed as a single molecule capable of molecular inclusion.[5] Although reports of similar hyperbranched macromolecules possessing micellar properties have appeared,[6] these materials are imperfectly branched and functionalized.

It has been shown that a degree of control can be obtained over the nature and functionality of both the internal building blocks[7] and the chain ends[8] in the convergent synthesis of dendritic macromolecules. Therefore, the possibility exists for the preparation of unimolecular dendritic micelles capable of specific non-bonding interactions through tailor-made molecular inclusion sites. To demonstrate this, and to further extend the concept of unimolecular micelles, the synthesis of carboxylate-terminated polyethers based on an electron-rich 3,5-dioxybenzyl building block by the convergent growth approach is reported. The ability to control molecular architecture is also exploited to prepare hybrid macromolecules with hydrophilic and hydrophobic chain-ends segregated in distinct sections of the globular structure, allowing for their preferential orientation at suitably selected interfaces.

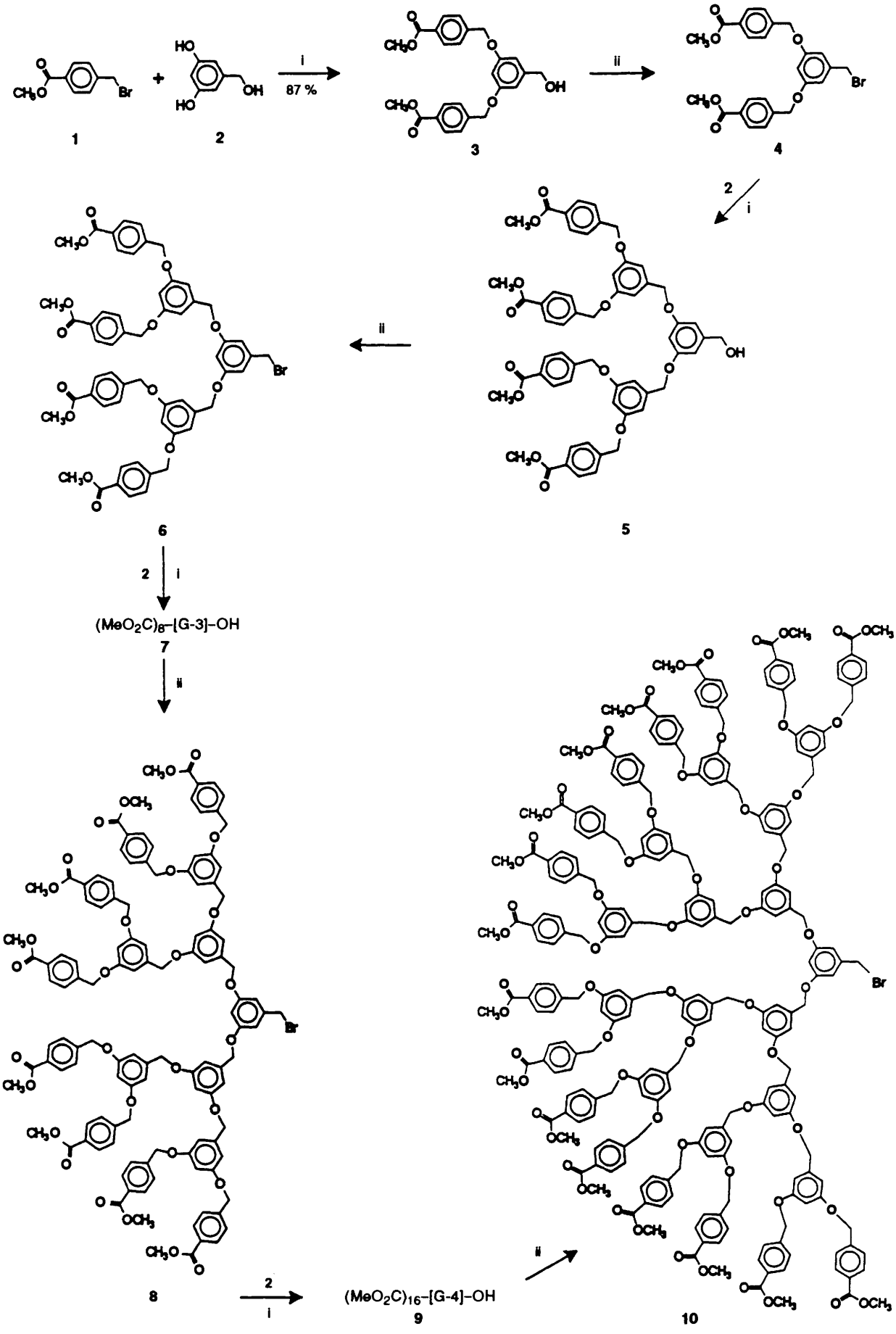
Results and Discussion

Synthesis.—To obtain a 'unimolecular micelle' using the convergent growth approach, the starting material, which will become the chain ends, must contain a potentially hydrophilic functional group. For comparison with our previous work, and to provide an interior containing electron-rich aromatic rings, we decided to employ 3,5-dihydroxybenzyl alcohol as the monomer unit and a two-step generation growth process

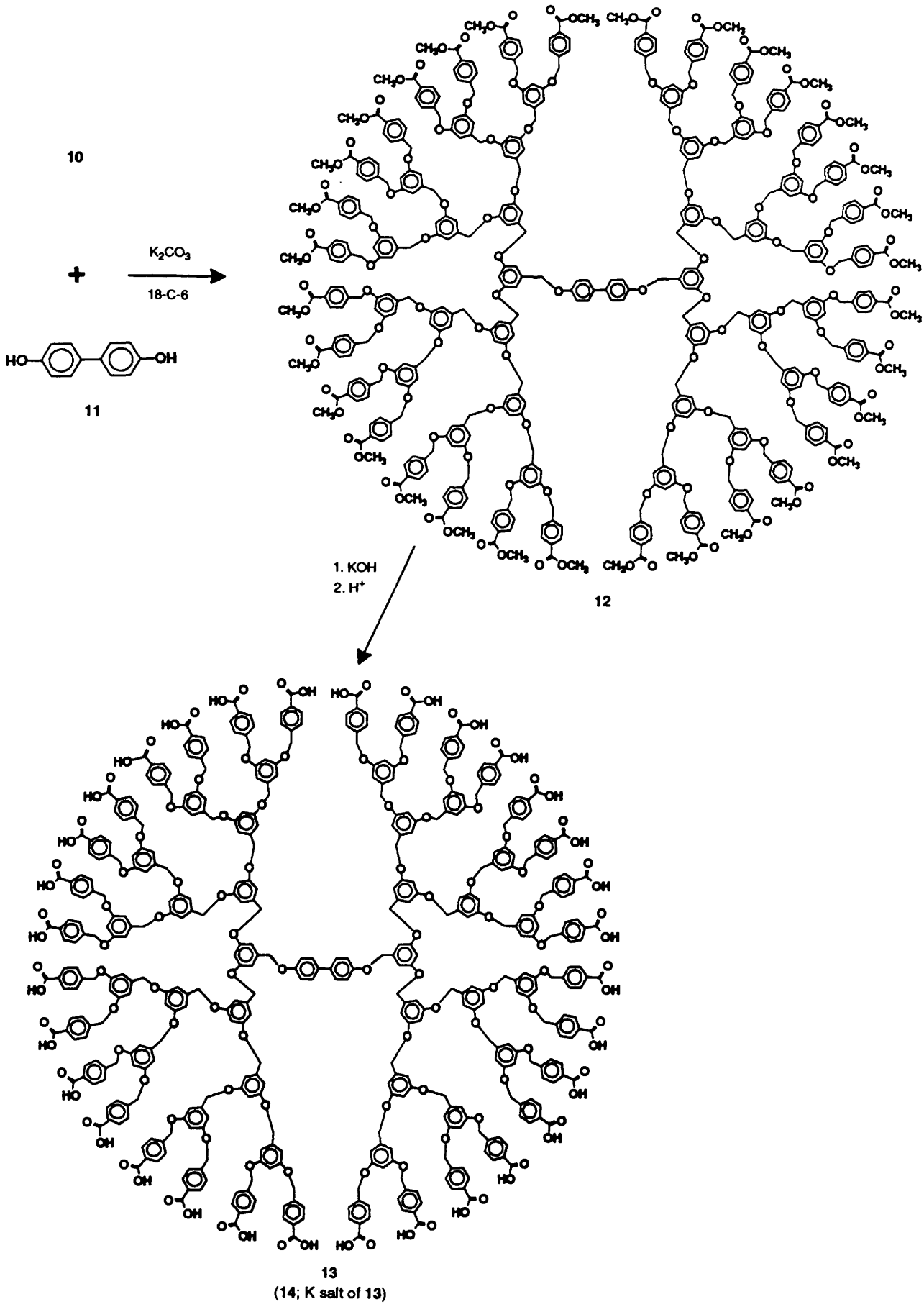
consisting of activation by bromination, and coupling by alkylation. Carboxylate groups were required as the chain ends of the final globular macromolecule, however their presence in the starting material or as chain ends in precursor dendritic fragments, was not feasible owing to side reactions in both the alkylation and bromination steps. Therefore the carboxy group had to be protected and the methyl esters we have used previously[8] appeared to meet the requirement of the various reactions in the convergent synthesis of polyethers using the above experimental conditions. Furthermore, the polyether core has been shown[9] to be stable to the alkaline hydrolysis conditions that are required for the conversion of the methyl ester end groups into the corresponding ionic carboxylate groups. The starting material was therefore chosen to be methyl *p*-bromomethylbenzoate **1**, which was obtained in 86% yield from the commercially available methyl *p*-hydroxymethylbenzoate by reaction with phosphorus tribromide in benzene. The synthesis of methyl ester-terminated dendrimers by the convergent growth approach is shown in Scheme 1. Coupling two molecules of **1**, which will become the terminal groups, to the monomer unit, 3,5-dihydroxybenzyl alcohol **2**, occurred readily in the presence of potassium carbonate and 18-crown-6 in acetone heated at reflux. This gave the first generation alcohol $(MeO_2C)_2$–[G-1]–OH **3**, with methyl ester chain ends in 87% yield after purification. Activation of the hydroxymethyl group at the focal point of **3** by reaction with carbon tetrabromide/triphenylphosphine proceeded smoothly to give the corresponding bromide $(MeO_2C)_2$–[G-1]–Br **4** in 83% yield. Reaction of 2.05 equiv. of $(MeO_2C)_2$–[G-1]–Br **4** with **2**, as above, gave the next generation alcohol $(MeO_2C)_4$–[G-2]–OH **5**, in 91% yield, which was brominated with CBr_4/PPh_3 to give $(MeO_2C)_4$–[G-2]–Br **6**. Conversion of **6** into the third generation alcohol, $(MeO_2C)_8$–[G-3]–OH **7**, was accomplished in 76% yield and activation by reaction with CBr_4/PPh_3 gave the bromide, $(MeO_2C)_8$–[G-3]–Br **8**, in 88% yield. During the process of growth from first to third generation, a gradual change in the solubility properties was observed on comparison with the corresponding unsubstituted polyethers prepared previously.[3] For both series, the first generation dendrimers were extremely soluble in dichloromethane, chloroform and acetone, however by the third generation the solubility of the methyl ester-terminated derivatives had decreased dramatically. In fact, the third generation bromide $(MeO_2C)_8$–[G-3]–Br **8**, was essentially insoluble in acetone even at reflux temperature. Therefore, no reaction occurred with **2** even after prolonged reflux under the above conditions. In comparison, the lower generation derivatives and all members of the unsubstituted series, up to the sixth generation, were very soluble in acetone at room temperature demonstrating the dramatic influence that the terminal groups have on the physical properties of dendritic macromolecules. Similar solubility differences, also attributed to the increasing influence of the terminal groups, have been observed for other dendrimers containing functional groups at the chain ends.[8] To overcome this solubility problem, the reaction of **8** and **2** was carried out in tetrahydrofuran heated at reflux in the presence of potassium carbonate and 18-crown-6. Utilizing these conditions allowed the fourth generation alcohol $(MeO_2C)_{16}$–[G-4]–OH **9**, to be obtained in 88% yield. For conversion into the corresponding bromide $(MeO_2C)_{16}$–[G-4]–Br **10**, 3 equiv. of carbon tetrabromide and triphenylphosphine were required to force the reaction to completion with purified **10** being isolated in 85% yield. The nominal molecular formula of $(MeO_2C)_{16}$–[G-4]–Br **10** is $C_{249}H_{219}BrO_{62}$ and corresponds to a molecular weight of 4279. All 16 of the chain ends are terminated with methyl ester groups while the focal point still contains a reactive bromomethyl group.

Coupling of **10** with the difunctional core, 4,4′-dihydroxybiphenyl **11**, allowed the use of the same alkylation conditions, though again the reaction had to be carried out in refluxing tetrahydrofuran due to the insolubility of **10** in acetone. The reaction was followed by size-exclusion chromatography. After purification by flash chromatography, the dendritic polyether macromolecule $(MeO_2C)_{32}$–$[G\text{-}4]_2$–[C] **12**, was isolated in 81% yeid. The macromolecule **12** contains 32 terminal methyl ester groups and has a nominal molecular weight of 8582. Owing to the choice of an ether framework, the transformation of the terminal methyl ester groups of the dendrimer into the desired carboxylate groups was accomplished by alkaline hydrolysis. Difficulties were initially found due to the insolubility of **12** in water and the concurrent insolubility of potassium hydroxide in solvents in which **12** was soluble. However, reaction of **12** with a large excess of potassium hydroxide was found to proceed satisfactorily in a mixed solvent system of tetrahydrofuran/water/methanol. Acidification of this reaction mixture then gave the carboxy-terminated dendrimer $(HO_2C)_{32}$–$[G\text{-}4]_2$–[C] **13**, in essentially quantitative yield. NMR spectroscopy showed **13** to be totally devoid of any unreacted methyl ester groups (Scheme 2). The polyacid **13** was insoluble in water but, on titration with potassium hydroxide, the solubility increased dramatically since the potassium salt **14** is very soluble in water without much apparent change in the viscosity of the solution. Similar solubility behaviour has been observed in other 'unimolecular micelle' systems.[6] It must be emphasized that though the structures shown in Scheme 2 and elsewhere are two-dimensional, they actually represent three-dimensional globular entities.

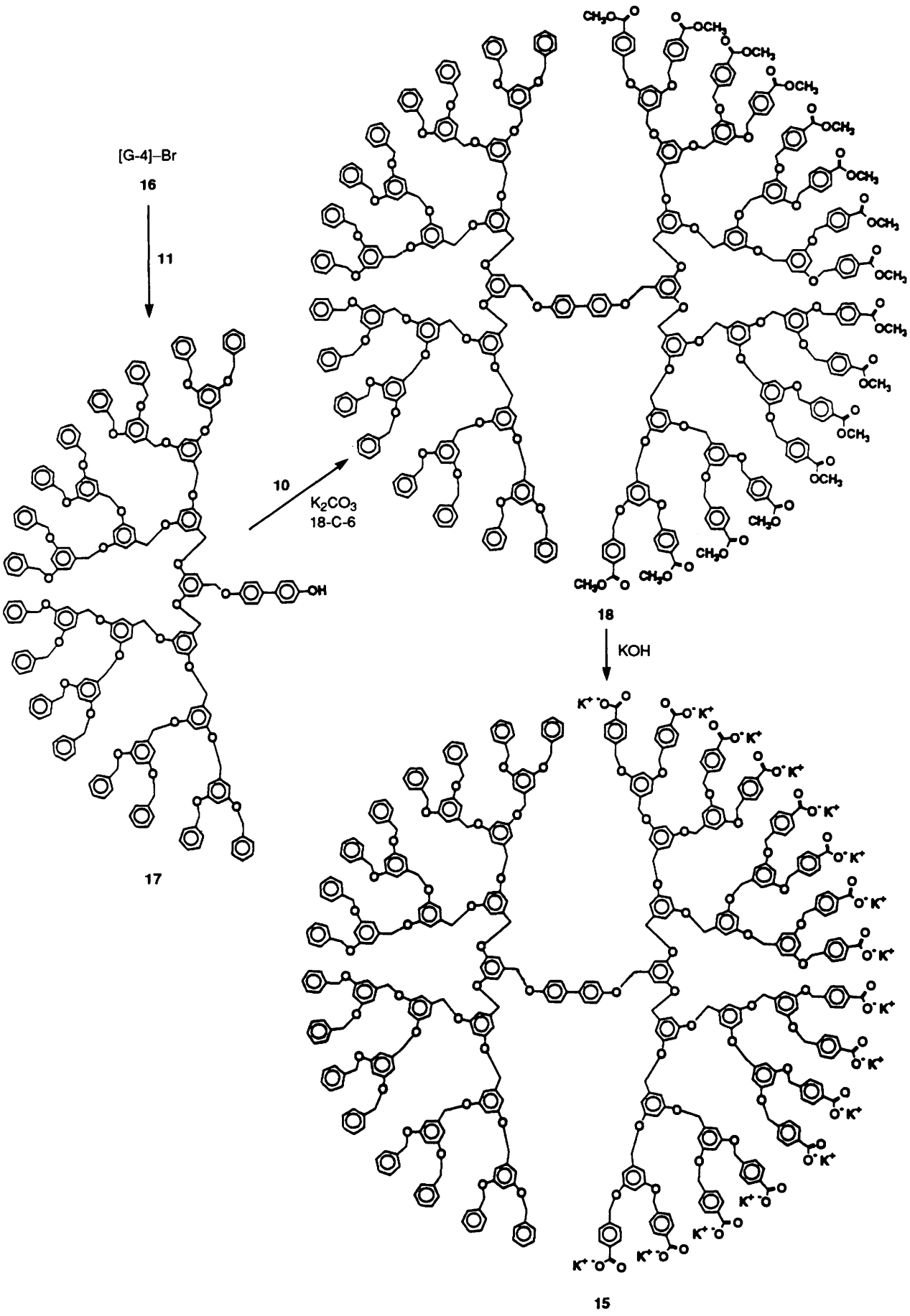
The functionality at the focal point can be used to prepare materials with specific properties. A large macromolecule, specifically a dendritic fragment for architectural consistency, was attached to the focal point of a hydrophilic carboxylate-terminated dendrimer (Scheme 3). This then lead to an unusual class of amphiphilic polymers which, due to their hydrophobic/hydrophilic nature, are expected to align readily at an interface as depicted in Fig. 1 for our target molecule **15**. The synthesis of **15** relies on the stepwise alkylation of a core molecule, which was chosen to be **11**. Reaction of the unsubstituted fourth generation bromide [G-4]–Br **16**, with a 10-fold excess of **11** gave the monophenolic derivative [G-4]–[C]–OH **17**, in 73% yield. The potential hydrophilic segment is then introduced by alkylation of **17** with the methyl ester-terminated bromide $(MeO_2C)_{16}$–[G-4]–Br **10**, to give the dendritic macromolecule $(MeO_2C)_{16}$–[G-4]–[C]–[G-4] **18**, in 71% yield. Hydrolysis of **18** under the conditions described above did not yield the fully protonated derivative $(HO_2C)_{16}$–[G-4]–[C]–[G-4] **20**, instead, a poorly defined partially protonated species was obtained. This is presumably due to the unusual solubility behaviour of the hybrid macromolecule which causes precipitation before full protonation is achieved. To overcome this problem, a silylation process was employed in order to effect complete protonation of the dendrimer salt. Therefore, the partially neutralized derivative was treated with trimethylsilyl chloride to give the fully trimethylsilylated compound, **19**. The solubility of the dendrimer was dramatically increased by silylation and it was found that hydrolysis was much more efficient. This process afforded the fully protonated hybrid dendrimer, **20**, which was titrated with potassium hydroxide to afford the unique dendritic amphiphile $(K^+{}^-O_2C)_{16}$–[G-4]–[C]–[G-4] **15**, in which one half of the macromolecule has 16 hydrophilic terminal carboxylate groups while the other half has 16 hydrophobic terminal phenyl groups. It is interesting to note that the hybrid dendrimer **15**, which is soluble in methanol, is insoluble in both water and dichloromethane. This is in direct contrast to the parent dendrimers $[G\text{-}4]_2$–[C] and $(K^+{}^-O_2C)_{32}$–$[G\text{-}4]_2$–[C] **14** which are extremely soluble in dichloromethane and water, respectively. Also, agitation of a mixture of water and dichloromethane to which a small amount of **15** had been added



Scheme 1 *Reagents: i*, K_2CO_3, 18-crown-6; ii, CBr_4, PPh_3. Reaction scheme for the preparation of methyl ester-terminated dendritic fragments.



Scheme 2 Reaction scheme for the preparation of carboxy-terminated dendritic macromolecule $\{(HO_2C)_{16}\text{-}[G\text{-}4]\}_2\text{-}[C]$



Scheme 3 Reaction scheme for the preparation of carboxy- and phenyl-terminated dendritic diblock copolymer $(KO_2C)_{16}$–[G-4]–[C]–[G-4]

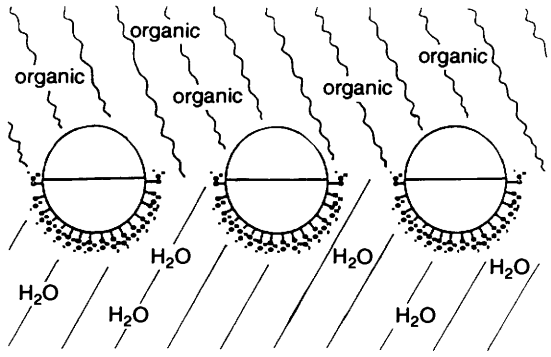


Fig. 1 Schematic representation of the carboxy- and phenyl-terminated dendritic diblock copolymer $(KO_2C)_{16}$–[G-4]–[C]–[G-4], aligning at an organic/aqueous interface

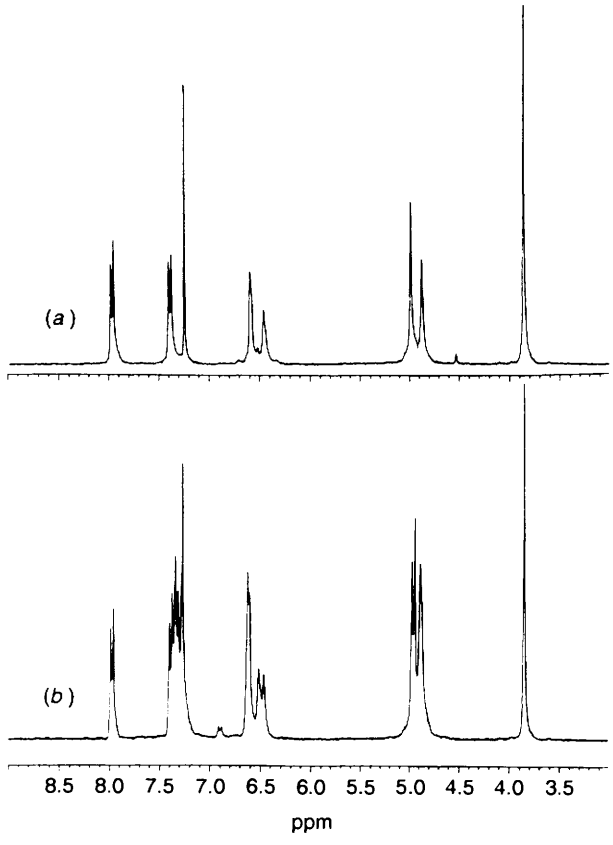


Fig. 2 300 MHz ^{1}H NMR spectra of compounds $(MeO_2C)_{16}$–[G-4]–OH, **9**, (a) and $(MeO_2C)_{16}$–[G-4]–[C]–[G-4], **18**, (b)

produced an emulsion which persisted for a period of weeks. This behaviour may be due to the solubilization of **15** at the dichloromethane/water interface which, in turn, stabilizes the interface. Further work to define and utilize this phenomenon is in progress.

Characterization.—As with our previous studies, the high symmetry of the dendrimers allowed ^{1}H and ^{13}C NMR spectroscopy to be of great use in confirming the structures produced according to our synthetic strategy and in determining the purity of these materials. Fig. 2(*a*) shows the ^{1}H NMR spectrum for the fourth generation alcohol $(MeO_2C)_{16}$–[G-4]–OH **9**, which has 16 methyl ester groups at the chain ends. Some distinct features are apparent: the terminal phenyl ring, which is *para*-substituted with a methyl ester, gives rise to an AB quartet at 7.40 and 8.00 ppm for the phenyl ring while the resonance for the methyl groups appears at 3.80 ppm. The resonances for the aromatic protons of the internal 3,5-dioxybenzyl groups are observed at 6.47–6.63 ppm and all benzylic protons resonate at 4.91–5.02 ppm, except those of the unique hydroxymethyl group at the focal point that appear at 4.58 ppm. Integration of these respective areas and comparison with each other confirms not only the generation number but also the structure. In accord with our previous work, changes in resonances occurring upon conversion of the dendritic alcohol to the corresponding bromide and on attachment of the bromide to the polyfunctional core **11**, were used to monitor product purities. The synthesis of hybrid macromolecules such as **18** was conveniently followed by size-exclusion chromatography (SEC) and NMR spectroscopy. Fig. 2(*b*) shows the ^{1}H NMR spectrum of **18** which, on comparison with **9**, reveals resonances for the two different types of terminal phenyl groups. The resonance for one half of the ABq for the *p*-(MeO_2C) substituted phenyl rings was observed at 8.00 ppm while the multiplet at 7.25–7.50 ppm is due to the unsubstituted phenyl rings as well as the other half of the ABq for the *p*-(MeO_2C) substituted phenyl rings and one half of the ABq resonances for the core protons. The small doublet at 7.00 ppm is due to the other half of an ABq for the core molecule. Added complexity is also observed in the benzyl CH_2 region. The above results for the ^{1}H NMR spectra were mirrored in the ^{13}C NMR spectra which added further support to the structural assignments. Each of the different carbon resonances were calculated for the structures and found to agree with the observed resonances of the spectra. The purity of the dendritic macromolecules was also confirmed by elemental analysis and size-exclusion chromatography (SEC). As shown previously,[9] size-exclusion chromatography was extremely useful due to the large molecular weight changes that occur on generation growth and on coupling to the core molecules. For example, the purity of hybrid macromolecule **18** is easily ascertained by SEC since the molecular weight of the product **18** is 7654 compared to less than 4000 for both individual starting materials.

Thermal Properties.—The thermal behaviour of dendritic macromolecules has recently been studied in detail.[10] The glass transition temperature was found to be dependent on the molecular weight of the dendrimer, the surface functional groups and the internal building blocks. For the methyl ester-terminated dendritic macromolecules, the glass transition temperature was also found to increase with molecular weight with $(MeO_2C)_{32}$–$[G\text{-}4]_2$–[C], **12**, having a T_g of 59 °C. On hydrolysis to give the corresponding acid-terminated dendrimer $(HO_2C)_{32}$–$[G\text{-}4]_2$–[C], **13**, the glass transition temperature increased to 142 °C. Since the interior polyether core is the same in both cases, the increase of 83 °C is due to the existence of hydrogen bonds involving the acid terminal groups. Therefore, the glass transition temperature is not due only to interactions between the surface functional groups but is a combination of effects from the surface functional groups as well as the interior building blocks. The hybrid macromolecule $(MeO_2C)_{16}$–[G-4]–[C]–[G-4], **18**, showed a single glass transition temperature at 48 °C. This value is intermediate between the values for the two parent hydrocarbons, 38 °C for $[G\text{-}4]_2$–[C][10] and 59 °C for $(MeO_2C)_{32}$–$[G\text{-}4]_2$–[C], **12**, and agrees with the value calculated from traditional equations for linear block copolymers. However, the acid-terminated hybrid macromolecule $(HO_2C)_{16}$–[G-4]–[C]–[G-4], **20**, showed two glass transition temperatures at 28 °C and 104 °C (Fig. 3). This is the first example of phase separation in dendritic block copolymers. It is interesting to note that the two glass transition temperatures are decreased when compared to the T_g's of the homopolymers, 38 °C for $[G\text{-}4]_2$–[C] and 142 °C for $(HO_2C)_{32}$–$[G\text{-}4]_2$–[C], **13**, respectively. This may be due to the existence of discrete domains resulting from the aggregation of like blocks within

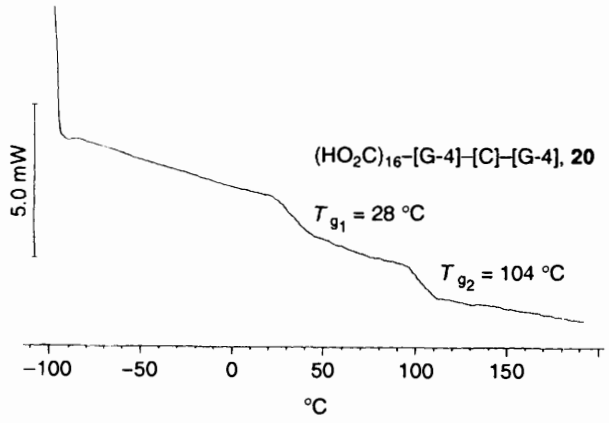
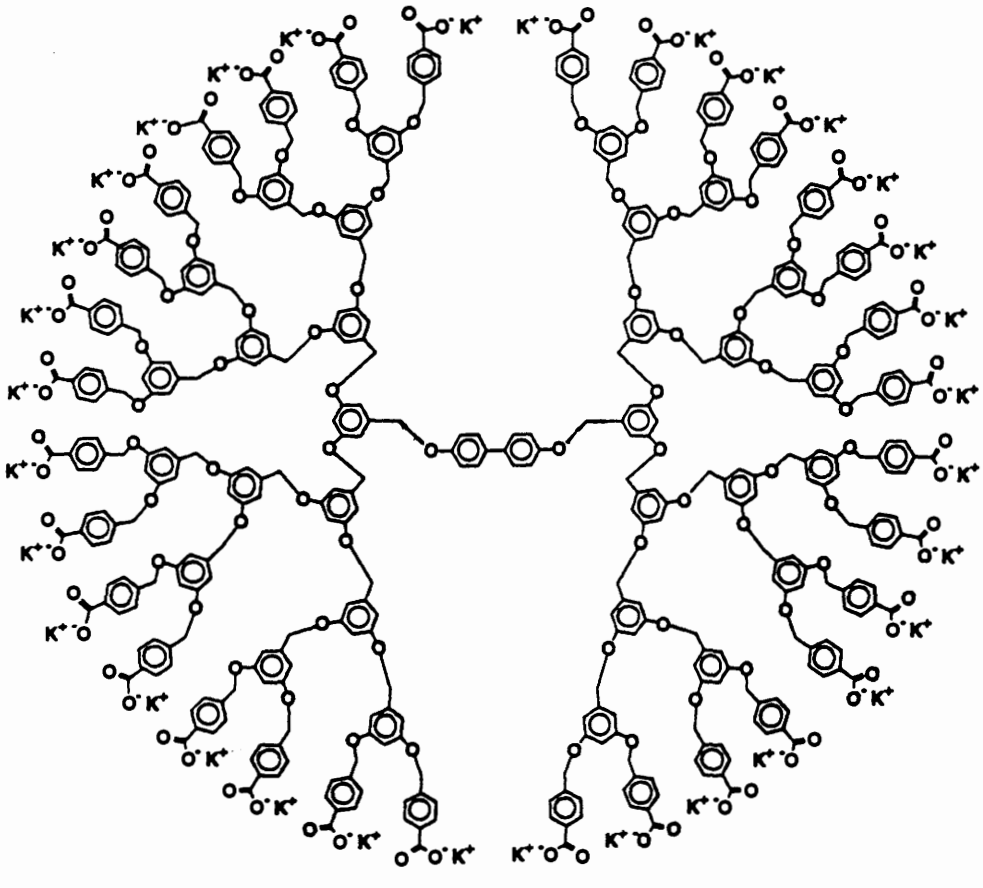


Fig. 3 DSC trace for the carboxy- and phenyl-terminated dendritic diblock copolymer $(HO_2C)_{16}$-[G-4]-[C]-[G-4], **20**

the bulk of the material. In view of the restricted geometrical structure of the globular copolymers these domains are expected to be quite small.

Solubilization Studies.—It has been widely documented that the solubility of hydrophobic compounds in water can be dramatically enhanced by the addition of a surfactant molecule at concentrations above its critical micelle concentration (CMC).[11] If dendritic macromolecules such as **14** (Fig. 4) behave as unimolecular micelles, it would be expected that the solubility of hydrophobic molecules would be increased. However, it should be stressed that since the critical micelle concentration has no meaning when applied to dendrimers, increased solubilization should be observed at all concentrations. Numerous methods and hydrophobic molecules have been used in solubility studies.[12] One of the most studied molecules is pyrene and a recent experimental technique used in solubilization studies involves sonication at elevated temperatures. Therefore, we initially employed both pyrene and sonication in our investigation. To test our system, an excess of pyrene was sonicated at 50 °C in doubly distilled water, filtered, and the resultant solution examined by UV–VIS spectroscopy. Since it has been shown[13] that within experimental error there is no change in the absorption coefficient with changes in solvent for various simple arenes, literature values for ε_{max} were used. This gave a saturated concentration of pyrene in water of 8.0×10^{-7} mol dm^{-3}, which is in good agreement with literature values.[14] Under the same conditions, saturation of pyrene in an aqueous solution of the dendrimer **14** (2.13×10^{-4} mol dm^{-3}) resulted in a significant increase in the concentration of pyrene to 9.47×10^{-5} mol dm^{-3}, *ca.* 120-fold increase when compared to pure water. Therefore, on average, a single dendrimer molecule dissolves 0.45 molecule of pyrene. The solubilizing ability of unimolecular dendritic micelles such as **14** can be better appreciated if we compare to the result obtained for a 9×10^{-3} mol dm^{-3} (*ca.* 10% above CMC) sodium dodecyl sulfate (SDS) solution where the saturation concentration of pyrene was 1.35×10^{-4} mol dm^{-3}, correlating to 0.93 pyrene molecules per micelle. In this calculation, it is assumed that the aggregation number for SDS is 62 molecules per micelle[15] for a 'micelle molecular weight' of nearly 18 000, over twice that of our dendritic molecule **14**.

The very high solubilizing power of the polyether dendrimers **14** may be related to formation of stabilizing π–π interactions with pyrene. To further investigate, the solubilization of a range of polycyclic aromatic compounds was studied. Under the same



14

Fig. 4 Water soluble unimolecular dendritic polyether micelle, **14**

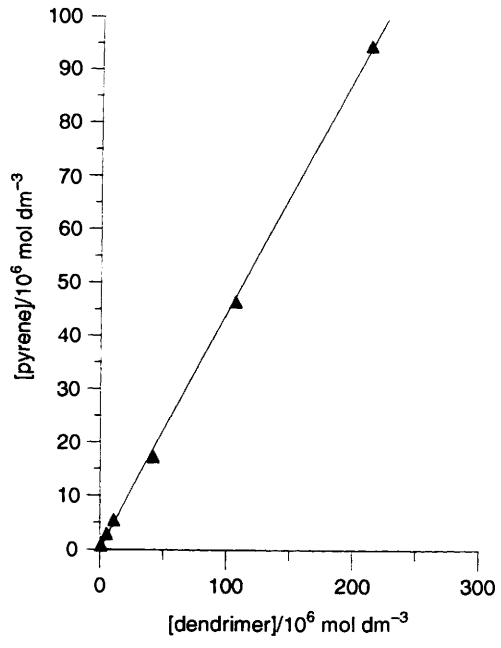


Fig. 5 Solubility of pyrene as a function of the concentration of dendrimer **14** in water

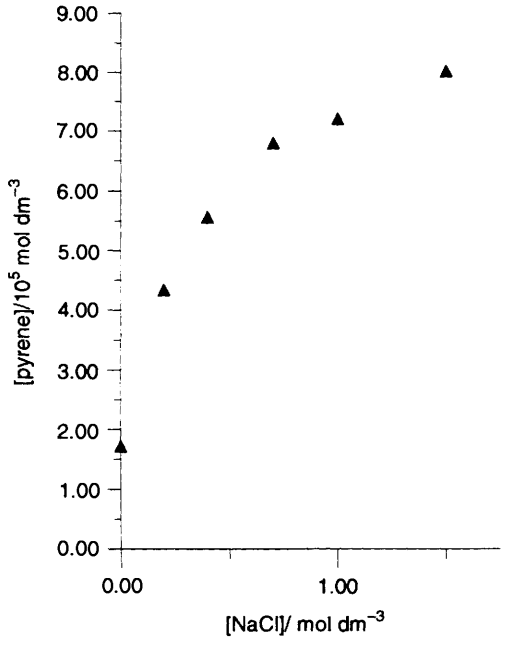


Fig. 6 Solubility of pyrene in a solution of 4.26×10^{-5} mol dm^{-3} dendrimer **14** as a function of NaCl molarity

conditions, and again using a 2.13×10^{-4} mol dm^{-3} dendrimer solution, the saturation concentration of anthracene was found to be increased by 58 times, 1,4-diaminoanthraquinone by 56 times, and 2,3,6,7-tetranitrofluorenone by 258 times on comparison with pure water. The much larger increase for the electron-deficient tetranitrofluorenone on comparison with the other polyaromatics supports the concept of stabilization by π–π interactions since the electron-deficient tetranitrofluorenone would be expected to be stabilized to a greater degree by the electron-rich 3,5-dioxybenzyl building blocks than would be the case for the other polycyclic aromatic compounds.

The change in the saturated concentration of pyrene with changes in the concentration of dendrimer **14** is shown in Fig. 5. As can be seen, there is a linear relationship between the concentration of pyrene and the concentration of dendrimer, with compound **14** demonstrating solubilizing ability at concentrations as low as 5×10^{-7} mol dm^{-3}. This is in marked contrast with traditional micelle behaviour where essentially zero solubility enhancement occurs below the critical micelle concentration (8.1×10^{-3} mol dm^{-3} for SDS).[15] The effect on the solubility of pyrene in dendrimer **14** solutions with the addition of neutral salts was also investigated. Fig. 6 shows the variation in saturated concentration of pyrene with increasing concentration of sodium chloride for a 4.26×10^{-5} mol dm^{-3} solution of **14**. A significant increase in the saturation concentration of pyrene was observed with increasing concentration of NaCl. At a NaCl concentration of 1.5 mol dm^{-3}, each dendrimer molecule dissolves an average of 1.9 molecules of pyrene. This salt effect may be due to a decrease in the concentration of water within the interior of the dendrimer as the ionic strength of the aqueous solution increases. This would lead to a corresponding increase in the hydrophobic nature of the local microenvironment within the dendrimer which would favour pyrene solubilization. A similar effect is observed in the solubilization of polycyclic aromatic by aqueous poly(methacrylic acid) solution at low degrees of neutralization.[16]

As we have demonstrated above, unimolecular dendritic micelles, such as **14**, do not display a critical micelle concentration and solubilize hydrophobic molecules even at very low concentrations. Therefore, the possibility exists for the development of a novel, recyclable, solubilization and extraction system. Upon solubilization of a hydrophobic molecule, such as pyrene, the molecules of pyrene reside in the interior of the dendrimer. When the pH of the solution is adjusted such that the dendrimer is precipitated, the pyrene molecules remain within the hydrophobic dendrimer interior and are precipitated with the dendrimer. Upon dissolution in an appropriate organic solvent, both the dendrimer and the pyrene become soluble and the pyrene migrates into the bulk solution. Treatment of this solution with aqueous base separates the pyrene from the dendrimer, as the dendrimer is extracted into the aqueous phase. Since the dendrimer is now present as its polyanion it is again able to extract hydrophobic molecules and the above cycle can be repeated. This concept was tested with the above polycarboxylate dendrimer **14** and pyrene as the hydrophobic solute. Addition of glacial acetic acid to an aqueous solution of **14**, saturated with pyrene, caused precipitation of the dendrimer as its carboxylic acid form **13**. Collection of this precipitate resulted in a +95% recovery of the original amount of **14** used in solubilizing the pyrene and gave a clear aqueous solution which was shown to contain essentially no pyrene. Upon dissolution of the precipitate in tetrahydrofuran, the UV–VIS spectrum showed peaks for both the carboxylic acid-terminated dendrimer **13** and pyrene. From the extinction coefficient for pyrene in tetrahydrofuran it was calculated that essentially all of the solubilized pyrene had been precipitated with the dendrimer and then subsequently redissolved in tetrahydrofuran. Extraction of this solution with aqueous KOH gave a tetrahydrofuran solution containing essentially only pyrene. Conversely, the aqueous solution was found to contain the dendrimer **14** with only trace amounts of pyrene. The dendrimer, **14**, which was recovered from the basic solution was capable of solubilizing pyrene with the same efficiency as above and, therefore, the potential exists for a cyclic procedure. It was also shown that sonication did not cause any detectable degradation of the dendrimer **14**.

Conclusion.—The use of *p*-(methoxycarbonyl)benzyl as a terminal group and 3,5-dihydroxybenzyl alcohol as a building block in the preparation of dendritic macromolecules that are subsequently treated with base to render the chain ends ionic

has extended the concept of unimolecular micelles to a family of electron-rich dendritic polyether macromolecules which act as micelles. The dendrimers were shown to have solubilizing abilities similar to sodium dodecyl sulfate micelles but are active over a much wider concentration range. It has also been demonstrated that non-covalent interactions between the dendrimer and solute can lead to preferential solubilization. Tailor-made and specific inclusion sites in unimolecular micelles are, therefore, possible. The potential to develop a recyclable solubilization and extraction system was demonstrated. The synthesis of hybrid macromolecules containing a hydrophobic surface sector and a hydrophilic surface segment was demonstrated using the control provided by the convergent growth approach. An example of this type of dendritic block copolymer was shown to have the first reported example of phase separation in a dendritic block copolymer.

Experimental

General Directions.—M.p.s and glass transition temperatures were determined on a Mettler DSC 30 instrument. IR spectra were recorded on a Perkin-Elmer spectrophotometer as thin films on NaCl disks. UV–VIS spectra were recorded on a Hewlett-Packard 210 spectrophotometer. ^{1}H NMR spectra were recorded on solutions in $CDCl_3$, unless otherwise noted, on a Bruker AM 200 (200 MHz) or WM 300 (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at either 50 or 75 MHz on a Bruker AM 200 (200 MHz) or WM 300 (300 MHz) spectrometer respectively, with the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 with EI ionization. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Size exclusion chromatography was carried out on an IBM LC/9560 chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed with GPC-PRO software, version 3.12 (Viscotek Corp.). Three 5 μm Polymer Laboratories columns (300 × 7.7 mm) connected in series in order of increasing pore size (500 Å, 1000 Å, mixed bed C) were used with THF as solvent.

Methyl p-*Bromomethylbenzoate* **1**.—A solution of methyl *p*-hydroxymethylbenzoate (50.0 g, 0.30 mol) in dry benzene was stirred under nitrogen at 0 °C. Phosphorus tribromide (27.1 g, 9.50 cm^3, 0.10 mol) was added dropwise to the solution which was then allowed to warm to room temperature. After 2 h, the reaction mixture was evaporated to dryness and partitioned between water (250 cm^3) and CH_2Cl_2 (250 cm^3). The aqueous layer was extacted with CH_2Cl_2 (2 × 150 cm^3) and the combined extracts were dried and evaporated to dryness. The crude product was recrystallized from heptane to give **1** as a white solid (86%); ν_{max}/cm^{-1} 1715, 1595, 1365 and 1160; $\delta_H(CDCl_3)$ 3.90 (s, 3 H, OCH_3), 4.49 (s, 2 H, CH_2Br) and 7.44 and 8.01 (ABq, 4 H, *J* 7, PhH); $\delta_C(CDCl_3)$ 33.23, 52.01, 126.78, 129.16, 129.55, 141.64 and 166.60; *m*/*z* (EI) 228/230 (*ca.* 1:1).

General Procedure for the Synthesis of Dendritic Benzyl Alcohols.—A mixture of the appropriate dendritic benzyl bromide (2.05 equiv.), 3,5-dihydroxybenzyl alcohol **2** (1.00 equiv.), potassium carbonate (2.50 equiv.) and 18-crown-6 (0.2 equiv.) in acetone was heated at reflux and stirred vigorously under nitrogen for 24 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2 and the aqueous layer was extracted with CH_2Cl_2 (× 3). The combined extracts were dried ($MgSO_4$) and evaporated and the crude product was purified as outlined in the following text.

General Procedure for the Synthesis of Dendritic Benzyl Bromides.—To a solution of the appropriate dendritic benzyl alcohol (1.00 equiv.) in the minimum amount of dry tetrahydrofuran was added triphenylphosphine (1.25 equiv.) and carbon tetrabromide (1.25 equiv.). The reaction mixture was stirred at room temperature under nitrogen, while being monitored by TLC. Additional aliquots of CBr_4 and PPh_3 were added at *ca.* 15 min intervals, if necessary to force completion of reaction. In some cases, decomposition products caused the reaction mixture to turn bright yellow. If this occurred, the reaction was immediately quenched to prevent further and rapid decomposition. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (× 3). The combined extracts were dried ($MgSO_4$) and evaporated to dryness and the crude product was purified as outlined in the following text.

$(MeO_2C)_2$–[G-1]–OH **3**. This compound was prepared from methyl 4-bromomethylbenzoate **1** and purified by flash chromatography eluting with CH_2Cl_2 and then with gradual increasing proportions of ether (to 1:9 ether–CH_2Cl_2) to give **3** as a white crystalline solid (87%), m.p. 115–117 °C; ν_{max}/cm^{-1} 3600–3100, 1715, 1600, 1370 and 1165; $\delta_H(CDCl_3)$ 3.55 (t, 1 H, *J* 5, OH), 3.90 (s, 6 H, OCH_3), 4.58 (d, 2 H, *J* 5, CH_2OH), 5.08 (s, 4 H, OCH_2), 6.42 (t, 1 H, *J* 2, ArH), 6.55 (d, 2 H, *J* 2, ArH) and 7.46 and 8.03 (ABq, 8 H, *J* 8, PhH); $\delta_C(CDCl_3)$ 51.83, 64.34, 68.83, 100.68, 105.37, 126.59, 128.99, 129.46, 141.79, 143.78, 159.38 and 166.55; *m*/*z* (EI) 436 (Found: C, 69.1; H, 5.4. Calc. for $C_{25}H_{24}O_7$: C, 68.8; H, 5.54%).

$(MeO_2C)_2$–[G-1]–Br **4**. This compound was prepared from $(MeO_2C)_2$–[G-1]–OH **3** and purified by flash chromatography eluting with hexane–CH_2Cl_2 (1:1) and then with gradually increasing proportions of $CHCl_2$ (to pure CH_2Cl_2) to give **4** as a white crystalline solid (83%); m.p. 139–140 °C; ν_{max}/cm^{-1} 1720, 1600, 1360 and 1160; $\delta_H(CDCl_3)$ 3.89 (s, 6 H, OCH_3), 4.39 (s, 2 H, CH_2Br), 4.95 (s, 4 H, OCH_2), 6.46 (t, 1 H, *J* 2, ArH), 6.58 (d, 2 H, *J* 2, ArH) and 7.41 and 8.01 (ABq, 8 H, *J* 8, PhH); $\delta_C(CDCl_3)$ 33.31, 52.14, 69.10, 102.12, 108.26, 126.95, 129.74, 129.87, 139.98, 141.68, 159.71 and 166.75; *m*/*z* (EI) 499 (Found: C, 59.8; H, 4.6. Calc. for $C_{25}H_{23}BrO_6$: C, 60.1; H, 4.64%).

$(MeO_2C)_4$–[G-2]–OH **5**. This compound was prepared from $(MeO_2C)_2$–[G-1]–Br **4** and purified by flash chromatography eluting with CH_2Cl_2 and then with gradually increasing proportions of ether (to ether–CH_2Cl_2, 1:9) followed by recrystallization from CH_2Cl_2–hexane (4:1) to give **5** as a white solid (91%); ν_{max}/cm^{-1} 3500–3100, 1715, 1600, 1375 and 1160; $\delta_H(CDCl_3)$ 2.48 (t, 1 H, *J* 5, OH), 3.85 (s, 12 H, OCH_3), 4.56 (d, 2 H, *J* 5, CH_2OH), 4.91 and 5.03 (each s, 12 H, OCH_2), 6.43 and 6.49 (each t, 3 H, *J* 2, ArH), 6.54 and 6.62 (d, 6 H, *J* 2, ArH) and 7.42 and 8.00 (ABq, 16 H, *J* 8, PhH); $\delta_C(CDCl_3)$ 52.00, 64.77, 69.14, 69.45, 100.85, 101.35, 105.40, 106.21, 126.79, 129.44, 129.68, 141.77, 143.67, 159.63, 159.68 and 166.66 (Found: C, 70.2; H, 5.2. Calc. for $C_{57}H_{52}O_{15}$: C, 70.1; H, 5.36%).

$(MeO_2C)_4$–[G-2]–Br **6**. This compound was prepared from $(MeO_2C)_4$–[G-2]–OH **5** and purified by flash chromatography eluting with hexane–CH_2Cl_2 (1:2) and then with gradually increasing proportions of CH_2Cl_2 (to ether–CH_2Cl_2, 1:19) to give **6** as a white solid (86%); ν_{max}/cm^{-1} 1715, 1595, 1370 and 1165; $\delta_H(CDCl_3)$ 3.90 (s, 12 H, OCH_3), 4.38 (s, 2 H, CH_2Br), 4.94 and 5.07 (s, 12 H, OCH_2), 6.45 and 6.52 (each t, 3 H, *J* 2, ArH), 6.58 and 6.64 (d, 6 H, *J* 2, ArH) and 7.45 and 8.02 (ABq, 16 H, *J* 8, PhH); $\delta_C(CDCl_3)$ 33.51, 52.12, 69.33, 69.78, 101.58, 101.79, 106.39, 108.10, 126.92, 129.64, 129.83, 139.20, 139.77, 141.81, 159.78 and 166.73 (Found: C, 66.0; H, 4.9. Calc. for $C_{57}H_{51}BrO_{14}$: C, 65.8; H, 4.94%).

$(MeO_2C)_8$–[G-3]–OH **7**. This compound was prepared from $(MeO_2C)_4$–[G-2]–Br **6** and purified by flash chromatography eluting with CH_2Cl_2 and then with gradually increasing proportions of ether (to ether–CH_2Cl_2, 1:9) to give **7** as a colourless glass (76%); ν_{max}/cm^{-1} 3500–3100, 1710, 1595, 1370

$\delta_H(CDCl_3)$ 2.17 (t, 1 H, *J* 5, OH), 3.88 (s, 24 H, OCH_3), 4.57 (d, 2 H, *J* 5, CH_2OH), 4.90 and 5.02 (each s, 28 H, OCH_2), 6.48–6.63 (m, 21 H, ArH) and 7.42 and 8.00 (ABq, 32 H, *J* 8, PhH); $\delta_C(CDCl_3)$ 52.06, 64.99, 69.26, 69.70, 101.09, 101.38, 101.49 105.60, 106.25, 106.35, 126.88, 129.57, 129.76, 139.30, 139.36 141.80, 143.68, 159.74, 159.84 and 166.69 (Found: C, 70.6; H, 5.3. Calc. for $C_{121}H_{108}O_{31}$: C, 70.6; H, 5.29%).

$(MeO_2C)_8$–[G-3]–Br **8**. This compound was prepared from $(MeO_2C)_8$–[G-3]–OH **7** and purified by precipitation into ether followed by flash chromatography eluting with CH_2Cl_2 and then with gradually increasing portions of ether (to 3% ether–CH_2Cl_2) to give **8** as a colourless glass (88%); ν_{max}/cm^{-1} 1715, 1600, 1370 and 1165; $\delta_H(CDCl_3)$ 3.89 (s, 24 H, OCH_3), 4.36 (s, 2 H, CH_2Br), 4.94 and 5.05 (s, 28 H, OCH_2), 6.50–6.52 and 6.60–6.63 (each m, 21 H, ArH) and 7.44 and 8.00 (ABq, 32 H, *J* 6, PhH); $\delta_C(CDCl_3)$ 33.48, 52.09, 69.44, 69.87, 70.02, 101.68, 102.28, 106.51, 108.28, 126.95, 129.75, 129.86, 139.13, 139.46, 139.85, 141.88, 159.89, 159.95, 160.00 and 166.73 (Found: C, 68.3; H, 5.0. Calc. for $C_{121}H_{107}BrO_{30}$: C, 68.5; H, 5.08%).

$(MeO_2C)_{16}$–[G-4]–OH **9**. This compound was prepared from $(MeO_2C)_8$–[G-3]–Br **8** and purified by flash chromatography eluting with 1.5% methanol–CH_2Cl_2 to give **9** as a colourless glass (88%); ν_{max}/cm^{-1} 3400–3100, 1715, 1600, 1370 and 1165; $\delta_H(CDCl_3)$ 3.86 (s, 48 H, OCH_3), 4.54 (s, 2 H, CH_2OH), 4.89 and 5.00 (each s, 60 H, OCH_2), 6.43–6.62 (m, 45 H, ArH), 7.39 and 7.96 (ABq, 64 H, *J* 6, PhH); $\delta(CDCl_3)$ 51.91, 64.80, 69.17, 69.63, 100.79, 101.45, 105.61, 106.22, 106.34, 126.78, 129.51, 129.65, 139.24, 139.34, 141.76, 143.76, 159.70, 159.82 and 166.53 (Found: C, 71.1; H, 5.29. Calc. for $C_{249}H_{220}O_{63}$: C, 70.9; H, 5.25%).

$(MeO_2C)_{16}$–[G-4]–Br **10**. This compound was prepared from $(MeO_2C)_{16}$–[G-4]–OH **9** and purified by precipitation into ether followed by flash chromatography eluting with 10% ether–CH_2Cl_2 to give **10** as a colourless glass (85%); ν_{max}/cm^{-1} 1715, 1595, 1370 and 1165; $\delta_H(CDCl_3)$ 3.87 (s, 48 H, OCH_3), 4.32 (s, 2 H, CH_2Br), 4.88 and 4.99 (s, 60 H, OCH_2), 6.45–6.70 (m, 45 H, ArH) and 7.43 and 8.03 (ABq, 64 H, *J* 7, PhH); $\delta_C(CDCl_3)$ 33.44, 51.95, 69.24, 69.69, 69.81, 101.52, 102.07, 106.27, 106.40, 108.21, 127.14, 129.58, 129.70, 139.11, 139.25, 139.37, 139.73, 141.79, 159.76, 159.87, 159.93 and 166.57 (Found: C, 70.0; H, 5.44. Calc. for $C_{249}H_{219}BrO_{62}$: C, 69.8; H, 5.15%).

$(MeO_2C)_{16}$–$[G-4]_2$–[C] **12**. A mixture of $(MeO_2C)_{16}$–[G-4]–Br **10** (2.75 g, 0.64 mmol), 4,4′-dihydroxybiphenyl **11** (54.0 mg, 0.29 mmol), potassium carbonate (1.0 g) and 18-c-6 (25 mg) in tetrahydrofuran (100 cm^3) was heated at reflux under nitrogen with vigorous stirring for 48 h. After completion of the reaction an excess of **11** (10 equiv.) was added to the reaction mixture. It was then evaporated to dryness and partitioned between CH_2Cl_2 (100 cm^3) and water (100 cm^3). The aqueous layer was then extracted with CH_2Cl_2 (3 × 50 cm^3) and the combined extracts were dried ($MgSO_4$) and evaporated to dryness. The crude product was purified by flash chromatography eluting with 10% ether–CH_2Cl_2 and then with gradually increasing portions of ether (to 15% ether–CH_2Cl_2) to give **12** as a colourless glass (81%); ν_{max}/cm^{-1} 1720, 1595, 1365 and 1170; $\delta_H(CDCl_3)$ 3.85 (s, 96 H, OCH_3), 4.85–5.07 (m, 124 H, OCH_2), 6.42–6.70 (m, 90 H, ArH), 6.89 (A of ABq, 4 H, *J* 9, core ArH) and 7.38 and 7.97 (ABq and B of ABq, 132 H, *J* 8, PhH and core ArH); $\delta_C(CDCl_3)$ 52.00, 69.34, 69.78, 69.92, 101.62, 106.37, 106.48, 115.03, 126.89, 127.55, 129.68, 129.77, 133.50, 139.33, 139.40, 139.44, 141.85, 159.83, 159.96, 160.02 and 166.63 (Found: C, 71.2; H, 5.45. Calc. for $C_{510}H_{446}O_{126}$: C, 71.3; H, 5.23%).

$\{(HO_2C)_{16}$–$[G-4]\}_2$–[C] **13**. To a solution of $(MeO_2)_{16}$–$[G-4]_2$–[C] **12** (1.00 g, 0.117 mmol) in tetrahydrofuran (25 cm^3) was added potassium hydroxide (2.00 g, 35.7 mmol) dissolved in water (3 cm^3). Methanol (*ca.* 10 cm^3) was then added to this two-phase system to give a homogeneous solution. This was then heated at reflux for 6 h during which time a precipitate formed; the reaction mixture was then evaporated to dryness and the residue redissolved in water (15 cm^3) and the mixture heated at reflux for 12 h. After cooling to room temperature the reaction mixture was added dropwise to a stirred mixture of water (600 cm^3) and glacial acetic acid (10 cm^3). The precipitate which formed was collected by vacuum filtration and dried to give acid **13** as a white solid (94%); ν_{max}/cm^{-1} 3500–2500, 1695, 1595 and 1160; $\delta_H([^2H_8]$-THF) 4.92 and 5.05 (s, 60 H, OCH_2), 6.51–6.70 (m, 45 H, ArH), 6.91 (A of ABq, 4 H, *J* 6, core ArH) and 7.45 and 7.98 (ABq, 64 H, *J* 7, PhH); $\delta_C(CDCl_3)$ 69.99, 70.47, 100.02, 101.76, 106.14, 106.56, 107.43, 115.07, 127.70, 130.60, 131.18, 133.65, 136.82, 140.11, 140.48, 140.72, 140.84, 143.21, 148.09, 157.65, 160.97, 161.11 and 167.45 (Found: C, 70.2; H, 4.9. Calc. for $C_{478}H_{382}O_{126}$: C, 70.5; H, 4.70%).

$(MeO_2C)_{16}$–[G-4]–[C]–[G-4] **18**. A mixture of $(MeO_2C)_{16}$–[G-4]–Br **10** (464 mg, 0.11 mmol), [G-4]–[C]–OH **17** (375 mg, 0.11 mmol), potassium carbonate (500 mg), and 18-c-6 (25 mg) in tetrahydrofuran (50 cm^3) was heated at reflux under nitrogen with vigorous stirring for 12 h. The reaction mixture was then evaporated to dryness and partitioned between CH_2Cl_2 (100 cm^3) and water (100 cm^3). The aqueous layer was then extracted with CH_2Cl_2 (3 × 50 cm^3) and the combined extracts were dried ($MgSO_4$) and evaporated to dryness. The crude product was purified by flash chromatography eluting with 2% methanol–CH_2Cl_2 to give **18** as a colourless glass (71%); ν_{max}/cm^{-1} 1715, 1595, 1365 and 1160; $\delta_H(CDCl_3)$ 3.89 (s, 48 H, OCH_3), 4.92, 4.98 and 5.01 (each s, 124 H, OCH_2), 6.50–6.67 (m, 90 H, ArH), 6.94 (A of ABq, 4 H, *J* 7, core ArH), 7.30–7.48 (m, 116 H, ArH) and 8.05 (B of ABq, 32 H, *J* 7, PhH); $\delta_C(CDCl_3)$ 51.96, 69.26, 69.73, 69.88, 69.97, 101.56, 106.33, 106.42, 115.01, 127.16, 127.86, 128.24, 128.45, 129.61, 131.96, 133.39, 136.74, 139.29, 139.40, 141.82, 157.71, 159.78, 159.92, 159.99, 160.07 and 166.60 (Found: C, 75.2; H, 5.6. Calc. for $C_{478}H_{414}O_{94}$: C, 74.9; H, 5.45%).

$(HO_2C)_{16}$–[G-4]–[C]–[G-4] **20**. To a solution of $(MeO_2C)_{16}$–[G-4]–[C]–[G-4] **18** (250 mg, 0.033 mmol) in tetrahydrofuran (15 cm^3) was added potassium hydroxide (500 mg, 8.9 mmol) dissolved in water (2 cm^3). Methanol (*ca.* 7 cm^3) was then added to this two-phase system to give a homogeneous solution. This was then heated at reflux for 3 h during which time a precipitate formed. The entire reaction mixture was then evaporated to dryness and the residue redissolved in water (10 cm^3). The hydrolysis was continued by heating at reflux for 12 h. After cooling to room temperature, the reaction mixture was added dropwise to a stirred mixture of water (600 cm^3) and glacial acetic acid (10 cm^3). Acidification with acetic acid only resulted in partial protonation of the product which precipitated from solution. In order to complete protonation of the dendrimer salt a silylation process was used. The partially neutralized precipitate which formed was collected by vacuum filtration, dissolved in THF and trimethylsilyl chloride (5 cm^3) was added to the solution. This mixture was stirred at room temperature for 15 min and then precipitated into water. The precipitate of fully protonated product was collected by suction filtration and dried to give the acid **20** as a white solid (93%); ν_{max}/cm^{-1} 3500–2500, 1690, 1595 and 1155; $\delta([^2H_8]$-THF) 4.93, 4.97 and 5.02 (s, 60 H, OCH_2), 6.52–6.69 (m, 45 H, ArH), 6.90 (A of ABq, 4 H, *J* 6, core ArH), 7.19–7.48 (m, 116 H, ArH) and 7.97 (B of ABq, 32 H, *J* 7, PhH); $\delta_C([^2H_8]$-THF) 69.95, 70.52, 101.61, 102.11, 106.78, 106.93, 107.08, 107.22, 125.78, 126.03, 127.66, 128.24, 128.53, 129.04, 129.15, 130.62, 131.17, 138.38, 140.64, 140.71, 140.83, 143.21, 160.96, 161.18 and 167.42 (Found: C, 74.7; H, 5.03. Calc. for $C_{462}H_{382}O_{94}$: C, 74.6; H, 5.18%).

Solubility Measurements.—An excess of hydrophobic aromatic hydrocarbon (finely powdered) was sonicated at 50 °C

with the appropriate solution (water aqueous SDS, or aqueous dendrimer **14**) for 6 h, and then allowed to equilibrate at room temperature for 2 days. The solutions were then filtered twice through 0.45 μm filters. Samples of the clear solution were then transferred to absorption cells, or, if necessary, to volumetric flasks for dilution. The absorbances were measured with a Hewlett-Packard 210 spectrophotometer.

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