

ESI data

Modified calix[8]arenes as new cross-linkers in free radical copolymerization

Roselyne Baudry^a, Christian Graillat^b, Caroline Felix^a and Roger Lamartine^a

General Methods.

p-*tert*-butylcalix[8]arene and calix[8]arene were synthesized according to the literature.²⁹ Commercially available alkylating or acylating agents were used without any purification. Sodium hydride (60%) was used with the mineral oil. THF, toluene and *o*-xylene were refluxed overnight in the presence of sodium and benzophenone and distilled before use. DMF was freshly distilled (under CaH₂) before use. All reactions were carried out under nitrogen. Reactions were monitored by TLC on silica gel (SIL G/UV₂₅₄). Melting points were determined on an Electrothermal-9100 Capillary apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were obtained by using Brücker DRX400 or ALS 300 spectrometers, TMS as internal standard, chemical shifts in ppm. The precisions of the integrations performed using the Brücker WINNMR software were estimated to be 1% for the proton. Mass spectra were obtained by electrospray technique (positive mode).

¹³C NMR data are available as ESI.

As verified by other authors elemental analyses of calixarenes are very often incorrect because of the inclusion of solvent molecules and thus cannot be considered as an appropriate criterion of purity.²⁶ Nevertheless, the identities of the reported compounds have been confirmed by their structural data.

5, 11, 17, 23, 29, 35, 41, 47-Octa-*tert*-butyl-49, 50, 51, 52, 53, 54, 55, 56-octaacryloyloxycalix[8]arene (1a). In a 500 mL three-necked flask equipped with stirrer and condenser, 5 g (3.8 mmol) of *p*-*tert*-butylcalix[8]arene were suspended in 200 mL of THF and 25 mL of DMF under nitrogen. NaH (2.4 g, 57.6 mmol) was added with stirring. When the bubbling ceased, the suspension was refluxed (80°C). When the solution became slightly green (1 hour), 4.7 mL of acryloyl chloride (57.8 mmol) in 50 mL of THF were added drop wise into the charge. After refluxing for 12h, the system was cooled to room temperature, and the solvents were removed under vacuum to leave a residue which was suspended in 2N HCl (250 mL). The insoluble material was collected by filtration, washed with water (500 mL) and methanol (100 mL), and dried. The crude product was then refluxed in hexane (150 mL) for 15 minutes, filtered off and dried to afford 5.6 g of light brown powder, which was found to be essentially pure by ¹H NMR spectroscopy. Yield : 84 % of **1a**. ¹H NMR (CDCl₃, 298K) δ 1.12 (s, 72H, CH₃), 3.60 (s, 16H, Ar-CH₂-Ar), 5.6 (d, 8H, ³J = 10.3, H_{cis}), 5.95 (dd, 8H, ³J_{cis} = 10.3, ³J_{trans} = 17.3, H_{gem}), 6.23 (d, 8H, ³J = 17.3, H_{trans}), 6.99 (s, 16H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K) δ 31.29 (CH₃, *t*-Bu), 31.62 (Ar-CH₂-Ar), 34.34 (C, *t*-Bu), 126.11 (CH, Ar), 127.27 (CH=CH₂), 131.36 (C-CH₂, Ar), 132.42 (CH=CH₂), 144.96 (C-*t*-Bu, Ar), 148.30 (C-O, Ar), 163.84 (C=O) ; ES-MS (+) for C₁₁₂H₁₂₈O₁₆ (1728.92) m/z = 887.8 [M+2Na]²⁺, 1731.0 [M+H]⁺, 1752.9 [M+Na]⁺.

49, 50, 51, 52, 53, 54, 55, 56-Octaacryloyloxycalix[8]arene (1b). Same procedure with 5 g of calix[8]arene (5.9 mmol), 3.5 g of NaH (84 mmol), 7.2 mL of acryloyl chloride (86 mmol). Yield : 83 % of **1b**. ¹H NMR (CDCl₃, 298K) δ 3.63 (s, 16H, Ar-CH₂-Ar), 5.71 (d, 8H, ³J = 10.3 Hz, H_{cis}), 6.00 (dd, 8H, ³J_{cis} = 10.3, ³J_{trans} = 17.3, H_{gem}), 6.27 (d, 8H, ³J = 17.3, H_{trans}),

6.94-7.05 (m, 24H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K) δ 31.57 (Ar-CH₂-Ar), 126.46 (CH_p, Ar), 127.51 (CH_m, Ar), 129.51 (CH=CH₂), 132.73 (C_o-CH₂, Ar), 133.14 (CH=CH₂), 147.61 (C-O, Ar), 164.1 (C=O) ; ES-MS (+) for C₈₀H₆₄O₁₆ (1280.42) m/z = 663.4 [M+2Na]²⁺, 1281.5 [M+H]⁺, 1298.4 [M+NH₄]⁺, 1303.5 [M+Na]⁺, 1319.5 [M+K]⁺.

5, 11, 17, 23, 29, 35, 41, 47-Octa-tert-butyl-49, 50, 51, 52, 53, 54, 55, 56-octamethacryloyloxycalix[8]arene (2a). In a 1 L three-necked flask equipped with stirrer and condenser, 10 g (7.7 mmol) of *p*-tert-butylcalix[8]arene was suspended in 400 mL of THF and 50 mL of DMF under nitrogen. NaH (5 g, 120 mmol) was added in 3 steps with stirring. When the bubbling ceased, the suspension was refluxed (80°C). When the solution became slightly green (1 hour), 8 mL of methacryloyl chloride (81 mmol) in 100 mL of THF was added drop wise into the charge. After refluxing for 12h, the system was cooled to room temperature, and the solvents were removed under vacuum to leave a residue which was suspended in 2N HCl (400 mL). The insoluble material was collected by filtration, washed with water (1,5 L) and cold ethanol (100 mL), and dried under vacuum to give 15.2 g (94 %) of white powder which was found to be essentially pure by ¹H NMR spectroscopy. Analytic portions were recrystallised from ethanol/water. Mp : decomposed. ¹H NMR (CDCl₃, 298K) δ 1.14 (s, 72H, CH₃, *t*-Bu), 1.71 (s, 24H, CH₃), 3.63 (sb, 16H, Ar-CH₂-Ar), 5.39 (s, 8H, H_{cis}), 5.94 (s, 8H, H_{trans}), 6.97 (s, 16H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K) δ 18.67 (CH₃), 31.68 (CH₃, *t*-Bu), 31.68 (Ar-CH₂-Ar), 34.71 (C, *t*-Bu), 126.43 (CH, Ar), 127.49 (C=CH₂), 131.65 (C-CH₂, Ar), 135.57 (C=CH₂), 145.76 (C-*t*-Bu, Ar), 148.58 (C-O, Ar), 165.4 (C=O). IR: 1734 (C=O), 1638 (C=C) ; ES-MS (+) for C₁₂₀H₁₄₄O₁₆ (1841.04) m/z = 994.3 [M+2Na]²⁺, 1865.2 [M+Na]⁺.

49, 50, 51, 52, 53, 54, 55, 56-Octamethacryloyloxycalix[8]arene (2b). In a 250 mL three-necked flask equipped with stirrer and condenser, 796 mg (0.94 mmol) of calix[8]arene was suspended in 90 mL of THF and 10 mL of DMF under nitrogen. NaH (600 mg, 14.4 mmol) was added with stirring. When the bubbling ceased, the suspension was refluxed (80°C). After 30 minutes, 0.9 mL of methacryloyl chloride (9 mmol) in 10 mL of THF was added drop wise into the charge. After refluxing for 12h, the system was cooled to room temperature, and the solvents were removed under vacuum to leave a residue which was dissolved in 100 mL of dichloromethane. The organic layer was washed with 20 mL of 1N HCl, and 50 mL of water (twice), dried with MgSO₄, concentrated. The crude product was then recrystallised from CH₂Cl₂/*n*-hexane to give 970 mg (74 %) of light brown powder. Mp : decomposed. ¹H NMR (CDCl₃, 298K) δ 1.78 (s, 24H, CH₃), 3,68 (bs, 16H, Ar-CH₂-Ar), 5.49 (s, 8H, H_{cis}), 6.0 (s, 8H, H_{trans}), 6.93 (bm, 24H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K) δ 18.16 (CH₃), 31.08 (Ar-CH₂-Ar), 125.89 (CH_p, Ar), 127.41 (C=CH₂), 128.94 (CH_m, Ar), 132,26 (C_o-CH₂, Ar), 135.03 (C=CH₂), 147.45 (C-O, Ar), 164.80 (C=O) ; IR: 1733 (C=O) ; 1637 (C=C) ; ES-MS (+) for C₈₈H₈₀O₁₆ (1392.54) m/z = 1416.7 [M + Na]⁺.

5, 11, 17, 23, 29, 35, 41, 47-Octa-tert-butyl-49, 50, 51, 52, 53, 54, 55, 56-octakis-[(*p*-vinylbenzyl)oxy]calix[8]arène (3a). In a 100 mL three-necked flask equipped with stirrer and condenser, 150 mg (0.12 mmol) of calix[8]arene were suspended in 20 mL of DMF under nitrogen. After 15 minutes, NaH (69 mg, 1.7 mmol) was added with stirring. After one hour, NaI (20 mg, 0.13 mmol) was added and 0.25 mL of chlorovinylbenzene (1.37 mmol) was injected into the charge. After 2 days, the system was cooled, and the reaction was stopped by adding 50 mL of 1N HCl and extracted by 2 × 100 mL of chloroform. The organic layer was filtered off on celite, and concentrated under vacuum to give brown oil as a crude product. The residue was diluted with 2 mL of chloroform and stirred with 100 mL of methanol. The insolubles products were filtered off and then recrystallised from CHCl₃/MeOH to give 197

mg (70 %) of light brown powder. Mp : decomposed. RMN ^1H (C_6D_6 , 336K, 400MHz) δ 1,18 (s, 72H, CH_3 , *t*-Bu) ; 4,26 (s, 16H, Ar- CH_2 -Ar) ; 4,72 (db, 16H, CH_2) ; 4,94 (db, 8H, $^3\text{J} = 9,5$ Hz, H_{cis}) ; 5,48 (db, 8H, $^3\text{J} = 16,9$ Hz, H_{trans}) ; 6,45 (tb, 8H, H_{gem}) ; 6,96-7,37 (mb, 48H, H_{Ar}) ; ^{13}C NMR (C_6D_6 , 336K, 400 MHz) δ 31,06 (Ar- CH_2 -Ar) ; 31,82 (CH_3 , *t*-Bu) ; 34,56 (C, *t*-Bu) ; 75,02 (O- CH_2 -Ar₂) ; 113,91 ($\text{CH}_2=\text{CH}$) ; 125,7 ; 126,65 ; 128,9 (CH, Ar) ; 133,9 (C- CH_2 , Ar₁) ; 137,32 ($\text{CH}=\text{CH}_2$) ; 137,15 ; 137,4 (C, Ar₂) ; 146,7 (C-*t*-Bu, Ar₁) ; 153,8 (C-O, Ar₁) ; ES-MS (+) : for $\text{C}_{160}\text{H}_{176}\text{O}_8$ (2225.33) $m/z = 1136,4$ [$\text{M} + 2\text{Na}$] $^{2+}$; 2249,7 [$\text{M} + \text{Na}$] $^+$; 2265,7 [$\text{M} + \text{K}$] $^+$.

49, 50, 51, 52, 53, 54, 55, 56-Octakis-[(*p*-vinyl-benzyl)oxy]calix[8]arene (3b). In a 100 mL three-necked flask equipped with stirrer and condenser, 468 mg (0.55 mmol) of calix[8]arene was suspended in 25 mL of DMF under nitrogen. After 15 minutes, NaH (550 mg, 13.2 mmol) was added with stirring. When the bubbling ceased, the suspension was heated (60°C). After one hour, NaI (50 mg, 0.33 mmol) and 0.9 mL of chlorovinylbenzene (4.9 mmol) in 5 mL of DMF were added drop wise into the charge. After 2 days, the system was cooled, and the reaction was stopped by adding 50 mL of 1N HCl and extracted twice with 100 mL of dichloromethane. The organic layer was filtered off on celite, concentrated under vacuum and dried by azeotropic distillation (toluene) to give a brown oil as a crude product. The residue was diluted with 2 mL of dichloromethane and stirred with 100 mL of ethanol. The insoluble products were filtered off and then recrystallised from $\text{CHCl}_3/\text{MeOH}$ to give 350 mg (36 %) of light brown powder. Mp : decomposed. ^1H NMR (CDCl_3 , 298K) δ 4.05 (s, 16H, Ar- CH_2 -Ar), 4.58 (s, 16H, CH_2), 5.17 (d, 8H, $^3\text{J} = 10.7$ Hz, H_{cis}), 5.64 (d, 8H, $^3\text{J} = 17.3$ Hz, H_{trans}), 6.60 (dd, 8H, $^3\text{J}_{\text{cis}} = 10.7$ Hz, $^3\text{J}_{\text{trans}} = 17.3$, H_{gem}), 6.77-7.2 (m, 56H, H_{Ar}) ; ^{13}C NMR (CDCl_3 , 298K) δ 30.41 (Ar- CH_2 -Ar), 75.11 (O- CH_2 -Ar₂), 114.28 ($\text{CH}_2=\text{CH}$), 124.83 (CH_p , Ar₁), 126.66, 128.10, 129.58 (CH_m , Ar₁, CH, Ar₂), 134.72 (Co- CH_2 , Ar₁), 137.02 ($\text{CH}=\text{CH}_2$), 137.44 (Cp-CH, Ar₂), 137.61 (Cp- CH_2 , Ar₂), 155.46 (C-O, Ar₁) ; ES-MS (+) for $\text{C}_{128}\text{H}_{112}\text{O}_8$ (1776.8) $m/z = 912$ [$\text{M}+2\text{Na}$] $^{2+}$, 1778.7 [$\text{M}+\text{H}$] $^+$, 1795.8 [$\text{M}+\text{NH}_4$] $^+$, 1800.8 [$\text{M}+\text{Na}$] $^+$, 1816.7 [$\text{M}+\text{K}$] $^+$.

5, 11, 17, 23, 29, 35, 41, 47-Octa-*tert*-butyl-49-butoxycalix[8]arene-50, 51, 52, 53, 54, 55, 56-heptol (4). In a 500 mL three-necked flask equipped with stirrer and condenser, 3 g (2.3 mmol) of *p-tert*-butylcalix[8]arene in 200 mL of THF and 25 mL of DMF was refluxed under stirring until a clear solution was obtained (20 min) ; then 5.11 g (3.7 mmol) of K_2CO_3 were introduced and stirring was continued for an additional 20 min under nitrogen. A solution of *n*-bromobutane (2 mL, 18.5 mmol) in 25 mL of THF was added drop wise into the charge. After refluxing for 24h (the starting calix[8]arene is still detected in the reaction mixture) the system was cooled to room temperature, and the solvents were removed under vacuum to leave a residue which was suspended in 1N HCl (100 mL). The insoluble material was collected by filtration, washed with methanol (100 mL) and dried under vacuum. The crude product was purified by chromatography ($\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ 3/2) and fractions which contained traces of starting material or polysubstituted were recrystallized from $\text{CHCl}_3/\text{CH}_3\text{CN}$ to give 1.68 g (54 %) of white powder. Mp : decomposed. ^1H NMR (Pyridine- d_5 , 363K, 400 MHz) δ 0.85 (t, 3H, $^3\text{J} = 7.3$ Hz, CH_3), 1.16 (s, 9H, CH_3 , *t*-Bu), 1.28 (db, 45H, CH_3 , *t*-Bu), 1.3 (s, 18H, CH_3 , *t*-Bu), 1.45 (m, 2H, $^3\text{J} = 7.3$ Hz, CH_2-CH_3), 1.82 (m, 2H, $^3\text{J} = 7.3$ Hz, $\text{CH}_2-\text{CH}_2-\text{CH}_3$), 3.95 (t, 2H, $^3\text{J} = 7.3$ Hz, O- CH_2), 4.15 (s, 4H, Ar- CH_2 -Ar), 4.16 (s, 4H, Ar- CH_2 -Ar), 4.20 (s, 4H, Ar- CH_2 -Ar), 4.24 (s, 4H, Ar- CH_2 -Ar), 7.29-7.35 (m, 16H, H_{Ar}), 9.41 (s, 7H, OH) ; ^{13}C NMR (Pyridine- d_5 , 363K) δ 13.92 (CH_3), 19.51 (CH_2-CH_3), 31.52, 31.76, 31.83 (CH_3 , *t*-Bu), 31.91 ($\text{CH}_2-\text{CH}_2-\text{CH}_3$), 32.56, 32.63, 32.70 (Ar- CH_2 -Ar), 34.24, 34.27, 34.48 (C, *t*-Bu), 74.75 (O- CH_2), 125.96, 126.02, 126.08, 126.16, 126.22, 126.30 (CH, Ar), 127.93, 128.48, 128.57, 128.68, 128.70, 128.71, 128.78, 128.82 (C- CH_2 , Ar), 143.35,

143.80, 143.87, 143.93, 144.17 (C-*t*-Bu, Ar), 149.77, 149.85, 150.65 (C-O, Ar) ; ES-MS (+) for C₉₂H₁₂₀O₈ (1352.8) m/z = 1354.7 [M+H]⁺, 1376.7 [M+Na]⁺.

5, 11, 17, 23, 29, 35, 41, 47-Octa-*tert*-butyl-49-butoxy-50, 51, 52, 53, 54, 55, 56-heptakisacryloyloxycalix[8]arene (1c). In a 100 mL three-necked flask equipped with stirrer and condenser, 200 mg (0.29 mmol) of **4** was suspended in 35 mL of toluene under nitrogen. After 15 minutes, NaH (230 mg, 5.5 mmol) was added with stirring and the suspension was refluxed. After one hour, a solution of acryloyl chloride (0.3 mL, 3.67 mmol) in 10 mL of toluene was added drop wise into the charge. After 3 days, the system was cooled to room temperature, and the reaction was stopped by adding 20 mL of 1N HCl. The organic layer was washed twice with 50 mL of water and concentrated. The crude product was recrystallised from ethanol/water to give 177 mg (69 %) of white powder. Mp : decomposed. ¹H NMR (CDCl₃, 298K, 300 MHz) δ 0.84 (m, 3H, CH₃), 1.11 (s, 9H, CH₃, *t*-Bu), 1.13 and 1.24 (s, 63H, CH₃, *t*-Bu), 1.47 (m, 4H, CH₂-CH₃), 3.4-3.8 (m, 18H, Ar-CH₂-Ar + O-CH₂), 5.52 (m, 7H, CH=CH₂), 5.88 (m, 7H, CH=CH₂), 6.16 (m, 7H, CH=CH₂), 6.85, 6.90, 6.94 and 7.00 (s, 16H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K) δ 13.0(CH₃-CH₂), 14.52, 18.66, 20.13 (CH₃-C=), 23.10 (CH₂-CH₃), 30.10 (Ar-CH₂-Ar), 31.67, 32.33, 33.16 (CH₃, *t*-Bu), 34.71 (C, *t*-Bu), 37.50 (CH₂-CH₂-CH₃), 37.78 (C, *t*-Bu), 126.45 (CH_{Ar}), 127.48 (C=CH₂), 131.63 (C_{Ar}-CH₂-Ar), 135.54 (CH₃-C=CH₂), 145.0 (C_{Ar}-C-*t*-Bu), 148.56 (C_{Ar}-O), 166.0 (C=O) ; ES-MS (+) : for C₁₁₃H₁₃₄O₁₅ (1730.97) m/z = 889 [M+2Na]²⁺/2, 1732.7 [M+H]⁺, 1754.8 [M+Na]⁺, 1770.7 [M+K]⁺.

5, 11, 17, 23, 29, 35, 41, 47-Octa-*tert*-butyl-49-butoxy-50, 51, 52, 53, 54, 55, 56-heptakismethacryloyloxycalix[8]arene (2c). Same procedure with 134 mg (0.1 mmol) of **4**, 191 mg (4.6 mmol) of NaH, 0.15 mL (1.5 mmol) of methacryloyl chloride and 30 mL of *o*-xylene. Recrystallisation from ethanol/water gave 117 mg of white powder (65 %). Mp : decomposed. ¹H NMR (CDCl₃, 298K, 300 MHz) δ 0.85, 0.87 and 0.90 (s, 21H, CH₃-C=), 0.85-0.90 (m, 3H, CH₃-CH₂), 1.14 and 1.30 (s, 72H, CH₃, *t*-Bu), 2.33 (m, 4H, CH₂-CH₂), 3.65 (m, 18H, Ar-CH₂-Ar + O-CH₂), 5.42 and 6.02 (m, 14H, =CH₂), 6.97 (bs, 16H, H_{Ar}) ES-MS (+) : for C₁₂₀H₁₄₈O₁₅ (1829.08) m/z = 1831.1 [M+H]⁺ ; 1853 [M+Na]⁺ ; 1868.9 [M+K]⁺.

5, 11, 17, 23, 29, 35, 41, 47-Octa-*tert*-butyl-49-butoxy-50, 51, 52, 53, 54, 55, 56-heptakis-[(*p*-vinylbenzyl)oxy]calix[8]arene (3c). In a 50 mL three-necked flask equipped with stirrer and condenser, 204 mg (0.15 mmol) of **4** and 60 mg (1.5 mmol) of NaH were suspended in 15 mL of DMF under nitrogen. The solution was heated (60°C) during 2 hours. 4-vinylbenzyl chloride (0.25 mL, 1.6 mmol) was added and the suspension was heated until the starting material was no longer detected in the reaction mixture. The system was then cooled to room temperature and most of the organic solvent was removed under vacuum. The crude product was dissolved with CH₂Cl₂ (100 mL) and washed with 2N HCl (20 mL). The organic layer was washed twice with 100 mL of water, dried with MgSO₄ and concentrated. Recrystallization from CH₂Cl₂/EtOH gave 113 mg (35 %) of light yellow powder. Mp : decomposed. ¹H NMR (C₆D₆, 333K) δ 0.83 (sb, 3H, CH₃), 1.1-1.7 (mb, 76H, CH₃, *t*-Bu, CH₂-CH₂), 3.6-4.6 (mb, 18H, Ar-CH₂-Ar, O-CH₂, *n*-Bu), 4.7-5 (mb, 14H, CH₂-O, Ar₂), 5.1 (sb, 7H, H_{trans}), 5.7 (sb, 7H, H_{cis}), 6.7 (sb, 7H, H_{gem}), 7.1-7.6 (mb, 44H, H_{Ar}) ; ¹³C NMR (CDCl₃, 298K, 400MHz) δ 13.52 (CH₃), 18.82 (CH₂-CH₃), 29.71, 30.05, 30.17 (Ar-CH₂-Ar), 31.39 (CH₃, *t*-Bu), 31.94 (CH₂-CH₂-CH₃), 34.14 (C, *t*-Bu), 74.22, 74.7 (O-CH₂), 113.85 (CH=CH₂), 125.27, 126.06, 126.63, 127.68, 128.46 (CH, Ar), 133.11 (C-CH₂, Ar), 136.58 (CH=CH₂), 137.45, 137.94 (C-CH₂, Ar), 146.06 (C-*t*-Bu, Ar), 152.59, 152.90, 153.54 (C-O, Ar) ; ES-MS (+) for C₁₅₅H₁₇₆O₈ (2165.33) m/z = 1106.2 [M+2Na]²⁺, 2189.4 [M+Na]⁺.