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The synthesis of dendrimers bearing alkyl chains and their behavior at air-water interface

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Summary

A new kind of amphiphilic polyether dendrimer bearing eight alkyl chains at the periphery were synthesized step by step using the convergent method. Their structures were confirmed by FT-IR spectra, ^{1}H NMR spectra and mass spectra etc. The π–A isotherms, hysteresis and molecular area-time curves at air water interface were reported. These results showed that they could form stable monolayers at water surface.

Introduction

A new kind of synthetic polymers, which are called dendrimers, have received extraordinary scientific attention in recent years (1-4).These tree-like molecules are of hyperbranched structures that emanate from a center core, contain a large number of terminal groups, and lack chain entanglement. They are of unique properties because their size, shape, topology, flexibility, and surface chemistry can be controlled at molecular level (1-3,5). Dendrimers are prepared layer by layer using either divergent or convergent method (3). Amphiphilic dendrimers or dendritic fragments are of great interest, there are a lot of publications about this aspect. Fréchet group reported that amphiphilic dendrimers form liquid membrane at oil-water interface (1,6). Amphiphilic compounds wherein a hydrophobic dendrimer resides at one end of a hydrophilic polyethylene oxide polymer aggregate in aqueous solution (1) and act as surfactants (7). Bola-amphiphilic arborols stack to form rod-shaped assemblies, resulting in gel formation in aqueous solution (8). Meijer and coworkers reported that amphiphilic block dendrimers showed generation-dependent aggregation and pH-dependent aggregation in aqueous solution (9,10). Zimmerman et al. found that dendritic fragment containing two isophthalic acid could self-assemble in organic solvent to form disk-shaped nano particles (11). Sallive et al. carefully studied amphiphilic dendrimer fragments with hydroxyl group at focal point at air water interface (12,13).

In our previous work (14-18), amphiphilic polymer with hydrophobic chains connected to a soft hydrophilic network were synthesized, their behaviors at air water interface were carefully studied, and reversed Duckweed polymeric LB film were fabricated. In this paper, we synthesized two kinds of amphiphilic dendrimer fragments with eight alkyl chains at the surface and with a hydroxyl group and a carboxyl group at the focal point, respectively. Their behavior at air water interface were also reported.

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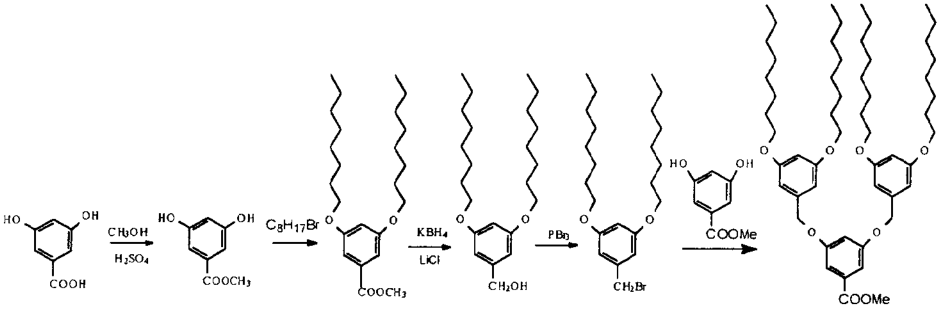
Experimental

IR spectra were recorded on a ISF-66V spectrometer as thin films on KBr plates. ^1H NMR were recorded with $CDCl_3$ solutions on a Varian 400 (400MHz) or a Varian 80 (80MHz) spectrometer using TMS proton signal as an internal standard. Molecular weight of the ultimate compounds was measured on a LD 11700-TOF MS mass spectrography. THF was distilled from sodium benzophenone ketyl. Acetone and cyclohexanone were dried with anhydrous K_2CO_3 and distilled with the middle fraction being collected. LiCl was dried at 120°C for 4h and stored with P_2O_5 . The other reagents were all analytical grade and used without further purification.

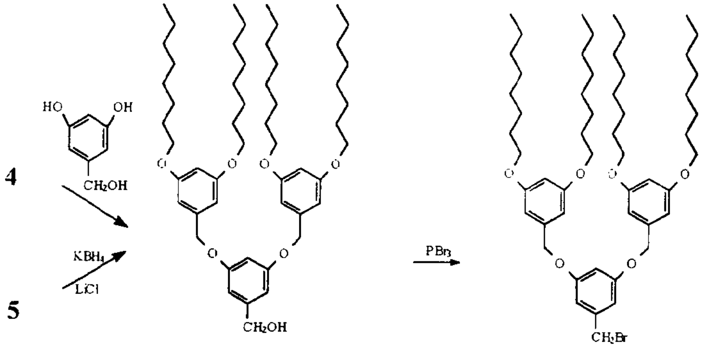
Synthetic route

The amphiphilic dendrimer fragments bearing long alkyl chains were synthesized by adopting the convergent method shown in Scheme 1.



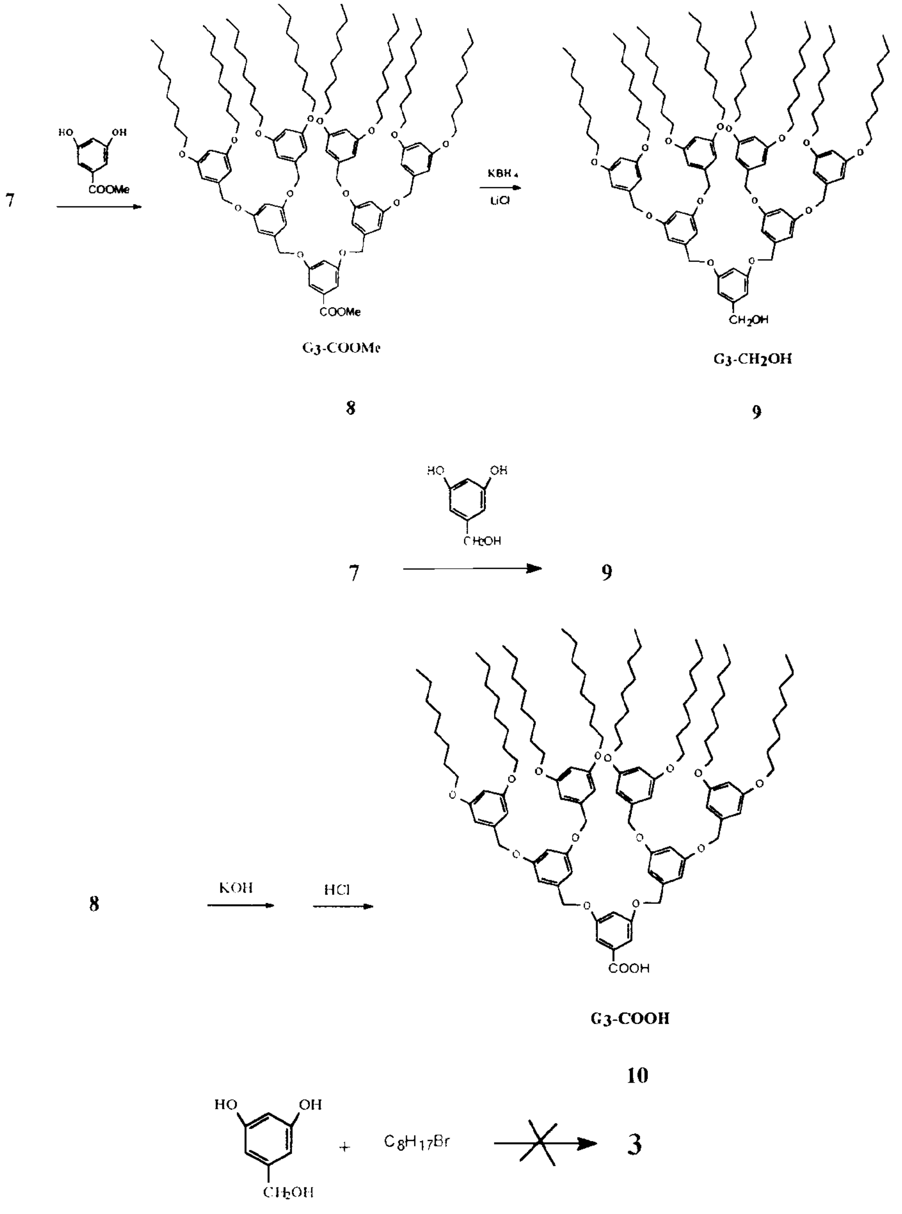
G1-COOMe G1-CH2OH G1-CH2Br G2-COOMe

1 2 3 4 5



G2-CH2OH G2-CH2Br

6 7



Scheme 1. The synthetic route of dendrimer fragments bearing alkyl chains

Methyl 3,5-dihydroxy benzoate (1)

3,5-Dihydroxy benzoic acid (20g, 0.13mol), methanol (200ml) and H_2SO_4 (5ml) were refluxed 10h under N_2. The excess of methanol was distilled under water bath, then the reaction mixture was partitioned between water (20ml) and dichloromethane (100ml). The oil layer was washed with saturated sodium bicarbonate solution (10ml), water (2×10ml), dried, and evaporated to dryness. The obtained solid was recrystalized from water to give white crystal. The yield is 89.0%. m.p. 164.5 °C

G_1-COOMe (methyl 3,5-bisoctyloxybenzoate) (2)

n-Octyl bromide (17.02g, 88mmol), methyl 3,5-dihydroxybenzoate (6.2g, 40mmol), anhydrous K_2CO_3 (22.13g, 160mmol), 18-Crown-6 (20mg) and cyclohexanone (100ml) were refluxed under argon. After 18h, the reaction mixture was evaporated to dryness under vacuum. The obtained solid was added water 100ml, and extracted with dichloromethane(3×50ml), dried and evaporated to dryness. The resultant solid was recrystalized from ethanol (100ml) to give white solid 15.0g. The yield is 95.0%. IR 2927.0 cm^{-1}; 2855.8 cm^{-1};1722.3 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.13-6.68ppm(m); 3.96ppm(s); 3.89ppm(t); 1.79ppm(m); 1.32ppm(m); 0.88pp(t).

G_1-CH_2OH (3,5-bisoctyloxybenzyl alcohol) (3)

KBH_4(4.77g, 0.09mol),LiCl (3.90g, 0.09mol) was refluxed in dry THF(50ml) for 2h. Then G_1-COOMe (1.43g, 1.75mmol) in 10ml THF was added dropwise to the solution, which was allowed to reflux for 5h. The mixture was evaporated to dryness with water-bath, cooled, added dilute HCl (50ml), and extracted with dichloromthane (3×50ml). The combined extracts were dried, and evaporated to dryness. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give G_1-CH_2OH as light yellow liquid. The yield is 95%. IR 3374.8 cm^{-1}; 2927.0 cm^{-1}; 2855.8 cm^{-1}; ^1H NMR($CDCl_3$) δ: 6.31-6.18ppm(m); 4.45ppm(s); 3.84ppm(t); 1.73ppm(m); 1.31(m); 0.88ppm(t).

G_1-CH_2Br (3,5-bisoctyloxybenzyl bromide) (4)

G_1-CH_2OH (11.35g, 31mmol) was dissolved in dry benzene and cooled to 0-5 °C under stirring, then PBr_3(1.5ml, 11mmol) was added dropwise. The mixture was kept to react for further 3h at room temperature. Then water (30ml) was added to the reaction mixture, benzene was evaporated under vacuum, and the mixture was extracted with CH_2Cl_2 (3×30ml). The combined extracts were dried with anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by column chromatography on silica gel eluting CH_2Cl_2 to give light yellow thick liquid product in 83.0% yield. IR 2926.7 cm^{-1}; 2855.4 cm^{-1}; 564.0 cm^{-1}; ^1H NMR($CDCl_3$) δ: 6.38-6.35ppm (m); 4.29ppm(s); 3.85ppm(t);1.72ppm(m); 1.31ppm(m); 0.88ppm(t)

G_2-COOMe (5)

G_1-CH_2Br (2.0g, 4.66mmol), methyl 3,5-dihydroxybenzoate (0.38g, 2.27mmol), K_2CO_3 (1.2g, 8.68mmol), catalytic amount 18-Crown-6 were dissolved in acetone (50ml) and the mixture was heated at reflux and stirred for 24h under argon. Then acetone was evaporated with water bath, water (20ml) was added to the residue and the obtained mixture was extracted with CH_2Cl_2 (3×20ml). The combined extracts were dried, and evaporated to dryness, and the crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2\cyclohexane(1:1\v:v) to give G_2-COOMe as light yellow thick liquid in 89.0% yield. IR 2926.6 cm^{-1}; 2855.6 cm^{-1}; 1726.0 cm^{-1}; ^1H NMR($CDCl_3$) δ: 6.53–6.39ppm(m); 4.98ppm(s); 3.90ppm(t); 1.75ppm(m); 1.32ppm(m); 0.89ppm(t).

G_2-CH_2OH (6)

G_2-CH_2OH was obtained by reduction of G_2-COOMe (1.43g, 1.75mmol)with KBH_4(0.45g, 8.34mmol) and LiCl (0.36g, 8.34mmol) in THF (25ml). The reaction procedure is similar to the preparation of G_1-CH_2OH. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give G_2-CH_2OH as light yellow thick liquid in 91.0% yield. IR 3416.8 cm^{-1}; 2925.5 cm^{-1}; 2855.3 cm^{-1}; ^1H NMR($CDCl_3$) δ: 6.55–6.39ppm(m); 4.49ppm(s); 4.61ppm(s); 3.93ppm(t); 1.75ppm(m); 1.32ppm(m); 0.88ppm(t).

G_2-CH_2Br (7)

This compound was prepared from G_2-CH_2OH, and the reaction procedure is similar to the preparation of G_1-CH_2Br. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give G_2-CH_2Br as light yellow thick liquid in 66.2% yield. IR 2925.9cm^{-1}; 2855.3 cm^{-1}; 564.0cm^{-1}; ^1H NMR($CDCl_3$) δ: 6.54-6.38ppm(m); 4.94ppm(s); 4.30ppm(s); 3.88ppm(t); 1.75ppm(m); 1.32ppm(m); 0.88ppm(t).

G_3-COOMe (8)

This compound was prepared from G_2-CH_2Br (0.50g, 0.56mmol), and methyl 3,5-dihydroxy benzoate (45.8mg, 0.27mmol). The procedure is similar to the preparation of G_2-COOMe. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give G_3-COOMe as light yellow thick liquid in 84.5% yield. IR 2925.7cm^{-1}; 2855.3 cm^{-1}; 1726.5 cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 6.66-6.39ppm(m); 4.95ppm(d);3.98ppm(s); 3.92ppm(t); 1.75ppm(m) 1.32ppm(m); 0.88ppm(t).

G_3-CH_2OH (9)

This compound can be prepared by reduction of G_3-COOMe in 77.1% yield. The procedure is similar with the preparation of G_1-CH_2OH. It can also be prepared from G_2-CH_2Br and 3,5-dihydroxy benzyl alcohol et al. in 85.4% yield. Its reaction procedure is similar with the preparation of G_2-COOMe. The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give light yellow thick liquid product. IR 2925.7 cm^{-1}; 2855.3 cm^{-1}; 1726.5 cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 6.66-6.40ppm(m); 4.94ppm(d); 4.62ppm(d); 3.92ppm(t); 1.75ppm(m);1.31ppm(m); 0.88ppm(t). m\e:1700.9 (calc.1700.0).

G_3-COOH (10)

The mixture of G_3-COOMe (200mg, 0.11mmol), KOH (50mg, 1.25mmol), catalytic amount of 18-Crown-6, and ethanol (95%, 20ml) were refluxed under argon for 6h, then the mixture evaporated to dryness. Dichloromethe (30ml) and dilute HCl (1N,10ml) were added and stirred to dissolve the solid, the organic layer was separated, dried with sodium sulphatate, evaporated to dryness and purified with column chromatography on silica gel eluting with CH_2Cl_2/CH_3CH_2OH (19 / 1; V /V) to give light yellow thick liquid product in 75.6% yield. IR 2500-3000cm^{-1}; 2925.6 cm^{-1}; 2855.3 cm^{-1}; 1692.6 cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 7.35-6.39ppm; 5.01ppm(s); 4.96ppm(s); 3.92ppm(t); 1.75ppm(m); 1.31ppm(m); 0.88ppm(t).m\e;1784.7(calc. 1784.6).

Spreading behavior experiments

Monolayer experiments were performed on a computer controlled KSV-5000 instrument with a whilhelmy plate system. The monolayers were spread on pure milli-Q water (15Ω) from chloroform solution in the concentration of 1mg/ml. The temperature was thermostated at 25°C.

Result and discussion

Synthesis

To obtain amphiphilic dendrimer fragments with alkyl chain at periphery, convergent method must be adopted. At first, in order to reduce the synthetic steps, we chose 3,5-dihydroxy benzyl alcohol as the monomer unit, which react with octyl bromide in potassium carbonate\acetone media to synthesize the desired product 3,5-bisoctyloxybenzyl alcohol, but failed. The reaction product can be easily distinguished with the product obtained by reducing methyl 3,5-bisoctyloxybenzoate using IR spectra and TLC method. In IR spectra, the absorbance of hydroxyl group at 3400cm-1 was not observed. We could deduce that this side reaction is different from the well-known side reaction of C-alkylation of phenol, which would give phenol and alkyl hydroxyl absorbance in IR spectra. So we choose methyl 3,5-dihydroxybenzoate as reactant. At first potassium carbonate\acetone were used as reaction media, the desired product could be obtained only in lower yield even in prolonged time experimental conditions. But in potassium carbonate\cyclohexanone media, the product could be obtained in high yield. The reduction step using LiCl\KBH_4 in THF could give Gn-CH_2OH in high yield, and the product was easy to purify. Gn-CH_2Br was easily obtained by reaction of Gn-CH_2OH with phosphorous tribromide in benzene, and the product was easy to separate. Gn-CH_2Br react with methyl 3,5-dihydroxy benzoate in potassium carbonate\acetone media give the next generation Gn-COOMe in high yield. The reaction of G_1-CH_2Br or G_2-CH_2Br with 3,5-dihydroxy benzyl alcohol in potassium carbonate\acetone media could give the next generation G_2-CH_2OH or G_3-CH_2OH. In this reaction conditions, the side reaction was almost not observed. G_3-COOMe was hydrolyzed with KOH in 95% ethanol and acidified with dilute HCl in dichloromethane readily give the product G_3-COOH.

Characterization of the amphiphilic dendrimer

IR spectroscopy could be used in characterizing the series of dendrimer fragments. The different substituent groups at focal point of dendrimer fragments bearing alkyl chains showed special characteristic IR absorption. Figure 1 shows the IR spectra for G_2-COOMe, G_2-CH_2OH and G_2-CH_2Br.

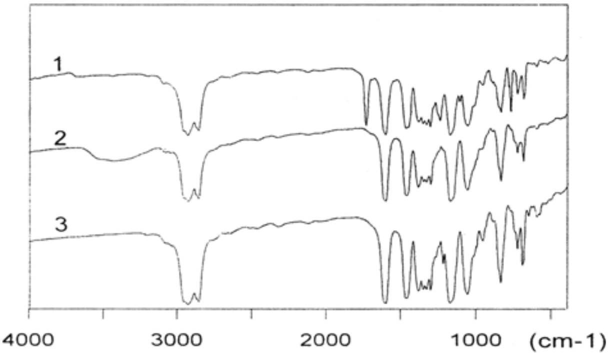
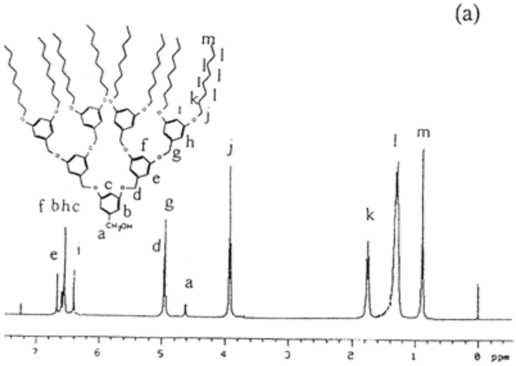


Fig.1. IR spectra for G_2-COOMe(1), G_2-CH_2OH(2) and G_2-CH_2Br(3), respectively.

The absorption of carbonyl group in G_2-COOMe occurs at 1700 cm^{-1}. In G_2-CH_2OH the ester group was reduced to hydroxyl group, the absorption of carbonyl group disappeared and a new band of O-H stretch absorption occurred at 3400cm^{-1}. In G_2-CH_2Br the absorption of hydroxyl group was not observed and a new absorption of C-Br stretch occurred at 564.0 cm^{-1}.

^1H NMR spectroscopy is a powerful tool in characterizing the polyarylether dendrimer. Figure 2 shows the ^1H NMR spectra of G_3-CH_2OH and G_3-COOH, respectively. All the protons in the structure could be identified and assigned. Also the integration data for these protons could fit well to the structures.



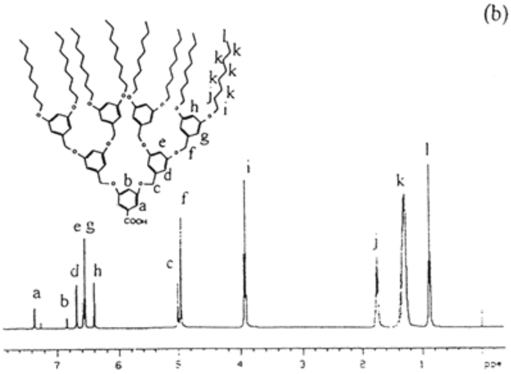


Fig. 2. ^{1}H NMR spectra of G_3-CH_2OH(a) and G_3-$COOH$(b)

monolayer at water surface

The surface pressure to molecular area isotherms of mono-molecular film of the amphiphilic dendrimer fragments bearing alkyl chains at air-water interfaces are shown in figure3. They both showed typical π–A curves, but with pretty lower collapse surface pressure. The G_3-$COOH$ monolayer showed a little higher collapse surface pressure than that of G_3-CH_2OH, because of G_3-$COOH$ with more hydrophilic -COOH group.

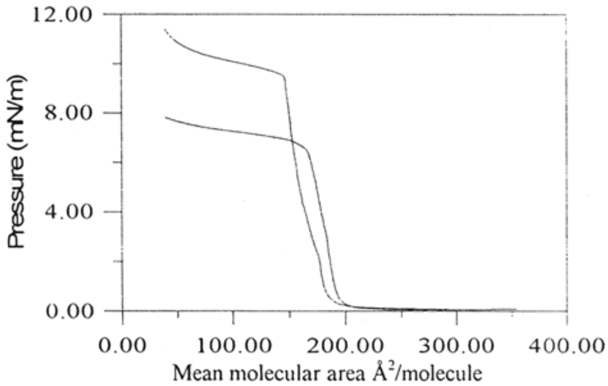


Fig. 3. The isotherms of amphiphilic alkyl containing dendrimer fragments Langmiur film at water surface

Figure4 shows the hysteresis of G_3-CH_2OH and G_3-$COOH$ at pure water surface. The monomolecular films were compressed to the surface pressure 5mN\m. Then the Barrier moved backward until the surface pressure reached zero. This process was repeated two times. The hysteresis curves of G_3-CH_2OH and G_3COOH Langmiur films showed good reversible compression and extension properties at surface pressure not more than 5mN\m. The monomolecular films were compressed to a surface pressure of 5mN\m, and then the film areas were controlled to hold the surface pressure of 5mN\m. If the monomolecular film is unstable, its monomolecular area changes with time. The monomolecular area of G_3-CH_2OH and G_3-$COOH$ did not change their value with time, which indicated that G_3-CH_2OH and G_3-$COOH$ could form stable Langmiur films at air water interface. From these curves, we could find that the monomolecular area of G_3-CH_2OH and G_3COOH at water surface are almost equal. This is reasonable, because the difference between G_3-CH_2OH and G_3-$COOH$ only exist at focal point.

Their interface behaviors are different from either that of the dendrimer fragments not bearing alkyl chains or that of the 'duckweed' amphiphilic molecules. As reported by Sallive et al., the amphiphilic dendrimer fragments without alkyl chains at periphery could not form stable monolayer at water interface. They have carefully studied the hydroxy terminal amphiphilic dendrimer fragments at air water interface using neutron scattering technique. Their results showed that the dendrimer fragments form bilayers at water surface(13).

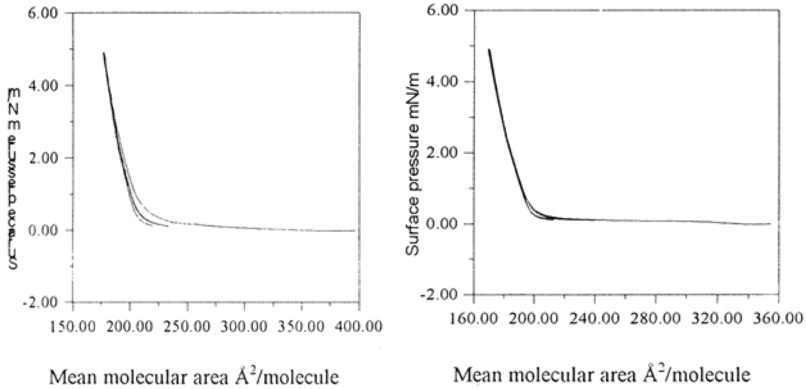


Fig.4. Hysteresis of G_3-COOH (left) and G_3- CH_2OH (right) at pure water surface

In summary, the two kinds of dendrimers bearing long alkyl chains were synthesized and it was found that these dendrimers could form stable monolayers at air water interface. Considering the conformation of these dendrimers, this kind of Langmiur film should have fixed porous, which could be used to separate some gaseous molecules and accommodate other functional molecules to form complex film.

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