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Orthogonal chain length control in calix[5]arene-based AB-type supramolecular polymers

Claudia Gargiulli^a, Giuseppe Gattuso^{a,*}, Anna Notti^a, Sebastiano Pappalardo^b, Melchiorre F. Parisi^{a,*}

^a Dipartimento di Chimica Organica e Biologica, Università di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy ^b Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

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ABSTRACT

New AB-type supramolecular polymers have been prepared by acid-promoted self-assembly of an aminododecyloxy-calix[5]arene monomer precursor. The number-average degree of polymerization has been found to be dependent on the concentration of the salt monomer and on the nature of the counterion (i.e., chloride, picrate or hexafluorophosphate).

Chain-length regulation experiments have been carried out, employing orthogonal chain stoppers capable of selectively interacting with a given moiety of the AB-type monomer/polymer. Competitive calix[5]arene 'caps' and *n*-butylammonium ion 'plugs' have been used to control the extent of self-assembly of the polymer, in turn interacting with the ammoniumdodecyloxy or with the cavity end-groups of the supramolecular calixarene assembly. These experiments, conveniently carried out at a 10 mM concentration, can be easily followed by ¹H NMR spectroscopy.

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Supramolecular polymers,¹ that is, polymers whose monomeric units are held together by means of reversible noncovalent interactions, rather than covalent bonds, are the latest frontier in advanced materials research. Their advantage over classical covalently-linked counterparts lies in the ease of preparation, which does not require chemical reactions, but simply relies on the self-assembly of pre-programmed monomers.² Supramolecular polymers have been actively investigated over the past 10 years. They have been designed around different recognition motifs, by taking advantage of the most diverse noncovalent interactions, such as hydrogen-bonding,^{1a,b} π – π stacking^{1a,3} or host–guest interactions.⁴

When dealing with supramolecular polymers, chain-length regulation is a crucial factor. In fact, as most supramolecular polymerizations are thermodynamically controlled self-assembly processes,² they cannot be stopped at will at a given extent of reaction, and the uncontrolled growth of polymeric chains may ultimately yield materials which cannot be easily handled.⁵

Typically, the degree of polymerization of these materials depends on: (i) the stability constant of monomer–monomer interactions (i.e., their association constant) and (ii) the monomer concentration, according to the equation $\bar{X}_n \approx (K \times [M])^{1/2}$, where \bar{X}_n is the number-average degree of polymerization, *K* is the monomer–monomer association constant, and [*M*] is the monomer

concentration.⁶ Because of this, direct control over the degree of polymerization can in principle be achieved either by indirectly acting on the association constant (by means of solvent effects⁷ or, in the case of charged monomers, by selecting appropriate counterions⁸), or by varying the monomer concentration.¹ However, a third possibility, borrowed from classical polymer chemistry,⁵ has recently been proposed, relying on the use of monofunctional monomers—that is, chain-stoppers—capable of making the degree of polymerization concentration independent.⁹

Among the many different building blocks employed for the construction of self-assembling monomers, calixarenes¹⁰ are playing an increasingly significant role. These versatile receptors have recently been used as a scaffold for the preparation of both hydrogen-bonded¹¹ and host-guest type¹² polymers. On our part, owing to the ability of calix[5]arenes locked in a regular cone conformation¹³ to act as receptors for linear primary alkylammonium ions, we have been able to design a number of supramolecular oligo-/ polymers based on the calix[5]arene/alkylammonium recognition motif.¹⁴ AB-type (self-complementary heteroditopic monomer) aggregates⁸ have been obtained by the acid-promoted iterative inclusion of aminododecyloxy-functionalized calix[5]arenes. AA/ BB-type (complementary homoditopic monomer pair) oligomers,¹ on the other hand, have been obtained from a series of divergentcavity bis-calix[5] arenes capable of binding α, ω -alkanediyldiammonium salts with a (poly)capsular topology.¹⁶

In the present Letter, we report on the chain-length control of an AB-type supramolecular polymer, prepared from a new highly lipophilic aminododecyloxy-calix[5]arene monomer precursor (1, see below). Control over the self-assembly of 1 was equally achieved





^{*} Corresponding authors. Tel.: +39 090 6765241; fax: +39 090 392840 (G.G.); tel.: +39 090 6765170; fax: +39 090 392840 (M.F.P.).

E-mail addresses: ggattuso@unime.it (G. Gattuso), mparisi@unime.it (M.F. Parisi).

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by using either A-type or B-type monofunctional chain stoppers, that is, a different calix[5]arene, and a *n*-butylammonium salt.

Monomer amino-precursor **1** was prepared in two steps, starting from the known phthalimidododecyloxy-calix[5]arene derivative⁸ **2** (Scheme 1). Calixarene **2** was fully alkylated in refluxing MeCN with 1-bromohexadecane, in the presence of K_2CO_3 , to give **3** in a 62% yield after column chromatography.¹⁷ Compound **3** was then treated with $H_2NNH_2 \cdot H_2O$ in refluxing ethanol to give the desired amino-derivative **1**, after precipitation from CHCl₃/MeOH, in a 43% yield.¹⁸

According to ¹H NMR data, the calixarene cavity of derivative **1** is arranged in a regular *cone* conformation, showing a very high



Scheme 1. Synthesis of amino-calix[5]arene 1.



Figure 1. ¹H NMR spectra (500 MHz, CDCl₃, 10 mM, 298 K) of: (a) 1, (b) 1 HCl, (c) 1 HPic and (d) 1 HPF₆. The asterisk indicates residual solvent peak.

degree of symmetry, with a single AX system accounting for 10 H assigned to the ArCH₂Ar hydrogens (as opposed to the expected three AX systems for C_s symmetric calix[5]arenes¹⁹), and a single broad resonance for the aromatic hydrogen atoms.

Exposure of amino-monomer precursor **1** to a variety of acids (HCl, picric acid—henceforth referred to as HPic—and HPF₆)²⁰ caused protonation of the amino group, thus activating the self-assembly tendency of the newly formed monomer **1**·HX. As a consequence, growth of the expected supramolecular polymeric species $(1 \cdot HX)_n$ takes place, by means of an iterative *endo*-cavity inclusion process, where the pendant dodecylammonium group of one monomer penetrates the cavity of the next.

The ¹H NMR spectra showing the formation of $(1 \cdot HX)_n$ are reported in Figure 1. In the three cases under study, assembly/disassembly of the ammonium monomer was found to be on a slow exchange regime on the NMR timescale.¹⁴ Supramolecular polymer formation is consistent with the appearance, in the high-field region ($\delta = -2.0-0.8$ ppm), of the telltale resonances generated by the α - ϵ -methylenes of the newly formed ammoniumdodecyloxy chain as they experience the shielding effect of the calixarene aromatic moieties, along with a broad peak ($\delta = 5.74$ ppm) assigned to the included $-NH_3^+$ moiety involved in hydrogen bonding with the calixarene phenolic oxygen atoms.^{8,14,21}

¹H NMR dilution experiments were carried out on the three protonated monomers (i.e., **1**·HCl, **1**·HPic, and **1**·HPF₆) to gain an insight into the concentration² and counterion^{8,22} dependence of the average degree of polymerization.²³ Analysis of the data reported in Table 1 led to two interesting observations: (i) in the concentration range examined (2–25 mM in CDCl₃) a relatively small but significant increase in the percentage of complexation (and hence of the degree of polymerization), in line with the known behavior of supramolecular polymers;²⁴ (ii) a remarkable dependence of the degree of polymerization on the nature of the counterion, in agreement with the increasing tendency of chloride, picrate, and hexafluorophosphate anions to form contact ion pairs with ammonium cations in low polarity solvents—the looser the ion pair, the higher the \bar{X}_n value.^{8,25}

Chain-length regulation experiments were carried out by progressively adding, to a 10 mM solution²⁶ of $(1 \cdot \text{HPF}_6)_n$, of either a competitive calix[5]arene 'cap', able to prevent the chain growth by binding to the dodecylammonium pendant chains, or an alkylammonium 'plug', capable of filling the calixarene cavity of the monomers, thus inhibiting monomer–monomer iterative inclusion.

For the capping of the terminal ammonium group of the monomer, the pentaester, penta-*tert*-butylpentakis(*tert*-butoxycarbonylmethoxy)calix[5]arene²⁷ (**4**), was selected, owing to its superior binding ability-toward alkylammonium ions-with respect to pentaether calixarene derivatives.^{14a} In addition, alkylammonium guests penetrate deeper into the cavity of pentaester derivatives compared with pentaether ones, giving rise to distinct sets of NMR peaks for the dodecylammonium groups included into **1** and those included into **4**.¹⁶

Table 1

Percentages of complexation for 1 HCl, 1 HPic, and 1 HPF₆ and corresponding calculated number-average degree of polymerization $(\bar{X}_n)^a$

	[1 ·HCl] (mM)				[1 ·HPic] (mM)				$[1 \cdot \text{HPF}_6] (\text{mM})$			
	2	5	10	25	2	5	10	25	2	5	10	25
$% \operatorname{compl}^{\mathbf{b}} \\ \bar{X}_n$	43 1.7	44 1.8	44 1.8	45 1.8	78 4.5	79 4.8	81 5.3	83 5.9	94 16.7	95 20	95 20	96 25

^a For calculation of \bar{X}_n values see Ref. 23.

^b Determined by ¹H NMR (500 MHz) at 298 K in CDCl₃. Values derived from the average of three independent measurements. Standard error <10%.



Figure 2. Selected regions of the ¹H NMR (500 MHz; CDCl₃, 298 K) titration experiment of $1 \cdot \text{HPF}_6$ (trace a, 10 mM) with calix[5]arene **4** (b, 1 mM; c, 2 mM; d, 3 mM; e, 5 mM; f, 10 mM; g, 20 mM; h, 50 mM). $n \ge 1$, $m \ge 1$.



Figure 3. Selected regions of the ¹H NMR (500 MHz; CDCl₃, 298 K) titration experiment of $1 \cdot \text{HPF}_6$ (trace a, 10 mM) with *n*-BuNH₃⁺PF₆⁻ (b, 1 mM; c, 2 mM; d, 3 mM; e, 5 mM; f, 10 mM; g, 20 mM; h, 50 mM). $n \ge 1$.



Figure 4. Decrease of the number-average degree of polymerization (\bar{X}_n) of (1 HPF₆)_n upon addition of: (a) calix[5]arene 4, and (b) n-BuNH⁺₂PF⁻_n.

¹H NMR spectra relating to this chain-length regulation experiment (Fig. 2) showed that in the high-field region, upon increasing the concentration of the chain stopper **4** (from 0.1 to 5 equiv), a new set of signals for the included methylene hydrogen atoms appeared and progressively grew, matched by the progressive disappearance of the signals belonging to $(\mathbf{1} \cdot \text{HPF}_6)_n$. This observation is compatible with the formation of $(\mathbf{1} \cdot \text{H}^+)_n \subset \mathbf{4}$ assemblies, in which the terminal dodecylammonium groups reside within the cavity of the chain stopper **4**. In addition, in the region where the included NH₃⁺ hydrogen atoms resonate, the peak for the pentaether-included ammonium group ($\delta = 5.54$ ppm) progressively decreased in intensity, whereas two overlapping peaks ($\delta = 6.10-6.14$ ppm) grew.²⁸ Integration of the relevant peaks indicates that the average degree of polymerization rapidly decreases during the early stages of the titration, and then slowly stabilizes toward the final value of 2 (Fig. 4a, see below).²⁹ Similar behavior has previously been observed for hydrogen-bonded supramolecular polymers.^{9c-e}

n-Butylammonium hexafluorophosphate was selected as a potential 'plug' for the 'cavity-plugging' chain-length control experiment. ¹H NMR spectra detailing the outcome of this titration are shown in Figure 3. In this case, discrimination between monomermonomer cavity-included and *n*-BuNH₃⁺⊂(1·H⁺)_n was made possible by the appearance, for the latter species, of the distinctive resonance of the methyl group of the included *n*-BuNH₃⁺ ion ($\delta = -0.34$ ppm), given that the peaks of the α -, β -, and γ -CH₂s are either partially or fully overlapping. As expected, addition of increasing amounts of *n*-BuNH₃⁺ PF₆⁻ led to the progressive filling of the cavities, as demonstrated by the replacement of the (1·H⁺)_n diagnostic peaks with those of *n*-BuNH₃⁺ ⊂(1·H⁺)_n. In this case, however, the included NH₃⁺ group gave rise to a single new resonance. Again,

integration of the relevant peaks showed a trend consistent with a decrease in the average degree of polymerization, similar to that observed in the 'capping' experiment (Fig. 4b). Similarly, beyond the point of equivalence the cavities of the monomers are almost fully 'plugged' with *n*-BuNH₃⁺ chain stoppers (i.e., $\bar{X}_n = 2$).³⁰

In conclusion, new calix[5]arene-based supramolecular polymers—that is, $(1 \cdot \text{HCl})_n$, $(1 \cdot \text{HPic})_n$, and $(1 \cdot \text{HPF}_6)_n$ —have been synthesized, and their concentration- and counterion-dependence have been investigated. In addition, we have demonstrated that the chain-length control of these AB-type supramolecular polymers can be efficiently achieved by independently acting on both terminals of the monomeric unit. Addition of either a competitive receptor—a polymerization-inert calix[5]arene—or a competitive guest—a polymerization-inert linear alkylammonium ion—resulted in a progressive decrease in the number-average degree of polymerization, opening the way for greater control over the macroscopic properties of these novel materials. Further studies aimed at the elucidation of the behavior of the chain stoppers at higher concentration ranges are currently in progress.

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- 31-[12-N-(Phthalimidododecyl)oxy]-32,33,34,35-tetra-hexadecyloxy)-5,11,17,23,29-penta-tert-butylcalix[5]arene 3: Calix[5]arene 2 (200 mg, 0.18 mmol), 1-bromohexadecane (652 mg, 2.14 mmol) and K₂CO₃ (295 mg, 2.14 mmol) were suspended in anhydrous CH₃CN (25 mL) and refluxed for 16 h, under vigorous stirring. Inorganic salts were filtered off and washed with CHCl₃. The combined filtrates were evaporated to dryness under reduced pressure, and the residue was purified by column chromatography (SiO₂, petroleum ether-Et₂O 8:1) to give **3** (225 mg, 62%) as a white powder. Mp 71-73 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.90 (t, J = 7.0 Hz, CH₂CH₃, 12 H), 1.04, 1.05 and 1.08 (3 × s, ratio 1:2:2, C(CH₃), 45 H), 1.20-1.55 (m, CH₂, 122 H), 1.69 (bq, J = 7.0 Hz, CH_2 , 2 H), 1.91 (bq, J = 7.0 Hz, CH_2 , 8 H), 3.26 and 4.56 (AX, J = 14.0 Hz, ArCH₂Ar, 10 H), 3.60–3.70 (m, NCH₂ and OCH₂, 12 H), 6.92, 6.94 and 6.97 (3 × s, ratio 1:2:2, Ar, 10 H), 7.69–7.72 and 7.84–7.87 (2 × m, Pht, 4 H) ppm; ¹³C NMR (75 MHz, CDCl₃), δ 14.1, 22.7, 26.4, 27, 0, 28.7, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2, 30.3, 30.6, 31.4, 31.9, 33.9, 38.0, 74.0, 123.1, 125.3, 125.4, 132.2, 133.8, 133.9, 144.4, 152.8, 168.4 ppm. ESI MS m/z (rel. int. %) 2045.5 ([M+Na]⁺, 100), and 2061.6 ([M+K]⁺, 78). Anal. Calcd for C₁₃₉H₂₂₅NO₇: C, 82.55; H, 11.21; N, 0.69. Found: C, 82.31; H, 11.33; N, 0.68.
- 18. 31-[(12-Aminododecyl)oxy]-32,33,34,35-tetra-hexadecyloxy-5,11, 17.23.29penta-tert-butylcalix[5]arene 1: A stirred mixture of calix[5]arene 3 (202 mg, 0.10 mmol) and hydrazine monohydrate (49 µL, 1.0 mmol) in EtOH (20 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure. The residue was dissolved in CHCl₃, washed with aqueous NaOH (5% w/w), dried (Na₂SO₄), and the solution was evaporated to dryness. Precipitation of the residue from CHCl₃/MeOH afforded 1 (81 mg, 43%). Mp 78-80 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, J = 6.7 Hz, CH₂CH₃, 12 H), 1.02, 1.03 and 1.05 (3 × s, ratio 1:2:2, C(CH₃), 45 H), 1.20–1.60 (m, CH₂, 122 H), 1.80–2.00 (m, CH₂, 10 H), 2.67 (t, J = 6.8 Hz, CH₂NH₂, 2 H), 3.24 and 4.54 (AX, J = 14.1 Hz, ArCH₂Ar, 10 H), 3.60-3.70 (m, OCH₂, 10 H), 6.91, 6.92 and 6.93 (3 × s, ratio 1:2:2, Ar, 10 H) ppm; ¹³C NMR (75 MHz, CDCl₃), δ 14.1, 22.7, 26.4, 27.0, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2, 30.6, 31.4, 32.0, 33.9, 42.3, 74.1, 125.3, 125.4, 133.9, 144.4, 152.8 ppm. ESI MS *m*/*z* (rel. int. %) 1893.3 ([M+H]⁺, 100), and 1915.7 ([M+Na]⁺, 3). Anal. Calcd for C₁₃₁H₂₂₃NO₅: C, 83.15; H, 11.88; N, 0.74 Found: C, 82.87; H, 11.99; N, 0.69.
- 19. The isochronous nature of these signals likely reflects the similar size of the hexadecyloxy and aminododecyloxy substituents present at the lower rim.
- 20. A solution of the amino precursor 1 (30 mg in 5 mL of HCl-free CHCl₃ was treated with 5 mL of the pertinent acid solution (1 M HCl/H₂O for 1 HCl, 1% picric acid in H₂O for 1 HPic and 1 M HPF₆/H₂O for 1 HPF₆). The organic layer was separated, washed with H₂O (3×5 mL), dried (MgSO₄), and concentrated to dryness under reduced pressure. The solid residue obtained was kept under vacuum (2 h, rt) and each sample used as such to prepare the relevant stock solutions. HCl-free CDCl₃ was obtained by percolation through neutral alumina prior to use.
- 21. Assignments derive from H-H COSY spectra (not shown).
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- 23. For supramolecular polymers, the average degree of polymerization can be determined by applying Carother's equation $[X_n = 1/(1-p)]$, where the 'extent of reaction' *p* can be obtained by direct integration of the peaks belonging to the free end-groups and to the self-assembled core moieties. See Ref. 8 for a more extensive discussion.
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- 26. Carrying out these experiments in relatively diluted conditions allowed ¹H NMR monitoring of the decrease in the average degree of polymerization.
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- 28. Owing to the fact that the higher-field peak firstly grows in intensity and then disappears, in favor of the lower-field one, these two peaks have been tentatively assigned to the pentaester-included ammonium moieties of the 1.H⁺⊂4 complex and the differently-sized (1.H⁺)_m⊂4 (m>1) assemblies, respectively.
- 29. As far as the \bar{X}_n determination is concerned, chain stoppers are considered equivalent to monomers, so that a $\bar{X}_n = 2$ represents the complete capture of the monomers by the relevant chain stoppers, with the exclusive formation of 1:1 1·H⁺⊂4 complexes in this case.
- 30. It should be mentioned that, due to the poor solubility of n-BuNH₃⁺PF₆, the last two spectra of the titration (i.e., 20 mM, 1:2; 50 mM, 1:5) were recorded in the presence of some undissolved salt. However, this had no influence on the \bar{X}_n calculations.