Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Kawabata, Hirosuke , Aoki, Masayoshi , Murata, Kazutaka and Shinkai, Seiji(1993) 'Assembly of functionalized calixarenes', Supramolecular Chemistry, 2: 1, 33 — 39
To link to this Article: DOI: 10.1080/10610279308027504
URL: http://dx.doi.org/10.1080/10610279308027504

SUPRAMOLECULAR CHEMISTRY, Vol. 2, pp. 33–39
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Assembly of functionalized calixarenes

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(Received July 30, 1992)

Calixarene-based functional assemblies having potential for metal ion and/or molecular recognition were obtained: they are (1) gelators and (2) polymers. Calix[*n*]arenes bearing aliphatic chains at the *p*-position (2_nC_m, $n = 4$, 6, and 8; $m = 6$, 12, and 18) have been synthesized by direct acylation from calix[*n*]arenes (1_n) and serve as novel gelators of organic fluids. It has been established that the gelation process is thermally reversible, and the formation mechanism of the gels is ascribed to C=O···HO hydrogen bonding. On the other hand, insoluble polymer gels could also be obtained from a mixture of monovinyl- and divinyl-calix[4]arenes and they showed ion-selective swelling.

INTRODUCTION

Calixarenes are cyclic oligomers made up of phenol and formaldehyde and are useful as a basic skeleton in the design of new functionalized host molecules. Recently, many chemists have turned their attention to these compounds to create novel recognition system.[1] It is of great interest to assemble functionalized calixarenes because the chemical and physical properties may be varied by the assembled and/or controlled states. To the best of our knowledge, few papers for assembled calixarenes have been published.[2]

Our purpose is to construct such 'calixarene-based functional assemblies' and to put them to practical use as gelators and polymers. Recently, we reported that calix[*n*]arenes having aliphatic chains at the *p*-position can act as gelators of organic fluids.[3] Hence we have thrown some light on the gel formation mechanism by spectroscopic, optical microscopic, and thermographic methods.[4] On the other hand, some researchers had reported the synthesis of polymeric calix[4]arenes, but the molecular weight of the resultant polymer was not so high.[5] We have recently started new work on synthesizing novel polymerizable calixarene derivatives, from which we could obtain insoluble polymer gels exhibiting ion-selective swelling.

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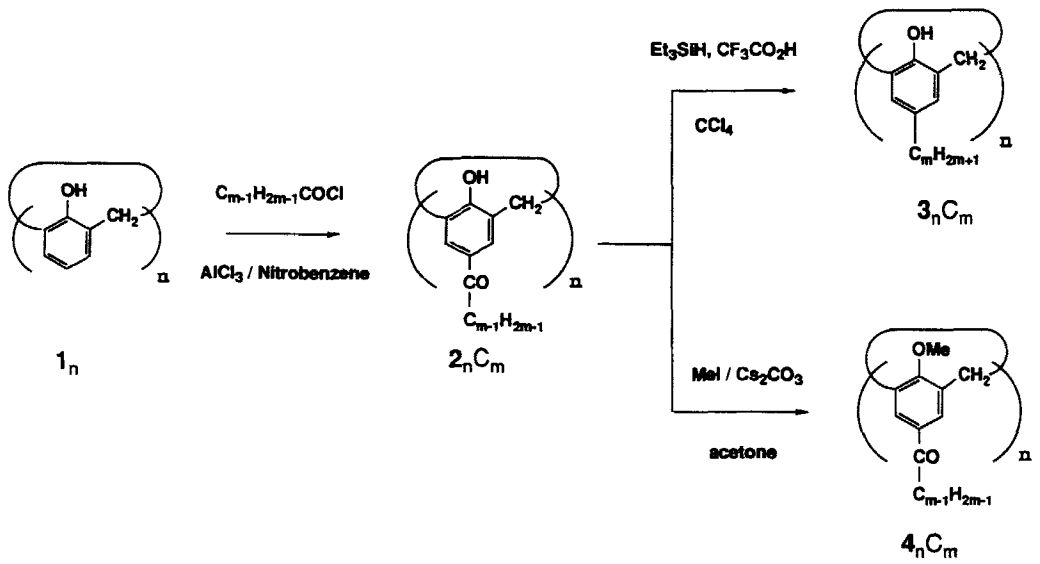
RESULTS AND DISCUSSION

Gelators

Calix[*n*]arenes having aliphatic chains at the *p*-position have been of increasing interest in host–guest chemistry and Langmuir monolayer formation.[6–8] We previously developed a new synthetic route from $\mathbf{1}_n$ to $\mathbf{3}_nC_m$ via $\mathbf{2}_nC_m$ (Fries rearrangement and Wolff–Kishner reduction).[3] In the course of this study, we experienced a surprising finding that the recrystallization of certain *p*-acylcalix[*n*]arenes from benzene, *n*-hexane, or cyclohexane results in organic gels. New gelators containing cholesterols or condensed aromatic rings have been reported by Lin *et al.*[9] To the best of our knowledge, however, our finding is the first example of a gelator derived from macrocycles. We thus considered that physical and chemical characterization of this gel would be of great significance in providing a guiding principle for the molecular design of new macrocycle-based gelators.

We firstly found that recrystallization of $\mathbf{2}_8C_{12}$ from benzene, *n*-hexane, or cyclohexane results in gels. We thus performed the extensive gelation test of $\mathbf{2}_8C_{12}$ for various organic solvents. As shown in Table 1, gelation at room temperature (method A) was observed for carbon disulphide, hydrocarbon solvents such as *n*-hexane, *n*-decane and cyclohexane, and alcohols such as isopropanol, *n*-butanol, and *n*-hexanol. When the solution was cooled to −20°C (method B), gelation occurred in carbon tetrachloride and aromatic hydrocarbon solvents such as toluene and benzene.

Gelation temperatures (T_g) were determined for the heating process by means of the inverted test-tube method. It is seen in Figure 1 that (i) T_g increases with increasing $\mathbf{2}_8C_{12}$ concentration, (ii) T_g for *n*-hexane (35–43°C) is much higher than that for cyclohexane (16–27°C) and CS_2 (18–24°C), and (iii) the slope [$= dT_g/dC$, °C $(mg \cdot g^{-1})^{-1}$] is in the order of cyclohexane ($dT_g/dC = 0.107$) > *n*-hexane (0.092) > CS_2 (0.041). The phase transition from gel to isotropic solution in the heating process was also detected by



Scheme I

Table 1 Organic fluids tested for gelation by 2_8C_{12}[a]

Organic fluids	*Room temperature (method A)*	*0°C[b] (method B)*
Toluene	S	G
Benzene	S	G[c]
Carbon tetrachloride	S	G
Chloroform	S → P	P
Dichloromethane	S	S
Carbon disulphide	S → G	G
n-Hexane	S → G	G
n-Decane	S → G	G
Cyclohexane	S → G	G
Acetone	I	I
Ethyl acetate	S → P	P
Dioxane	S → P	P
Tetrahydrofuran	S	P
Methanol	I	I
Ethanol	I	I
Isopropanol	S → G	G
n-Butanol	S → G	G
n-Hexanol	S → G	G

[a] S, soluble; P, precipitate formed; G, gel formed; I, insoluble. [b] The solution was cooled to −20°C to grow the gel and then returned to 0°C for the estimation of the gel. [c] The gel was formed before the benzene solvent solidified.

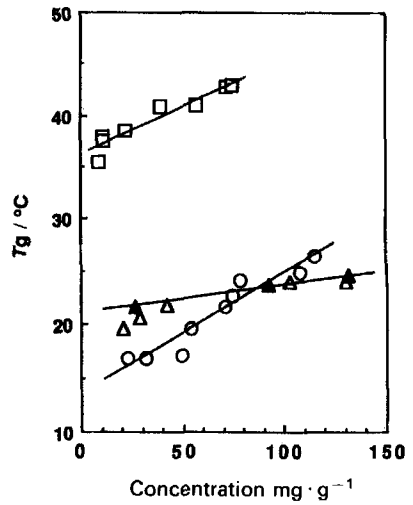


Figure 1 Plots of T_g vs. 2_8C_{12} concentration (2_8C_{12} mg per g of added solvent): □ *n*-hexane, ○ cyclohexane, △ carbon disulphide, ▲ carbon disulphide (T_g values were determined by a DSC method).

differential scanning calorimetry (DSC). In CS_2, for example, an endothermic peak appeared at around 23°C and the peak shifted to a higher temperature region with increasing 2_8C_{12} concentration. Similar curves were obtained for the cooling process, indicating that the sol–gel phase transition occurs reversibly. As shown in Figure 1, the phase transition temperature determined by DSC showed good agreement with the T_g value determined by the 'melting point' measurement.

Interestingly, the aggregates formed from 2_8C_{12} in CS_2 could be directly observed by optical microscopy. When the homogeneous solution was cooled below T_g, a network formed from fibrillar aggregates with ca. 1 μm diameter appeared. When the gel was heated, the network disappeared at around T_g. This observation could be repeated many times. The result clearly shows that the gelation process is reversible.

We considered here why 2_8C_{12} is capable of gelatinizing certain organic solvents. In order to make the molecular network 2_8C_{12} must aggregate intermolecularly with the aid of some secondary valence foeces. The forces expected for the intermolecular aggregation of 2_8C_{12} are the C=O···HO hydrogen

bonding interaction and the C=O···C=O dipole–dipole interaction. To discriminate between these two interactions we synthesized $\mathbf{3}_n\mathbf{C}_m$ ($n = 4$, 6, and 8; $m = 6$ and 12), which do not have the carbonyl group, and $\mathbf{4}_8\mathbf{C}_{12}$ in which the OH groups are converted to methoxy groups. We found that none of these compounds could gelatinize the organic solvents tested in Table 1. This finding establishes that the network is formed basically from the C=O···HO hydrogen bonding interactions but not from the C=O···C=O dipole–dipole interaction.

As shown in Table 1, the gel formation is limited to hydrocarbon solvents (except for a few alcohols) which do not involve oxygen atoms. This suggests that the oxygen atom in solvent molecules can compete with the C=O groups for the formation of the hydrogen bond and can destroy the gel network. We measured the DSC thermograph for the carbon disulphide gel in the presence of a small amount of acetone. As shown in Figure 2, the peak maximum gradually shifted to a lower temperature region and finally disappeared at 20.5 mg of acetone in 1 g of carbon disulphide. The result clearly indicates that the formation of the intermolecular C=O···HO hydrogen bonds plays a crucial role in stabilizing the gel network.

We tested the gelation ability of nine $\mathbf{2}_n\mathbf{C}_m$ homologues. Among three $\mathbf{2}_8\mathbf{C}_m$ homologues ($m = 6$, 12, and 18), $\mathbf{2}_8\mathbf{C}_{12}$ and $\mathbf{2}_8\mathbf{C}_{18}$ showed gelation ability, but $\mathbf{2}_8\mathbf{C}_6$ did not. A similar trend was observed for $\mathbf{2}_4\mathbf{C}_m$ homologues: $\mathbf{2}_4\mathbf{C}_{18}$ showed gelation ability, but $\mathbf{2}_4\mathbf{C}_6$ and $\mathbf{2}_4\mathbf{C}_{12}$ did not. As mentioned above, the first prerequisite for gel formation is moderate intermolecular interaction of gelator molecules. The data in Table 2 reveal that the second prerequisite is a moderate 'affinity' between gelator and solvent, because the formation of stable organic gels is limited to $\mathbf{2}_8\mathbf{C}_{12}$, $\mathbf{2}_8\mathbf{C}_{18}$, and $\mathbf{2}_4\mathbf{C}_{18}$ which have the longer aliphatic chains. The solvent effect observed for alcohols may be explained on the same basis. $\mathbf{2}_8\mathbf{C}_{12}$ is insoluble in methanol and ethanol whereas it is soluble in isopropanol, *n*-butanol, and *n*-hexanole (Table 1). Thus, provided that the moderate intermolecular interactions exist in the latter solvents and the network is formed, $\mathbf{2}_8\mathbf{C}_{12}$ can act as a gelator of these solvents. Basically, the OH group in alcoholic solvents can act as both a proton donor and a proton acceptor and therefore may destroy the gel network of $\mathbf{2}_8\mathbf{C}_{12}$. The gel formation observed for $\mathbf{2}_8\mathbf{C}_{12}$ implies that the $(\mathbf{2}_8\mathbf{C}_{12})$C=O···HO$(\mathbf{2}_8\mathbf{C}_{12})$ interaction is stronger than the $(\mathbf{2}_8\mathbf{C}_{12})$C=O···HO(alcohol) interaction and the $(\mathbf{2}_8\mathbf{C}_{12})$OH···OH(alcohol) interaction. It is clear that the C=O oxygen is more electronegative than the alcoholic OH oxygen,[10] and the phenolic OH proton in $\mathbf{2}_8\mathbf{C}_{12}$ is more acidic than the alcoholic OH proton.[11–14] Thus, the aggregation of $\mathbf{2}_8\mathbf{C}_{12}$ is achieved by the combination of the more electronegative proton acceptors and the more acidic proton donors. This is why gelation can take place even in some alcoholic solvents. Anyhow, $\mathbf{2}_8\mathbf{C}_{12}$ is a rare example showing a gelation ability for alcohols. Strangely, none of the $\mathbf{2}_6\mathbf{C}_m$ homologues showed any significant gelation ability. This reason is not well understood at present. We only know that the solubility of $\mathbf{2}_6\mathbf{C}_m$ homologues is much inferior to that of the $\mathbf{2}_4\mathbf{C}_m$ and $\mathbf{2}_8\mathbf{C}_m$ homologues. Presumably, $\mathbf{2}_6\mathbf{C}_m$ homologues cannot satisfy the second prerequisite of a moderate affinity between gelator and solvent.

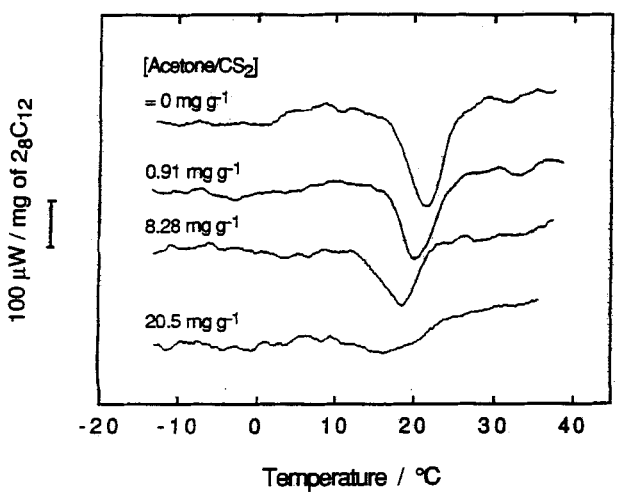


Figure 2 DSC heating curves for the $\mathbf{2}_8\mathbf{C}_{12}$–$CS_2$. Heating rate: 2°C·min^{-1}, $\mathbf{2}_8\mathbf{C}_{12}$ concentration: 40.1 mg·g^{-1}. Acetone concentration 0, 0.91, 8.28, and 20.5 mg·g^{-1} as indicated on the figure.

Table 2 Gelation ability of $\mathbf{2}_n\mathbf{C}_m$[a]

	n		
m	4	6	8
6	X	X	X
12	X	X	O (20°C)[b]
18	O (31.2°C)[b]	X	O (31.4°C)[b]

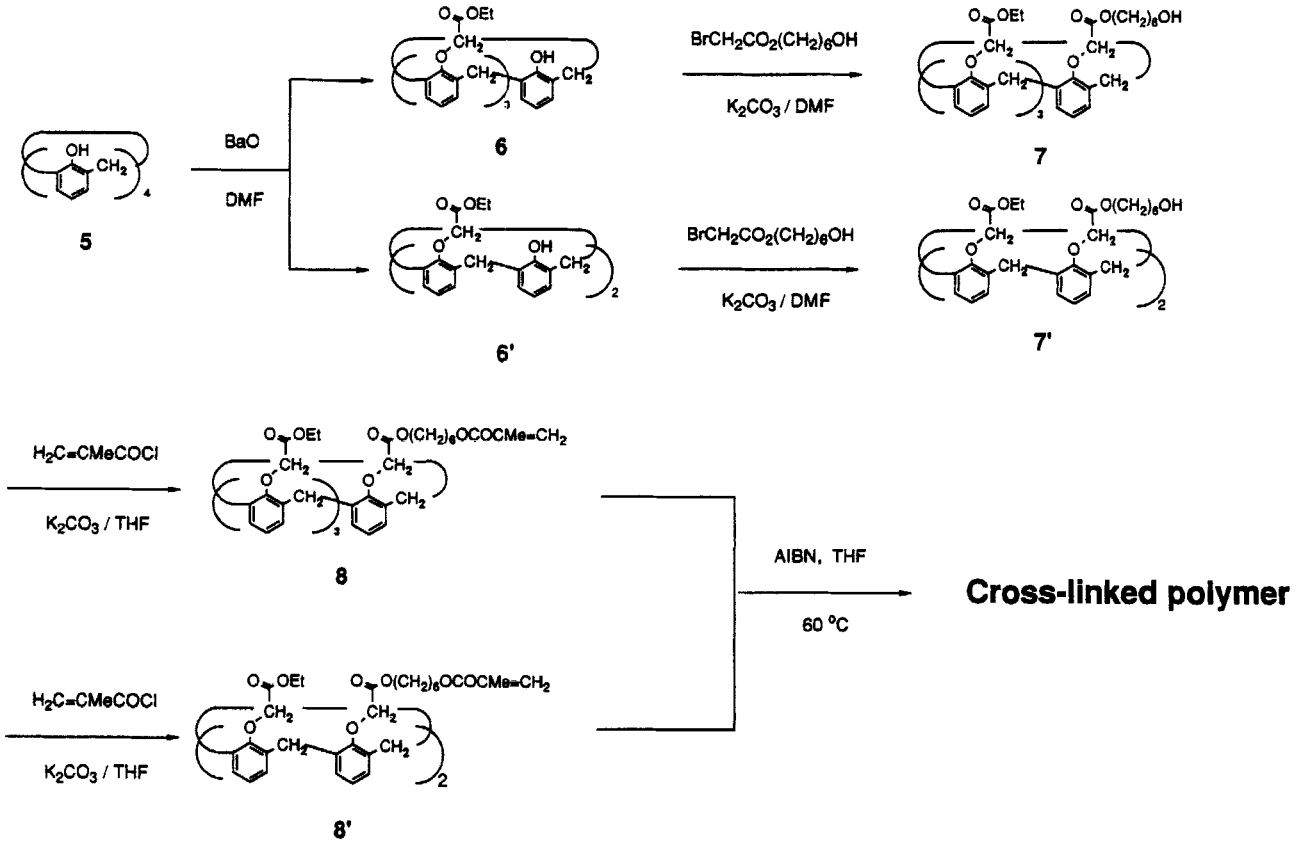
[a] O denotes that the compound is capable of gelating hydrocarbon solvents (toluene, benzene, *n*-hexane, and cyclohexane), carbon tetrachloride, or carbon disulphide at 0°C. X denotes that gelation is not observed with any solvents listed in Table 1. [b] T_g in toluene (concentration 80 mg·g^{-1}).

Calixarene-containing polymers

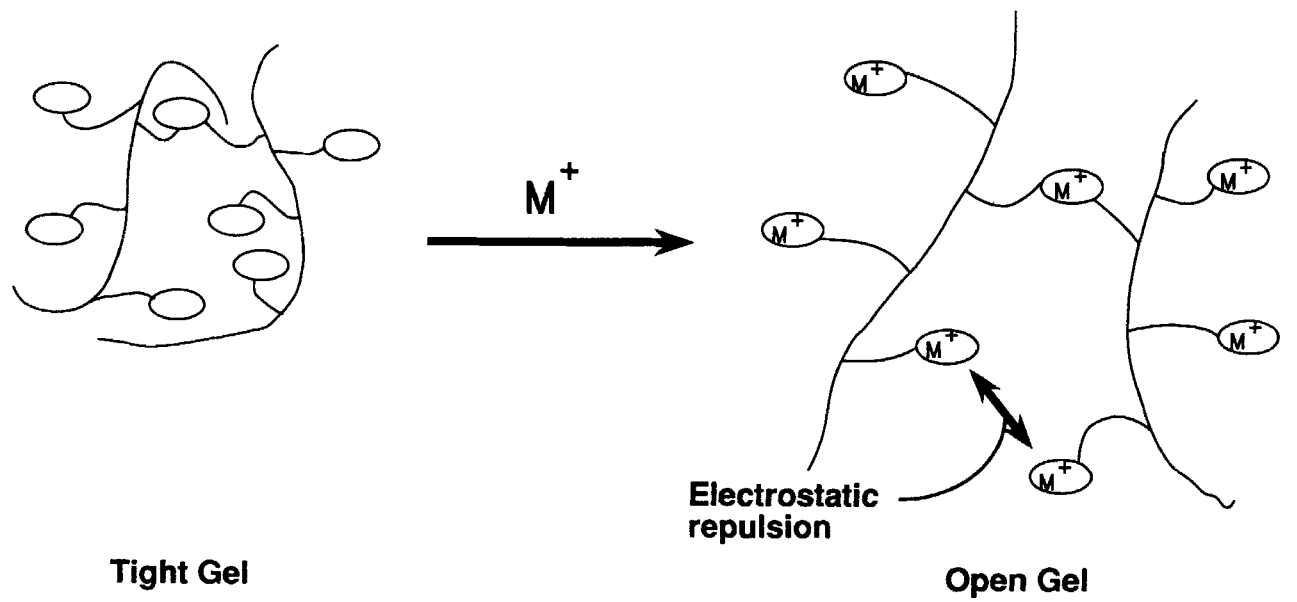
Harris *et al.*[5] reported the synthesis, polymerization, Na^+ complexation, and extraction of metal picrates from aqueous into organic media, of a polymeric calixarene having a methacrylate group. The molecular weight of the resultant polymer ($M_n = 6745$) was not satisfactorily high.[5] It seems to us that the low molecular weight is attributed to the short ethylene

spacer between the bulky calix[4]arene and the vinyl group. With a view to obtaining a high molecular weight polymer, we synthesized a novel polymerizable calix[4]arene derivative with a long hexamethylene spacer chain (Scheme II). In the course of the synthesis of intermediate, **6**, however, an infinitesimal amount of disubstituted byproduct (**6'**) was produced. The elimination of this compound **6'** was very difficult. We thus used the mixture for further reactions.

Radical polymerization of **8** (Scheme II) was carried



Scheme II



Scheme III

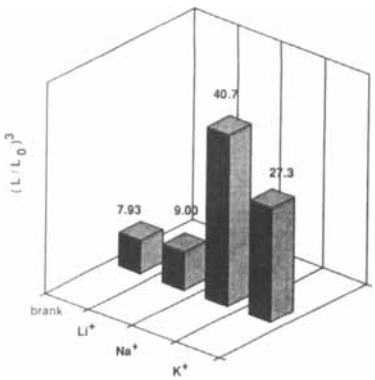


Figure 3 The swelling ratio of calixarene-based polymer gels in acetone. L_0 and L are the lengths of the gels before and after swelling, respectively.

out according to the usual sealed tube technique in tetrahydrofuran (THF) at 60°C for 24 h by using 2,2′-azobis(isobutyronitrile) as initiator to yield the calix[4]arene-containing polymethacrylate. The product was divided into a soluble polymer and an insoluble gel. The M_n of the soluble polymer, 35,000, was higher by 5.2 times than the polymer without a spacer synthesized by Harris *et al.*[5] The gel swelled in THF and acetone whereas it contracted in methanol. The swelling ratio of this gel was affected selectively by alkali metal cations. As shown in Figure 3, this gel exhibited ion-selective swelling towards Na^+ in acetone. The selectivity is attributed to the selective binding of Na^+ to the ionophoric calix[4]arene cavity (Scheme III).

CONCLUSIONS

Calix[n]arenes having long acyl groups at the p-position ($\mathbf{2}_n\mathbf{C}_m$) serve as excellent and unique gelators of various organic solvents. The sol–gel phase transition occurs thermoreversibly. We propose the prerequisites for the formation of the stable organic gels as: (i) intermolecular C=O···HO hydrogen bonding to form a three-dimensional network; and (ii) the moderate affinity of the gelators to the solvent molecules. The results offer important strategies for the molecular design of new gelators of organic fluids. Also important are the findings that high molecular weight polymers can be obtained by introducing a long spacer between the calix[4]arene and the vinyl group, and that calixarene-based polymer gels show ion-selective swelling for Na^+.

EXPERIMENTAL SECTION

Materials

Preparations of $\mathbf{2}_n\mathbf{C}_m$ and $\mathbf{3}_n\mathbf{C}_m$ (n = 4, 6, and 8; m = 6 and 12) were reported previously.[3] $\mathbf{2}_n\mathbf{C}_{18}$ (n = 4, 6, and 8) were synthesized from $\mathbf{1}_n$ and octadecanoyl chloride according to the method described previously.[3]

5,11,17,23-Tetraoctadecanoylcalix[4]arene-25,26,27,28-tetrol ($\mathbf{2}_4\mathbf{C}_{18}$)

M.p. 108–109°C, yield 72%; IR (KBr) ν_{OH} 3193 cm^{-1}, $\nu_{C=O}$ 1676 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 10.07 (s, 4H, OH), 7.75 (s, 8H, ArH), 3.99 (br s, 8H, $ArCH_2Ar$), 2.83 (t, J = 7.0 Hz, 8H, $COCH_2$), 1.63–1.26 [m, 120H, $CH_2(CH_2)_{15}CH_3$], 0.88 [br t, 12H, $CH_2(CH_2)_{15}CH_3$]. Anal. calcd. for $C_{100}H_{160}O_8$: C, 80.58, H, 10.83. Found: C, 80.18; H, 10.21.

5,11,17,23,29,35-Hexaoctadecanoylcalix[6]arene-37,38,39,40,41,42-hexol ($\mathbf{2}_6\mathbf{C}_{18}$)

M.p. > 200°C, yield 63%; IR (KBr) ν_{OH} 3250 cm^{-1}, $\nu_{C=O}$ 1682 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 10.40 (s, 6H, OH), 7.85 (s, 12H, ArH), 3.98 (s, 12H, $ArCH_2Ar$), 2.90 (t, J = 7.0 Hz, 12H, $COCH_2$), 1.59–1.26 [m, 180H, $CH_2(CH_2)_{15}CH_3$], 0.88 [br t, 18H, $CH_2(CH_2)_{15}CH_3$]. Anal. calcd. for $C_{150}H_{240}O_{12}$: C, 80.58; H, 10.83. Found: C, 80.53; H, 10.85.

5,11,17,23,29,35,41,47-Octaoctadecanoylcalix[8]-arene-49,50,51,52,53,54,55,56-octol ($\mathbf{2}_8\mathbf{C}_{18}$)

M.p. > 200°C, yield 60%; IR (KBr) ν_{OH} 3339 cm^{-1}, $\nu_{C=O}$ 1682 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 9.54 (s, 8H, OH), 7.80 (s, 16H, ArH), 4.00 (s, 16H, $ArCH_2Ar$), 2.81 (t, J = 7.0 Hz, 16H, $COCH_2$), 1.67–1.26 [m, 240H, $CH_2(CH_2)_{15}CH_3$], 0.88 [br t, 24H, $CH_2(CH_2)_{15}CH_3$]. Anal. calcd. for $C_{200}H_{320}O_{16}$: C, 80.58; H, 10.83. Found: C, 80.09; H, 10.67.

5,11,17,23,29,35,41,47-Octaoctadecanoyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene ($\mathbf{4}_8\mathbf{C}_{12}$)

Compound $\mathbf{2}_8\mathbf{C}_{12}$ (0.5 g; 0.34 mmol), Cs_2CO_3 (1.13 g; 3.46 mmol), and MeI (1 g; 7.0 mmol) were mixed in dehydrated acetone (20 ml) and the reaction mixture was stirred at reflux temperature for 110 h. The solid material was removed by filtration, the filtrate being evaporated to dryness. The solid residue was subjected to purification by column chromatography (silica gel, $CHCl_3$) and finally recrystallized from chloroform–methanol: m.p. 93.3–94.3°C, yield 40%; IR (KBr), no ν_{OH}: ^{1}H-NMR ($CDCl_3$, 30°C) δ 7.57 (s, 16H, ArH), 4.05 (s, 16H, $ArCH_2Ar$), 3.48 (s, 24H, OCH_3), 2.75 (t, J = 7.0 Hz, 16H, $COCH_2$), 1.54–1.24 [m, 144H, $CH_2(CH_2)_9CH_3$], 0.87 [br t, 24H, $CH_2(CH_2)_9CH_3$]. Anal. calcd. for $C_{160}H_{240}O_{16}$: C, 79.42; H, 10.00. Found: C, 80.23; H, 10.06.

25,26,27-Tris(ethoxycarbonylmethoxy)-28-hydroxycalix[4]arene (6)

2.12 g (5 mmol) of calix[4]arene and 2.42 g (15 mmol) of BaO were mixed in 50 ml of distilled dimethylformamide (DMF) under a stream of N_2, and the mixture was stirred at 55–60°C for 30 min. Then, 2.5 ml (22.5 mmol) of ethyl bromoacetate was added and the mixture was stirred at 55–60°C for 50 h. The insoluble material was removed by filtration. The filtrate was poured into 100 ml of $CHCl_3$ and treated with 10 ml of aqueous 1N HCl. The organic layer was washed with water for neutralization and dried over anhydrous $MgSO_4$. The solution was filtered and concentrated under vacuum to yield the pale white solid. This residue was recrystallized from ethanol to give 1.75 g (51%) of powder: m.p. 129.7–130.5°C; IR (KBr) ν_{OH} cm^{-1}, $\nu_{C=O}$ 1771, 1748, 1732 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 7.10 (d, J = 7.6 Hz, 2H, ArH), 7.04 (d, J = 7.6 Hz, 2H, ArH), 6.92 (t, J = 7.3 Hz, 1H, ArH), 6.70 (t, J = 7.3 Hz, 1H, ArH), 6.54–6.45 (m, 6H, ArH), 6.16 (s, 1H, OH), 5.10 (s, 2H, OCH_2), 4.95 (d, J = 13.4 Hz, 2H, $ArCH_2Ar$), 4.62 (d, J = 15.9 Hz, 2H, OCH_2), 4.50 (d, J = 15.6 Hz, 2H, OCH_2), 4.37 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 4.26 (q, J = 7.0 Hz, 4H, OCH_2CH_3), 4.14 (q, J = 7.3 Hz, 2H, OCH_2CH_3), 3.32 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 3.30 (d, J = 13.4 Hz, 2H, $ArCH_2Ar$), 1.32 (t, J = 7.0 Hz, 6H, OCH_2CH_3), 1.25 (t, J = 7.3 Hz, 6H, OCH_2CH_3). We noticed, however, that the product includes 5 mol% of 25,27-bis(ethoxycarbonylmethoxy)-26,28-dihydroxycalix[4]arene (**6′**), which was identified by comparison of the ^{1}H-NMR spectrum and the HPLC peak (ODS column, methanol) of the authentic sample.[15] The removal of **6′** by recrystallization was very difficult.

6-Hydroxyhexyl bromoacetate (10)

1,6-Hexanediol (36.3 g, 0.307 mol), bromoacetic acid (4.27 g, 30.7 mmol) and *p*-toluenesulphonic acid (catalytic amount) were dissolved in benzene (100 ml) in a 3-necked flask connected to a Dean-Stark trap, and the solution was refluxed for 2 h. After cooling, the reaction mixture separated. The upper layer was recovered and evaporated to dryness. The oily residue containing **10** was purified by distillation with a glass tube oven to give a colourless liquid: b.p. 80–100°C/0.25 mmHg, yield 14%; IR (neat) ν_{OH} 3400 cm^{-1}, $\nu_{C=O}$(ester) 1735 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C), δ 4.18 (t, J = 6.2 Hz, 2H, CO_2CH_2), 3.83 (s, 2H, OCH_2CO_2), 3.64 (t, J = 6.2 Hz, 2H, CH_2OH), 1.76–1.46 [m, 8H, $CH_2(CH_2)_4CH_2$]; GC–MS (CI, column; TC-1, inj. temp. 240°C, column temp 180°C), m/z 239.

25,26,27-Tris(ethoxycarbonylmethoxy)-28-(6-hydroxyhexyl)carbonylmethoxycalix[4]arene (7)

6 (1.36 g, 2 mmol) was dissolved in distilled DMF (40 ml) under nitrogen atmosphere. Finely ground potassium carbonate (11 g, 80 mmol) and 6-hydroxyhexylbromo acetate (2.39 g, 10 mmol) were suspended in the DMF solution, and the mixture was heated at 50–60°C for 16 h. After K_2CO_3 was removed, the filtrate was poured into $CHCl_3$. The $CHCl_3$ solution was diluted with aqueous 1N HCl, washed with water, and then dried over anhydrous $MgSO_4$. Evaporation of the solution gave the yellow oily crude product. This crude product was purified using size exclusion chromatography (Shephadex LH-20) to give 1.55 g (92%) of yellow viscous liquid: IR (neat) ν_{OH} 3500 cm^{-1}, $\nu_{C=O}$ 1760, 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 6.63 (s, 12H, ArH), 4.87 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 4.86 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 4.72 (s, 8H, OCH_2CO_2), 4.21 (q, J = 7.2 Hz, 6H, $CO_2CH_2CH_3$), 4.14 [t, J = 6.8 Hz, 2H, $CO_2CH_2(CH_2)_5$], 3.63 (t, J = 6.8 Hz, 1H, CH_2OH), 3.24 (d, J = 13.7 Hz, 4H, $ArCH_2Ar$), 1.67 [m, 2H, $CO_2CH_2CH_2(CH_2)_4$], 1.56 (t, J = 6.8 Hz, 2H, CH_2OH), 1.39 [m, 6H, $(CH_2)_4$], 1.29 (t, J = 7.2 Hz, 9H, $CO_2CH_2CH_3$); MS [SIMS (+)] m/z 863 $(M + Na)^+$. The HPLC analysis (ODS column, methanol) showed that the produce contained 5 mol% of 25,27-bis(ethoxycarbonylmethoxy)-26,28-bis(6-hydroxyhexyl)carbonylmethoxycalix[4]arene (**7′**).

25,26,27-Tris(ethoxycarbonylmethoxy)-28-(6-methacryloyloxyhexyl)carbomethoxycalix[4]arene (8)[16]

To a solution of 1.55 g (1.84 mmol) of **7**, a small amount of 2,6-di-*tert*-butylphenol, 6.08 g (44 mmol) of K_2CO_3, and two drops of pyridine in 20 ml of THF were added 2.90 ml (29.7 mmol) of freshly distilled methacryloyl chloride in 2.0 ml of THF at 0°C. The mixture was vigorously agitated under a nitrogen atmosphere at 0°C for 1 h and then stirred at room temperature for 20 h. After concentration, the residue was poured into water with stirring. The white viscous product was thus obtained by decantation. This product was dissolved in $CHCl_3$, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residual yellow oil was subjected to size exclusion chromatography (Shephadex LH-20) to give the yellow oily product of 0.38 g (17%): IR (neat) $\nu_{C=O}$ 1760, 1740, 1725 cm^{-1}, $\nu_{C=C}$ (vinyl) 1638 cm^{-1}, $\nu_{C=C}$ (aromatic) 1586 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 30°C) δ 6.64 (s, 12H, ArH), 6.09 (s, 1H, $CMe{=}CH_2$), 5.55 (s, 1H, $CMe{=}CH_2$), 4.88 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 4.86 (d, J = 13.7 Hz, 2H, $ArCH_2Ar$), 4.74 [s, 2H,

$OCH_2CO_2(CH_2)_6$], 4.73 (s, 6H, $OCH_2CO_2CH_2CH_3$), 4.21 (q, J = 7.1 Hz, 6H, $CO_2CH_2CH_3$), 4.13 [t, J = 6.8 Hz, 4H, $CO_2CH_2(CH_2)_5$], 3.74 (d, J = 13.7 Hz, 4H, $ArCH_2Ar$), 1.94 (s, 3H, $CCH_3 = CH_2$), 1.66–1.59 [m, 4H, $CO_2CH_2CH_2(CH_2)_2CH_2CH_2$], 1.40–1.38 [m, 4H, $CO_2CH_2CH_2(CH_2)_2CH_2CH_2$], 1.29 (t, J = 7.2 Hz, 9H, $CO_2CH_2CH_3$); MS [SIMS (+)] m/z 931 $(M + Na)^+$. The HPLC analysis (ODS column, methanol) showed that this product contains 25,27-bis(ethoxycarbonylmethoxy)-26,28-bis(6-methacryloyloxyhexyl)carbonylmethoxycalix[4]arene (**8'**).

Radical polymerization of 8[17]

A freshly distilled THF solution (1 ml) containing **8** plus **8'** (0.37 g, 0.41 mmol) and 2,2'-azobis(isobutyronitrile) (0.67 mg, 0.0041 mmol) was degassed in a glass tube by the freeze-pump-thaw technique and sealed under vacuum. The polymerization was conducted in a thermocontrolled oil bath at 60°C for 24 h. The solution gelated. The gel was washed with THF and dried at 60°C for 24 h in vacuum to afford **9** in 81% yield (colourless solid). From THF used for washing was recovered the soluble polymer in 11% yield. The M_n determined by GPC (monodispersed polystyrene as standard) was 35,000.

Gelation tests

$\mathbf{2}_n\mathrm{C}_m$ (17.3 mmol in the benzene unit mole: e.g. 5 mg for $\mathbf{2}_8\mathrm{C}_{12}$) was mixed with test solvent (0.5 ml) in a septum-capped test tube and the mixture was heated until the solid dissolved. The solution was cooled to room temperature and concentrated gradually at room temperature (method A). Then, the solution was adjusted to 0.10 ml and cooled to −20°C (method B). All solvents used herein were special grade.

T_g measurements

To determine the sol–gel phase transition temperature (T_g), an inverted test tube containing the gel in a thermocontrolled water bath was set up. We raised the bath temperature at a speed of 1.0°C min^{-1} and determined the temperature when the gel melted down. The T_g values could be reproduced with an accuracy of ±1.0°C.

Miscellaneous

The gel formation was observed by using an optical microscope (Olympus BH-2) with or without a phase differential condenser. Thermographic measurements were carried out by using a DSC apparatus (Seiko Denshi DSC-220). Spectroscopic data were obtained by means of Bruker 250 MHz FT-NMR (AC-250P) for ^{1}H-NMR spectroscopy and Shimazu FT-IR 8100 for IR spectroscopy.

Swelling ratio[17]

The gels were immersed in solvents for 1 week at room temperature. The length of the swollen gels was determined by taking their photographs. The swelling ratio is defined by $(L/L_0)^3$ before (L_0) and after (L) the swelling: [Gel] = 1.43×10^{-4} unit mol dm^{-3}, $[M^+Pic^-] = 1.43 \times 10^{-2}$ mol dm^{-3}.

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