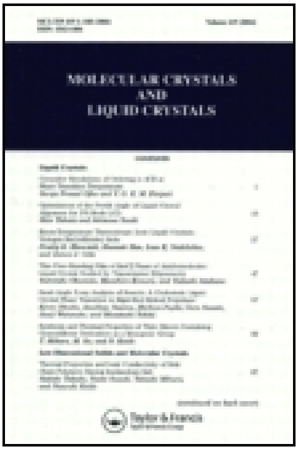

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Nanostructured Materials from Radially Layered Copolymeric Amidoamine-Organosilicon (PAMAMOS) Dendrimers

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Radially layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers have been prepared with hydrophilic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors. At low degrees of surface derivitization with trimethylsilyl- groups these dendrimers significantly reduce water surface tension. At higher degrees they become insoluble and form spread monolayers on water which on compression can sustain surface pressures of over 50 mN/m due to the strong attraction of the PAMAM core to the water surface. When reactive organosilicon terminating units such as methoxysilyl- groups are incorporated, the copolydendrimers can be crosslinked into networks. These new elastomeric or plastomeric dendritic materials have well-defined, nanoscopic domains with the ability to complex and encapsulate within the PAMAM domains, a wide variety of metal compounds and metal atoms.

Keywords: dendrimers; copolymers; surface activity; network formation; encapsulation; nanocomposites

INTRODUCTION

Copolymerization, particularly of blocks of repeat units with very different characteristics, is a common approach to the tailoring of novel polymeric materials and additives. The resulting hybrid macromolecules combine attributes of the parent homopolymers and lead to varied technical applications. For example, homopolymeric polydimethylsiloxane (PDMS), being insoluble in and of lower surface energy than, polymerizing urethanes, is an excellent defoamer in the manufacture of polyurethane elastomers and coatings. However, when copolymerized with alkylene oxides which provide compatibility with the reacting medium, the resultant silicone polyether copolymers are widely used for stabilizing polyurethane foam.

Such exploitation of surface phenomena is a natural consequence of the low surface energy of PDMS which derives primarily from the low interaction forces between methyl groups. As a result, PDMS has a lower surface energy than most common polymers, with the exception of aliphatic fluorocarbon based ones, conferring on its copolymers the thermodynamic potential for accumulation in the surface of other polymers with consequent modification of their surface properties[1]. Since the size of the modified surface region is of the order of the dimensions of the PDMS blocks, i.e. in the nanoscopic regime, such copolymer modified surfaces are essentially two-dimensional nanocomposites.

The behavior of block polymers is dictated not only by the nature of the constituent blocks (i.e. chemical composition) but also by the structure or architecture in which they are united. It has recently been shown that there are four major classes of polymer architecture known to date; linear, cross-linked, randomly branched and dendritic[2]. The dendritic polymer class is the most recent to be recognized and is inevitably the least commercially exploited. However, provided there are adequate examples of the value of a particular compositional component in the other three architectures, there is good reason to anticipate probable new application opportunities in the newer dendritic polymer arena. This is clearly the case for silicones with many established surface applications providing a major sector of industrial interest in these polymers. Consequently, the success of silicone containing copolymers of traditional architecture explains our interest in the surface properties of organosilicon polymer containing copolymeric dendrimers.

Various linear AB, ABA and $(AB)_n$ type polymers have been extensively used to modify material surface properties where A is a compatible or "anchor" block and B is a surface active PDMS block. More recently AXB type terpolymers have also been introduced where X is a functional group or polymer whose presence is desired in a polymer surface but which would be unable to accumulate there were it not for the surface activity or "tethering" capability of the PDMS chain[3]. "Smart surfaces" have been proposed that respond to environmental changes based on this concept. For example, Koberstein et al.[4] have shown that when the functional component is a receptor group such as SiH, the surface switches from the usual PDMS release character to an adhesive nature when presented to an appropriate substrate containing vinyl, allyl or other suitable unsaturated functionality.

Copolymeric surface modifiers based on cross-linked components are less common but do exist. For example, MQ resins modified with poly(alkylene oxides) have been used as dispersants in silicone antifoam compositions and as stabilizers in the mechanical frothing of PVC plastisols[5]. Randomly branched PDMS containing copolymers are very familiar. The previously mentioned silicone-polyether copolymers which dominate the polyurethane foam stabilization market are branched, rake-like structures with the poly(alkylene oxide) chains attached to a PDMS backbone. Many other silicone polymeric surfactants are based on this branched rake architecture.

SYNTHESIS OF PAMAMOS DENDRIMERS

There are two general methods that have been developed for dendrimer preparation, the divergent (core to branch units to surface group) and the convergent (surface group to branch units to central core) synthesis. Our PAMAMOS preparation starts from amine-terminated, ethylenediamine core PAMAM dendrimers obtained from Dendritech Inc., Midland MI USA, which can be used without any further purification. They are prepared by a divergent growth method involving a reiterative sequence of a Michael addition reaction of methyl acrylate to primary amines followed by amidation of the resulting methyl ester intermediate with ethylene diamine. By terminating with only the first of these paired reactions PAMAMs with carbomethoxy terminal functionality can also be formed. The main sequence, however, can be repeated up to generation 10 with approximately a 10 Angstrom (1 nm) increase in dendrimer diameter per generation. At about generation 10 the so-called "dense-packed stage" is reached where reaction rates at the dendrimer surface decrease dramatically and there are major deviations from branching ideality. We have used generation 0 through 4 PAMAMs with ethylenediamine (EDA)cores for PAMAMOS preparation and are far from this sterically limiting region in our present studies. The theoretical molecular weight, number of $-NH_2$ end-groups (providing double that number of -NH reactive sites) and some size data by size exclusion chromatography (SEC) and dilute solution viscometry (DSV) are given in Table I.[6,7] These PAMAM dendrimers are shown in the reaction schemes below as G_x-$(NH_2)_z$, where x is the generation and z the number of terminal amine groups. The size exclusion chromatography (SEC) data are calibrated relative to poly(oxyethylene) standards. DSV stands for dilute solution viscometry. Both techniques were used at 25°C in 0.1 molar citric acid in water of pH 2.7.

TABLE I Molecular characteristics of EDA core PAMAM dendrimers

Generation	Number of End-Groups	MW	Hydrodynamic Radius (Angstroms)	
			SEC	DSV
0	4	517	7.6	-
1	8	1,430	10.8	10.1
2	16	3,256	14.3	14.4
3	32	6,909	17.8	17.5
4	64	14,215	22.4	25.0
5	128	28,826	27.2	32.9
6	256	58,048	33.7	-

Two synthetic routes have been developed for converting from PAMAM to PAMAMOS dendrimers employing different cross-over reactions to go from the wholly organic, divergent PAMAM synthesis to an organosilicon sequence. These are (a) a Michael addition reaction of silicon-containing acrylates shown as Reaction Scheme 1, and (b) a haloalkylation with various silanes and siloxanes shown as Reaction Scheme 2. If the organosilicon intermediate has further reactivity, for example, vinyl functionality, there is the potential for further divergent OS generation development although in this particular case preforming of OS dendrons is preferred because of excess Pt catalyst consumption resulting from complexation of the metal with the PAMAM core.

Scheme 1 (R_1, R_2 and R_3 can be methyl, methoxy or $OSiMe_3$):

$$G_x\text{-}(NH_2)_z + CH_2{=}CHCO_2(CH_2)_3SiR_1R_2R_3 \rightarrow G_x\text{-}[NH_{2-x}\{(CH_2)_2CO_2(CH_2)_3SiR_1R_2R_3\}_x]_z \qquad (1)$$

Scheme 2 (X can be Cl, Br or I and R_1, R_2 and R_3 can be methyl or vinyl):

$$G_x\text{-}(NH_2)_x + XRSiR_1R_2R_3 \rightarrow G_x\text{-}[NH_{2-x}(RSiR_1R_2R_3)_x]_z \qquad (2)$$

For the Michael addition reactions (Scheme 1) methanol was the best solvent. Temperature had no great effect on the reaction progress. Typically, as high as 80-85 % degree of modification of -NH groups was obtained, regardless of which particular acrylate was used. For haloalkylation of PAMAM dendrimers, 1-methyl-2-pyrrolidinone (NMP) was found to be a good solvent. In contrast to Scheme 1, higher temperature had a great influence on these reactions, producing higher degrees of surface modification up to 100%. Two different strategies were used to separate the HX by-product from the resulting copolydendrimers. Either the amino groups of the reacting PAMAM dendrimer were permitted to entrap the by-product during the reaction and the separation was performed in the late stage by adding sodium bicarbonate, or sodium bicarbonate was present from the beginning in the reaction mixture. Since the salts are insoluble in NMP, they could be easily removed by filtration. Under appropriate conditions, this procedure yields quantitative modification of the NH groups of PAMAM dendrimers. The products are soluble in THF, $CHCl_3$, toluene and methanol and either insoluble or only slightly soluble in water.

Further details of the preparation and characterization of PAMAMOS dendrimers are available elsewhere[8-10]. Routinely, these radially layered copolymeric dendrimers are characterized by ^1H, ^{13}C and ^{29}Si NMR, DSC and TGA, GPC, and MALDI-TOF and Electrospray MS. In what follows, the PAMAMOS dendrimers are identified by designations such as 3-1-45TMS. The first number indicates the generation of the PAMAM reagent used in preparation. The second number is the number of OS generations with the 45TMS indicating that 45% of available -NH end-groups were derivatized by trimethylsilyl- functionality. Other acronyms used in this nomenclature include VDM, vinyldimethylsilyl- and MDMO, methyldimethoxysilyl- functionality.

SURFACE PROPERTIES OF PAMAMOS DENDRIMERS

Most of our dendrimers are water insoluble and can conveniently be studied as spread films on water by the Langmuir trough technique. For a polymer to form a spread film there must be sufficient attraction to the subphase which usually derives from polar, hydrophilic entities. Although long-chain hydrocarbon oils do not form spread films, PDMS polymers do, implying a sufficient water attracting contribution from the backbone siloxane linkages. The relatively low collapse pressures of PDMS films on water, *circa* 10 mN/m, indicate that this is a relatively weak attraction, consistent with the siloxane/water hydrogen bond. The PAMAM interiors of the PAMAMOS dendrimers have amide and amine groups capable of much stronger hydrogen bonding with the water surface, so higher surface pressures than those achieved with PDMS ought to be possible, provided the organosilicon component does not prevent these hydrophilic groups from interacting with the water surface.

Another feature of PDMS spread films is the plateau region where surface area changes markedly with little additional surface pressure. The traditional model[11] assumed PDMS and other similar siloxane polymer spread films to be in a highly extended configuration at low surface pressure with every siloxane bond in contact with the water surface. As surface pressure increases a transition to a 6-unit helical coil whose axis is parallel to the water surface was postulated. This reconfiguration explained the distinctive plateau in the PDMS surface pressure-area isotherm. Doubts have recently been cast on the validity of this long-standing hypothesis[12], but the plateau can still be seen as a manifestation of the extreme flexibility of the PDMS chain and one would not expect to see similar features in PAMAMOS surface pressure-area isotherms.

The experimental results are in good agreement with these conjectures. Figure 1 is an example of such behavior and Table II summarizes the surface areas for various PAMAMOS dendrimers with one OS layer obtained from such plots. Expectedly, these areas increase with size of the parent PAMAM dendrimer and with the degree of substitution of the NH groups; the compression cycle values are in good agreement with the DSV area data taken from the hydrodynamic radii shown in Table I and assuming the added OS generation can be approximated by the next higher PAMAM generation data.

TABLE II PAMAMOS surface areas

Sample Number	Calculated MW	Area per Molecule (A^2/mol) Compression	Expansion	DSV
3-1-92TMS	11,976	1,640	1,080	2,000
4-1-68TMS	21,760	3,540	2,280	3,400
4-1-88TMS	23,941	3,700	2,510	3,400
4-1-100TMS	25,249	4,490	2,530	3,400
2-1-83VDM	5,880	890	570	1,000
3-1-85VDM	12,245	1,060	830	2,000
4-1-98VDM	26,700	3,590	2,660	3,400

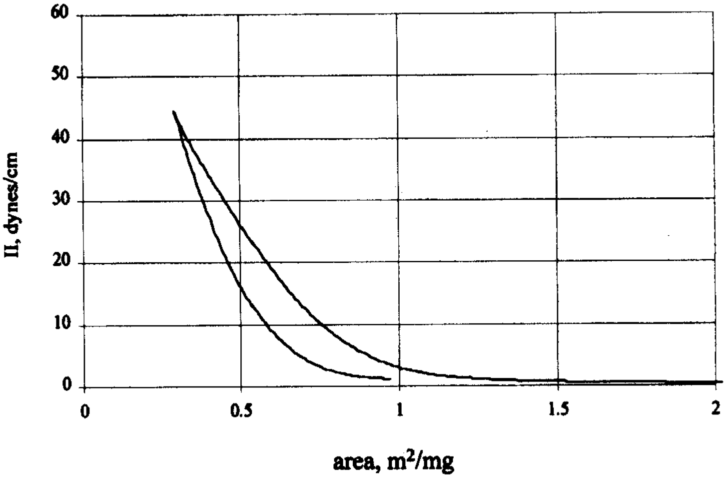

Figure 1 Surface Pressure/Area Isotherm of 4-1-88 TMS

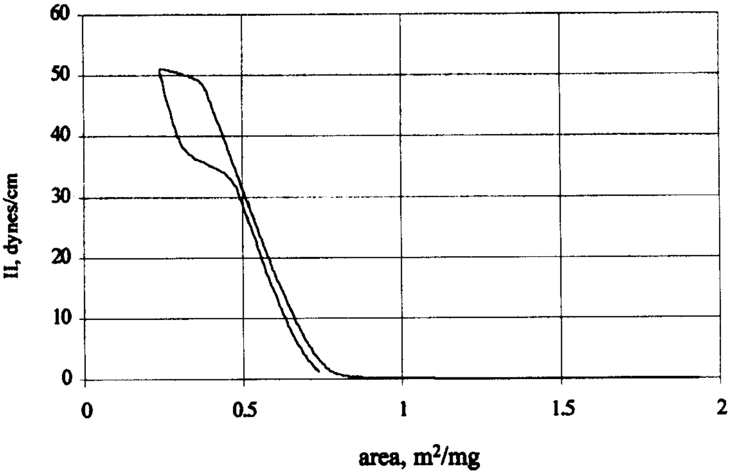

Figure 2 Surface Pressure/Area Isotherm of 3-2-83 TMS

All of the Langmuir plots obtained show some degree of hysteresis with the expansion portion of the plot not reversibly following the preceding compression cycle. Hysteresis is commonplace in polymer surface studies such as contact angle and contact mechanics studies and its occurrence here is not unexpected. The extent of hysteresis experienced is dependent on procedural conditions such as the rate of compression and expansion and the amount of material delivered to the surface. Because of this, we have chosen standard measurement conditions for all the data presented herein, which included a barrier sweep rate of 50 mm/min and an amount of 20 μl chloroform solution. The hysteresis is more marked for dendrimers with lower generation PAMAM interiors and less OS surface modification. In other words, the more open, less congested the dendrimer surface, the more prominent appears to be water penetration of the interior causing the observed hysteresis.

Behavior of PAMAMOS dendrimers with two OS layers is similar to those with one layer. Three OS layers causes a reduction in maximum surface pressure as presumably the polar NH groups of the PAMAM interior are becoming too well sheathed for optimal interaction with the water molecules in the trough surface. One unique surface pressure/area behavior was found for the (3-2-83TMS) PAMAMOS dendrimer shown in Figure 2. This shows a high pressure hysteresis loop but much less significant hysteresis at lower pressure. The plateau-like region at the highest surface pressure is unlikely to be a reconfiguration within the individual macromolecules as happens at much lower pressure for linear PDMS but is believed to be the probable formation of two layers because of the areas occupied in this hysteresis loop. The area of the expansion portion is half that of the compression portion. Double and multiple layer formation on compressing organosilicon polymer spread films have been postulated by other researchers, most notably Godovsky and co-workers[13]. They found up to seven plateaus in surface pressure/area isotherms of cyclolinear polysiloxanes and showed by scanning force microscopy that this stepwise collapse is associated with the formation of mutilayers.

At lower degrees of surface derivitization the copolydendrimers are too water soluble to be studied as spread films, but their surface activity can be characterized by direct solution surface tension measurement using a Cahn balance equipped with a platinum Wilhelmy plate. Plots of surface tension of aqueous solution versus log concentration have been given previously[10] for some water soluble PAMAMOS dendrimers resulting from partial chloromethylsilylation: 3-1-6TMS, 3-1-19TMS and 3-1-45TMS. The degree of surface activity is considerable with values less than 30 mN/m being attained. Although some kinks are evident in these plots, no definite break to a plateau surface tension value, indicative of a critical micelle concentration, is seen up to the highest concentrations (0.5%) we examined. Clearly, micellization would be unlikely with this globular polymer architecture.

Limiting surface areas for these dendrimers, obtained from the approximate form of the Gibbs adsorption isotherm[14] assuming no ionization, are unreasonably low, over a magnitude smaller than expected from the PAMAM dendrimer sizes obtained by dilute solution viscometry and other methods, and from molecular modeling of PAMAMOS dendrimers. Clearly the assumptions are unjustified but we have no estimate of the degree of ionization. Others have also reported unexpectedly low limiting surface area values for related systems, for example, Mahan and Chapman[15] for their fluorinated hydraamphiphiles.

PAMAMOS DENDRIMER-BASED NETWORKS

Functionalized PAMAMOS dendrimers with reactive groups in the outermost surface layer are useful precursors for the preparation of polymer networks of remarkable architecture and composition. They provide new, crosslinked dendritic materials with well-defined, nanoscopic domains of hydrophilic PAMAM and hydrophobic and oleophilic OS compositions. For example, PAMAMOS dendrimers having methyldimethoxysilyl- end-groups can directly form such networks in a facile two-step process. Firstly, water hydrolysis of the methoxysilyl- entities into the corresponding silanols is performed, followed by the condensation of these silanols with the elimination of water to form siloxane interdendrimer bridges. This latter reaction is self-catalyzed by the basic PAMAM interior of the PAMAMOS dendrimer precursor, and, in practice, this whole cross-linking procedure is readily accomplished either by direct exposure to atmospheric moisture, or by controlled addition of water vapor or liquid. These PAMAMOS dendrimer-based networks are clear, transparent and colorless films with very smooth surfaces, and are insoluble in solvents such as methanol, methylene chloride, THF, acetone or water. Depending on the dendrimer precursor used, and on its density of functionality, these films may be either elastomeric or plastomeric. The rate of cure can be accelerated by heating. Efficient curing can be achieved by heating between 60 and 100^{o}C when stable glass temperature products can be achieved within a few hours curing.

Expectedly, the glass temperatures depend on the particular PAMAMOS dendrimer chosen and the composition of the curing system. In general, PAMAMOS dendrimers containing only one layer of the organosilicon branch cells in their exteriors, show T_gs little different from those of the parent PAMAM from which they are derived. However, the T_gs decrease with introduction of a second layer of organosilicon branch cells, reflecting an increase in the content of flexibilizing -Si-C- and -Si-O-Si- units. Thus the thicker the OS exterior of the PAMAMOS dendrimer precursor, the lower the T_g and the more elastomeric is the resultant network. Flexibility also depends on the curing system. Incorporation of tetraethoxysilane (TEOS) leads to an increase in T_g from 10-14^{o}C for an unmodified network to 37^{o}C when 60 mole % of TEOS relative to the amount of methoxy- end-groups present is used. Conversely, addition of α,ω-telechelic linear oligomeric PDMS of 600 M_n decreases the glass temperature to -25^{o}C. Thermal and thermo-oxidative stability of the PAMAMOS dendrimers is predetermined by the stability of the less thermally stable PAMAM interior. TGA patterns of all PAMAMOS samples were similar to their PAMAM parents.

Measurement of quasi-equilibrium contact angles of various liquids show these dendrimer-based networks to have low solid surface energies. Typically, an elastomeric network shows contact angles of 109, 74 and 31 degrees for water, methylene iodide and *n*-hexadecane, respectively. These translate to a solid surface energy of 23.1 mN/m using the geometric mean, Owens and Wendt approach[16]. This is close to the value obtained for an all-methyl surface such as that provided by PDMS (22.8 mN/m) or paraffin wax (25.4 mN/m), expectedly implying that the lowest surface energy entity, the methyl groups, dominate the surface. It also suggests any nano-roughness deriving from the dendritic structure is of too small a scale to affect the measured contact angles. Similar parallels between the contact angle behavior of hyperbranched perfluorinated polymers[17] and similarly substituted, conventional, cross-linked polymers have been reported. Elastomeric dendrimer film samples were also characterized by SEM/EDS, XPS and AFM.

One of the remarkable properties of these PAMAMOS dendrimer networks is their ability to complex and encapsulate within their nanoscopic hydrophilic domains, a wide variety of metals, metal ions, metal oxides, metal sulfides or other metal salts and water soluble organic and organometallic molecules. Examples include Ag^{+1}, Cu^{+2}, Ni^{+2}, Co^{+2}, Pt^{+4}, Fe^{+3} and Au^{+3} ions. The sulfides can be reduced to the metal with hydrazine or sodium borohydride.

SUMMARY

An unusual new family of nanostructured macromolecules has been synthesized and characterized. These radially layered copolymeric poly(amidoamine-organosilicon) (PAMAMOS) dendrimers consist of hydrophiliic polyamidoamine (PAMAM) interiors and hydrophobic organosilicon (OS) exteriors. Two versatile siliconization reactions of amine-terminated PAMAM dendrimers have been exploited for their preparation, Michael addition reaction of silicon-containing acrylates and haloalkylation with various silanes and siloxanes. These structures have been characterized with a wide range of bulk and surface analytical techniques including NMR, DSC, TGA, GPC, MS, surface tension, contact angle, Langmuir trough, SEM/EDS, AFM and XPS.

Derivatives of these dendrimers with inert trimethylsilyl-terminating groups may be viewed as globular, covalently bonded "inverted micelles" with unusual surface properties. On water, they form liquid-like spread films capable of sustaining much higher surface pressures than linear polydimethylsiloxane. Values of over 50 mN/m are attained, providing a marked example of the impact of macromolecular architecture on surface properties of organosilicon-containing polymers. Surface area obtained from Langmuir trough studies are in good agreement with expected PAMAMOS dendrimer sizes from dilute solution viscometry and molecular modeling. Increases in area occur both with increasing degree of organosilicon substitution of the parent PAMAM dendrimer surfaces and with increasing number of PAMAM generations.

Derivatives of these dendrimers with reactive methoxysilyl-terminating groups are excellent precursors for unique tractable dendrimer-based materials. These dendrimer-based networks consist of nanoscopic well-controlled domains, of predetermined size and shape evenly distributed in a continuous hydrophobic organosilicon matrix. They can be conveniently shaped into elastomeric or plastomeric films, sheets, membranes, coatings and objects. These new nanostructured materials show exceptional complexation abilities towards inorganic and organic electrophiles and offer unique opportunities for nano-technology of semi-permeable membranes, molecular "sponges" and "reactors", nanoscopic inorganic-organic composites and functional protective coatings for a wide variety of different substrates.

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