Synthesis and montmorillonite-intercalated behavior of dendritic surfactants

Cheng-Che Tsai,^{*a*} Tzong-Yuan Juang,^{*a*} Shenghong A. Dai,^{*a*} Tzong-Ming Wu,^{**a*} Wen-Chiung Su,^{*b*} Ying-Ling Liu^{*c*} and Ru-Jong Jeng^{**a*}

Received 13th January 2006, Accepted 1st March 2006 First published as an Advance Article on the web 20th March 2006 DOI: 10.1039/b600544f

A series of novel dendrons serving as surfactants for surface modification of montmorillonite (MMT) have been synthesised *via* a convergent approach. The most distinguishing characteristic of the prepared dendrons is the long alkyl chain at the periphery. This would certainly bring about good solubility, high yield and easy purification. By simple acidification of the "head group" upon the dendron and then ion-exchange with Na⁺-MMT, the interlayer distance could be enlarged significantly between the layered silicates. The organic/inorganic ratio determined by thermogravimetric analysis (TGA) is in the range of 60%–91%. This also confirms the occurrence of dendron ion-exchange with Na⁺-MMT. Transmission electronic microscopy (TEM) reveals the intercalated and exfoliated morphology of the dendron-modified MMTs. Modification using the generation 2 dendritic surfactant (G2) with molecular weight (M_w) = 2887.5 has achieved the exfoliated morphology in this work.

1 Introduction

Dendritic macromolecules with architectural and functional superiority have been attracting great interest.^{1–3} Unlike linear polymers and traditional branched polymers, dendrimers are monodisperse and highly branched macromolecules that consist of multiple functional groups at the periphery, which are synthesized through covalent bonds with a divergent or convergent strategy.^{4,5} Because of these unique advantages, their molecular size, shape and nature can be precisely controlled. Dendrimers are nanostructures with specific, precise and predictable physical properties (lower intrinsic viscosity and higher solubility)⁶ that make them especially useful for various applications including drug delivery,^{7–9} self-assembly systems,^{10–13} electro-optical materials,^{14–17} catalysts,^{18–20} etc.

Montmorillonite (MMT) is the most commonly used layered silicate with high aspect ratio.²¹ Employing suitable surfactants with simple ion-exchange reactions could achieve different natures of morphologies: intercalated, intercalated-and-flocculated and exfoliated.²² Many studies indicate that incorporating very small amounts of layered silicate into a polymer matrix can greatly improve the mechanical and physical properties.²³ In general, most of the traditional surfactants are linear forms; even though the interlayer *d*-spacing can be increased, they still retain the intercalated features of nanocomposites. Theoretically incorporating a 3-D structure into a layered silicate should have a significant

influence on the intercalated technique. Singh and Balazs²⁴ had studied the effect of polymer architecture in polymer/clay nanocomposites by using linear and branching units. At the same molecular weight, a linear structure tends to be intercalated; increasing the extent of branching units decreases the free energy of interaction between surfactants and MMT, so the layered silicates tend to be exfoliated. Furthermore, the hydrophilicity property at the periphery of the dendron was utilized as a surfactant in an organically-modified layered silicate system. However, the shape and size of dendrons did not have any discernable influence on the intercalation or exfoliation behavior.

Unlike other previous studies, Månson and co-workers²⁵ exploited the external multiple hydroxyl groups of a dendritic structure as a polar feature, and there were no cation-exchange reactions with layered silicate. Their results only showed intercalated silicates. Furthermore, Simanek and co-workers²⁶ identified another dendritic surfactant based on triazines and diamines since the dendritic part did not fully stretch out between layered silicates but hung outside. Therefore, they believed this dendritic structure could not afford expectable exfoliation, but only increased the *d*-spacing slightly.

In this report, we suggest a new method to modify the surface of MMT using polyurea/malonamide dendrons synthesized previously in our laboratory using [4-isocyanato-4'-(3,3-dimethyl-2,4-dioxo-acetidino)diphenylmethane] (MIA) and diethyltriamine (DETA) without painstaking protection-deprotection or activation methodology.²⁷ The same efficient convergent route was introduced to successfully synthesize a series of dendrons consisting of decyl chain groups on the exterior with high yield and easy purification (Scheme 1). Subsequently, a secondary aliphatic amine of different generation dendrons (G1–G3) was utilized as the hydrophilic segment by simple acidification, with a long alkyl chain as the hydrophobic segment. Therefore, the resultant dendritic

^aDepartments of Chemical Engineering and Materials Engineering, National Chung Hsing University, Taichung 402, Taiwan, ROC E-mail: rjjeng@dragon.nchu.edu.tw

^bChung-Shan Institute of Science and Technology, Lungtan, Taoyuan 325, Taiwan, ROC

^cDepartment of Chemical Engineering and R&D Center for Membrane Technology, Chung Yuan Christian University, Taoyuan 320, Taiwan, ROC



Scheme 1 Synthesis of G1, G2 and G3 dendrons from MIA and 1-decanol.

surfactants were incorporated into MMT to form an organically modified layered silicate system. Herein we could effortlessly achieve large *d*-spacings of intercalation or direct exfoliation by different 3-D structures and hydrophobicity of dendritic surfactants. Dendron-containing hybrids have been explored in various applications, such as nano-containers, reactive scaffolds and drug deliveries.^{28–30} *Via* respective incorporation of the different generation dendrons onto layered MMT, the interlayer distance of the intercalated hybrid can be precisely controlled to form a unique vessel. Moreover, exfoliated samples can be applied to serve as surface modifying agents or metal-encapsulated templates.^{31,32}

2 Experimental

Methylene di-*p*-phenyl diisocyanate (MDI), isobutyryl chloride, triethylamine, 1-decanol and diethyltriamine (DETA) were purchased from Aldrich and Acros, and used without further purification. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone before use. Na⁺-MMT was supplied by Nanocor Co., is a sodium type with a cationic exchange capacity (CEC) of 1.20 mequiv g^{-1} and a surface area of 750 m² g⁻¹.

¹H NMR spectra were taken on a Varian Gemini-200 FT-NMR spectrometer with chloroform-d₆ and DMSO-d₆.

IR measurements were performed on a Perkin Elmer Spectrum One Fourier transform infrared (FTIR) spectrometer. Elemental CHN analysis was performed on a Heraeus CHN-OS Rapid Analyzer. Thermal analysis was performed in N2 on a TA Instruments DSC2010 at a heating rate of 10 $^{\circ}$ C min⁻¹. Thermogravimetric analysis was performed by a Seiko SSC-5200 Thermogravimetric Analyzer (TGA) at a heating rate of 10 °C min⁻¹ under nitrogen. Fast atom bombardment mass spectrometry (FAB MS) analysis was performed on a JEOL JMS SX/SX 102A mass spectrometer equipped with the standard FAB source, whose upper limit for measuring molecular weight is 2000. Matrix-assisted laser desorption ionization with time of fight (MALDI-TOF) mass spectra were recorded on a Voyager DE-PRO (Applied Biosystems, Houston, TX) equipped with a nitrogen laser (337 nm) operating in linear detection mode to generate positive ion spectra with dithranol as a matrix, dimethyl sulfoxide (DMSO) as a solvent and sodium trifluoroacetate as an additive agent. Gel permeation chromatography (GPC) was performed in THF as an eluent with a Waters Apparatus equipped with Waters Stygel columns with a refractive index (RI) detector and polystyrene calibration. The d-spacing of the intercalated MMT was analyzed by an X-ray powder diffractometer (XRD, Shimadzu SD-D1 using a Cu target at 35 kV, 30 mA). The d-spacing of the intercalated MMT was

analyzed by using Bragg's equation $(n\lambda = 2d \sin \theta)$. The value for n = 1 was calculated from the observed values for n = 2, 3, 4, etc. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902A and operated at 80 kV and samples of approximately 70 nm were microtomed at room temperature.

Synthesis of MIA

Synthesis of MIA was performed according to the literature.^{27,33} A solution of triethylamine (45 g, 0.445 mol) in xylene (100 mL) was added to a solution of methylene di-*p*-phenyl diisocyanate (MDI) (125 g, 0.5 mol) and isobutyryl chloride (38.6 g, 0.362 mol) in the same solvent (250 mL). The reaction mixture was refluxed for 7 h and then cooled to room temperature. The resulting solution was filtered to remove the quaternary salt and concentrated to about 50 mL. The product was then crystallized from cyclohexane to give MIA (14.9 g, 33%) as white powder (Found: C, 71.32; H, 5.17; N, 8.96. $C_{19}H_{16}N_2O_3$ requires C, 71.24; H, 5.03; N, 8.74%); v_{max}/cm^{-1} 2260 (N=C=O), 1852 (C=O), 1731 cm⁻¹ (C=O); δ_H (CDCl₃; 200 MHz) 1.40 (6H, s, CH₃), 3.87 (2H, s, Ar–CH₂–Ar), 6.90– 7.69 (8H, m, Ar–H); *m*/*z* (FAB) 320 (M⁺).

Synthesis of G0.5 (Scheme 1)

Decanol (2.469 g, 15.60 mmol) was added to a solution of MIA (5 g, 15.63 mmol) in dry THF (100 mL). The solution was stirred at 80 °C under nitrogen for 3 h. The solvent was evaporated and purified by recrystallization from cyclohexane to give G0.5 (7.1 g, 95%) as white powder (Found: C, 72.70; H, 8.19; N, 6.18. C₂₉H₃₈N₂O₄ requires C, 72.77; H, 8.00; N, 5.85%); v_{max}/cm^{-1} 3300 (NH), 1856 (C=O), 1738 (C=O), 1700 cm⁻¹ [(NH)C=O(O)]; δ_{H} (DMSO; 200 MHz) 0.83 (3H, t, CH₃), 1.23 (14H, s, CH₂), 1.38 (6H, s, CH₃), 1.57 (2H, t, CH₂), 3.86 (2H, s, Ar–CH₂–Ar), 4.02 (2H, t, CH₂), 7.06–7.62 (8H, m, Ar–H); *m/z* (FAB) 478 (M⁺).

Synthesis of G1 (Scheme 1)

To a solution of G0.5 (5.1 g, 10.66 mmol) in dry THF (50 mL), DETA (0.539 g, 5.22 mmol) was added. The solution was stirred at 60 °C under a nitrogen atmosphere for 2 h. The solvent was evaporated and purified by recrystallization from acetone to give G1 (5.3 g, 95%) as white powder (Found: C, 69.82; H, 8.66; N, 9.67. C₆₂H₈₉N₇O₈ requires C, 69.82; H, 8.66; N, 9.67%); v_{max}/cm^{-1} 3300 (NH), 1700 [(NH)C=O(O)], 1650 [C=O(NH)]; δ_{H} (DMSO; 200 MHz) 0.83 (6H, t, CH₃), 1.23 (28H, s, CH₂), 1.38 (12H, s, CH₃), 1.57 (4H, t, CH₂), 2.55 (4H, t, CH₂(NH)), 3.30 (4H, m, CH₂(N)), 3.86 (4H, s, Ar–CH₂–Ar), 4.02 (4H, t, CH₂), 7.06–7.62 (16H, m, Ar–H); *m/z* (FAB) 1060 (M⁺).

Synthesis of G1.5 (Scheme 1)

To a solution of G1 (5 g, 4.72 mmol) in dry THF (50 mL), MIA (1.52 g, 4.75 mmol) was added. The solution was stirred at 60 °C under nitrogen for 2 h. The solvent was evaporated and the product was purified by silica gel chromatography with 2 : 1 ethyl acetate-hexane to give G1.5 (5.5 g, 86%) as yellow powder (Found: C, 69.96; H, 7.97; N, 9.19.

 $\begin{array}{l} C_{62}H_{89}N_7O_8 \mbox{ requires C, 70.46; H, 7.66; N, 9.13\%}; \mbox{v_{max}/cm^{-1}} \\ 3300 \mbox{ (NH), 1856 (C=O), 1738 (C=O), 1700 [(NH)C=O(O)];} \\ \delta_{H}(DMSO; 200 \mbox{ MHz}) \mbox{ 0.83 (6H, t, CH_3), 1.23 (28H, s, CH_2),} \\ 1.38 \mbox{ (12H, s, CH_3), 1.44 (6H, s, CH_3), 1.57 (4H, t, CH_2), 3.30 (8H, m, CH_2(N)), 3.86 (4H, s, Ar-CH_2-Ar), 3.94 (2H, s, Ar-CH_2-Ar), 4.02 \mbox{ (4H, t, CH_2), 7.06-7.62 (24H, m, Ar-H); m/z (FAB 1380 (M⁺). } \end{array}$

Synthesis of G2 (Scheme 1)

To a solution of G1.5 (5.1 g, 3.69 mmol) in dry THF (50 mL), DETA (0.187 g, 1.81 mmol) was added. The solution was stirred at 60 °C under a nitrogen atmosphere for 2 h. The solvent was evaporated and the product was purified by silica gel chromatography with acetone to give G2 (4.8 g, 90%) as yellow powder (Found: C, 69.23; H, 8.18; N, 10.33. C₁₆₆H₂₂₃N₂₁O₂₂ requires C, 69.60; H, 7.85; N, 10.27%); v_{max}/cm^{-1} 3300 (NH), 1700 [(NH)C=O(O)], 1650 cm⁻¹ [C=O(NH)]; $\delta_{\rm H}$ (DMSO; 200 MHz) 0.83 (12H, t, CH₃), 1.23 (56H, s, CH₂), 1.38 (36H, s, CH₃), 1.57 (8H, t, CH₂), 2.55 (4H, t, CH₂(NH)), 3.30 (20H, m, CH₂(N)), 3.86 (12H, s, Ar-CH₂-Ar), 4.02 (8H, t, CH₂), 7.06–7.62 (48H, m, Ar-H); *m/z* (MALDI-TOF) 2887.5 (M + Na⁺).

Synthesis of G2.5 (Scheme 1)

To a solution of G2 (5 g, 1.73 mmol) in dry THF (50 mL), MIA (0.56 g, 1.75 mmol) was added. The solution was stirred at 60 °C under a nitrogen atmosphere for 2 h. The solvent was evaporated and the product was purified by silica gel chromatography with ethyl acetate to give G2.5 (4.7 g, 86%) as yellow powder (Found: C, 70.09; H, 7.09; N, 9.90. C₁₈₅H₂₃₉N₂₃O₂₅ requires C, 69.76; H, 7.56; N, 10.11%); v_{max}/cm^{-1} 3300 (NH), 1856 (C=O), 1738(C=O), 1700 [(NH)C=O(O)]; $\delta_{\rm H}$ (DMSO; 200 MHz) 0.83 (12H, t, CH₃), 1.23 (56H, s, CH₂), 1.38 (36H, s, CH₃), 1.44 (6H, s, methyl), 1.57 (8H, t, CH₂), 3.30 (24H, m, CH₂(N)), 3.86 (12H, s, Ar-CH₂-Ar), 3.94 (2H, s, Ar-CH₂-Ar), 4.02 (8H, t, CH₂), 7.06–7.62 (48H, m, Ar-H); *m/z* (MALDI-TOF) 3208.1 (M + Na⁺).

Synthesis of G3 (Scheme 1)

To a solution of G2.5 (5.1 g, 1.59 mmol) in dry THF (50 mL), DETA (0.080 g, 0.78 mmol) was added. The solution was stirred at 60 °C under a nitrogen atmosphere for 2 h. The solvent was evaporated and the product was purified by silica gel chromatography with acetone to give G3 (4.5 g, 88%) as yellow powder (Found: C, 69.21; H, 8.26; N, 10.16. $C_{166}H_{223}N_{21}O_{22}$ requires C, 69.39; H, 7.65; N, 10.60%); v_{max}/cm^{-1} 3300 (NH), 1700 [(NH)C=O(O)], 1650 cm⁻¹ [C=O(NH)]; $\delta_{\rm H}$ (DMSO; 200MHz) 0.83 (24H, t, CH₃), 1.23 (112H, s, CH₂), 1.38 (84H, s, CH₃), 1.57 (16H, t, CH₂), 2.55 (4H, t, CH₂(NH)), 3.30 (52H, m, CH₂(N)), 3.86 (28H, s, Ar-CH₂-Ar), 4.02 (16H, t, CH₂), 7.06-7.62 (96H, m, Ar-H); *m/z* (MALDI-TOF) 6496.3 (M + Na⁺).

Acidification of dendritic surfactant

All of the dendrons (G1–G3) have structural characteristics such as secondary aliphatic amine located on one end and long

1000

500

alkyl chains on the other. For the G1, G2 and G3 dendritic surfactant solutions, the formulations of each were prepared by adding 254, 686 and 1553 mg, respectively, of the dendrons dissolved in 20 mL THF, followed by acidification of the secondary aliphatic amine by adding hydrochloric acid (37% in water, 24 mg, 0.24 mmol).

Modification of organoclay

A series of organoclays were prepared from each dendron. Typical experimental procedures are described below. First, clay suspensions were prepared by adding 20 mL of distilled water to 200 mg of MMT at 80 °C and stirring for 24 hours until fully swollen. Afterward, different generations (G1-G3) of dendritic surfactant solutions were added. The organic solvents were completely miscible with water. Finally, the suspensions were stirred for 24 hours at 80 °C. The resulting agglomerated precipitate was collected, and washed with water and with THF twice to thoroughly remove any residual ions and non-exchanged dendritic surfactants. The dendron-clay materials (G1/MMT-G3/MMT) were dried in a vacuum oven at 80 °C for 24 h and characterized by using XRD, TEM, TGA and DSC.

3 Results and discussion

In the synthesis of G0.5, MIA and 1-decanol were mixed at 80 °C with a molar ratio of 1 to 1. The addition reaction was completed with a high yield of 95%, and monitored by FTIR. As shown in Fig. 1, the peak at 2260 cm^{-1} (N=C=O absorption of isocyanate) disappeared, and a peak at 1700 cm⁻¹ (C=O stretching of urethane) appeared. The ¹H NMR spectrum (DMSO-d₆) of G0.5 exhibited chemical shifts at 3.86 (2H, s, Ar-CH₂-Ar) and 4.02 (2H, t, CH₂). The ratio of integrated areas conformed to the number of hydrogens. Subsequently, G1 was synthesized by ring-opening addition reaction of G0.5 with DETA with an inward secondary amine at the focal point and the reaction was completed at 60 °C with a high yield of 95%, and monitored by FTIR. As shown in



Fig. 1 Infrared spectrum of G0.5.



Fig. 2, the peaks at 1738 cm^{-1} and 1856 cm^{-1} (C=O stretching of azetidine-2,4-dione) disappeared, and a peak at 1675 cm⁻ (C=O stretching of malonamide) appeared. The ¹H NMR spectrum (DMSO-d₆) of G1 exhibited chemical shifts at 3.30 (4H, m, CH₂(N)), 3.86 (4H, s, Ar-CH₂-Ar) and 4.02 (4H, t, CH₂). The ratio of integrated areas conformed to the number of hydrogens. The syntheses and analysis of G1.5-G3 were also performed in the same manner.

The chemical structures of all fabricated specimens were fully confirmed by ¹H NMR, elemental analysis (CHN), and MALDI-TOF spectroscopy. In one example, Fig. 3 shows the mass spectrum of third generation dendron G3. In this mass spectrum, only one peak is observed at m/z = 6496.3 $(M + Na^{+})$, which is consistent with the theoretical molecular weight. Although MALDI-TOF offers much more accurate molecular weight, GPC provides invaluable information confirming the purity of these dendrons, and their globular conformation in solution.³⁴ Molecular weights and thermal properties of the dendrons are provided in Table 1. The polydispersity according to GPC still maintains a narrow range (PDI = 1.02-1.03), which is further evidence of a monodisperse distribution. For highly branched or globular materials,^{34,35} the relatively significant difference in molecular weights obtained from MALDI-TOF and GPC is due to the more pronounced change of hydrodynamic volume as



Fig. 3 MALDI-TOF MS spectrum of G3.

 Table 1
 Characteristics, polydispersities and thermal properties for dendritic compounds

Compound	Calcd. $M_{\rm w}$	$M_{\rm w}{}^a$	$M_{\rm w}{}^b$	$M_n^{\ b}$	PDI^b	$T_{\rm d}^{\ c}$	$T_{\rm m}^{\ \ d}$	$T_{\rm g}$
G0.5	478.6	478	565	547	1.03	260	99	ND
G1	1060.4	1060	1711	1654	1.03	234	163	ND
G1.5	1380.8	1380	2099	2054	1.02	272	ND^{e}	45
G2	2864.7	2864	3996	3917	1.02	265	ND	65
G2.5	3185.0	3185	4396	4283	1.02	254	ND	82
G3	6473.2	6473	8635	8465	1.02	254	ND	74
^a Determined by FAB MS and MALDI-TOF MS. ^b Determined								
by GPC analysis in THF (calibration with polystyrene standards).								
^c 5% weight loss. ^d Melting point. ^e Not detectable.								

compared to linear polymers. The degradation temperatures $(T_{\rm d})$ were in the range of 234–272 °C and only compounds G0.5 and G1 exhibited melting temperatures (T_m) at 99 and 163 °C, respectively. As the molecular weight and branching units increased, the other compounds (G1.5-G3) only revealed the presence of a glass-transition temperature (T_g) without any trace of melting temperature. There are two factors which influence the T_g value of a dendritic structure. Firstly, the increase of branching units leads to an increase of T_g , due to the decreased flexibility of adjacent chain segments. However, the increasing number of end groups diminishes the T_g because of the larger conformational flexibility of the end groups compared to segments of the dendritic core. The former factor affects the increasing tendency of T_g from 45 to 82 °C (G1.5 to G2.5). In addition, as a result of increasing number of end groups, the latter factor has higher priority in competition. Consequently the T_g of G3 decreases to 74 °C. This phenomenon was also observed in previous reports.^{27,36} The solubility of each dendron was qualitatively analyzed in various solvents, and the results are summarized in Table 2. All of them exhibited good solubility in a variety of polar solvents that can be attributed to the flexible alkyl chains at the periphery. Even the higher generation dendron still preserves excellent solubility. All the above evidence indicates that a series of dendrons with high yield, excellent solubility and easy purification have been successful synthesized.

Three generations of dendrons (G1–G3) were acidified by an equimolar ratio of hydrochloric acid in THF and then formed amphiphilic dendritic surfactants with a hydrophilic part (secondary amine salt) on one end and a hydrophobic part (long alkyl chain) on the other. After mixing these surfactants and MMT in solution, organically-modified MMTs were prepared by ion-exchange reactions and then characterized by using XRD, TEM, TGA and DSC.



Fig. 4 XRD patterns for various dendritic surfactant/MMT blends and pristine MMT.

The X-ray diffraction data of the pristine and organicallymodified MMTs are shown in Fig. 4. In this spectrum, the d-spacings of G1, G2 and G3 modified-MMTs based on Bragg's law $(n\lambda = 2d \sin\theta$ and the observed values for n =2, 3, 4, etc.) were 40 Å, 67 Å and 38 Å, respectively. The addition of G1 into MMT enlarged the d-spacing to 40 Å which was three times higher than that of pristine MMT. This result indicates that the amphiphilic dendritic surfactants could easily intercalate layered silicates. When the molecular weight increases to almost double (G2) or triple (G3) as compared to that of G1, the d-spacings of G2/MMT and G3/MMT would be expected to be larger than that of G1/MMT. The d-spacing of G2/MMT increased to 67 Å and was almost two times larger than that of G1/MMT. As anticipated, the number of hydrophobic end groups and the solidly packed volumes of dendritic molecules increased, so the modified MMT could achieve larger *d*-spacing effortlessly. However, the d-spacing of G3/MMT only reached 38 Å against prior anticipation. In order to confirm the previous assumptions observed by XRD patterns, TEM was utilized to visualize the spatial distribution among the modified MMTs.

As shown in Fig. 5a, the TEM micrograph of G1/MMT indicates ordered intercalation between oriented silicate layers with well-defined *d*-spacing (40 Å) corresponding to the analysis of the XRD pattern. Amazingly, the micrographs of G2/MMT either on widespread scale (Fig. 5b) or particule

Table 2 Solubility behavior for dendritic compounds

Sample	Toluene	Chloroform	THF	Acetone	Ethyl acetate	DMSO	Ethanol	Methanol
G0.5	_	+	+	+	+	+	_	_
G1		+	+		_	+		
G1.5	+	+	+	+	+	+	+	+
G2	+	+	+	+	+	+	+	+-
G2.5	+	+	+	+	+	+	+	+-
G3	+	+	+	+	+	+	+	+

^{*a*} Qualitative solubility was determined with 10 mg of sample in 1 mL of solvent. +: soluble at room temperature; +-: soluble after heating to 60 °C; -: insoluble even on heating to 60 °C.



Fig. 5 TEM micrographs: (a) intercalated morphology of G1/MMT; (b) exfoliated morphology of G2/MMT (200 nm); (c) exfoliated morphology of G2/MMT (50 nm); (d) intercalated and exfoliated morphology of G3/MMT.

scale (Fig. 5c) all exhibited exfoliated morphology with *d*-spacing larger than 300–500 Å between random and disordered single silicate platelets. However, the micrograph

of G3/MMT (Fig. 5d) revealed both intercalated and exfoliated morphology, but the *d*-spacing was even equal to or larger than 38 Å as calculated from the XRD pattern. At the intercalated region (left arrow of Fig. 5d), only a few lavered silicates were stacked without regular distribution. The phenomenon might result from increased steric hindrance arising from the high molecular weight dendritic surfactant. Consequently, part of G3 surfactants can not fully stretch and intercalate layered silicates.²⁶ Moreover, random and disordered single silicate platelets were found in more than half of the region (right arrow of Fig. 5d). Conceptual diagrams of MMTs intercalated by different generation dendrons (G1-G3) are illustrated in Scheme 2. A rough estimation of the length of the extended alkyl chain is 14 Å³¹ and the length of the building block is about 16 Å. The dimensions of different generation dendrons (G1-G3) are 30 Å, 46 Å, and 62 Å, respectively. According to prior X-ray results shown in Fig. 4 and the estimation of the molecular dimensions, we assumed that the conformation of G1/MMT was ordered intercalation containing G1 monolayers between layered silicates.^{37,38} For the G2/MMT series, as the periphery groups increase, the interpenetration of dendrons between silicate layers can be anticipated. Therefore the interlayer distance of G2/MMT is larger than that of the G2 monolayer. As the periphery groups continuously increase, a larger interlayer distance is expected. But the increasing periphery groups also induced significant steric hindrances of dendritic surfactants and parts of G3 surfactant are exposed to the exterior of layered silicates. Thus, the interlayer distance for G3/MMT was only 38 Å. Based on the above, this series of dendritic surfactants are effective in modifying MMT, especially G2/MMT.

As shown in Table 3, the organic/inorganic ratio was measured by TGA, conforming to the result calculated by CEC. Hence it is evident that this series of dendritic surfactants are powerful intercalating agents and could effortlessly attach to Na⁺-montmorillonite (yield > 90%). Furthermore, the modified organoclays could be well dispersed into organic solvents like toluene after a long period of time without precipitation or aggregation. The molecular mobility of dendritic surfactants attached to layered silicates was also monitored by DSC (Fig. 6). The ΔH (enthalpy of crystallinity at $T_{\rm m}$) of pristine G1 was 67.3 (mJ mg⁻¹) and then decreased to 0.3 (mJ mg⁻¹) after attachment to Na⁺-montmorillonite. In addition, the $\Delta C_{\rm p}$ (heat capacity difference at Tg) values of pristine G2 and G3 were 0.438 (mJ $^{\circ}C^{-1}$ mg⁻¹) and 0.471 (mJ $^{\circ}C^{-1}$ mg⁻¹), which decreased to 0.216 (mJ $^{\circ}C^{-1}$ mg⁻¹) and 0.186 (mJ $^{\circ}C^{-1}$ mg⁻¹), respectively, after modification. This tendency clearly reveals that the reduction in both enthalpy of crystallinity at $T_{\rm m}$ and heat capacity difference at $T_{\rm g}$ after modification may be due to the fact that the dendritic surfactants were restricted by the layered silicates without sufficient spaces for molecular relaxation. This conforms to the observations of the earlier literature.39,40

4 Conclusion

A new series of dendrons have been synthesized *via* a convergent approach with high yield, excellent solubility and



Scheme 2 Conceptual representation of conformations for MMTs intercalated by G1, G2 and G3 dendrons.

Table 3 Organic fraction and dispersibility of dendritic compounds

	Weight rat	Dispe	rsibility ^c		
Intercalation agent	Based on CEC ^a	Based on TGA^b	H ₂ O	EtOH	Toluene
G1/MMT	56/44	60/40		+	+-
G2/MMT	77/23	75/25		+-	+
G3/MMT	88/12	91/9		+	+
a					2

^{*a*} Values calculated from the following equation: $X \times 1.2 \times 10^{-3} \times M_w = Y$, where X is the pristine weight of clay, M_w is the molecular weight of the dendron, and Y is the weight of dendron. The theoretical organic ratio is given by Y/(X + Y). ^{*b*} Measured by thermogravimetric analysis (TGA) in air. ^{*c*} +: dispersible; +-: aggregate after 12h; -: aggregate.

easy purification, which consisted of active amine groups on one end and flexible alkyl chains on the other. The dendritic moieties were feasibly converted into amphiphilic structures by simple acidification of the "head group". The incorporation of dendritic surfactants can precisely control the *d*-spacing between layered silicates because of the presence of their geometric architecture and hydrophobic property. The dendritic structure even with low molecular weight could effectively intercalate the layered silicates and enlarge the *d*-spacing to 40 Å. On the other hand, dendritic structures with higher molecular weight would increase the steric hindrance and hydrophobic effect, which could effortlessly lead to exfoliated morphology as compared to the traditional linear surfactants.⁴¹ The utilities of these dendrons in other aspects are under investigation.

Acknowledgements

The authors thank NSC of Taiwan and Chung Shan Institute of Science and Technology for financial support. Partial financial support from the Green Chemistry Project (NCHU) and the Center-of-Excellence Program on Membrane Technology from the Ministry of Education, Taiwan, is gratefully acknowledged.



Fig. 6 DSC thermograms for pristine dendrons and modified organoclays: (a) G1 and G1/MMT; (b) G2, G2/MMT, G3 and G3/MMT.

References

- 1 A. W. Bosman, H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
- 2 S. M. Grayson and J. M. J. Fréchet, Chem. Rev., 2001, 101, 3819.
- 3 J. M. J. Fréchet, J. Polym. Sci., Part A: Polym. Chem., 2003, 41, 3713.
- 4 D. A. Tomalia, A. M. Naylor and W. A. Goddard, III, Angew. Chem., Int. Ed. Engl., 1990, 29, 138.
- 5 C. J. Hawker and J. M. J. Fréchet, J. Am. Chem. Soc., 1990, 112, 7638.
- 6 J. M. J. Fréchet and D. A. Tomalia, in *Dendrons and Other Dendritic Polymers*, ed. J. M. J. Fréchet and D. A. Tomalia, Wiley Series in Polymer Science, John Wiley & Sons, West Sussex, UK, 2001, ch. 1, pp. 31–40.
- 7 O. L. P. D. Jesus, H. R. Ihre, L. Gagne, J. M. J. Fréchet and F. C. Jr. Szoka, *Bioconjugate Chem.*, 2002, **13**, 453.
- 8 E. R. Gillies and J. M. J. Fréchet, J. Am. Chem. Soc., 2002, 124, 14137.
- 9 E. R. Gillies and J. M. J. Fréchet, Chem. Commun., 2003, 1640.
- 10 Y. Ma, S. V. Kolotuchin and S. C. Zimmerman, J. Am. Chem. Soc., 2002, 124, 13757.
- 11 C. Kim, S. J. Lee, I. H. Lee and K. T. Kim, Chem. Mater., 2003, 15, 3638.
- 12 H. S. Ko, C. Park, S. M. Lee, H. H. Song and C. Kim, *Chem. Mater.*, 2004, 16, 3872.
- 13 S. Srivastava, A. Verma, B. L. Frankamp and V. M. Rotello, *Adv. Mater.*, 2005, **17**, 617.
- 14 H. Ma, B. Chen, T. Sassa, L. R. Dalton and A. K. Y. Jen, J. Am. Chem. Soc., 2001, 123, 986.
- 15 H. C. Jeong, M. J. Piao, S. H. Lee, M. Y. Jeong, K. M. Kang, G. Park, S. J. Jeon and B. R. Cho, *Adv. Funct. Mater.*, 2004, 14, 64.
- 16 H. Ma, J. Luo, S. H. Kang, S. Wong, J. W. Kang, A. K. Y. Jen, R. Barto and C. W. Frank, *Macromol. Rapid Commun.*, 2004, 25, 1667.
- 17 S. Wang, X. Wang, L. Li and R. C. Advincula, J. Org. Chem., 2004, 69, 9073.
- 18 J. W. Kriesel and T. D. Tilley, Adv. Mater., 2001, 13, 1645.
- 19 W. J. S. Robert, M. W. Orla, S. K. Oh, A. K. Edward and M. C. Richard, J. Am. Chem. Soc., 2004, 126, 15583.

- 20 A. Dahan and M. Portnoy, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 235.
- 21 Y. Komori and K. Kuroda, in *Polymer-Layered Silicate Nanocomposites*, ed. T. J. Pinnavaia and G. W. Beall, John Wiley & Sons, West Sussex, UK, 2000, ch. 1, pp. 3–18.
- 22 S. S. Ray, K. Okamoto and M. Okamoto, *Macromolecules*, 2003, 36, 2355.
- 23 S. S. Ray and M. Okamoto, Prog. Polym. Sci., 2003, 28, 1539.
- 24 C. Singh and A. C. Balazs, Polym. Int., 2000, 49, 469.
- 25 C. J. G. Plummer, L. Garamszegi, Y. Leterrier, M. Rodlert and J. A. E. Manson, *Chem. Mater.*, 2002, 14, 486.
- 26 E. J. Acosta, Y. Deng, G. N. White, J. B. Dixon, K. J. McInnes, S. A. Senseman, A. S. Frantzen and E. E. Simanek, *Chem. Mater.*, 2003, **15**, 2903.
- 27 C. P. Chen, S. A. Dai, H. L. Chang, W. C. Su and R. J. Jeng, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 682.
- 28 J. H. Choy, S. Y. Kwak, Y. J. Jeong and J. S. Park, Angew. Chem., Int. Ed., 2000, 39, 4041.
- 29 M. Yang, E. M. W. Tsang, Y. A. Wang, X. Peng and H. Z. Yu, *Langmuir*, 2005, 21, 1858.
- 30 H. Yang and S. T. Lopina, J. Biomed. Mater. Res. A, 2005, 72A, 107.
- 31 S. Reemers, A. Mourran, H. Keul and M. Möller, J. Polym. Sci., Part A: Polym. Chem., 2006, 44, 1372.
- 32 M. R. Knecht, S. L. Sewell and D. W. Wright, *Langmuir*, 2005, **21**, 11981.
- 33 M. Okaniwa, K. Takeuchi, M. Asai and M. Ueda, Macromolecules, 2002, 35, 6232.
- 34 C. J. Hawker and J. M. J. Fréchet, J. Am. Chem. Soc., 1990, 112, 7638.
- 35 Y. Mai, Y. Zhou and D. Yan, Macromolecules, 2005, 38, 8679.
- 36 K. Lorenz, R. Mülhaupt, H. Frey, U. Rapp and F. J. Mayer-Posner, *Macromolecules*, 1995, 28, 6657.
- 37 I. Dékány, Pure Appl. Chem., 1992, 64, 149.
- 38 Á. Patzkó and I. Dékány, Colloids Surf., A, 1993, 71, 299.
- 39 J. J. Lin, I. J. Cheng, R. Wang and R. J. Lee, *Macromolecules*, 2001, 34, 8832.
- 40 R. A. Vaia, B. B. Sauer, O. K. Tse and E. P. Giannelis, J. Polym. Sci., Part B: Polym. Phys., 1997, 35, 59.
- 41 B. K. G. Theng, *The Chemistry of Clay–Organic Reactions*, Wiley & Sons, New York, 1974.